PAC study of the magnetic and structural first-order phase transition in MnAs

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ISOLDE project 487

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Outline

- MnAs/Motivation
- TDPAC experimental details and results
- Magnetization, XRD results
- Ab-initio calculations
- Conclusion

MnAs

- Studied since 1904

  1904 - F. Heusler, Z. Angew. Chem. 17 260

  1911 - S. Hilpert and T. Dieckmann, Ber. Dtsch. Chem. Ges. A 44 2378 (Ferromagnetic)

  1947 - A. Serres, Journal de Physique et le Radium 8(5):146-151

  1954 - B. T. Willis M and Rooksby H P Proc. Phys. Soc. London B 67 290

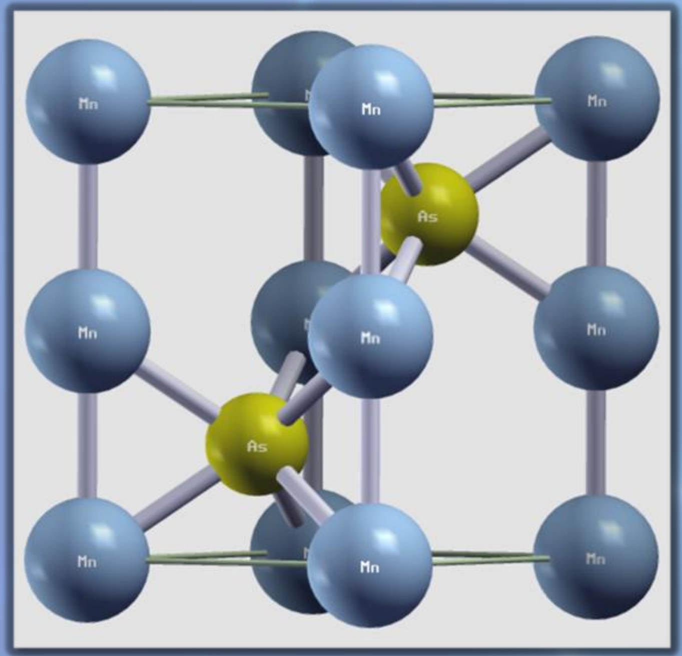
  1962 – C. P. Bean, D. S. Rodbell Physical Review 126(1):104

  ...

- Unusual transition
- Magnetocaloric effect
  (C. Kuhrt *et al.*, Phys. Status Solidi A 91, 105 1985)
- Spin injector for Spintronics
  (Daweritz Rep. Prog. Phys. **69** 2581 2006)
- Magnetoresistance effect
  (J. Mira *et al.*, PRL **90** 09273 2003)
- Spin-Phonon Coupling
  (J. Łazewski *et al.*, PRL **104**, 147205 2010)
- ...

MnAs Phases

Low temperature
Hexagonal structure (NiAs-type)
Ferromagnetic metal

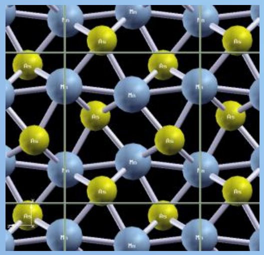


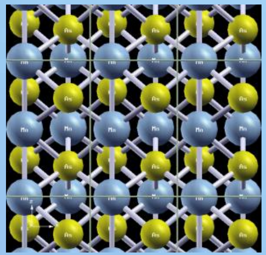
1st order phase transition at 42 C

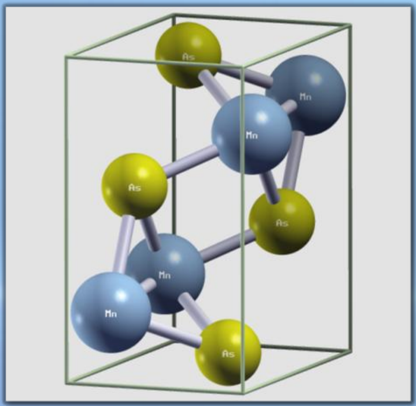
Increasing temperature:

- **2% volume loss**
- **Hexagonal-Orthorhombic**
- **Loss of Ferromagnetism**
- **Increase in resistivity**

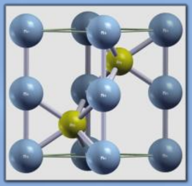
Orthorhombic structure (MnP-type), Paramagnetic(?)



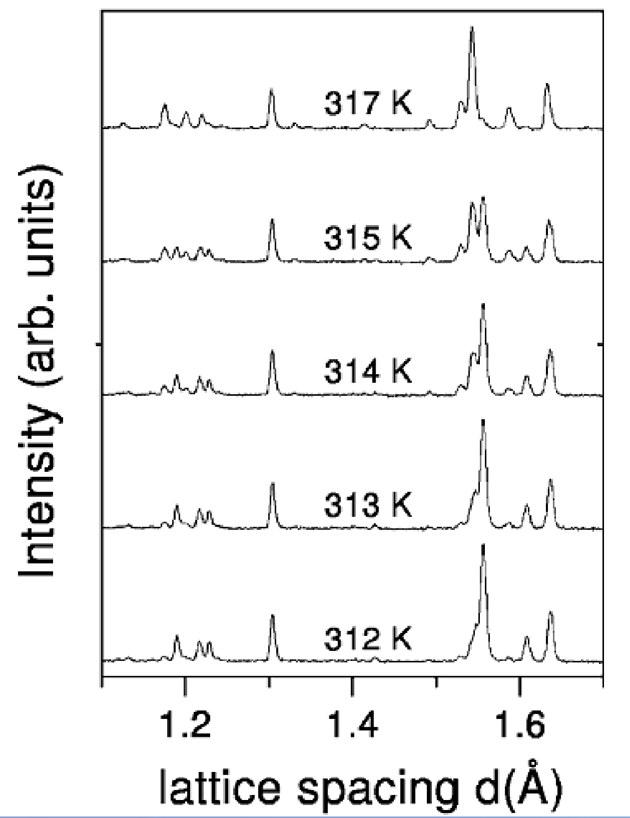


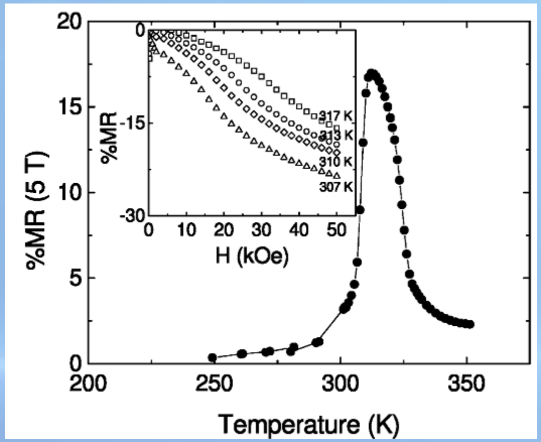


Between 42 C and 120 C the orthorhombic distortions disappear and the structure becomes again hexagonal of NiAs-type, paramagnetic (Curie-Weiss).



Magnetoresistance effect





"Colossal-like" Magneto-resistance

Neutron diffraction measurements and Magneto-Resistance effect.
J. Mira et al., Phys. Rev. Lett. **9** 097203 2009

Hyperfine Interactions in MnAs

Mössbauer

• B. Kirchschlager *et al.*, Physics Letters. 1981;82(1):46-50.
$Mn_{0.75}Fe_{0.25}As$
No hyperfine field.

•M. A. Abdelgadir *et al.*, Physica Scripta **37**(3):373-380(1988)
$Mn_xFe_{1-x}As$, with x=0.01, 0.03 and 0.15.
Hyperfine at the Fe probe is very small, or follows unusual dependence
$T_{C,d}$=2C for x=0.01 .

NMR

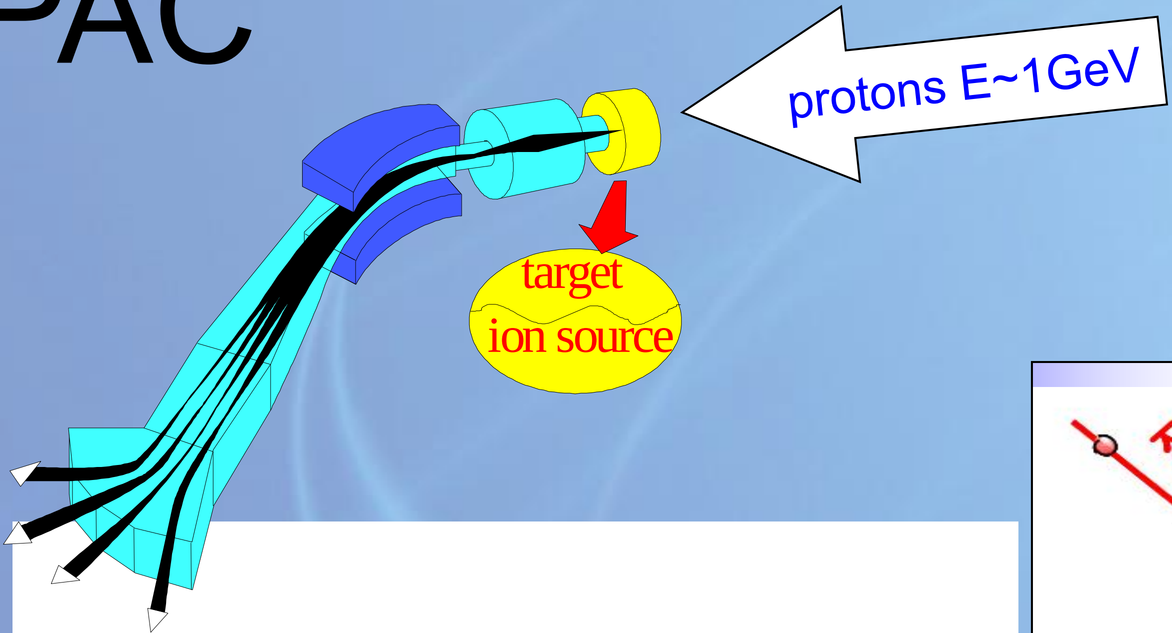
• S. Pinjare and K. Rama Rao, Journal of Magnetism and Magnetic Materials, 30, 27 (1982)
Double signals from Mn and As, attributed to nuclei at edge and centers of domain walls.
Anomaly at -50 C, due to atoms at domain walls.

