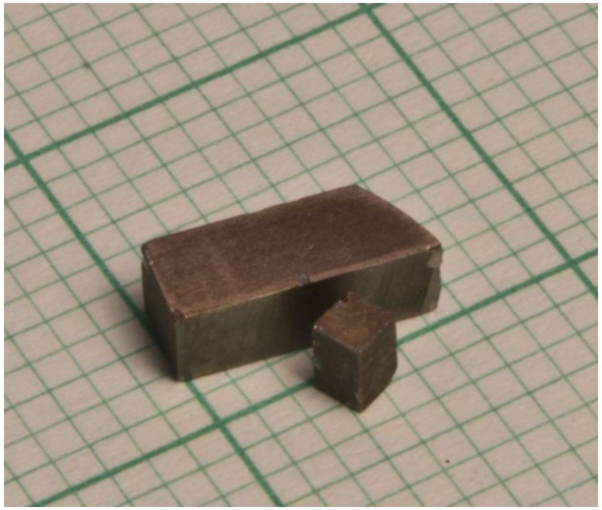
$MnFe_4Si_3$

A prototype material of a *second-order* phase transition with magnetocaloric effect



M. Herlitschke, P. Hering, I. Sergueev, B. Klobes, J. Perßon, and R. Hermann

FS-PE, Deutsches Elektronen-Synchrotron
Jülich Centre for Neutron Science JCNS, JARA-FIT, Forschungszentrum Jülich GmbH
Faculté des Sciences, Université de Liège
Materials Science and Technology Division, Oak Ridge National Laboratory

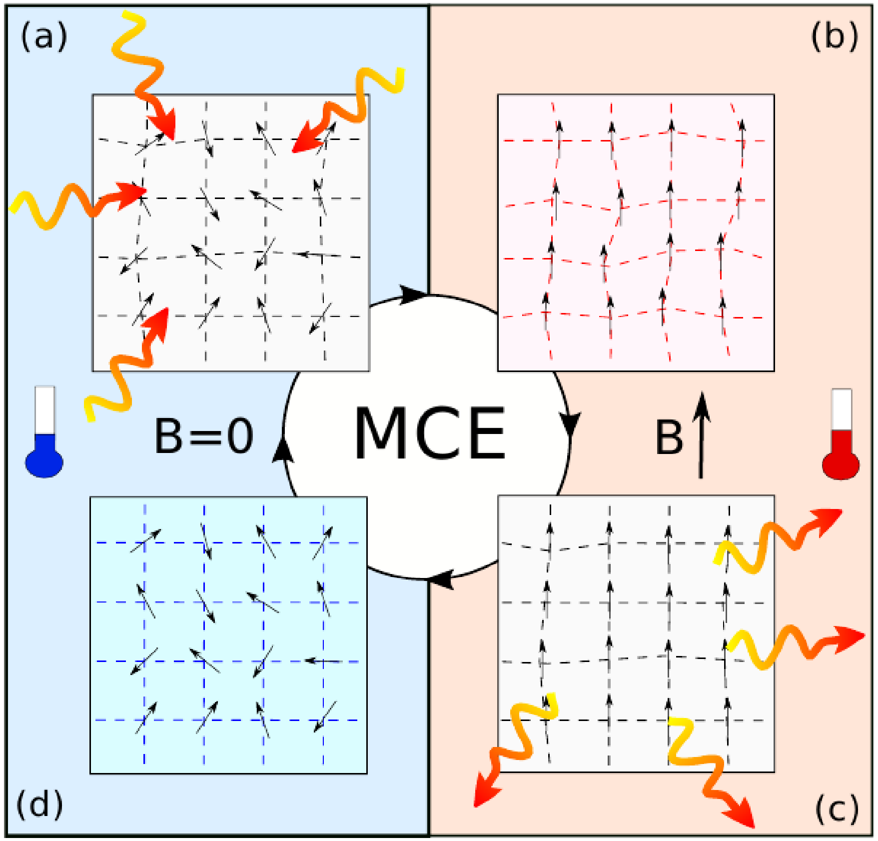
HELMHOLTZ ASSOCIATION

DESY

Magnetocaloric Effect (MCE)

- Magnetocaloric effect (MCE) is a reversible temperature change upon application or removal of an external magnetic field

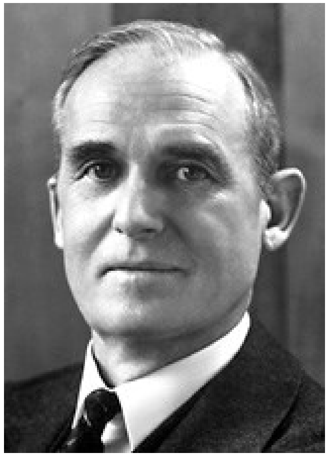
- Room-temperature refrigeration
  - Up to 30% potential energy saving[1]
  - Environmental friendly
  - No moving parts



[1] K. Gschneidne, *Rep. Prog. Phys.*, 2005, 68, 1479

Magnetocaloric Effect (MCE)

- 80 years ago : used for achieving ultra low temperatures (W. F. Giauque, Nobel price winner - 1949).



http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1949/

- Room-temperature refrigeration
  - Since 1997, after discovery of the giant MCE in $Gd_5(Ge_2Si_2)$
  - Patent by BASF and E. Brueck *et. al.* „Method for generating giant magnetocaloric materials”

