

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

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Projects:

CERN/FP/83506/2008

CERN/FP/83643/2008

O5KK1TSA(BMBF-Germany)

ISOLDE project 487

FCT Grant

SFRH/BD/42194/2007

# Outline

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

# MnAs

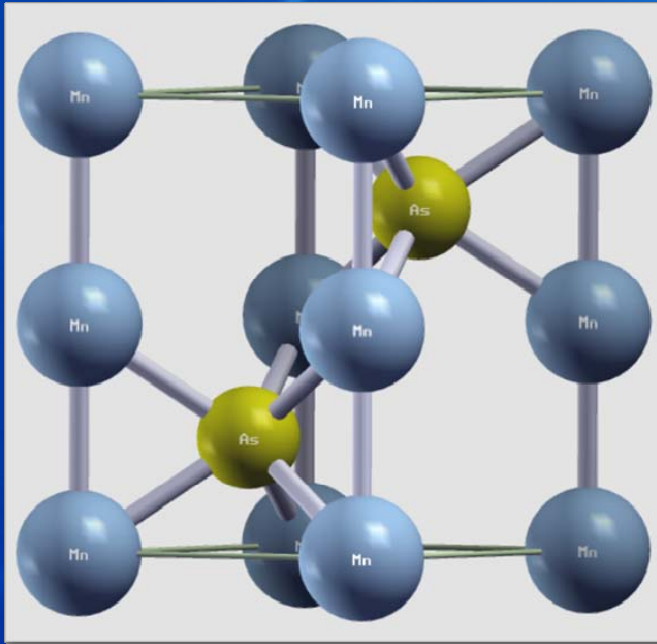
- Studied since 1904
  - 1904 - F. Heusler, Z. Angew. Chem. 17 260
  - 1911 - S. Hilpert and T. Dieckmann, Ber. Dtsch. Chem. Ges. A 44 2378  
(Ferromagnetic)
  - 1947 - A. Serres, Journal de Physique et le Radium 8(5):146-151
  - 1954 - B. T. Willis M and Rooksby H P Proc. Phys. Soc. London B 67 290
  - 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 )
- ...

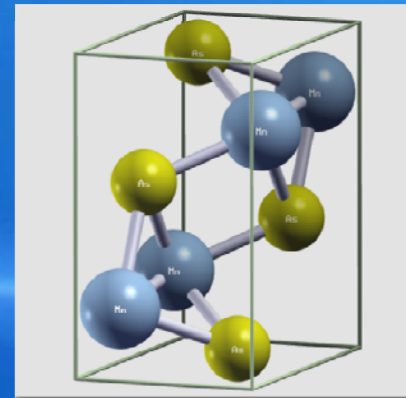
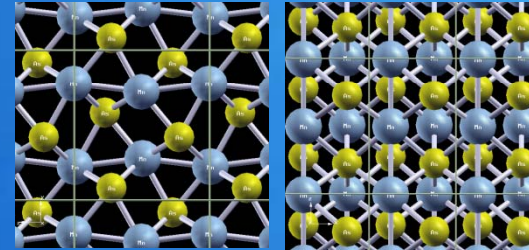
# MnAs Phases

Low temperature  
Hexagonal structure (NiAs-type)  
Ferromagnetic metal

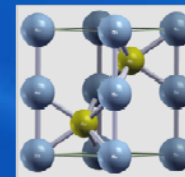


- 1st order phase transition at 42 C
- Increasing temperature:
- 2% volume loss
  - Hexagonal-Orthorhombic
  - Loss of Ferromagnetism
  - Increase in resistivity

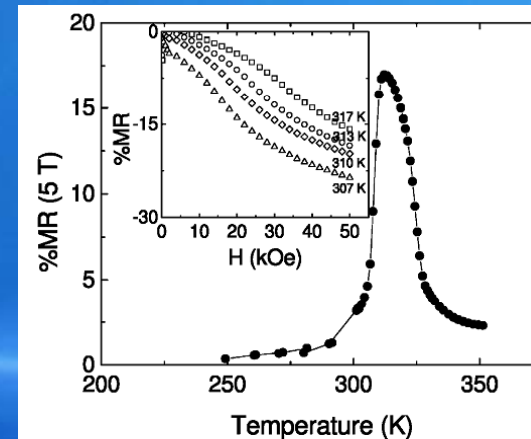
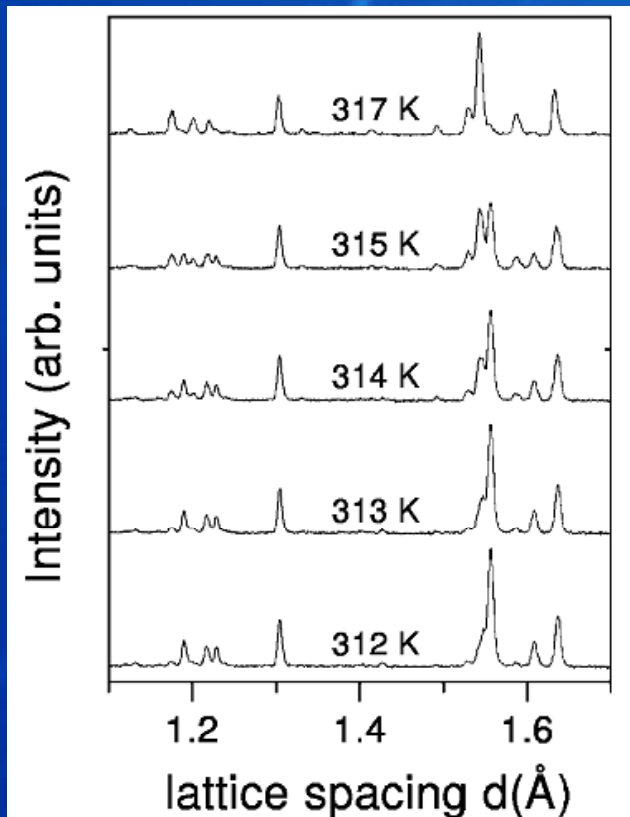
Orthorhombic structure (MnP-type),  
Paramagnetic(?)