Perturbed Angular Correlations

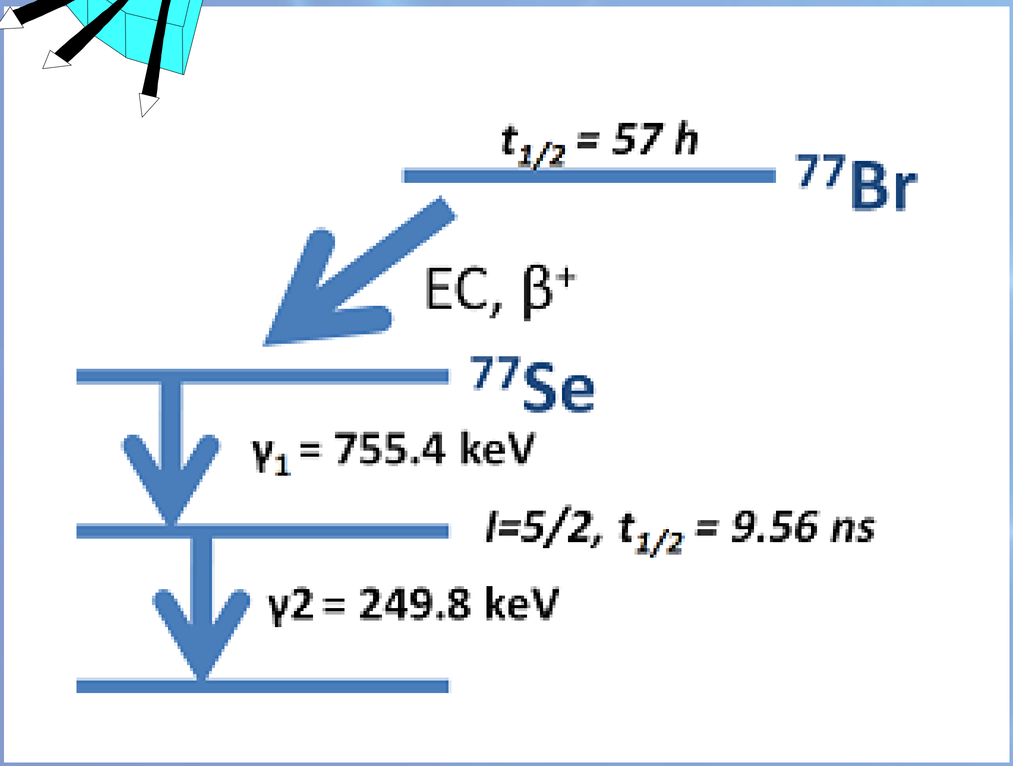
• Radioactive beam of selected isotope probes, implanted in the sample in vaccum

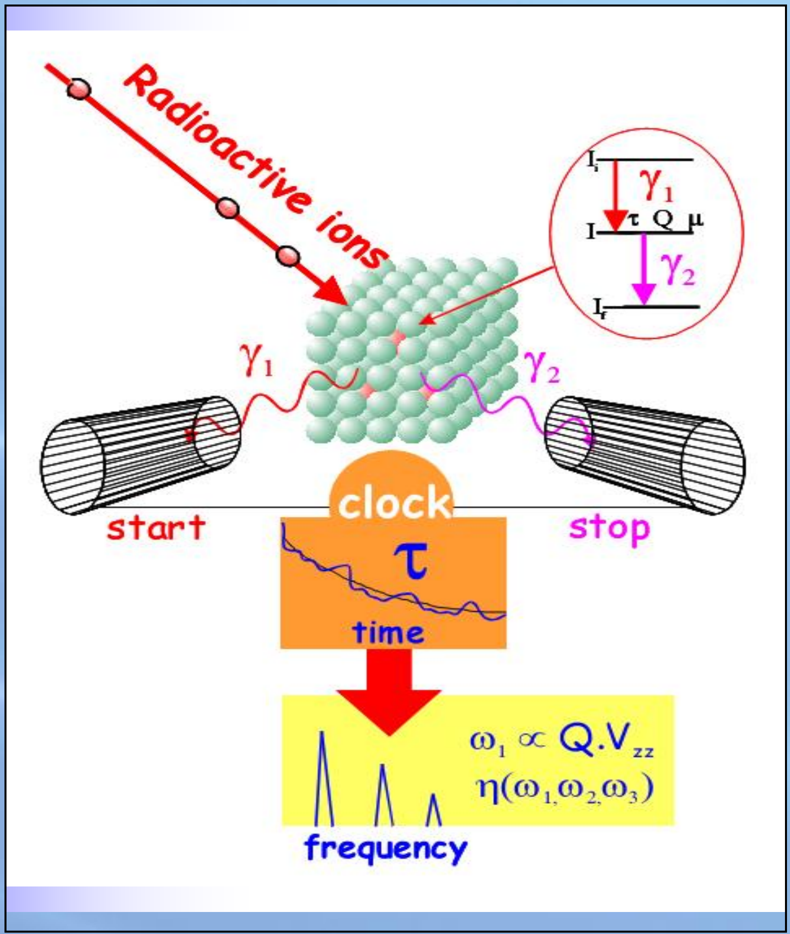
• Highly diluted concentrations of probes (parts per million)

PAC



CERN's Proton-Synchroton Booster





Quadrupole electric moment interacts with

Electric Field Gradient (EFG)

$V_{zz}(10^{21}\ V/m^2)$

$\eta=|V_{xx}-V_{yy}|/V_{zz}$

Magnetic dipole moment with

Magnetic Hyperfine Field B_{hf} (T)

MATERIAL SPECIFIC

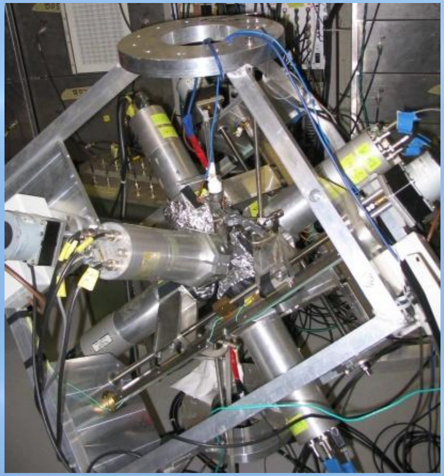
Interaction Frequencies:

$$\nu_Q = eV_{zz}Q/h$$

EXPERIMENTAL OUTPUT

$$\omega_L = Bg\mu_{nuc.}/\hbar$$

•Local scales of length (nm or Å) and time (ns)



Numerical fit of the hamiltonian of the hyperfine interactions.
All the fit parameters have physical meaning:

ω_0, η, ω_L,,σ

ω_0: frequency of the electric quadrupole interaction

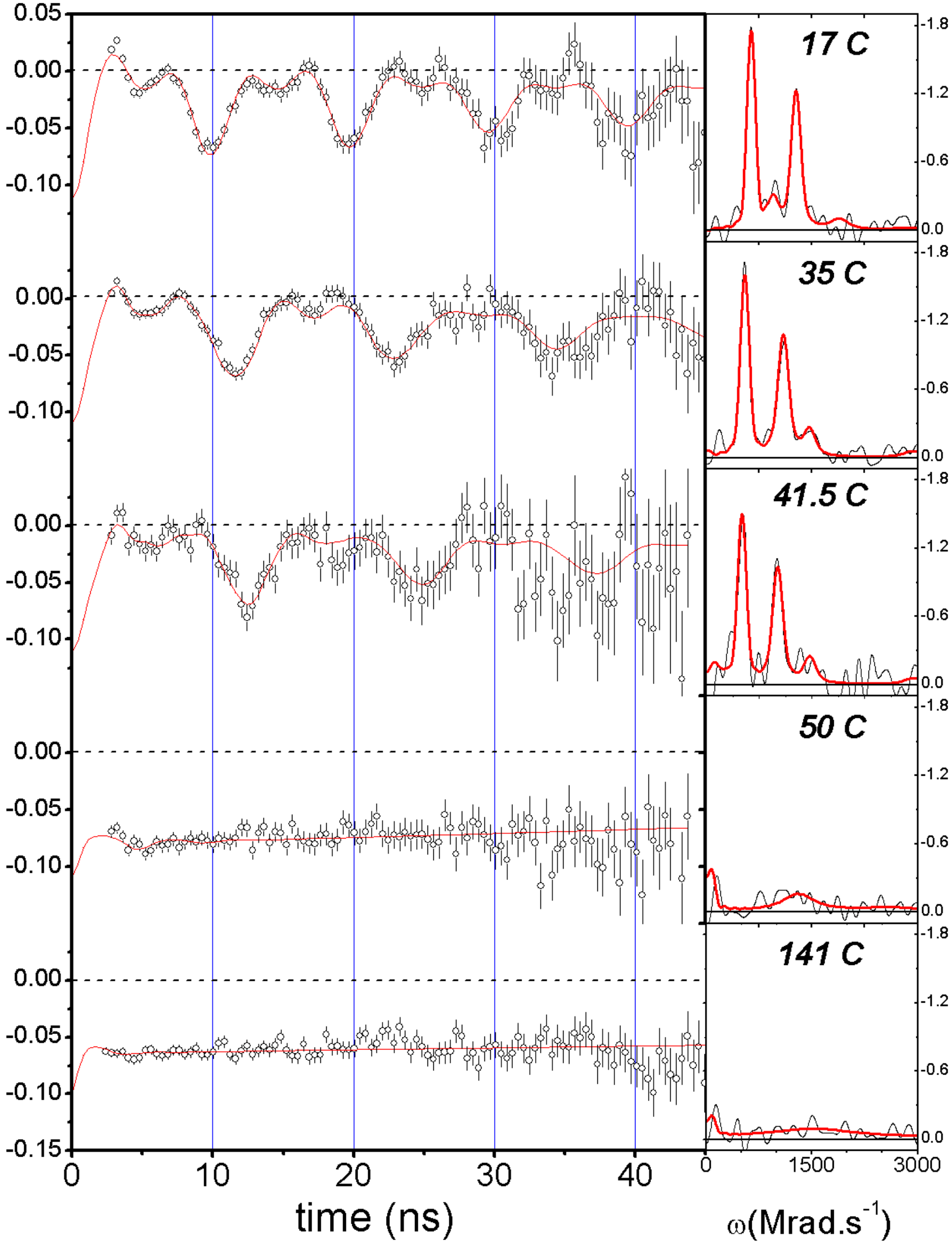
η : axial asymmetry parameters of electric quadrupole interaction

ω_L: frequency of the magnetic dipole interaction

σ: damping of the perturbation spectrum is simulated by a Lorentzian function of width σ

Heating

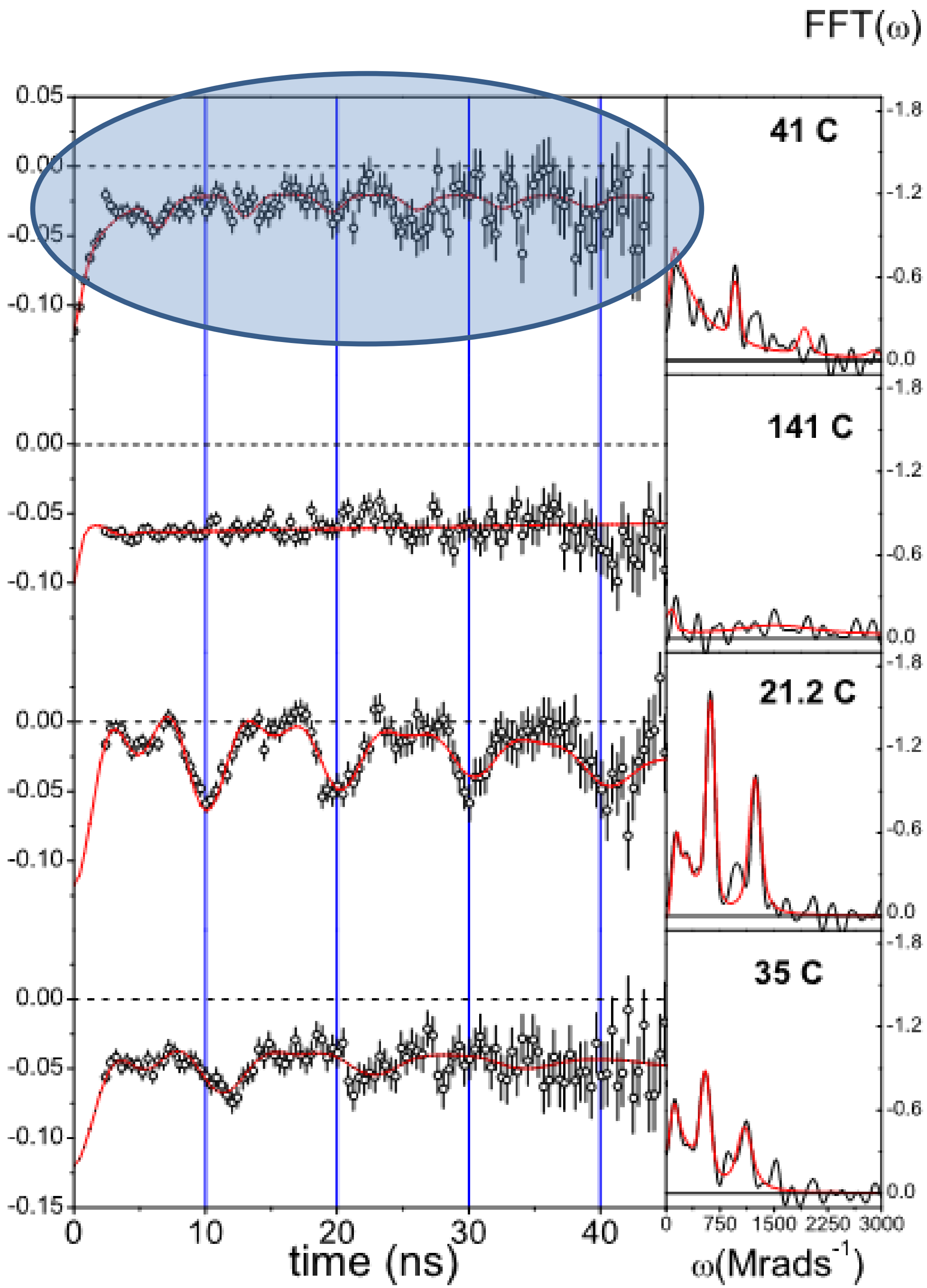
(chronological order)



- Ferromagnetic phase: nuclei interacting with a magnetic hyperfine field; EFG is too small to be resolved (< 1 x 10^{21} V/m^2).

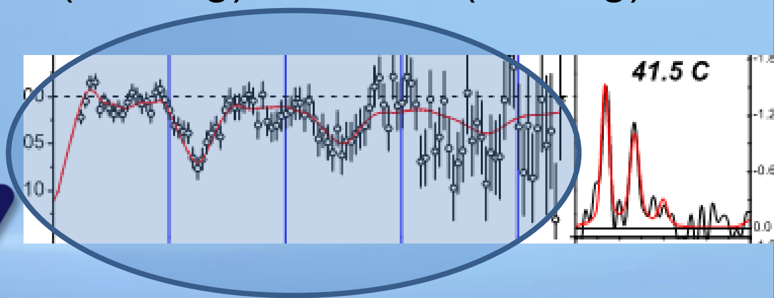
- Orthorhombic Phase: low electric field gradient (less than 1.1 x 10^{21} V/m^2)
- $\eta=0$

- For all cases, a constant fraction of nuclei interacting with a higher EFG must be considered, which we attributed to defects which were not annealed.