Source: Haier - magnetocaloric wine cooler

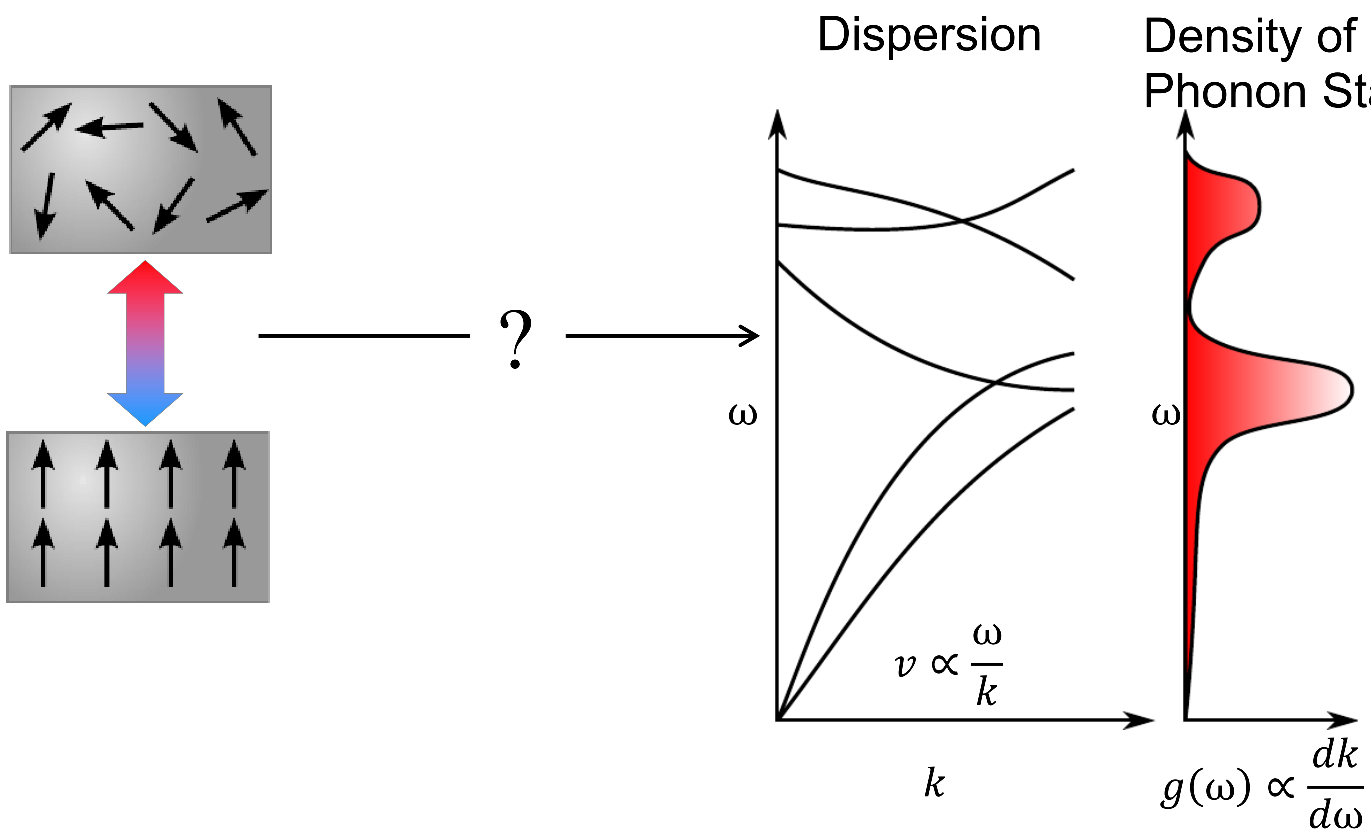
MCE & Entropy

Entropy : $S(T,B,p) = S_l(T,B,p) + S_e(T,B,p) + S_m(T,B,p)$,

Lattice Entropy

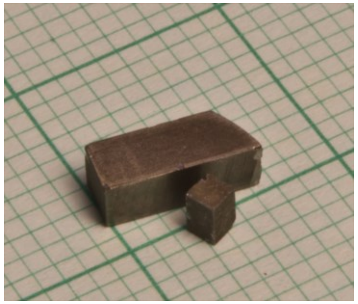
Entropy of conduction-electrons

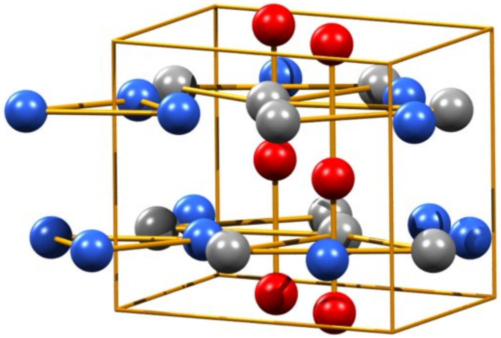
Magnetic entropy

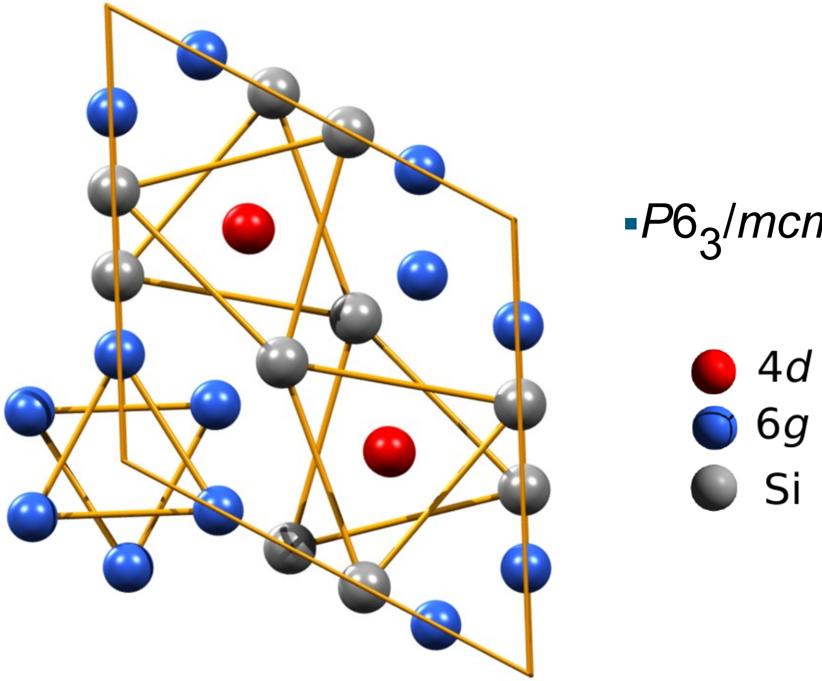


$MnFe_4Si_3$

- Prototype material
- Single crystal of $Mn_{5-x}Fe_xSi_3$ with $0 < x < 4$
- $x = 4$ exhibits moderate MCE at ~300 K
- Non-rare earth based
- Solid solution: Mn and Fe on *4d* and *6g*



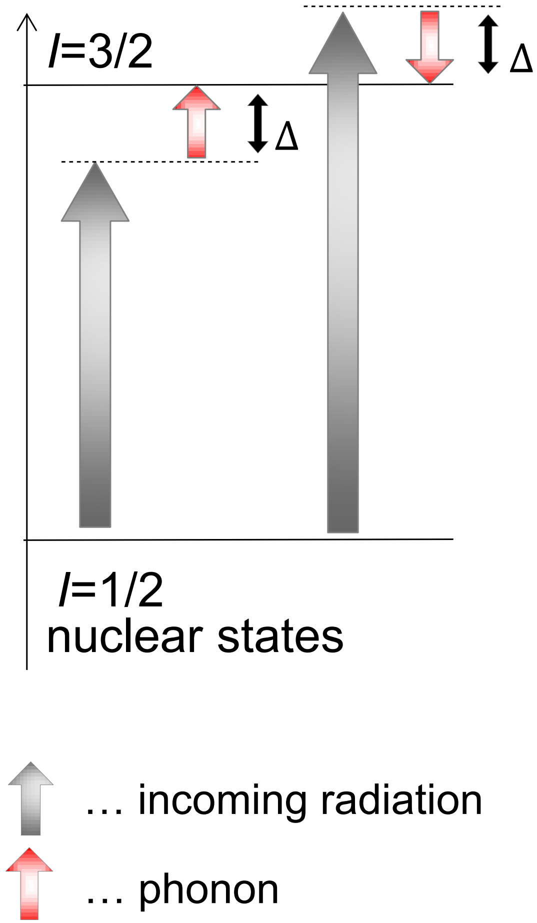




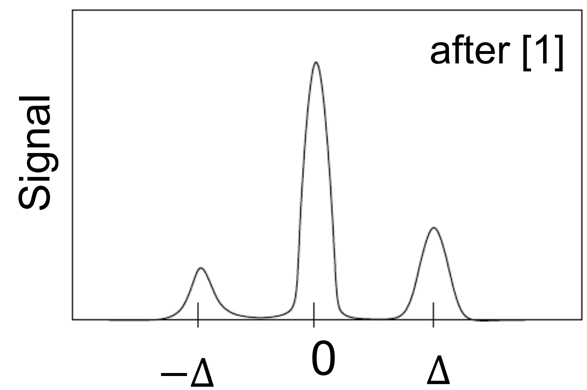
- $P6_3/mcm$

Nuclear Inelastic Scattering

P 01



- Phonon assisted nuclear absorption
- Direct measurement of density of phonon states



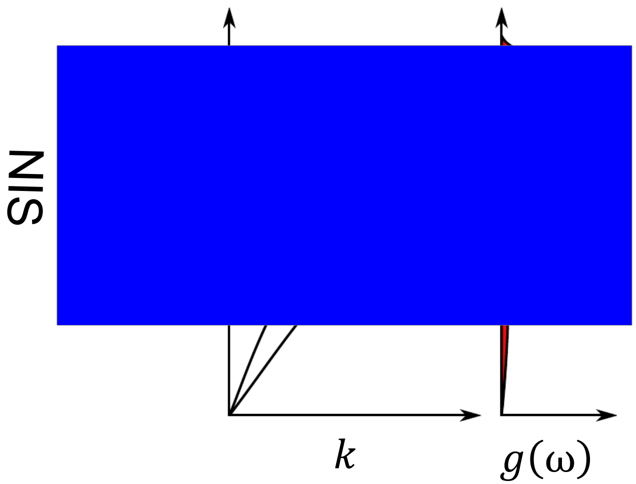
- Detection: measurement of radioactive decay or internal conversion
- about 1 meV resolution

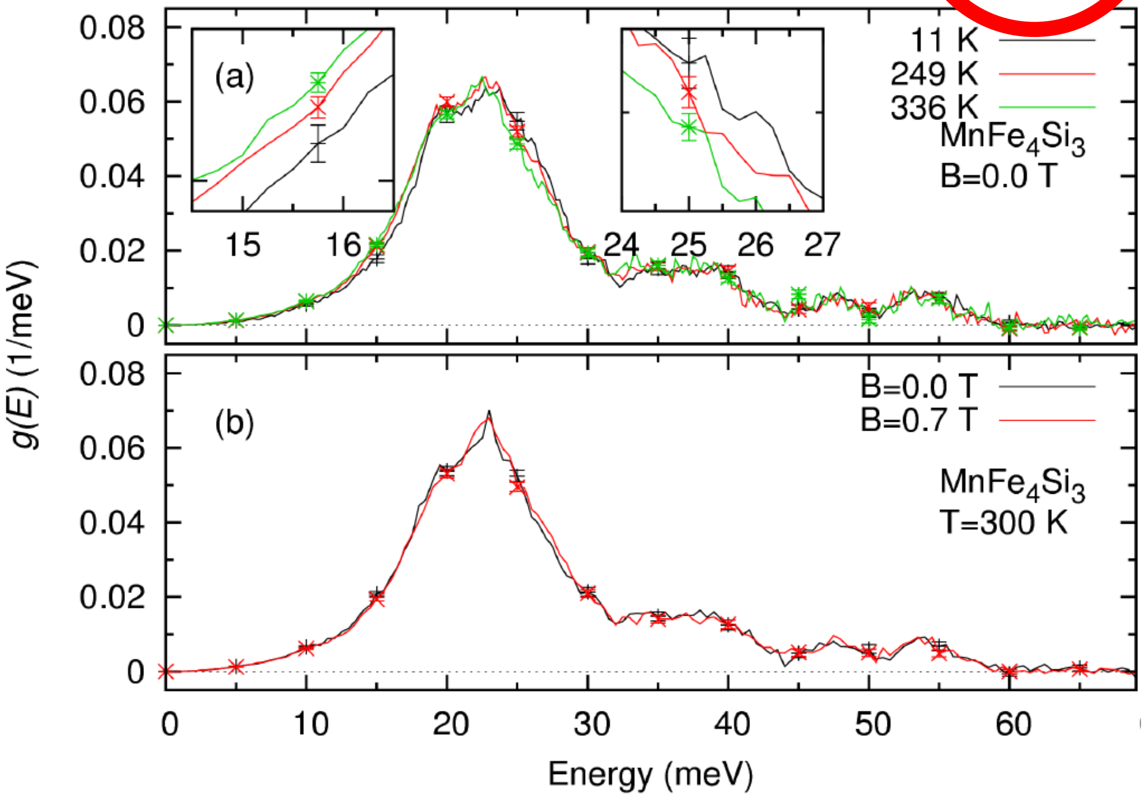
[1] Ralf Röhlsberger, *Nuclear Condensed Matter Physics with Synchrotron Radiation,* Springer, 2004

MnFe4Si3 - Density of phonon states

Iron resonant

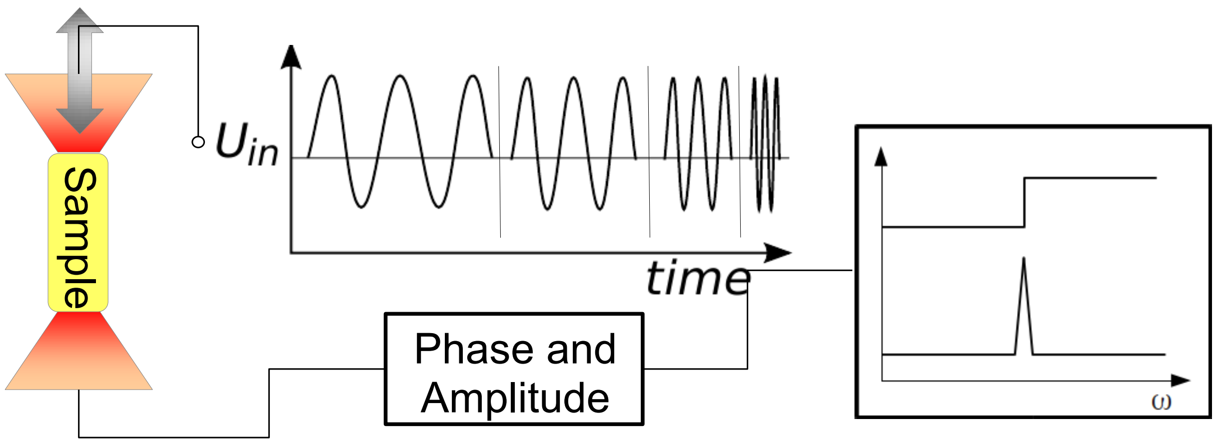
- NIS results at different temperatures and with applied magnetic field
- No significant change in DPS
- Obtained data >3 meV
- Entropy ~300 J/kg/K



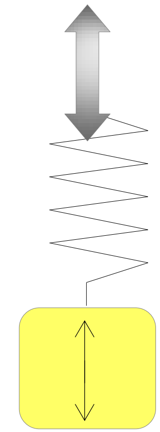


Resonant Ultrasound Spectroscopy (RUS)