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.  
 $\text{Mn}_{0.75}\text{Fe}_{0.25}\text{As}$   
**No hyperfine field.**
- M. A. Abdelgadir *et al.*,  
Physica Scripta **37**(3):373-  
380(1988)  
 $\text{Mn}_x\text{Fe}_{1-x}\text{As}$ , 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 vacuum
- Highly diluted concentrations of probes (parts per million)

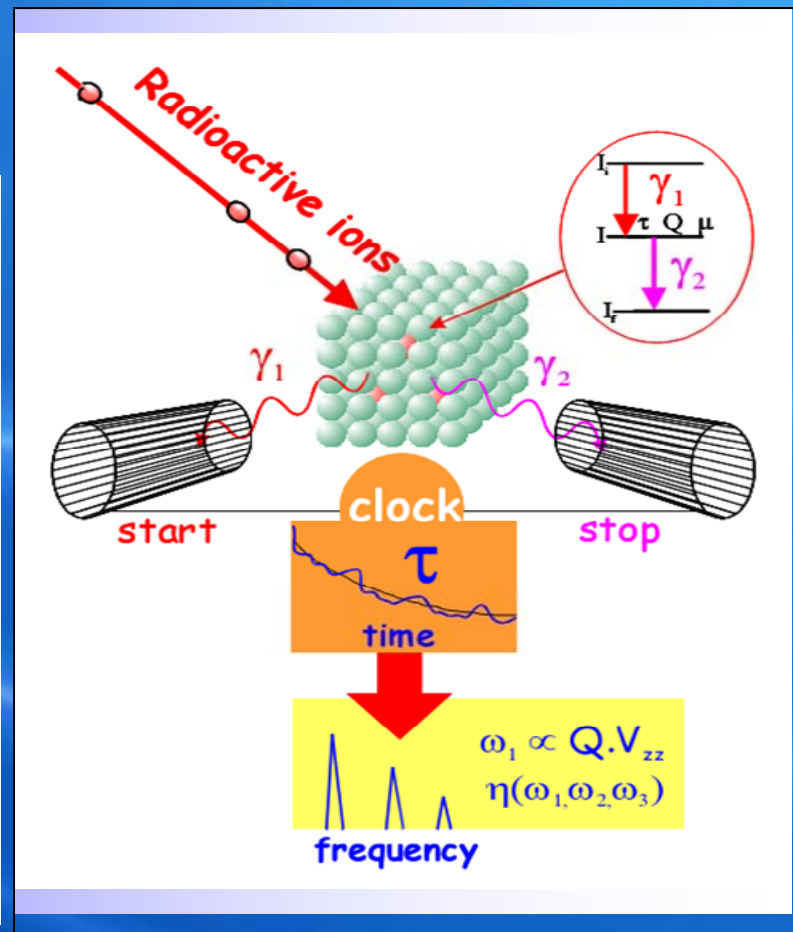
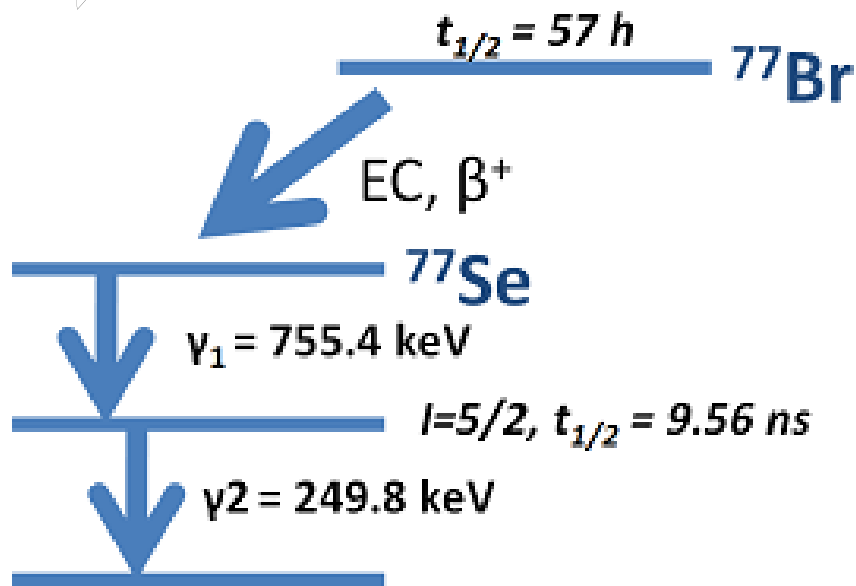


# PAC

CERN's Proton-Synchrotron Booster

protons  $E \sim 1 \text{ GeV}$

target  
ion source



Quadrupole electric moment interacts with  
**Electric Field Gradient (EFG)**

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

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

Magnetic dipole moment with  
**Magnetic Hyperfine Field  $B_{\text{hf}}$  (T)**

**MATERIAL SPECIFIC**

**Interaction**

**Frequencies:**

$$\nu_Q = e V_{zz} Q / h$$

**EXPERIMENTAL  
OUTPUT**

$$\omega_L = B g \mu_{\text{nuc.}} / \hbar$$

- 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:

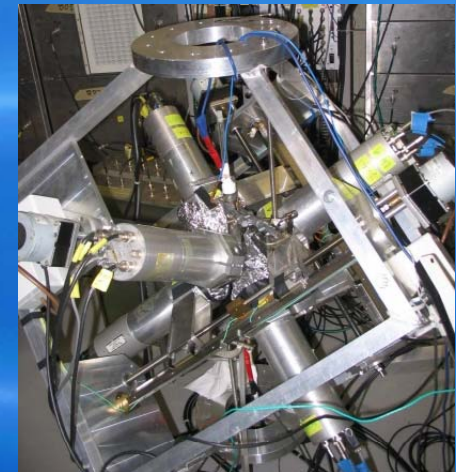
$\omega_0, \eta, \omega_L, \sigma$

$\omega_0$ : frequency of the electric quadrupole interaction

$\eta$ : axial asymmetry parameters of electric quadrupole interaction

$\omega_L$ : frequency of the magnetic dipole interaction

$\sigma$ : damping of the perturbation spectrum is simulated by a Lorentzian function of width  $\sigma$