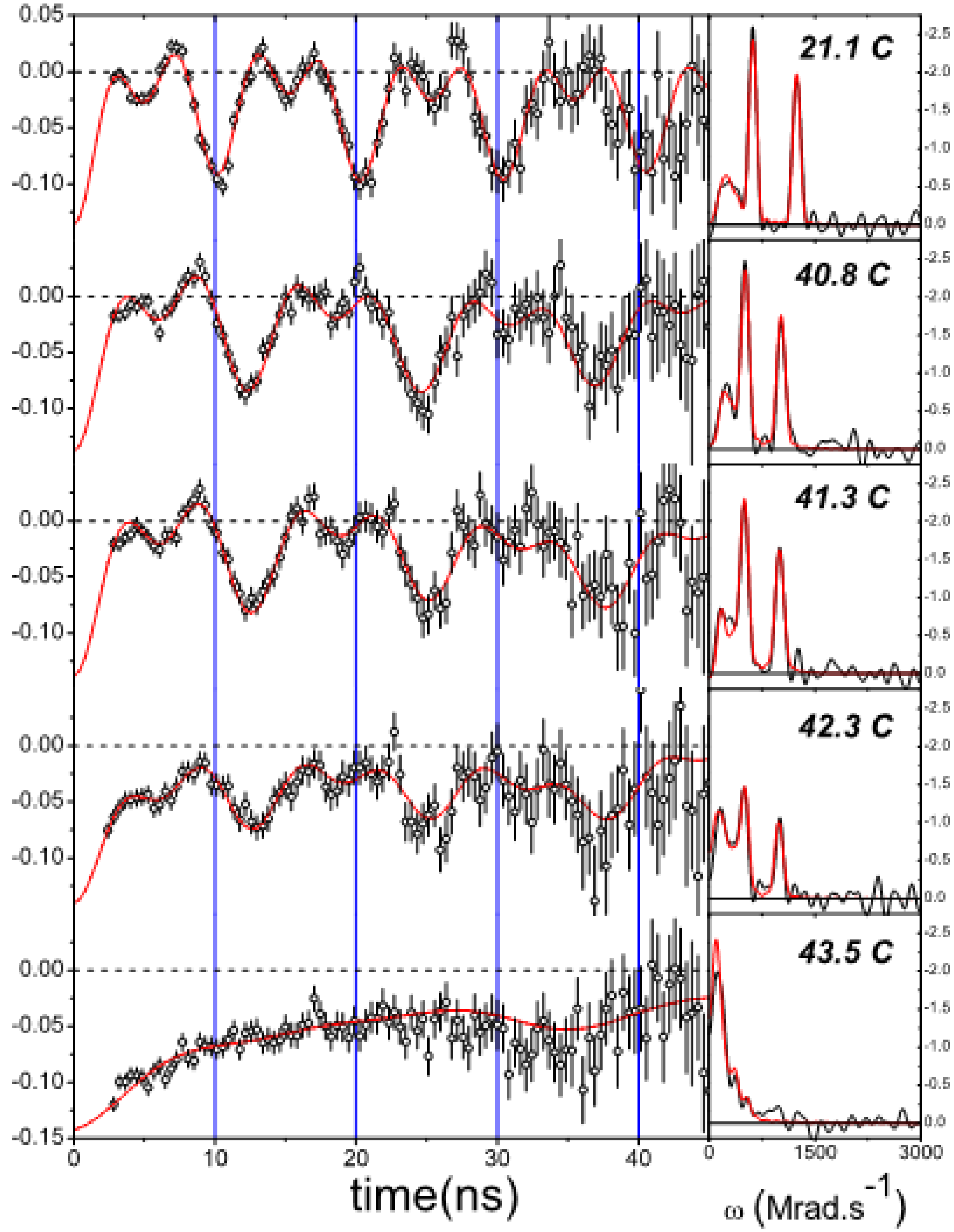
•141 – Above the second order transition. Continues with low V_{zz} and no MHF.

• Hysteresis clearly seen when comparing with previous 41.5 C (heating) with 41 C(cooling).Hel



Between 21.2 and 35 C the sample was heated to 100 C.

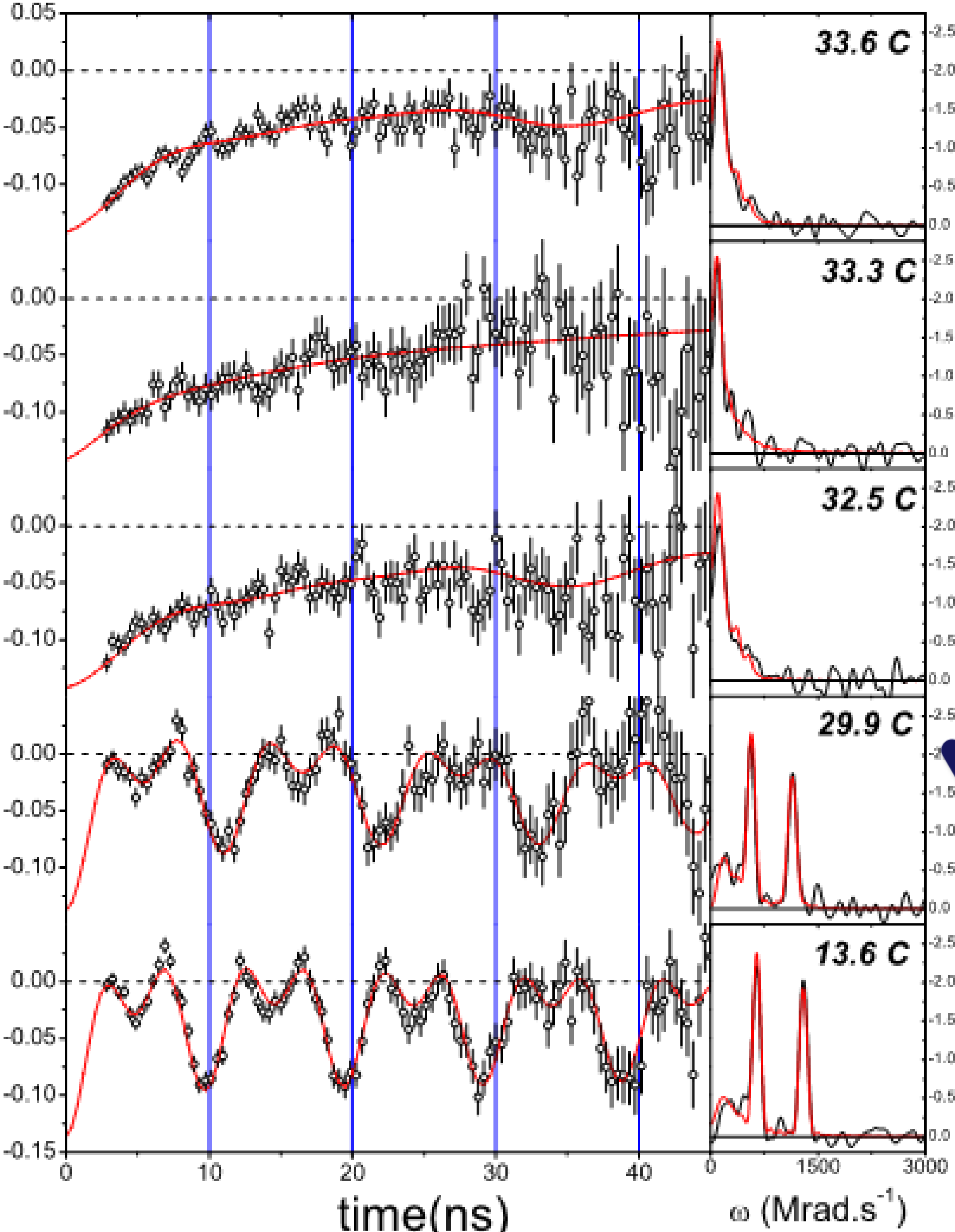
2nd set of experiments
First-order Transition



- 21.2, 40.8, 41.4: fraction of Hyperfine magnetic field (B) 70%

Within 1 C, the hyperfine field fraction disappears, but the hyperfine field is still large at 42.3 C, where phase coexistence is seen.

- Including am EFG in fits of all the spectra. Constant EFG, with constant fraction 30%. Accounts for perturbed environments remaining after annealing.



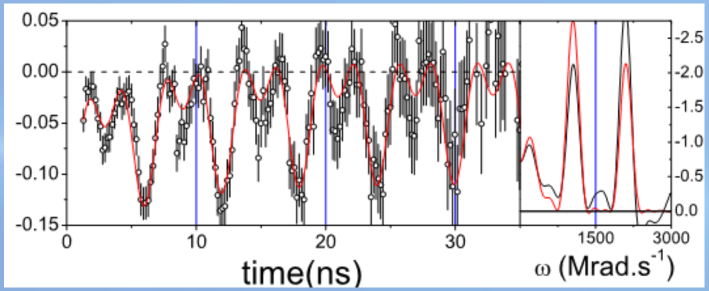
- Entering low T phase with $T_{C,d}$(Curie temperature when decreasing T) 10 degrees lower than $T_{C,I}$.