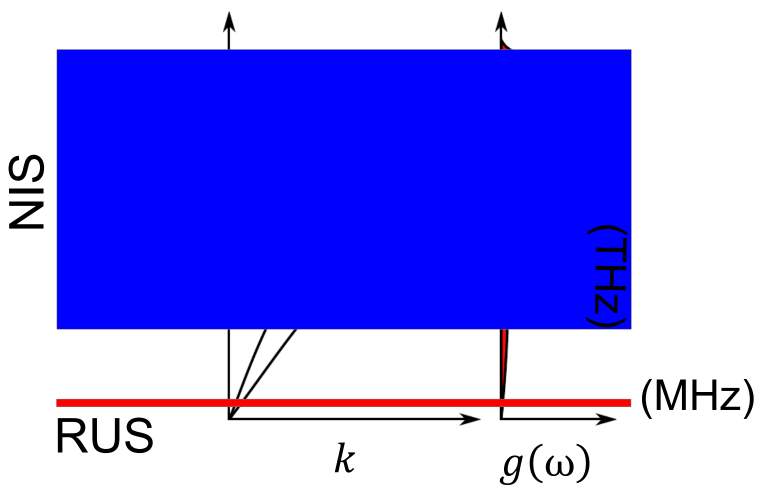
- Resonant Ultrasound Spectroscopy (RUS)



Analogy:
Spring pendulum



$\omega = \sqrt{(D/m)}$



Access to elastic properties

$$\sigma_{ij} = \sum_{kl} c_{ijkl}\epsilon_{kl}$$

σ … stress
ϵ … strain

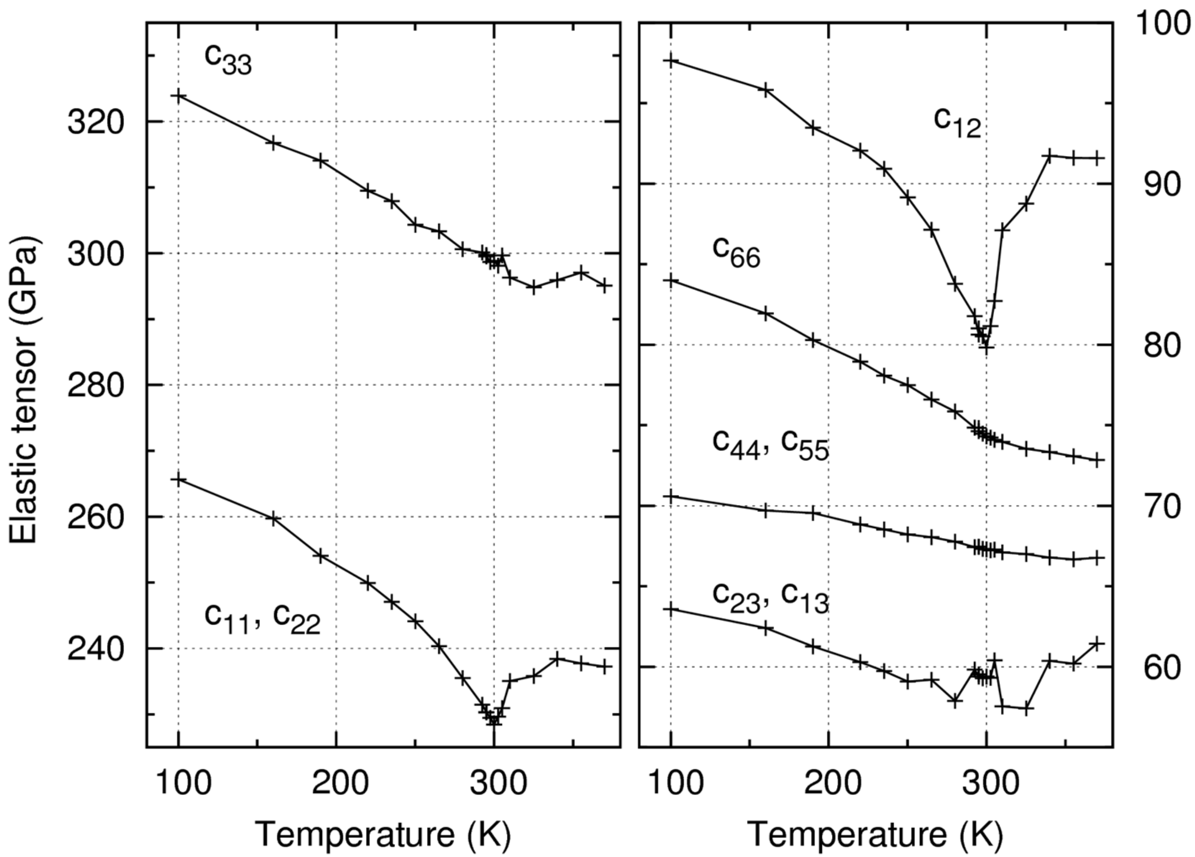
hexagonal

$$\begin{pmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{13} & 0 & 0 & 0 \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{c_{11}-c_{12}}{2} \end{pmatrix}$$

DESY

RUS

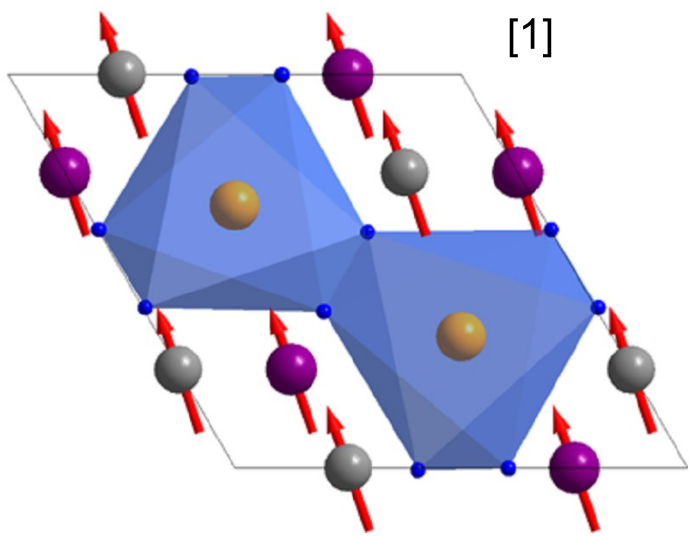
- RUS results at different temperatures



- Soft mode behaviour at 300 K
- Only in a,b plane components
- No discontinuity
- absolute errors: ~5%
- relative errors: <<1%

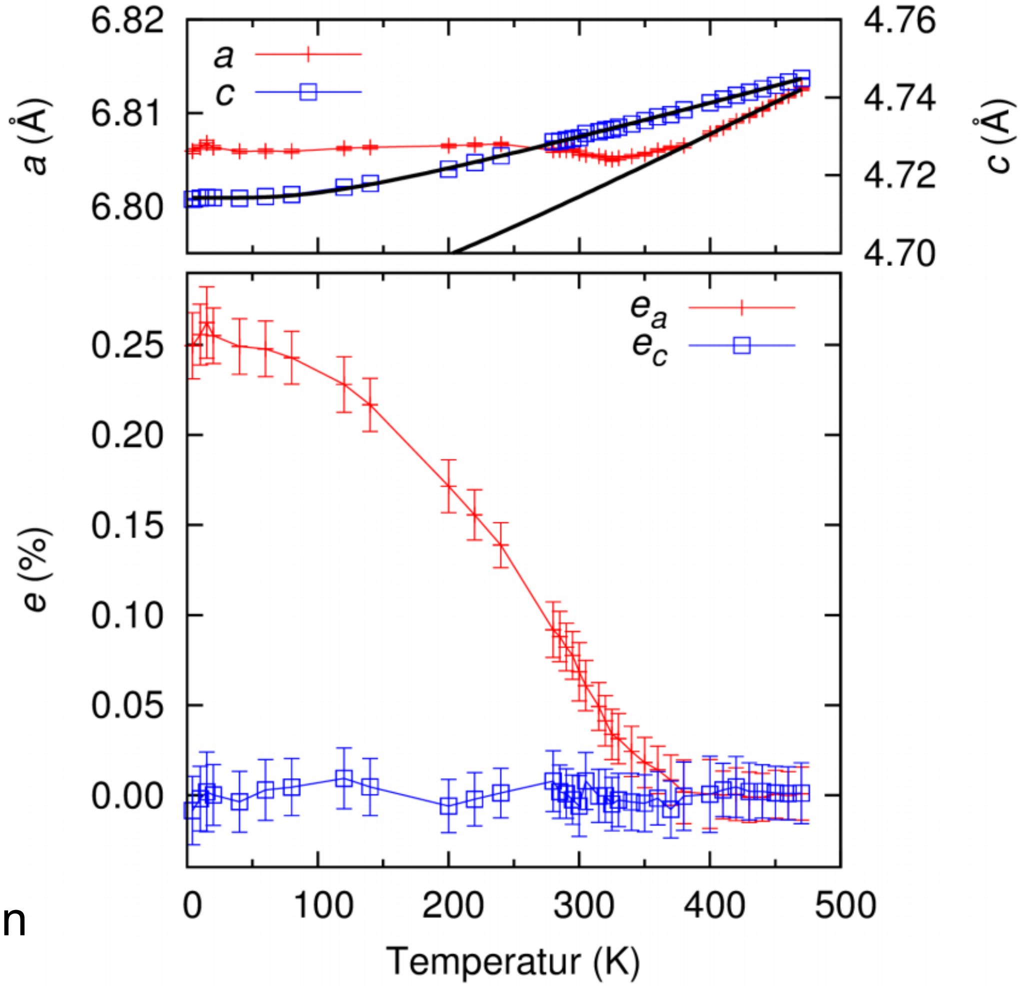
Neutron diffraction

- neutron diffraction (SPODI, MLZ)
- refinement of magnetic structure: $P\bar{6}$ >> *Pm‘*



[1]

In collaboration with [1]