# Heating

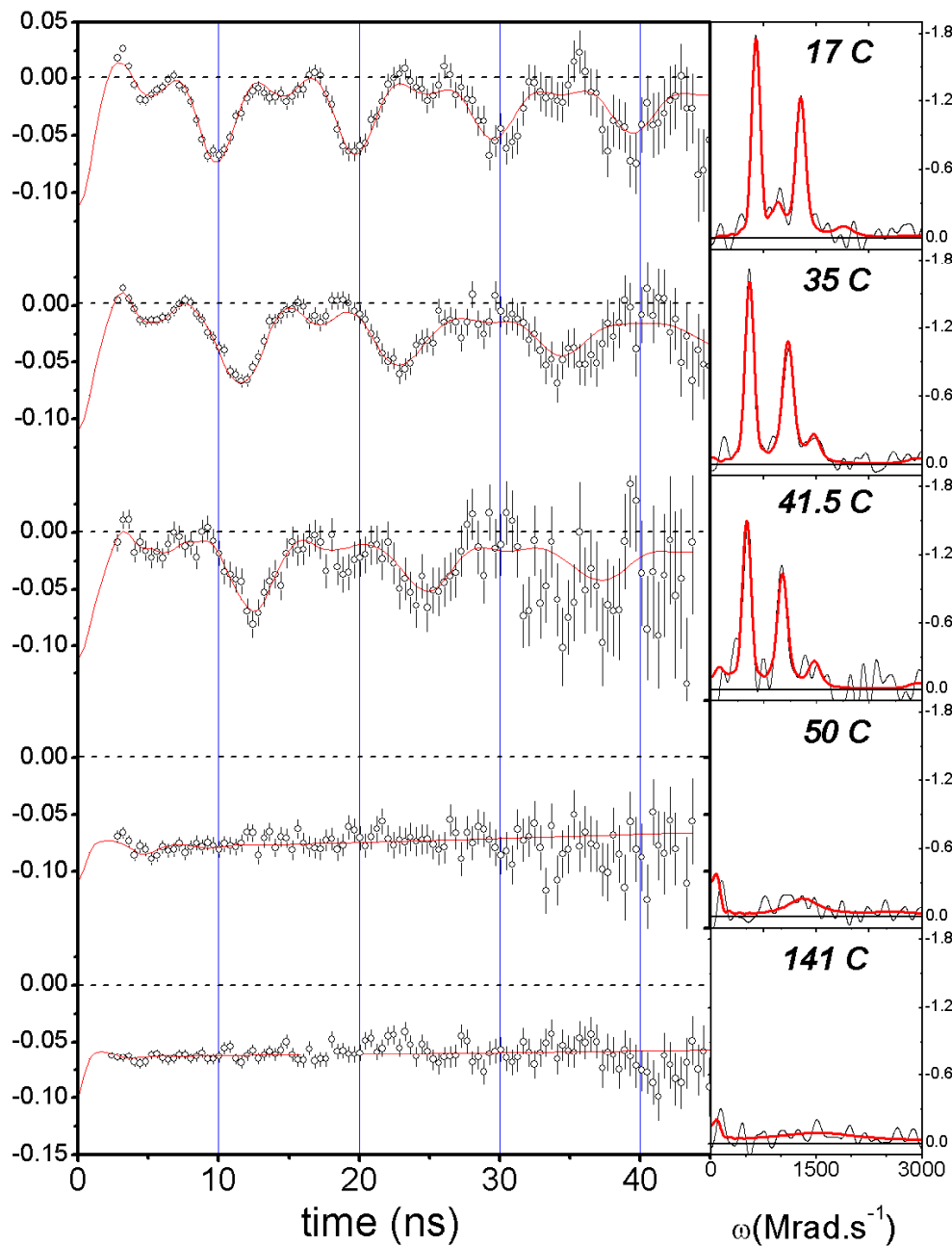
(chronological order)

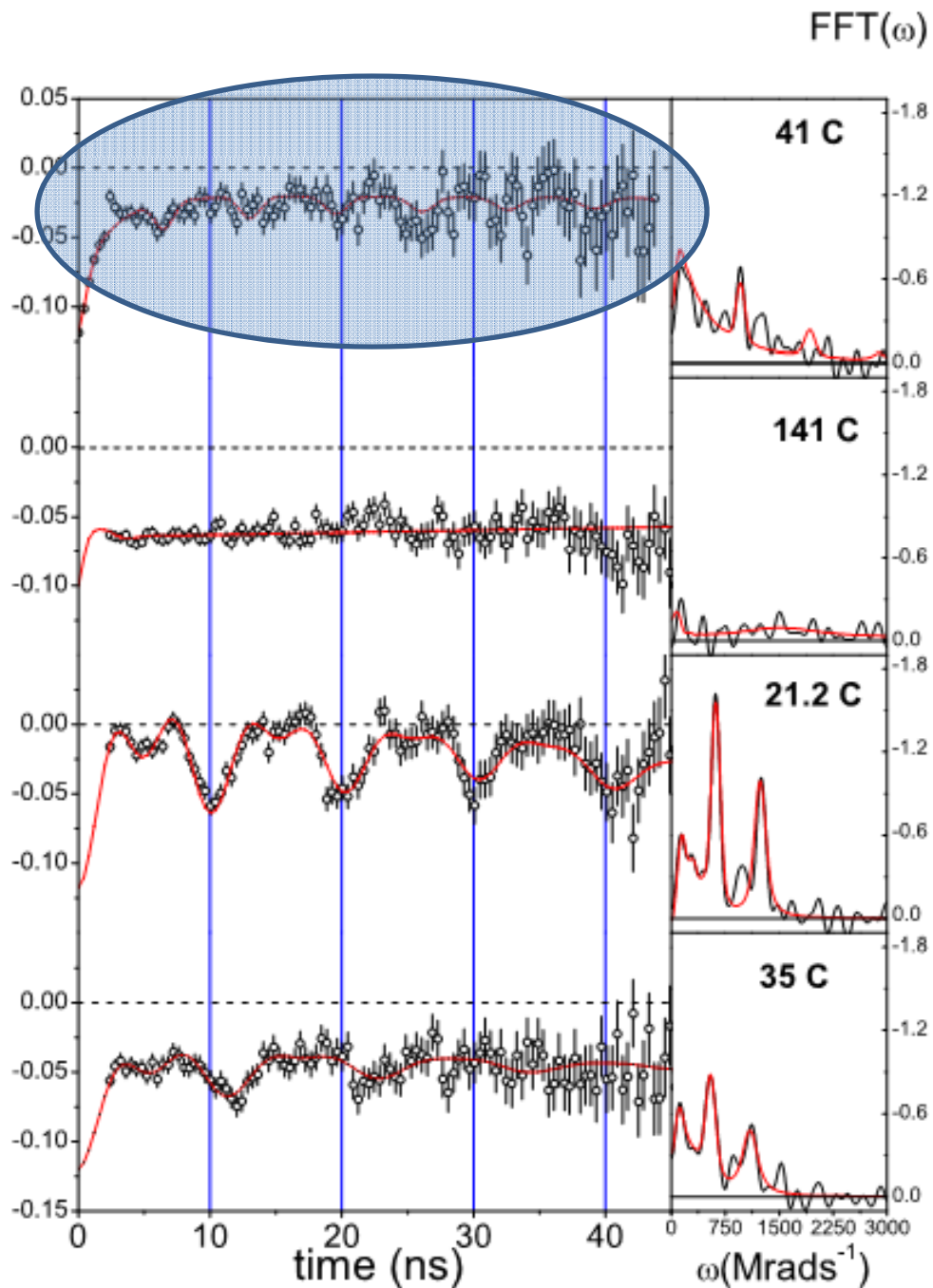
- Ferromagnetic phase: nuclei interacting with a magnetic hyperfine field; EFG is too small to be resolved ( $< 1 \times 10^{21} \text{ V/m}^2$ ).