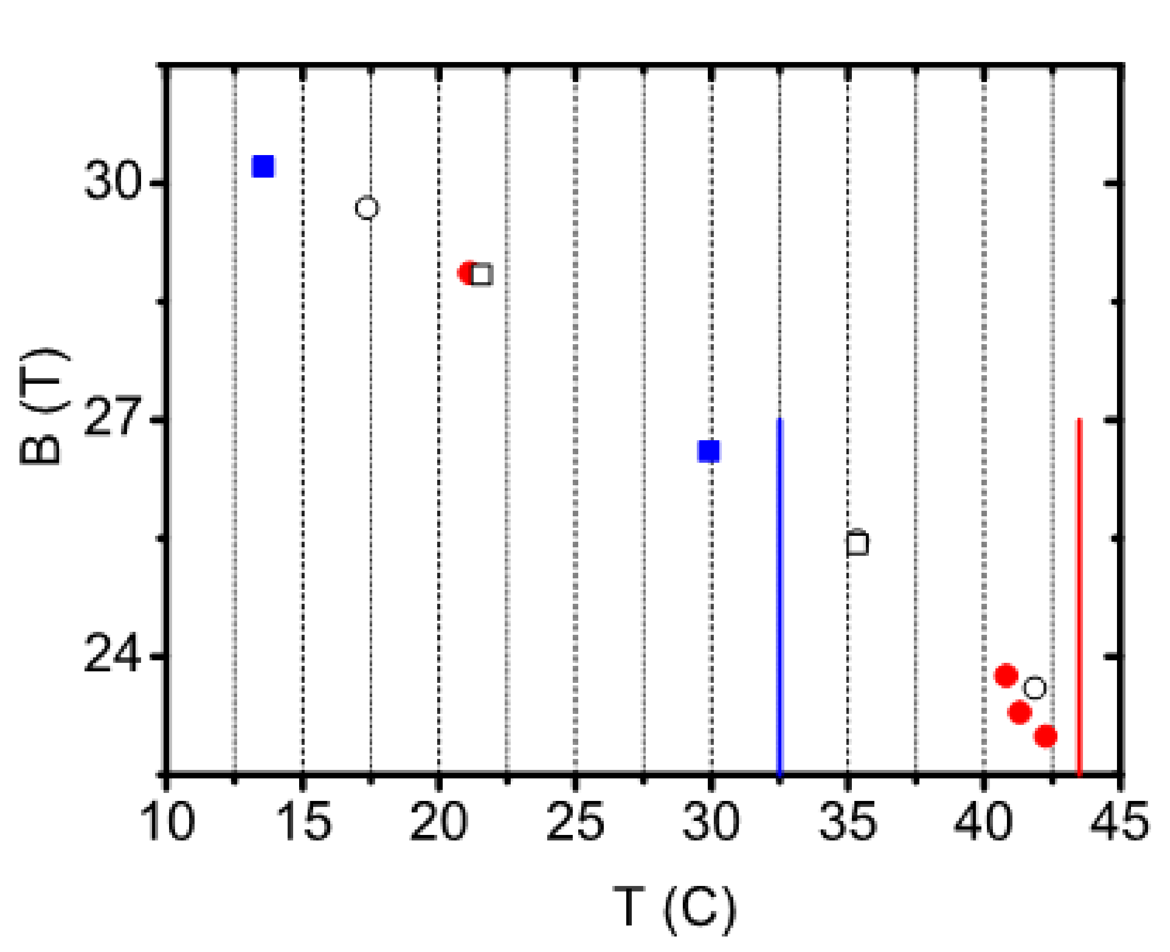
Fit parameters

$T(^\circ C)$	f_1	ω_{L1}	σ_1	f_2	$\omega 02$	σ_2	f_3	ω_{03}	σ_3	
21.1	70	619	3	-	-	-	30	176	23	
40.8	70	510	9	-	-	-	30	176	22	H
41.3	70	499	12	-	-	-	30	176	18	
42.3	40	495	10	30	28	20	30	176	10	H+O
43.5	-	-	-	70	28	24	30	176	9	
124.5	-	-	-	70	28	26	30	176	27	
41.4	-	-	-	70	28	36	30	176	17	
39.5	-	-	-	70	28	46	30	176	24	O
37.5	-	-	-	70	28	47	30	176	22	
34.5	-	-	-	70	28	29	30	176	14	
33.3	-	-	-	70	28	197	30	176	73	
32.5	-	-	-	70	28	20	30	176	11	
29.9	70	571	9	-	-	-	30	176	48	
13.6	70	648	4	-	-	-	30	176	98	H
-196	70	1050	0	-	-	-	30	57	29	

- The attenuation of the hyperfine field (σ_1)increseases towards the phase transition, and decreases when going away from the transition.

Dynamic processes near the transition such as spin fluctuactions may be responsible for this increase of attenuation.



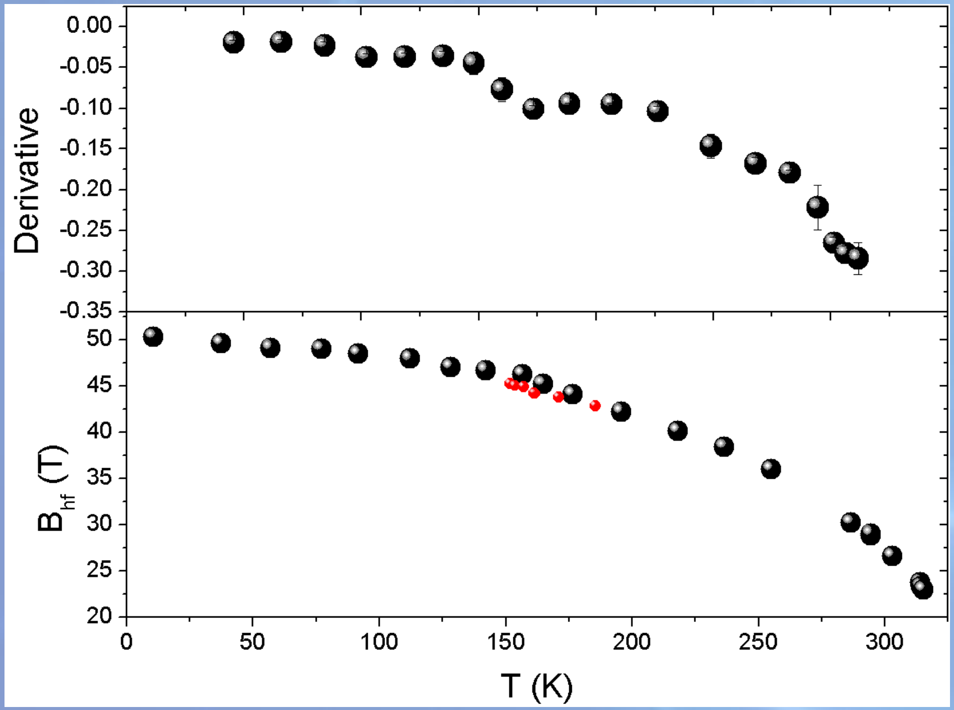


$T_{C,i}$ = 42.3-43.5 C
$T_{C,d}$ = 30-32.6 C
$\Delta T_{hysteresis}$ = 9.7-13.5 C

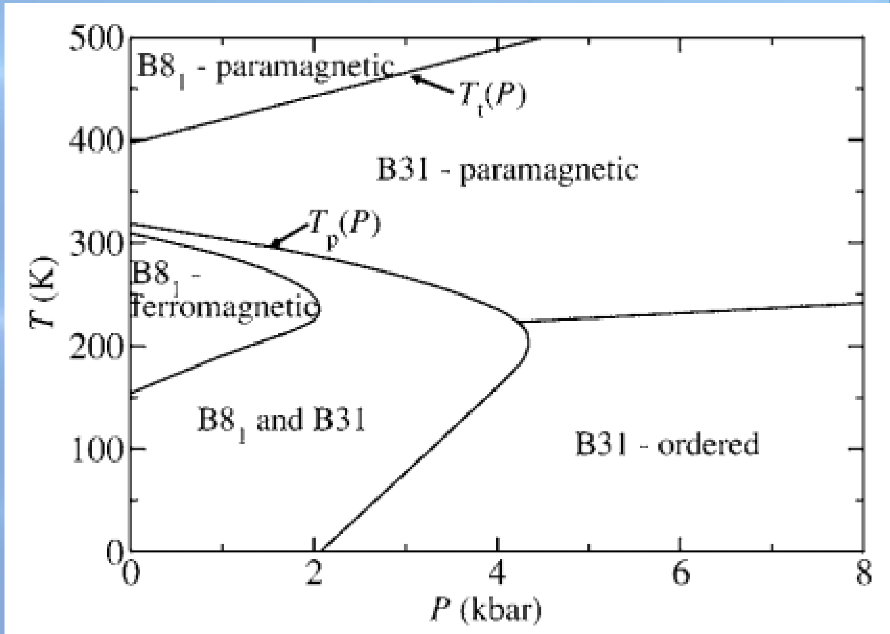
At a given T, the hyperfine field is the same, irrespective of cooling or heating the sample.