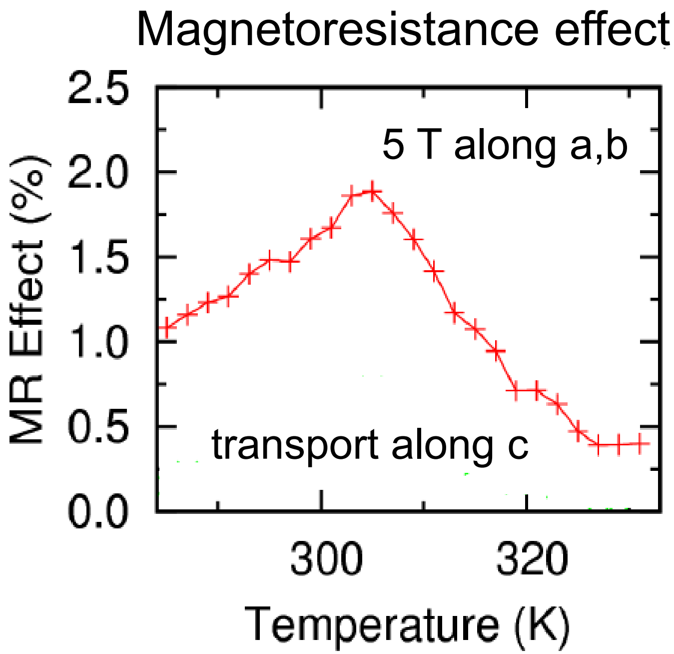


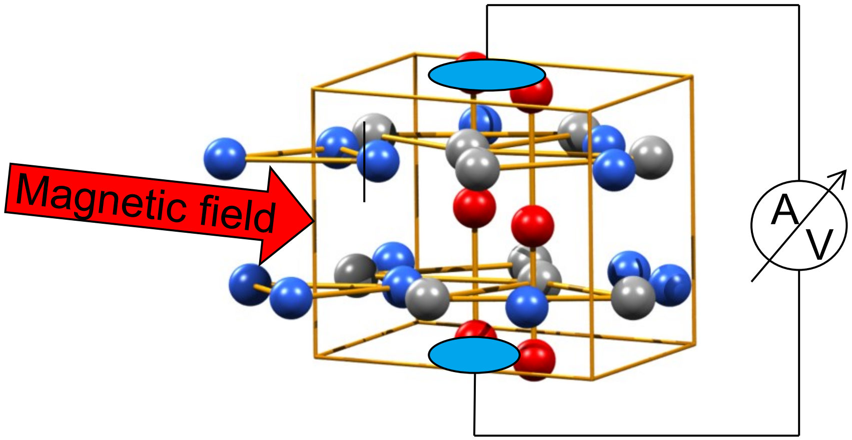
- again: sensitive to transition solely in *a,b* plane

[1] P. Hering, *Chem. Mater.*, 2015, 27 (20), pp 7128–7136

Resistivity

- temperature dependent resistivity sensitive for transition
- but magneto resistance (MR) effect only with field in *a,b* and transport along *c*
- up to 2% MR not large for GMR materials but for anisotropic resistance



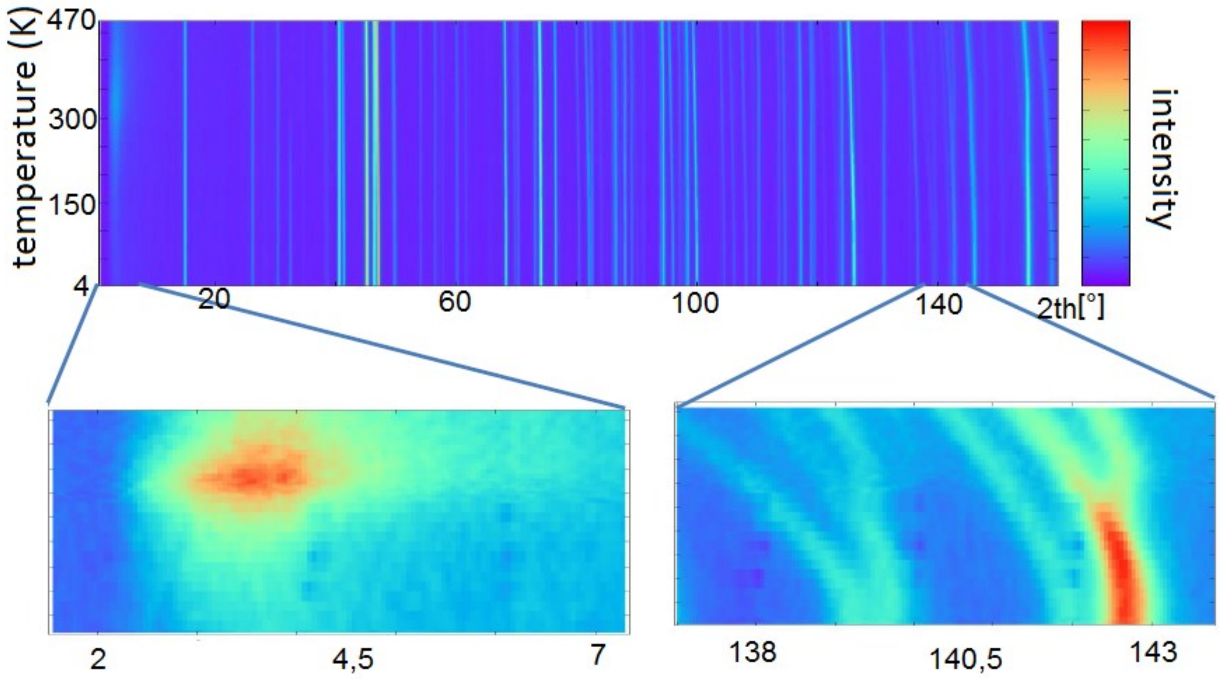


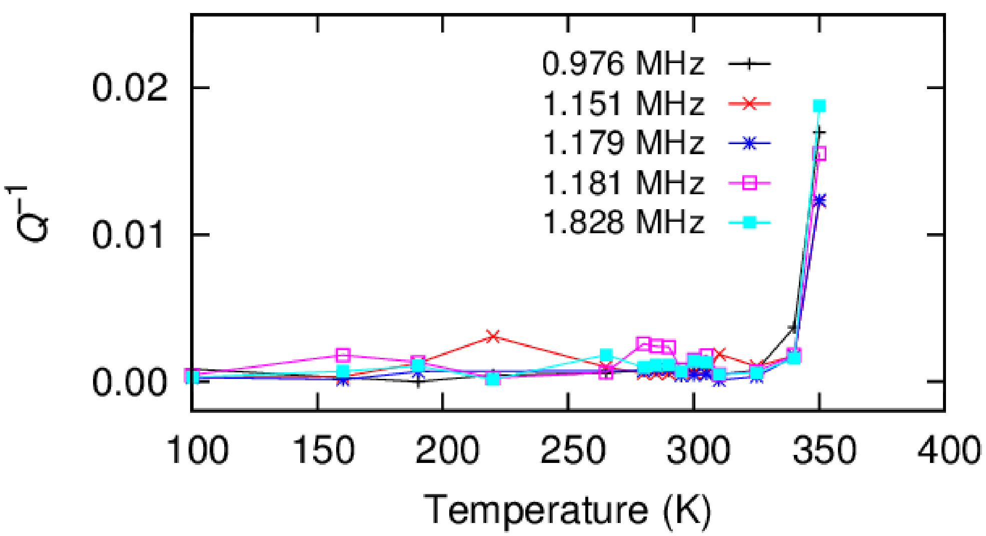
- might be ordering of spins in *a,b* plane

Small-Angle Scattering and anelastic Process

- unexpected SAXS signal in neutron diffraction data

- large increase in inverse quality factor of the RUS peaks





- inverse quality factor:

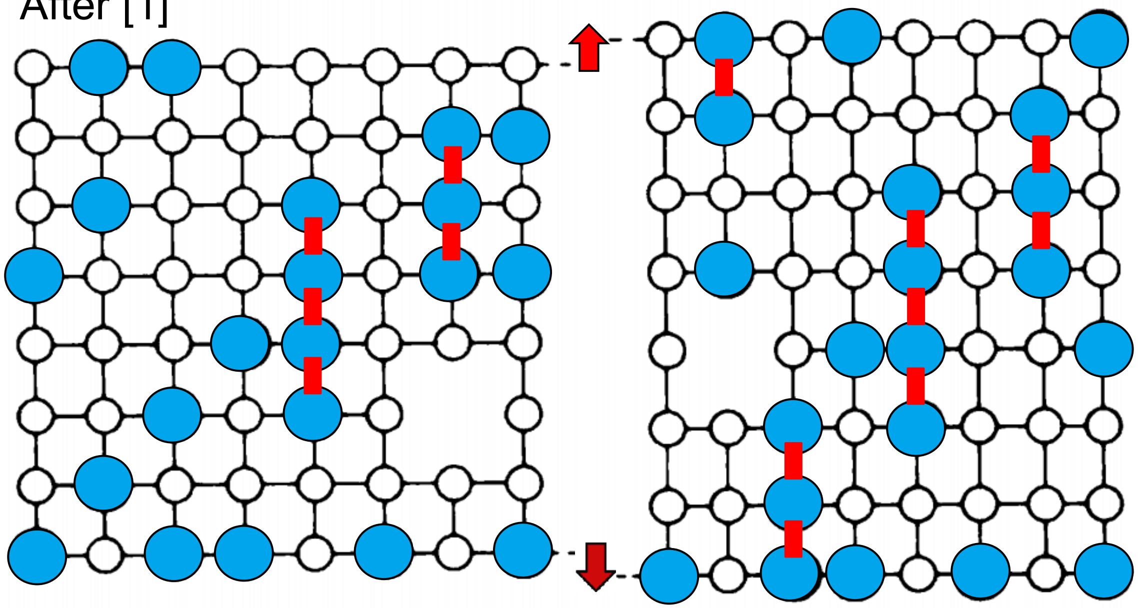
$$Q^{-1} = f/\Delta f$$

- relates to dissipation of energy

Small-Angle Scattering and anelastic Process

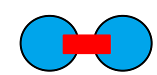
- maybe an anelastic process (**Zener**, Gorsky, Snoek …) :
    - Re-arrangment of atomic order / occupation
    - Know to be prominent in alloys / solid solution
    - Verification **? ? ?**

After [1]



(a) x5 (b) x8

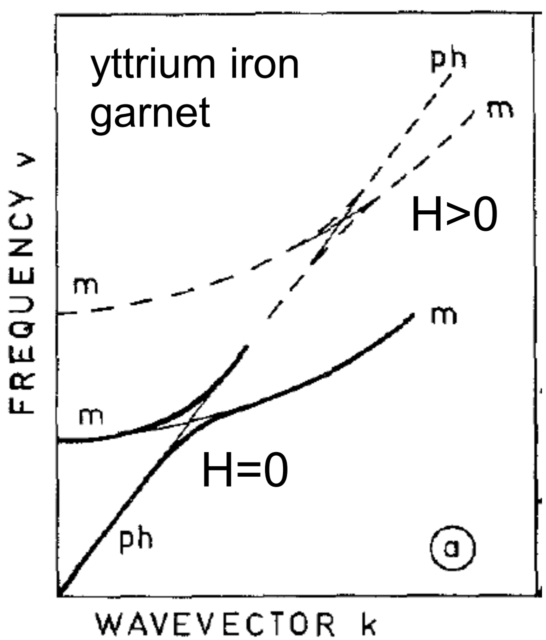
<u>Assumption:</u>
The blue-blue bond is longer than the other bonds