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

- $\eta=0$

- 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.



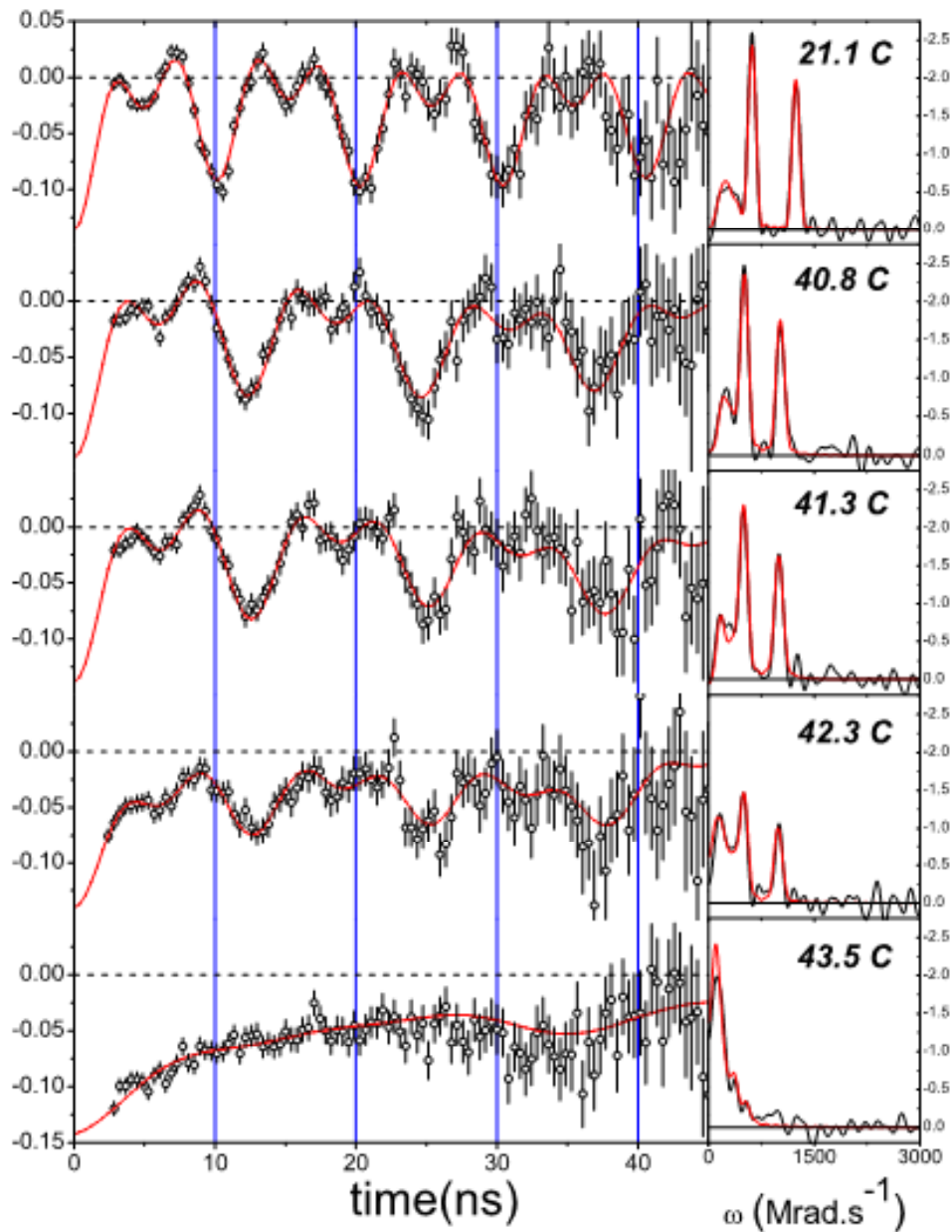


- 141 – Above the second order transition. Continues with low  $V_{zz}$  and no MHF.
- Hysteresis clearly seen when comparing with previous 41.5 C (heating) with 41 C (cooling). Hel