Red: heating
Blue: cooling
White: previous experiments

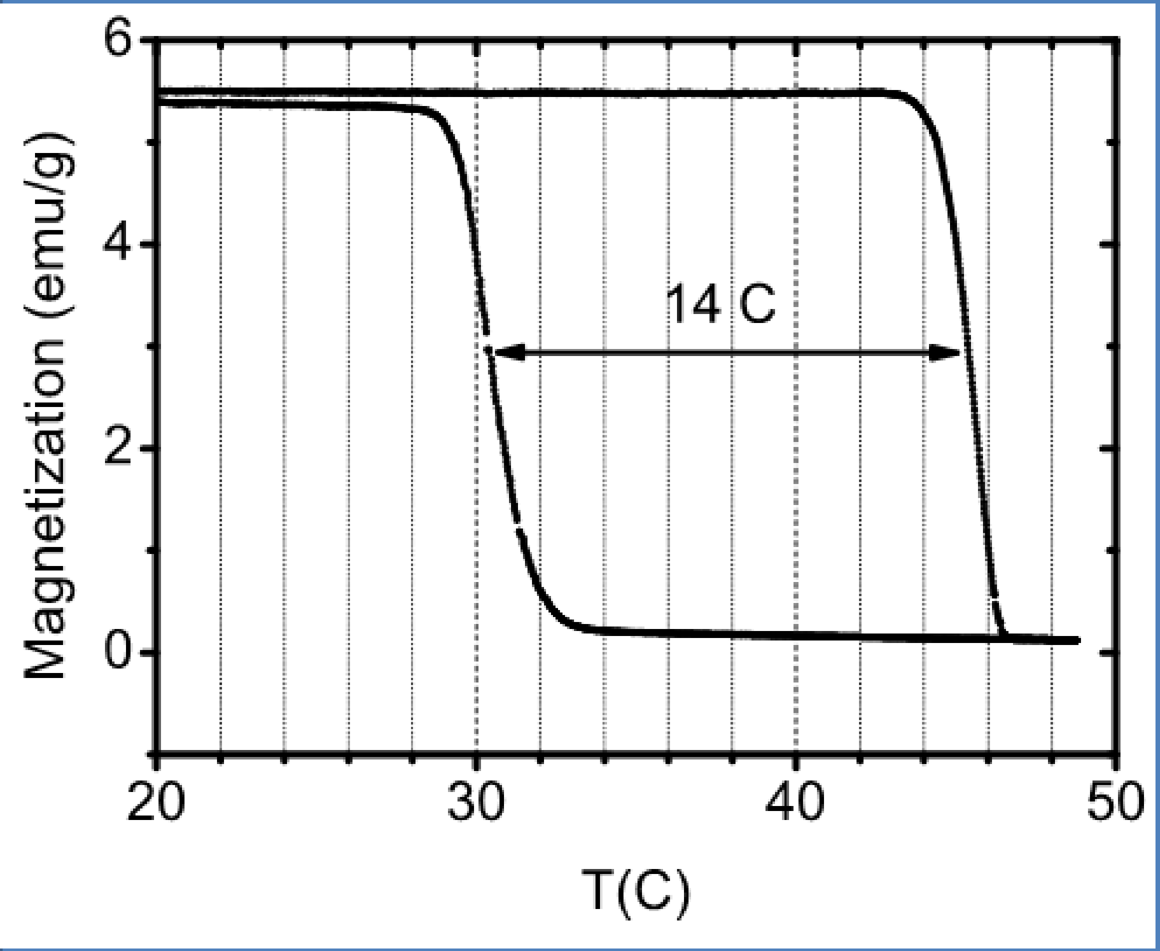
Low temperature PAC measurements



- There is a change of the MHF derivative around 140 K.
- Hyperfine field also shows anomalous measurements at that region.

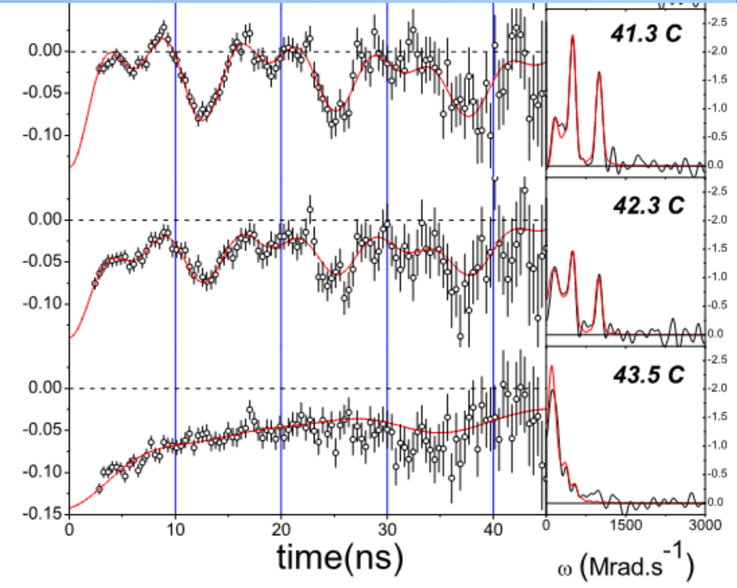


Magnetization



Transition width = 2-3 C
$T_{C,i}$ = 42 C
$T_{C,d}$ = 32 C

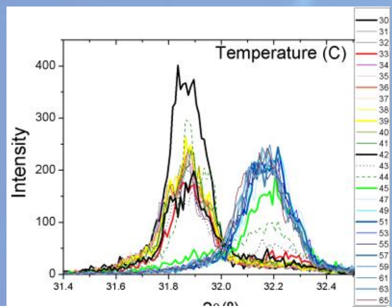
PAC: 41.3, 42.3, 43.5 C



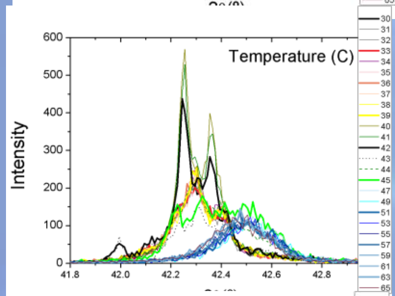
PAC: $\Delta T_{hysteresis}$ = 9.7-13.5 C

X-ray diffraction

Measurements on three 2θ ranges, 31.4-32.6, 41.8-43 and 48.6-50º.



(101)



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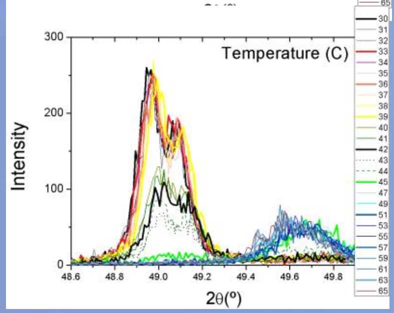
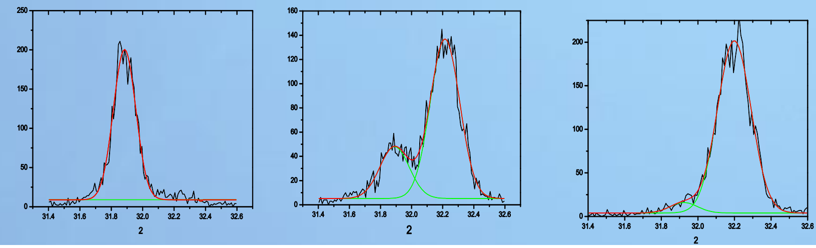
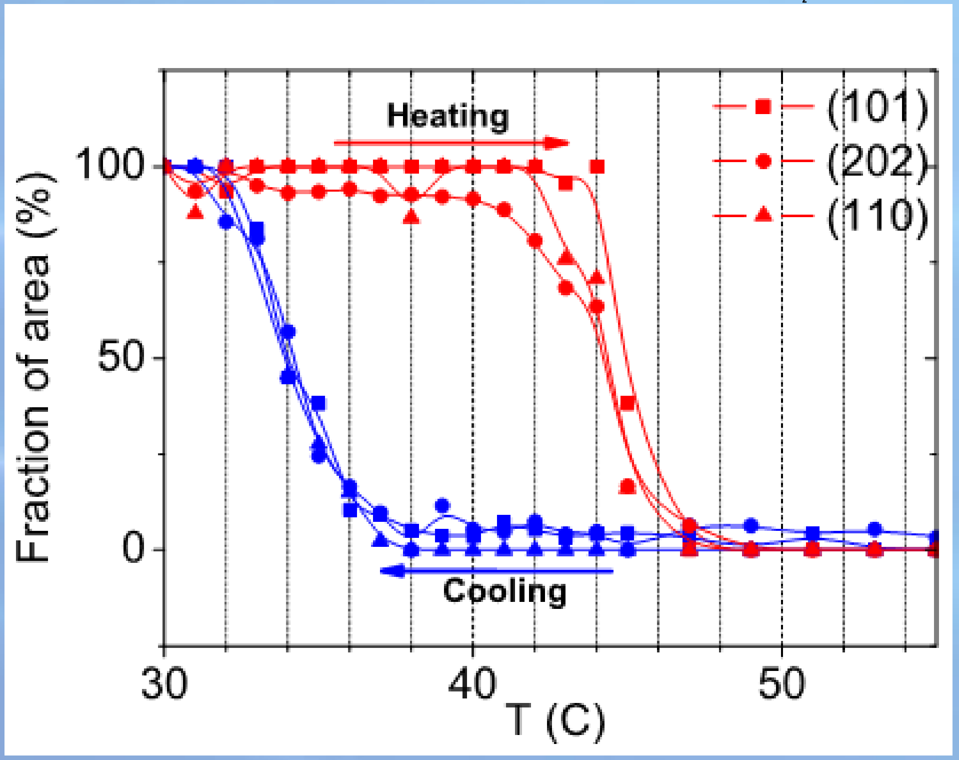


(110)





Density Functional Theory Calculations

Wien 2k code
P. Blaha et al., TU Vienna

Basis APW+lo /LAPW.

Periodic - Supercells to include probes in small concentrations

Optimization of structural parameters, by minimization of total energy or calculated forces.

Generalized Gradient Approximation (PBE)
LDA gives poor results for MnAs (Zhao et al., Phys. Rev. B 35, 113202)

Spin-polarized calculations (collinear), Ferromagnetism due to Mn atoms at the hexagonal phase.