[1] A. Nowick, Anelastic Relaxation in Crystalline Solids, Academic Press, 1972

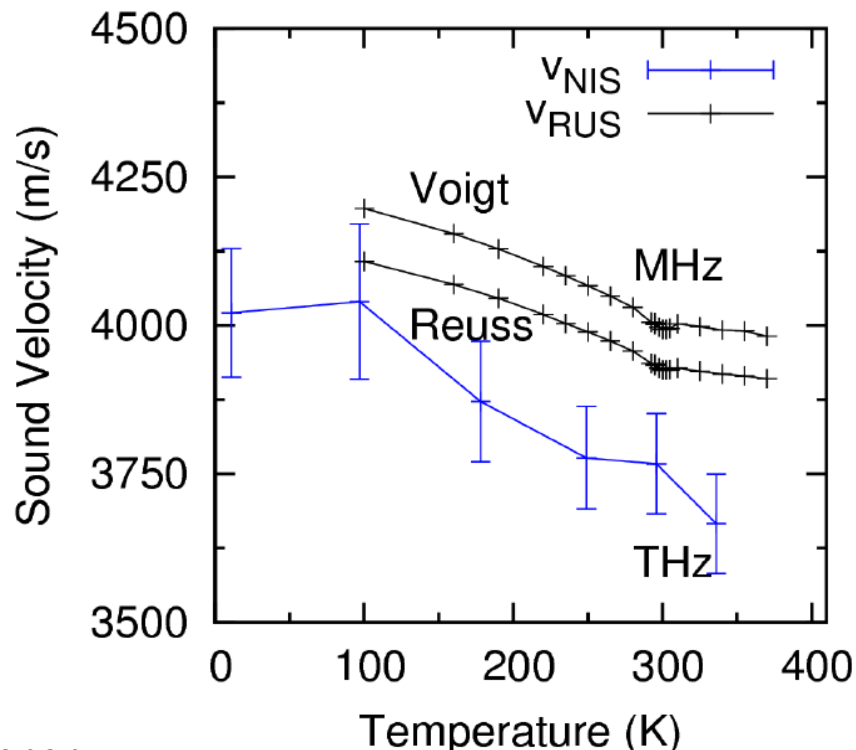
RUS & NIS – Comparison

- Extracted sound velocities do not match
- Magnon-phonon interaction or systematic deviation of methods



[1]

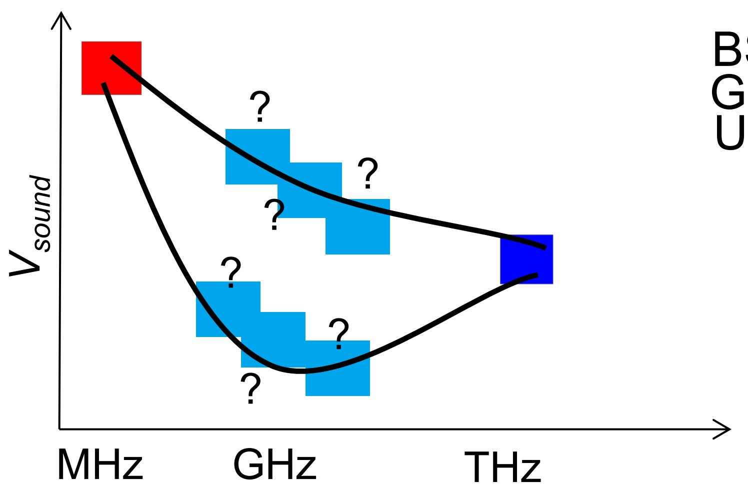
m=magnon, ph=phonon
Thin lines = without coupling
Thick lines= with coupling
Dashed = coupling at higher fields

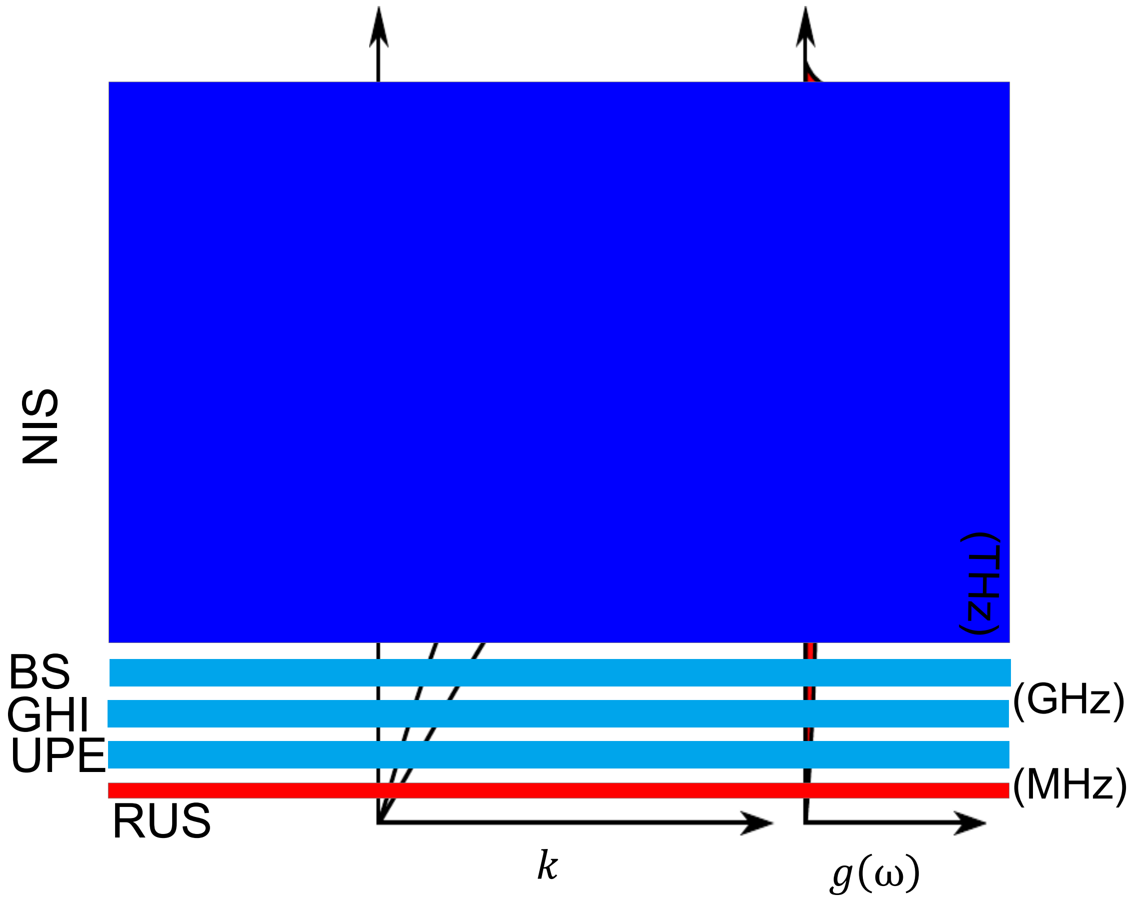


[1] Wettling, Jantz, Appl. Phys. 23, 195 (1980)

Outlook

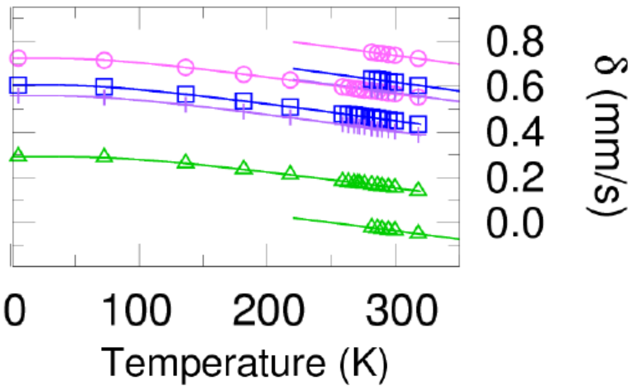
- Ultrasound Pulse Echo (UPE) - MHz to GHz
- Giga-Hertz Interferometry (GHI) - low GHz
- Brillouin Scattering (BS) - GHz





Conclusion

- No influence on iron specific DPS (above 3 meV), entropy estimation reveals: possible change only ~1 %



- Low energy elasticity (MHz) influenced by the magnetic transition, not magnetostriction due to diffraction results and isomer shift

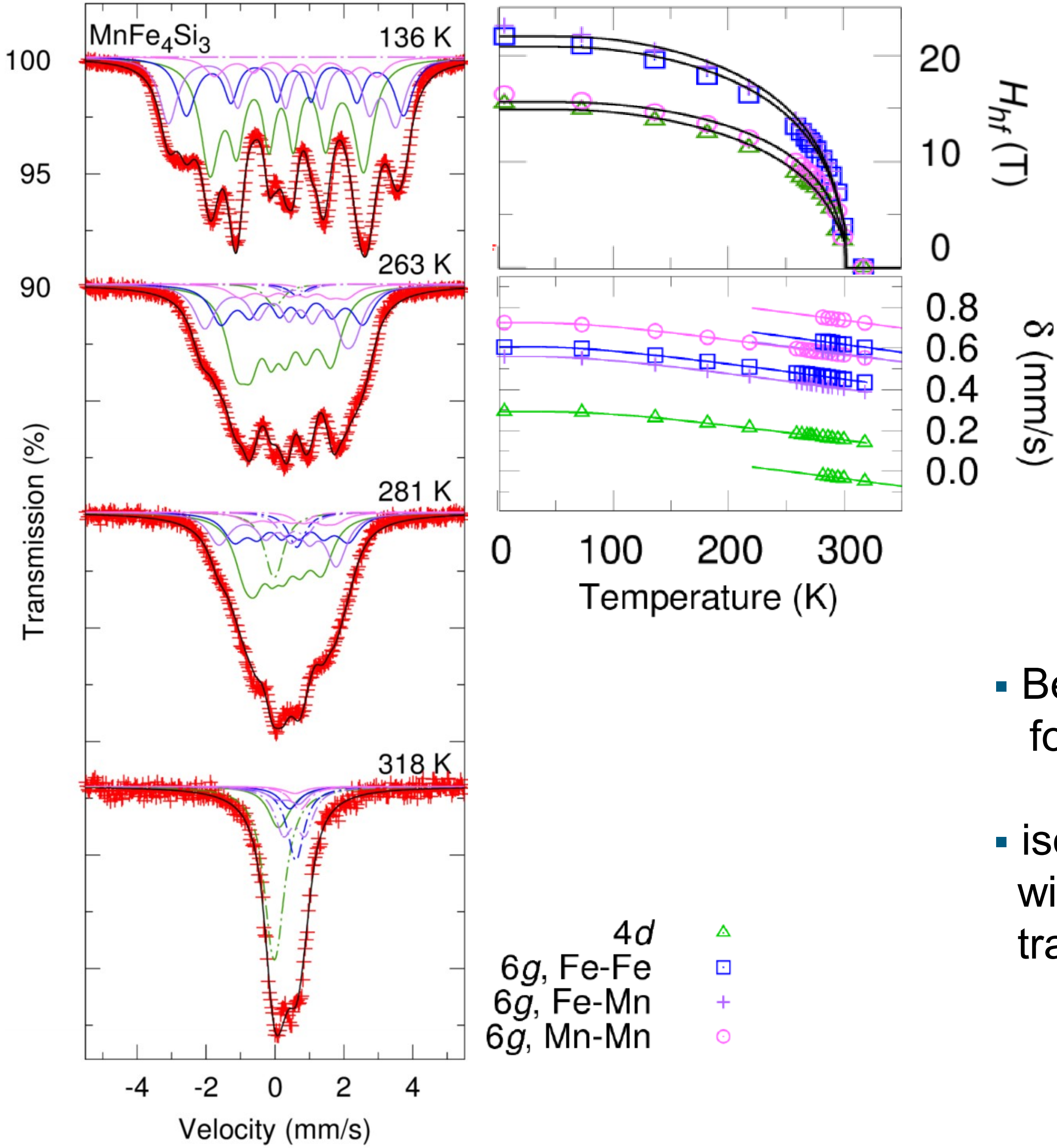
- Difference in the extracted sound velocities possibilities: systematic, spin-phonon interaction