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

# 2nd set of experiments

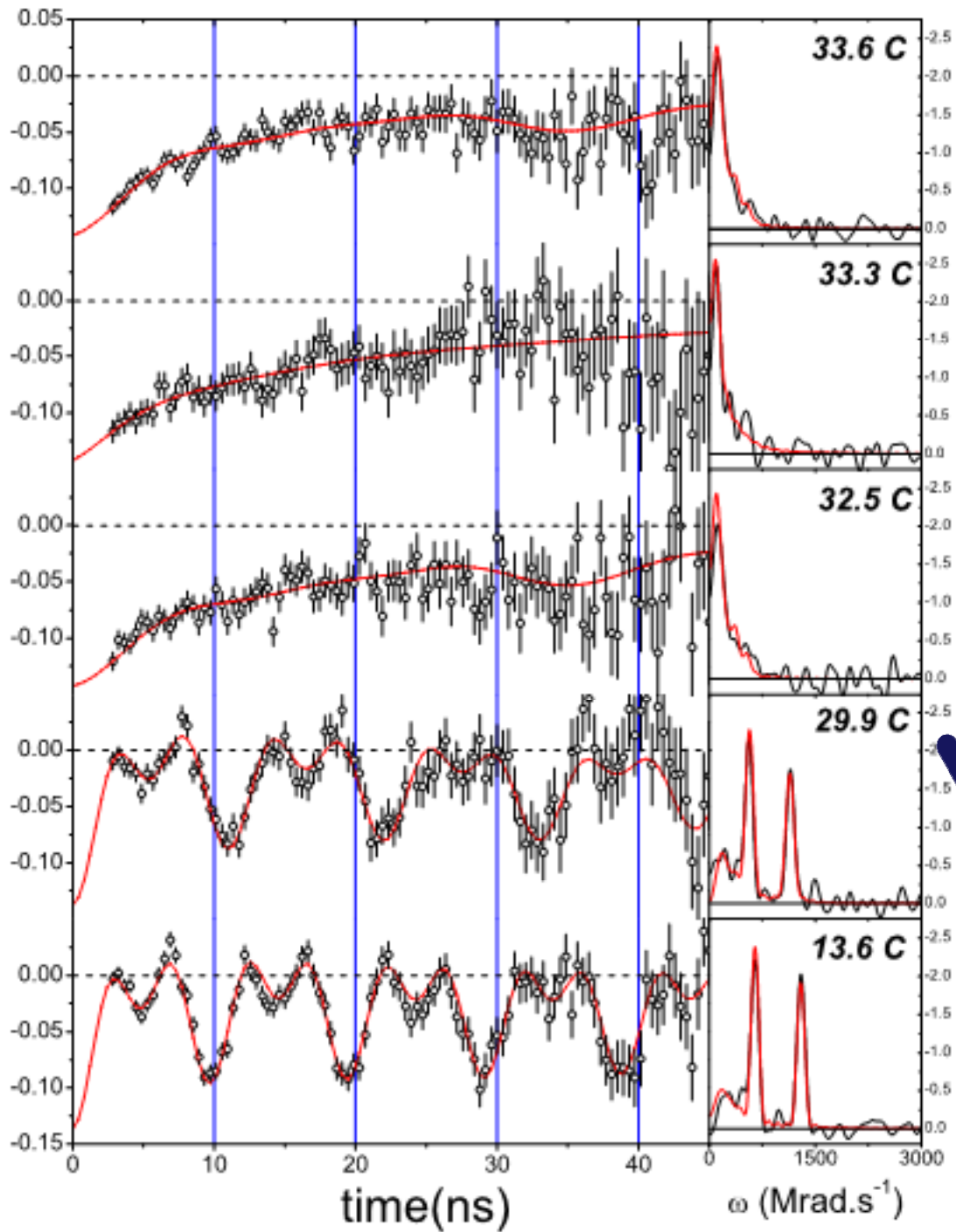
## First-order Transition



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



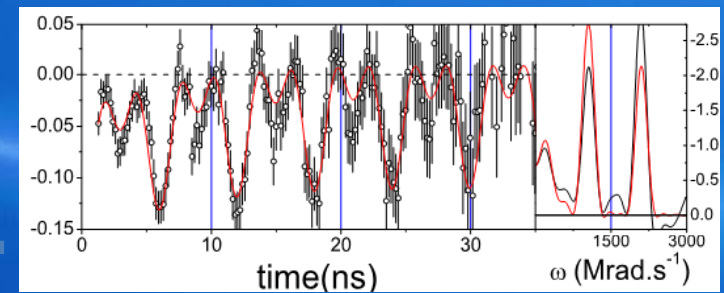
- Entering low T phase with  $T_{C,d}$  (Curie temperature when decreasing T) 10 degrees lower than  $T_{C,l}$ .

# Fit parameters

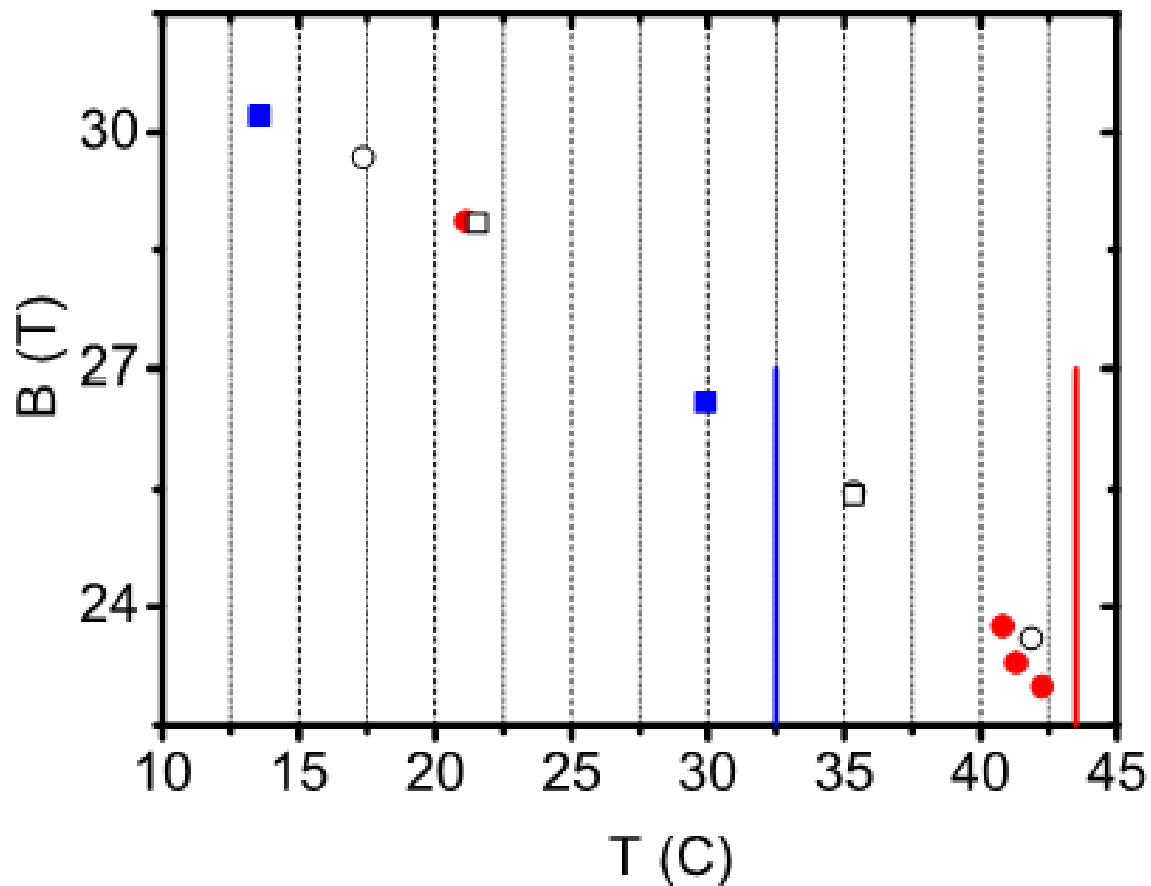
$T(^{\circ}C)$	$f_1$	$\omega_{L1}$	$\sigma_1$	$f_2$	$\omega_{02}$	$\sigma_2$	$f_3$	$\omega_{03}$	$\sigma_3$	
21.1	70	619	3	-	-	-	30	176	23	H
40.8	70	510	9	-	-	-	30	176	22	
41.3	70	499	12	-	-	-	30	176	18	
42.3	40	495	10	30	28	20	30	176	10	H+O
43.5	-	-	-	70	28	24	30	176	9	O
124.5	-	-	-	70	28	26	30	176	27	
41.4	-	-	-	70	28	36	30	176	17	
39.5	-	-	-	70	28	46	30	176	24	
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	H
13.6	70	648	4	-	-	-	30	176	98	
-196	70	1050	0	-	-	-	30	57	29	

- The attenuation of the hyperfine field ( $\sigma_1$ ) increases towards the phase transition, and decreases when going away from the transition.