Hyperfine Parameters – pure MnAs

Atom	$V_{zz}(10^{21}V/m^2)$	η	V_{zz} dir.
Mn	-3.63	0	(0,0,1)
As	1.53	0	(0,0,1)

Atom	B_C	core	valence
Mn	-6.5	-39.3	32.8
As	25.0	0.4	24.5

Exp. Room Temperature lattice constants

Calculations are exact only for T=0 K

Atom	B_C	core	valence
Mn	-6.1	-38.7	32.5
As	25.5	0.4	35.1

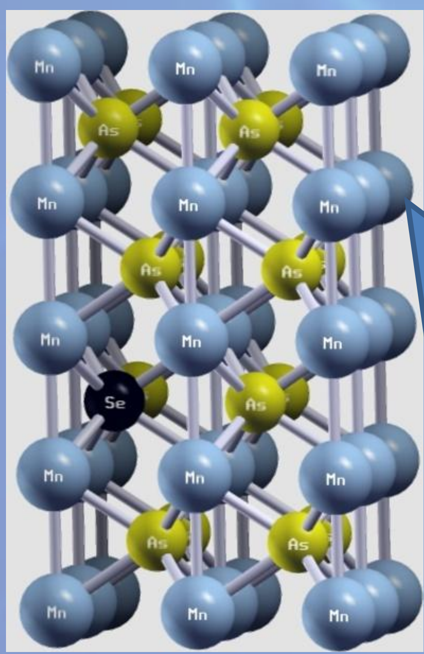
Exp. Low temperature lattice constants

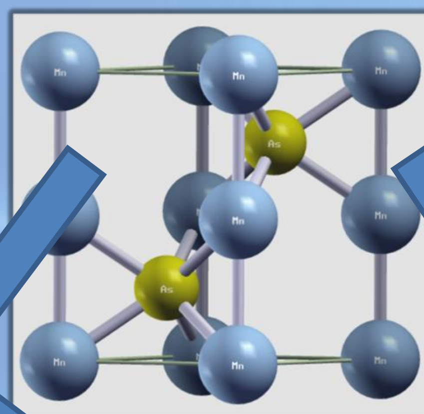
Supercells

• We consider the Se probe at the possible substitutional sites (As/Se)

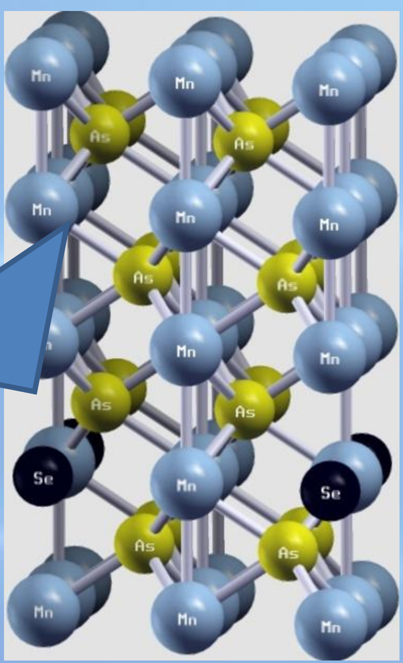
$MnAs_{1-x}Se_x$ $Mn_{1-x}AsSe_x$

$MnAs_{15/16}Se_{1/16}$





$MnAs_{1/16}Se_{5/16}$

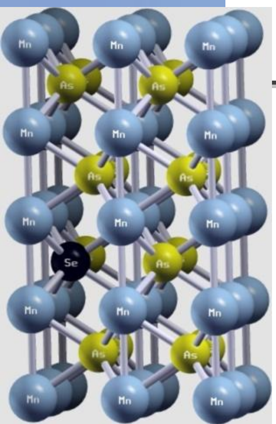


Hyperfine Parameters

Concentration: 1/16 of As atoms are subsituted by Se atoms

V_{zz} exp. ~ 0

B_{hf}. exp. ~ 50 T

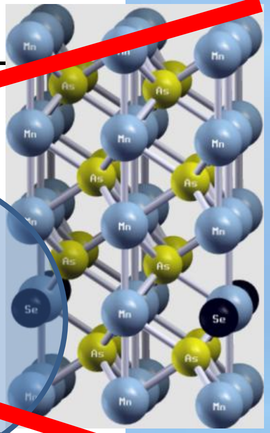


Se at As site		
$V_{zz}(V/Å^2)$	η	V_{zz} dir.
-2.7	0	(0,0,1)

B_C	core	valence	B_{orb}	B_{dip}	B_{hf} total
56.6	0.4	56.2	-2.1	-0.2	54.3

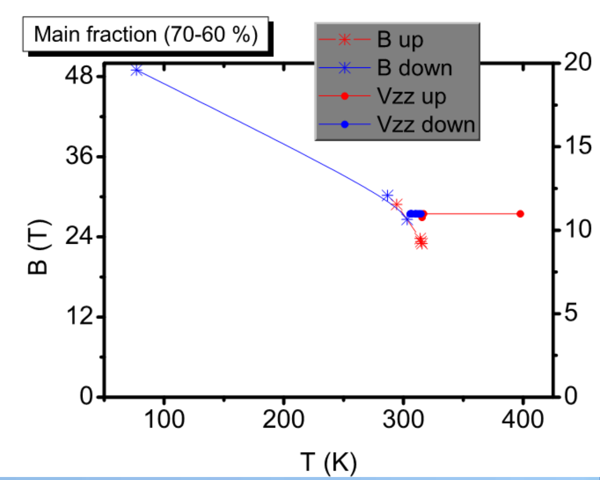
Se at Mn site		
$V_{zz}(V/Å^2)$	η	V_{zz} dir.
178.0	0	(0,0,1)

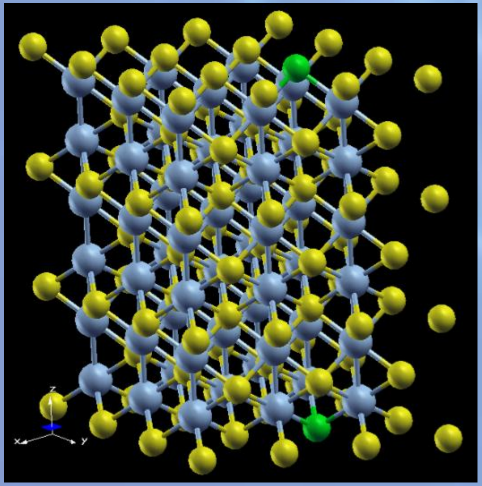
B_C	core	valence	B_{orb}	B_{dip}	B_{hf} total
-23.1	-22.9	-0.2	3.4	-1.8	-21.5



Hyperfine Parameters

Is the concentration low enough to reproduce the diluted impurity (parts per million) experimental situation?





x	V_{zz} (V/Å^2)	B_{hf} (T)
1/16	6	58
1/64	3	76

Hyperfine Parameters

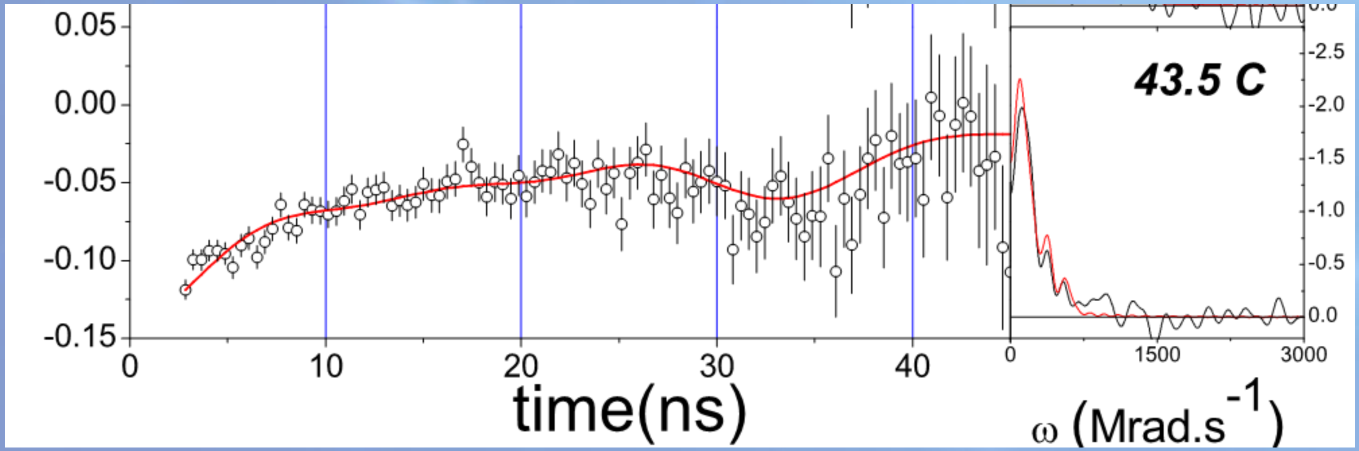
- What is the favorable site for the probe in the orthorhombic phase?