- Transition not second order, more likely tricritical point or complex interplay
  → first order: RUS, heat capacity (lattice)
  → second order: VSM, Mössbauer (magnetism)

- Remark: Conduction electrons influenced by magnetic transition
  → efficiency of MCE could be influenced

Backup $MnFe_4Si_3$

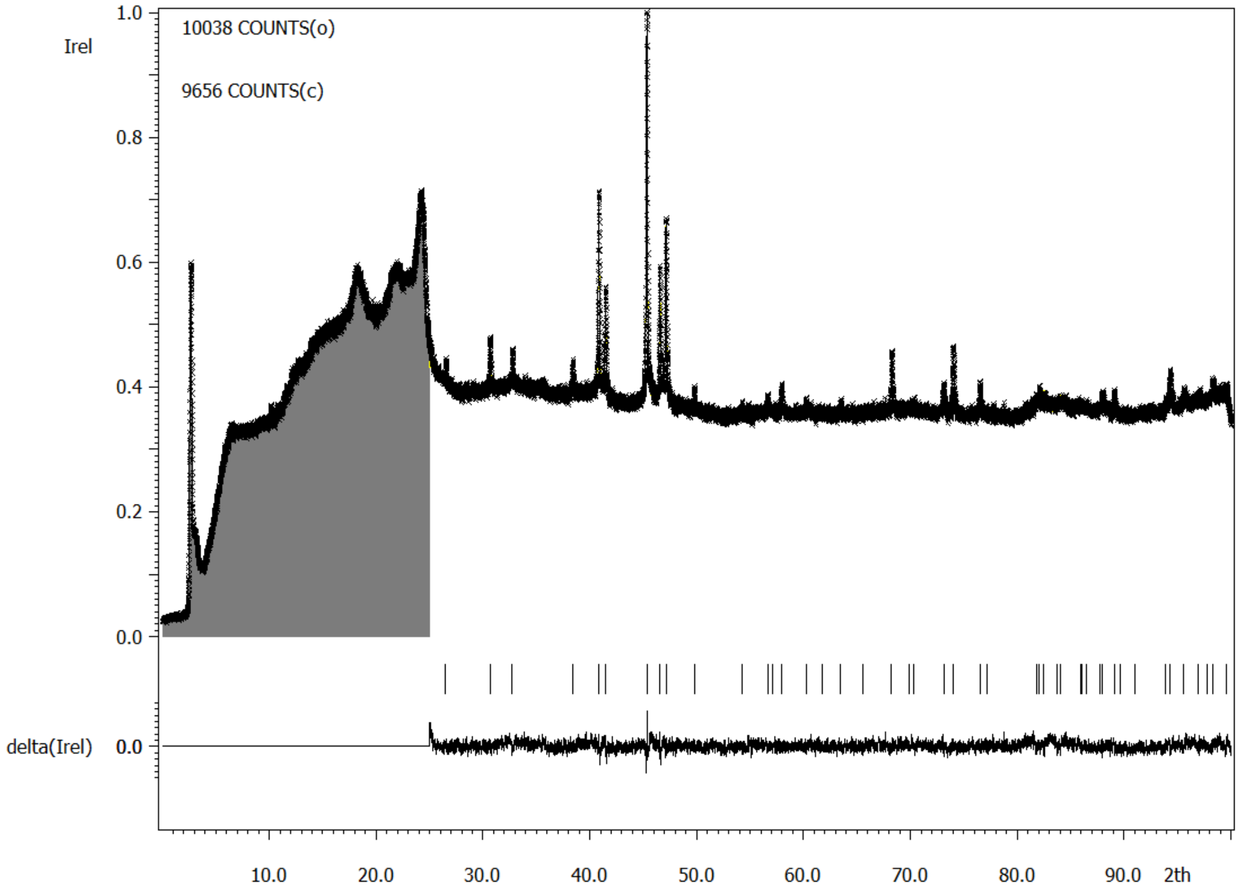
Mössbauer Spectroscopy



- 4 component MB fit (binomial distribution due to occupation)
- Bean and Rodbell fit indicative for second order transition
- isomere shift changes with opposite sign at the transition

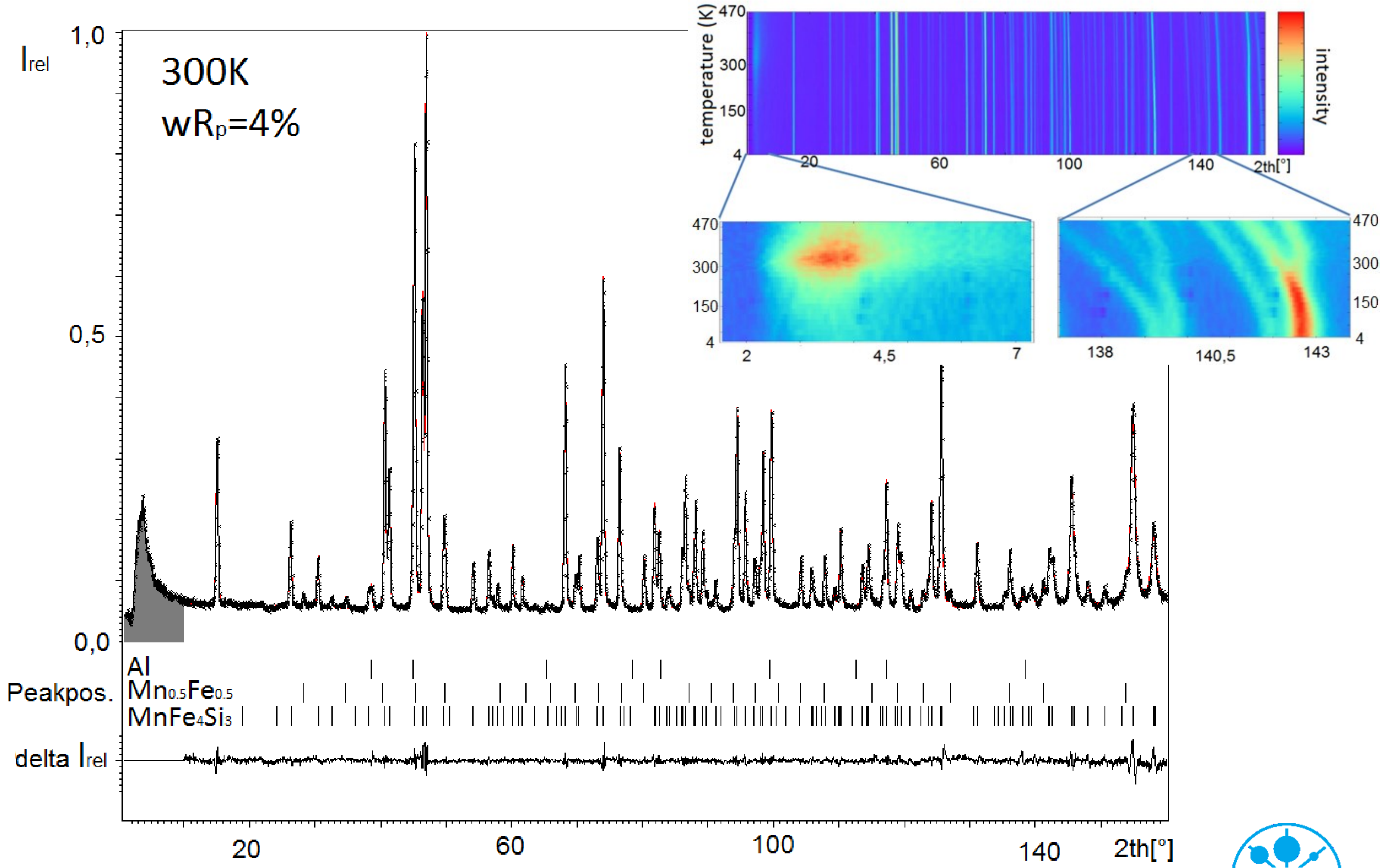
Characterization

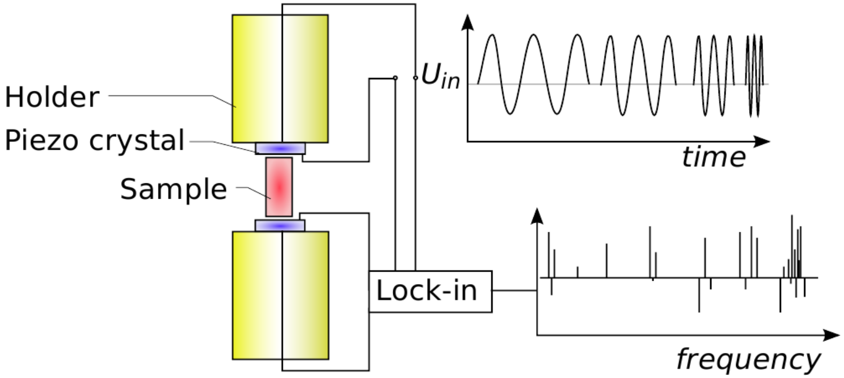
- Paul Hering:
- in-house XRD - x=4, 300K, wR=1.7 (**enriched powder**)