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







$$T_{C,i} = 42.3-43.5 \text{ C}$$

$$T_{C,d} = 30-32.6 \text{ C}$$

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

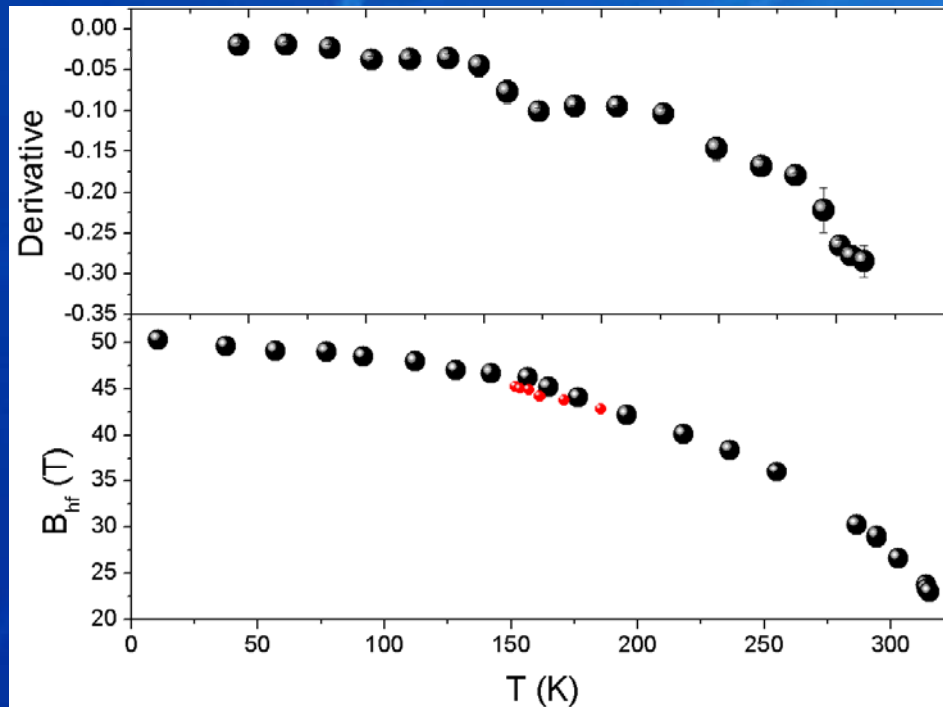
**At a given T, the hyperfine field is the same, irrespective of cooling or heating the sample.**