$MnAs_{47/48}Se_{1/48}$

V_{zz} (10^{21} V/Å^2)
-1.0

$Mn_{47/48}AsSe_{1/48}$

V_{zz} (10^{21} V/Å^2)
15.3



V_{zz} ~ 11 V/Å^2

Heat Formation Energies

$$\Delta H_f = E^{sup}_{imp} - 8 \times E^{MnAs} - \mu_{Se} + \mu_{As/Mn}$$

2x2x2 supercell

In the hexagonal phase:

Se subs. Mn: 2.84 eV

Se subs. As: 0.03 eV -> lower energy

The assignemt obtained with with the hyperfine parameters, is confirmed buy the heat formation energies.

Conclusions

• Transition measured at the atomic level. Coexistence of phases measured in a small interval (less than 2 C).

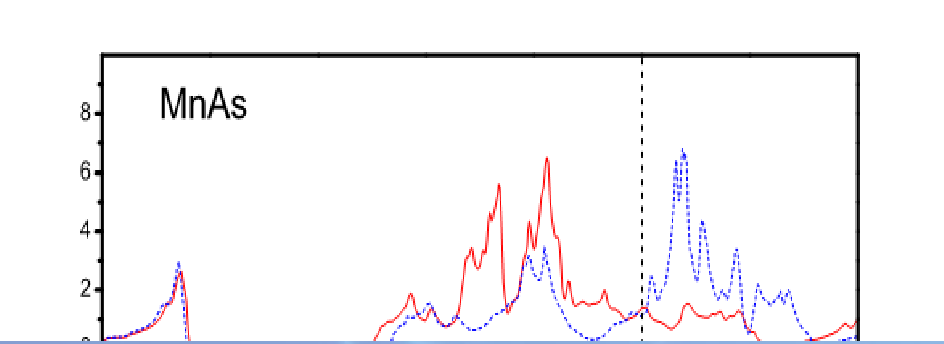
• First principles calculations are in good agreement with the low T hyperfine field, considering the probe Se substitutional at the As site.

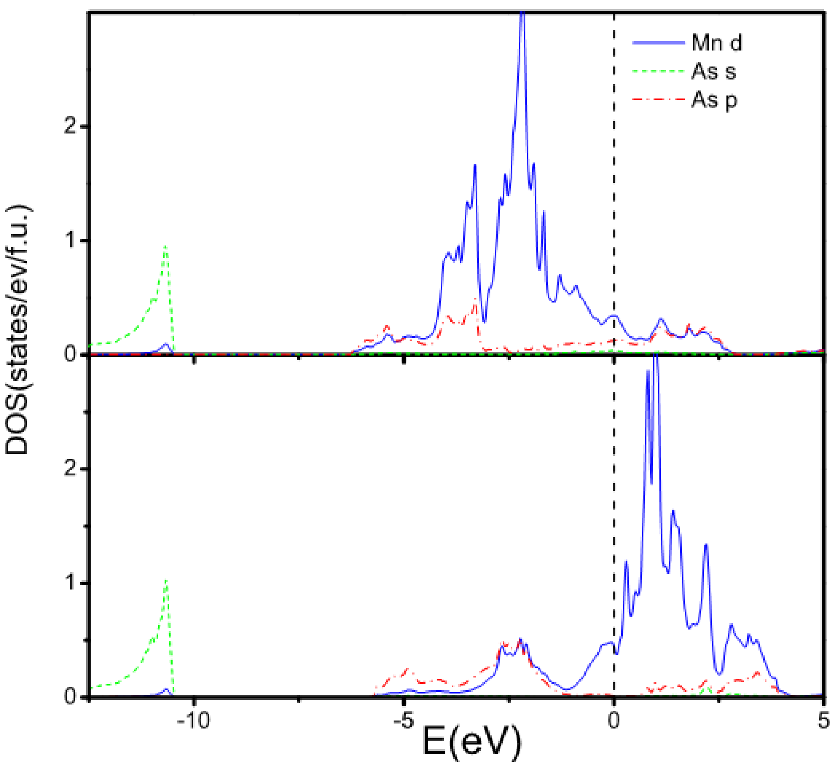
• The phase fractions are measured by PAC, showing that the magnetization changes are mostly due to the change of phase fractions, which can be correlated with the XRD measurements.

•Hysteresis is seen also from a microscopic point of view, consistent with the XRD and magnetization results.

Thank you

Hyperfine Parameters – pure MnAs

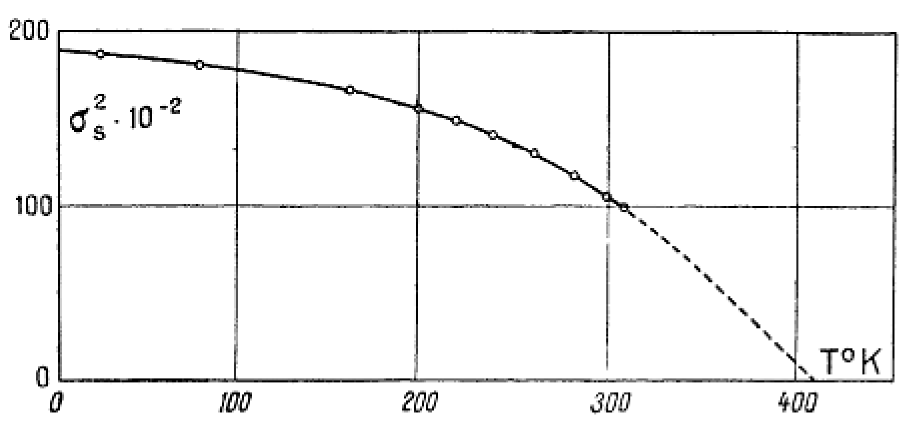




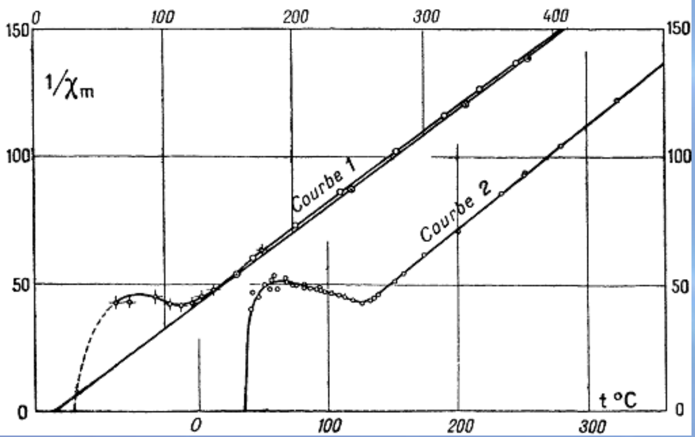
Compound	Atom	$V_{zz}(10^{21}V/m^2)$	V_{zz}^{p-p}	V_{zz}^{d-d}
MnAs	Mn	-3.63	-1.45	-1.70
	As	1.53	1.27	0.06

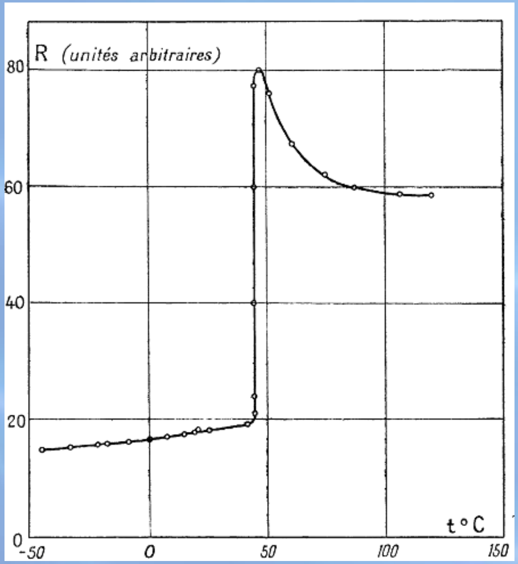
- In this case the hyperfine field masks the electric field gradient. The EFG is very low, due to the low quadrupole moment of the probe at the high symmetry of the position.

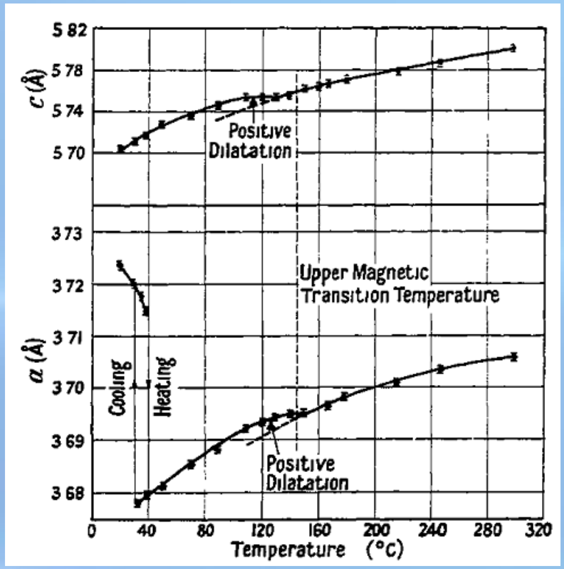
Other isotopes: ^{172}Lu



1947 - A. Serres, Journal de Physique et le Radium 8(5):146-151







Why is it still studied?