Characterization

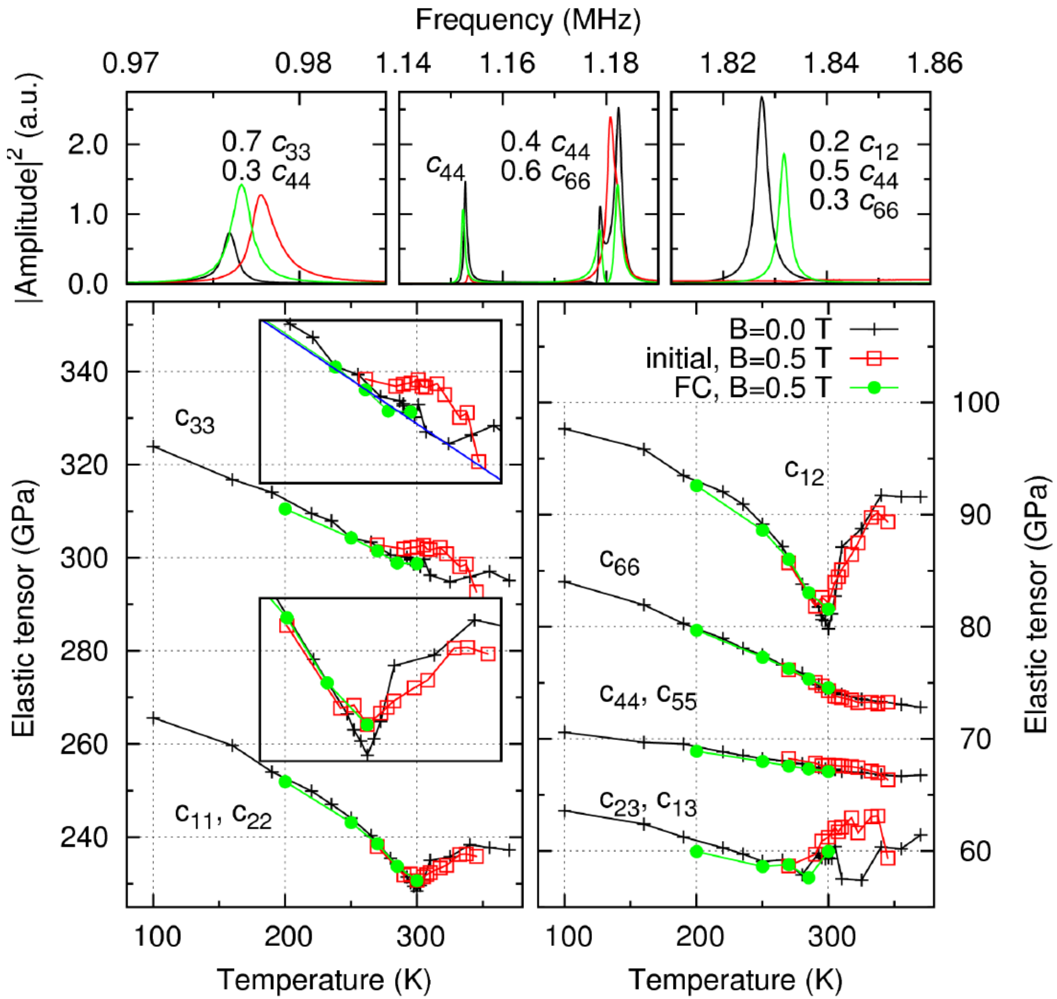
- Paul Hering:
- Neutron Powder diffraction (SPODI), non-enriched powder x=4

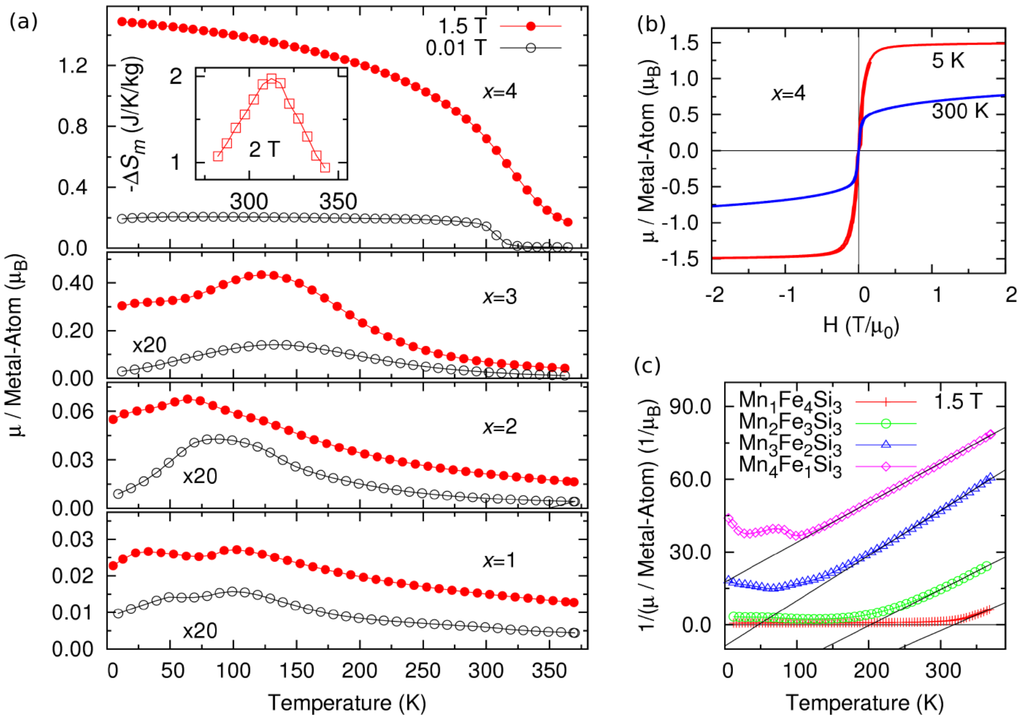




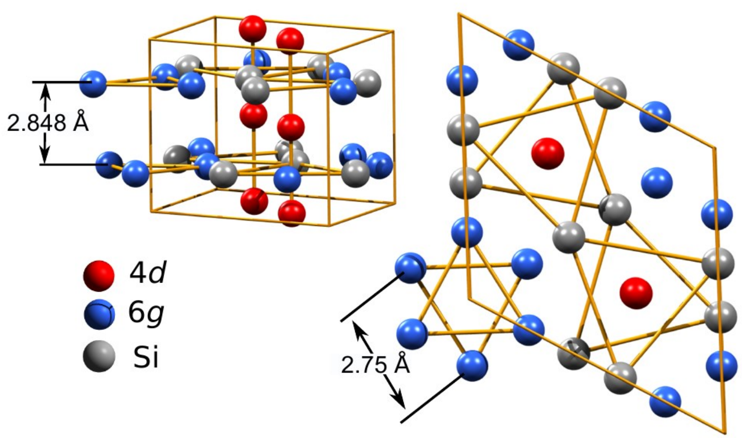
Cubic - long wavelength limit

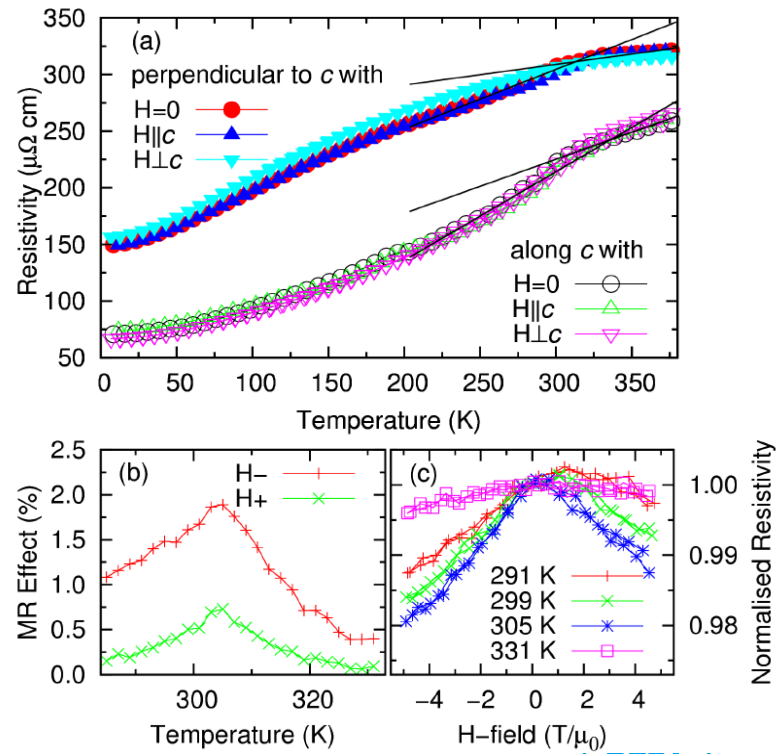
$$\rho\omega^2 = c_{11}k_x^2$$
$$\rho\omega^2 = c_{44}k_x^2$$