*Red: heating*

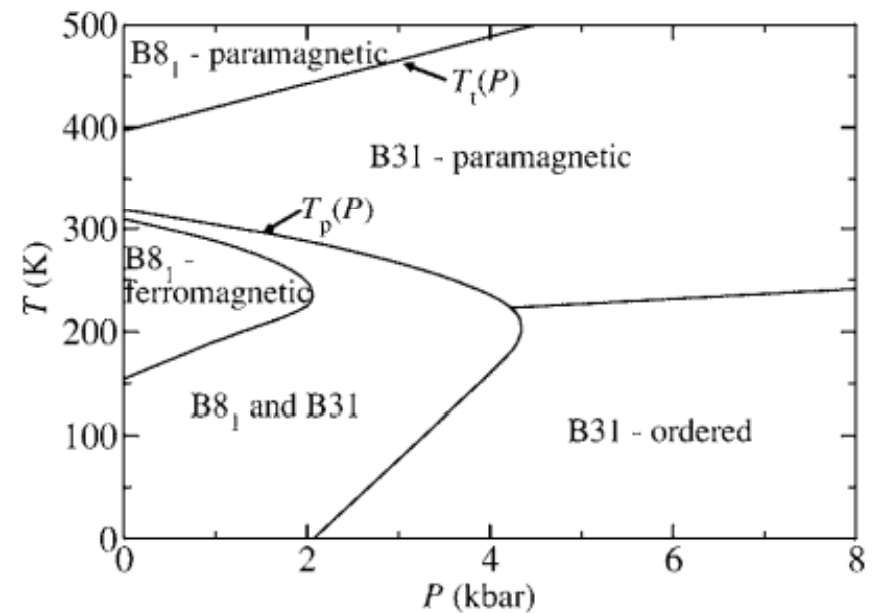
*Blue: cooling*

*White: previous experiments*

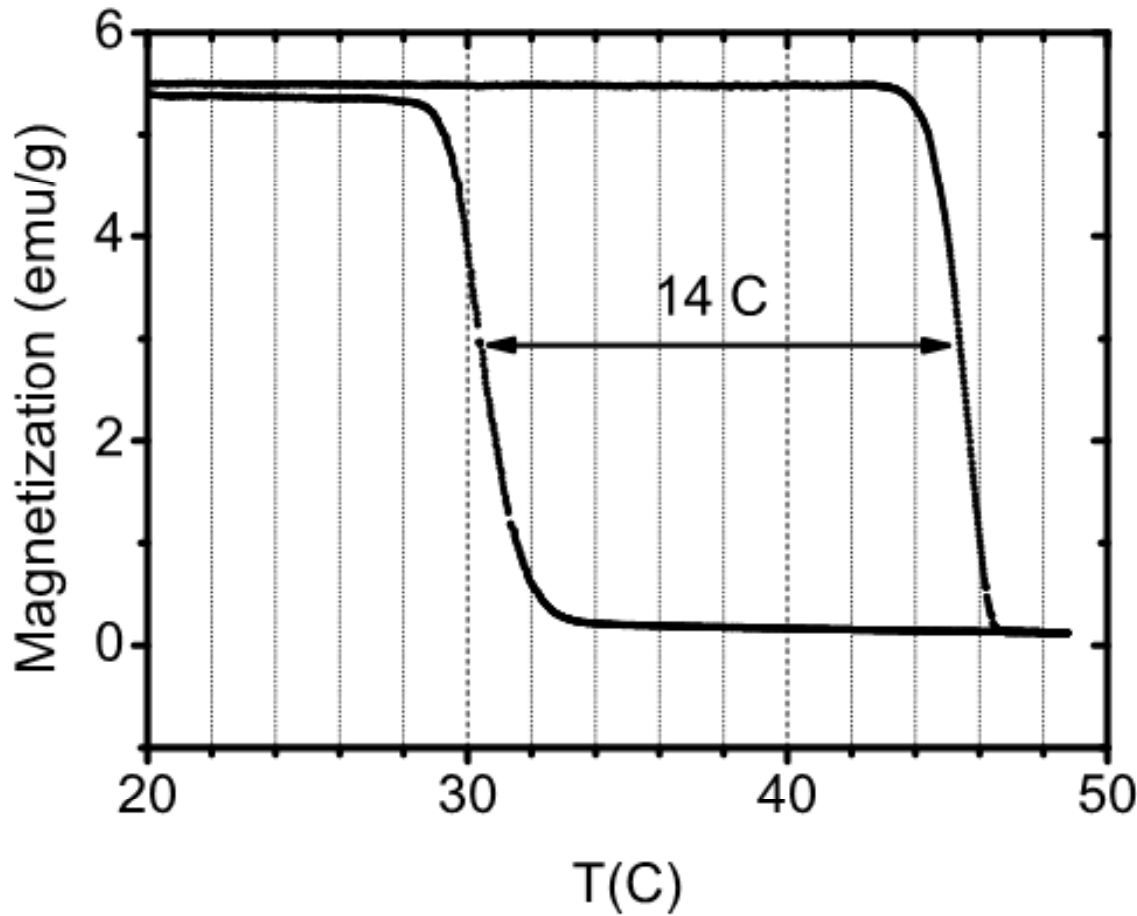
# Low temperature PAC measurements



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



# Magnetization



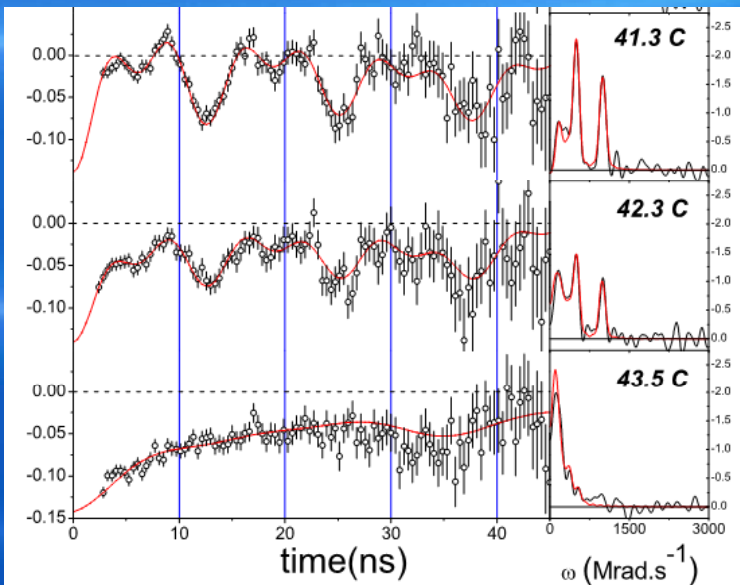
Transition width = 2-3 C

$T_{C,i} = 42 \text{ C}$

$T_{C,d} = 32 \text{ C}$

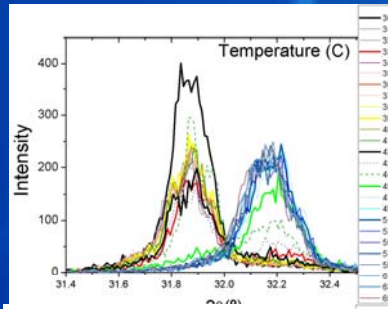
PAC: 41.3, 42.3, 43.5 C

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

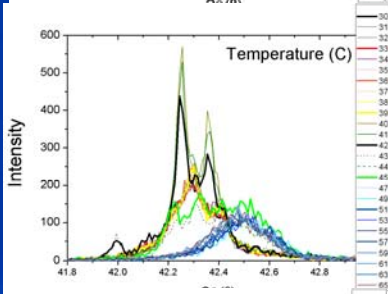


# X-ray diffraction

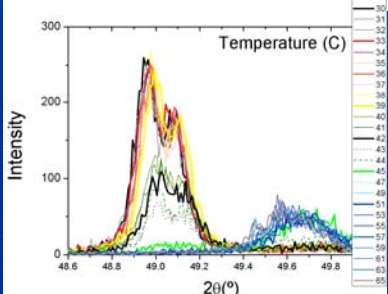
Measurements on three  $2\theta$  ranges,  $31.4-32.6$ ,  $41.8-43$  and  $48.6-50^\circ$ .



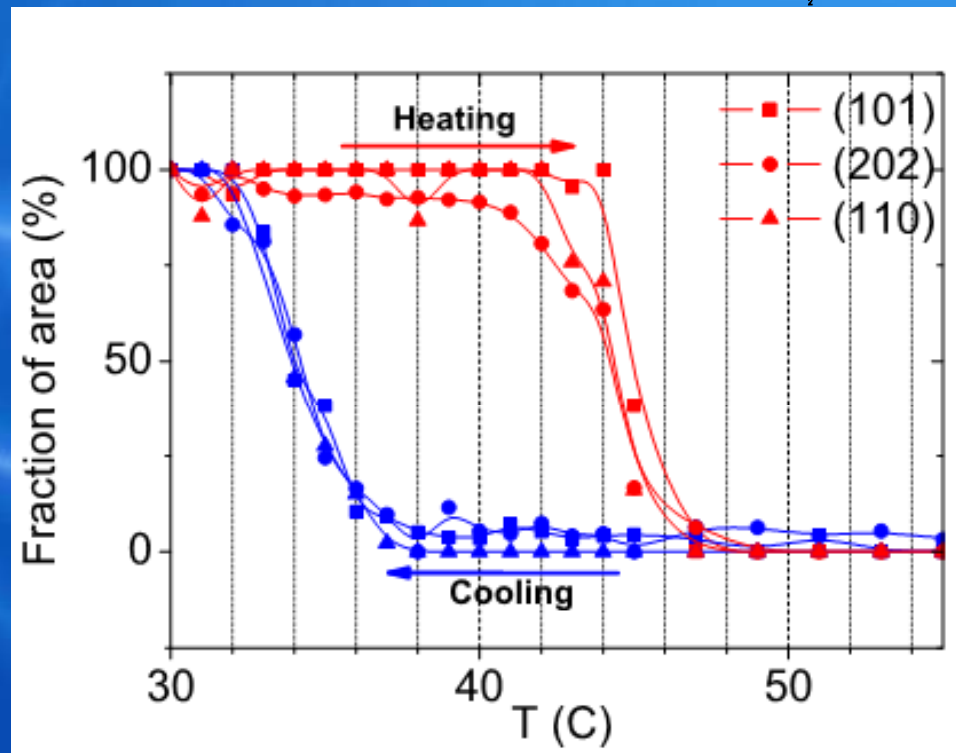
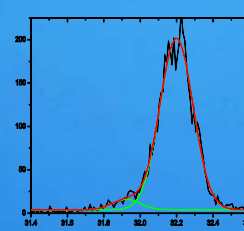
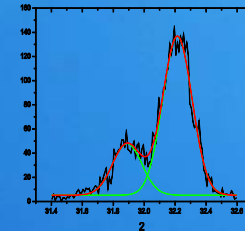
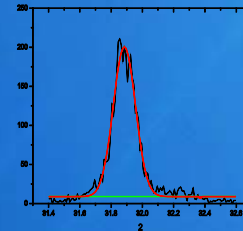
(101)