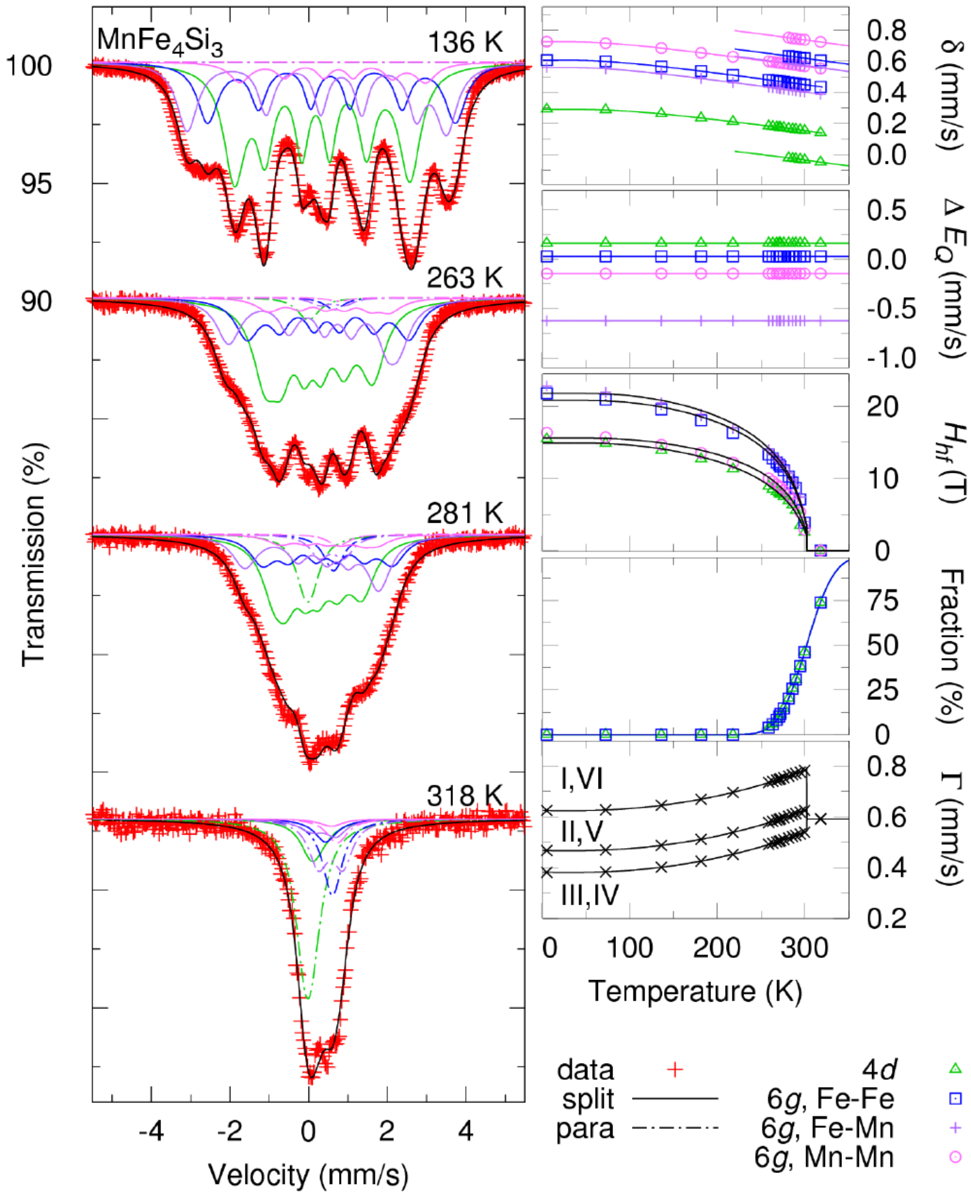




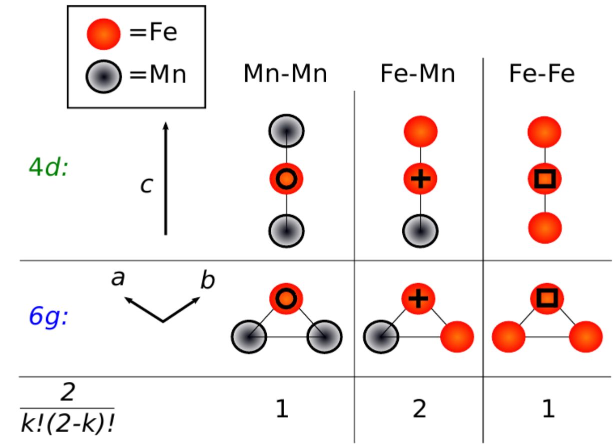
x	θ (K)	μ_{eff} (μ_B)
1	-107(2)	4.3(1)
2	47(2)	4.0(2)
3	203(3)	4.5(2)
4	320(20)	4.8(8)







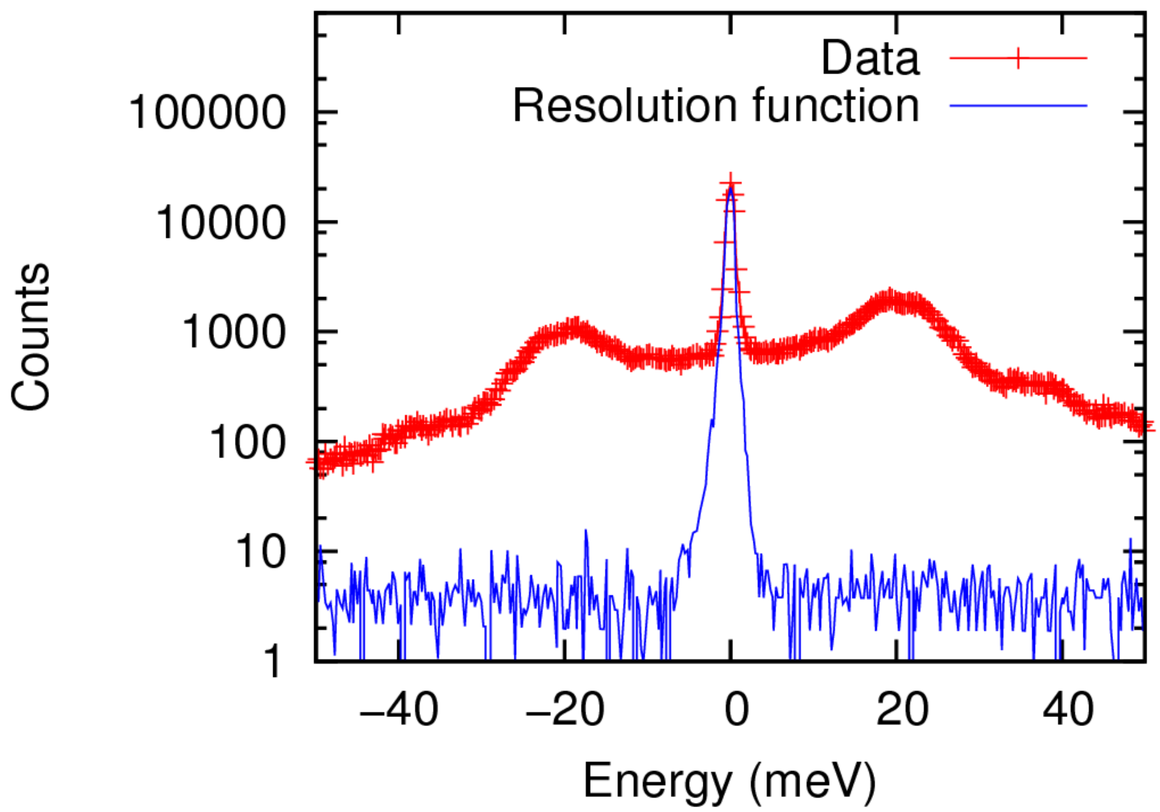
MnFe4Si3
136 K
263 K
281 K
318 K
Transmission (%)
Velocity (mm/s)
δ (mm/s)
ΔEQ (mm/s)
Hhf (T)
Fraction (%)
Γ (mm/s)
I,VI
II,V
III,IV
Temperature (K)
data
split
para
4d
6g, Fe-Fe
6g, Fe-Mn
6g, Mn-Mn



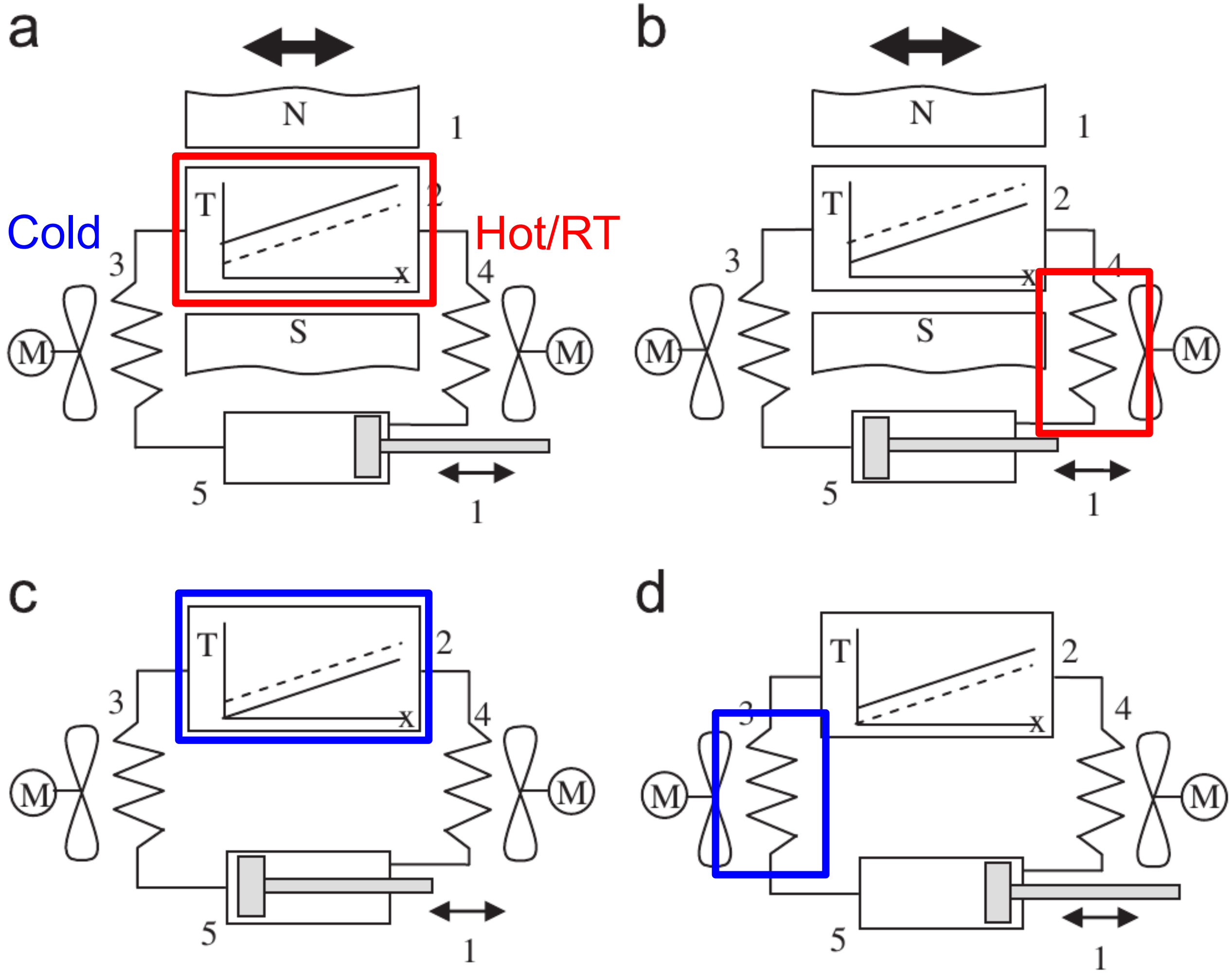
=Fe
=Mn
Mn-Mn
Fe-Mn
Fe-Fe
4d:
c
6g:
a
b
2
k!(2-k)!
1
2
1

NIS

- Subtraction of elastic line



MCE- Refrigeration - Example



a) exchange-liquid heated by MCE
c) exchange-liquid cooled by MCE

b) transporting warm liquid to hot side
d) transporting cold liquid to cold side

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