(102)

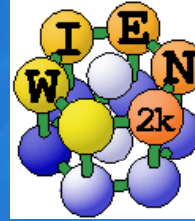


(110)



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

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

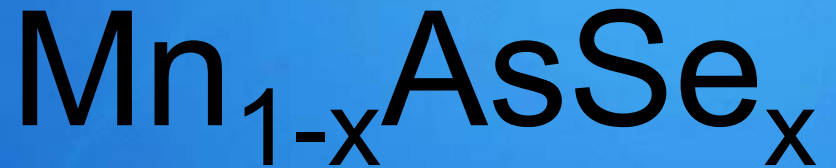
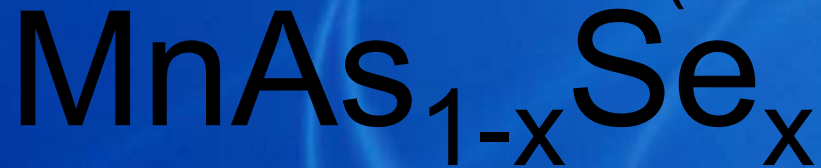
Exp. Room  
Temperature lattice  
constants

Exp. Low  
temperature lattice  
constants

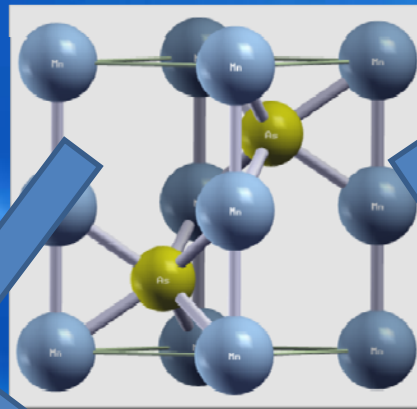
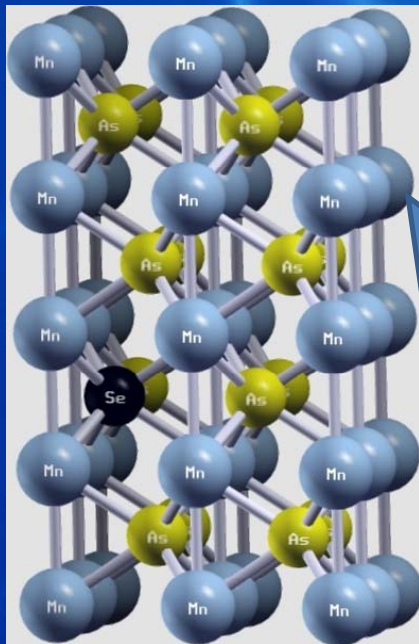
Calculations are exact  
only for T=0 K

# Supercells

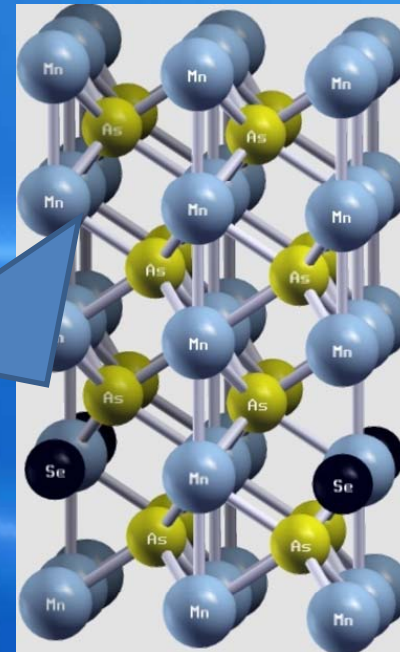
- We consider the Se probe at the possible substitutional sites (As/Se)



$\text{MnAs}_{15/16}\text{Se}_{1/16}$



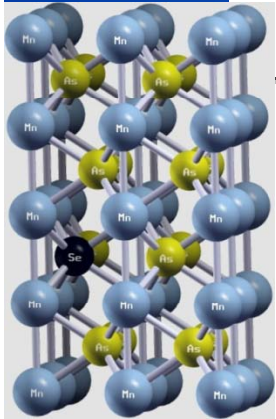
$\text{MnAs}_{1/16}\text{Se}_{5/16}$





# Hyperfine Parameters

Concentration: 1/16 of As atoms are substituted by Se atoms  $V_{zz}$  exp.  $\sim 0$



Se at As site

$V_{zz} (V/\text{\AA}^2)$

-2.7

$\eta V_{zz}$  dir.

0 (0,0,1)

$B_C$

56.6

core valence

0.4

$B_{orb}$

56.2

$B_{dip}$

-2.1

$B_{hf}$  total

-0.2

$B_{hf}$  total

54.3

$B_{hf}$  exp.  $\sim$   
50 T

~~Se at Mn site~~

~~$V_{zz} (V/\text{\AA}^2)$~~

~~178.0~~

~~$\eta V_{zz}$  dir.~~

~~0 (0,0,1)~~

~~$B_C$~~

~~-23.1~~

~~core valence~~

~~-22.9~~

~~$B_{orb}$~~

~~-0.2~~

~~$B_{dip}$~~

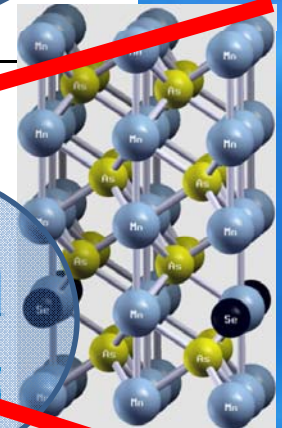
~~3.4~~

~~$B_{hf}$  total~~

~~-1.8~~

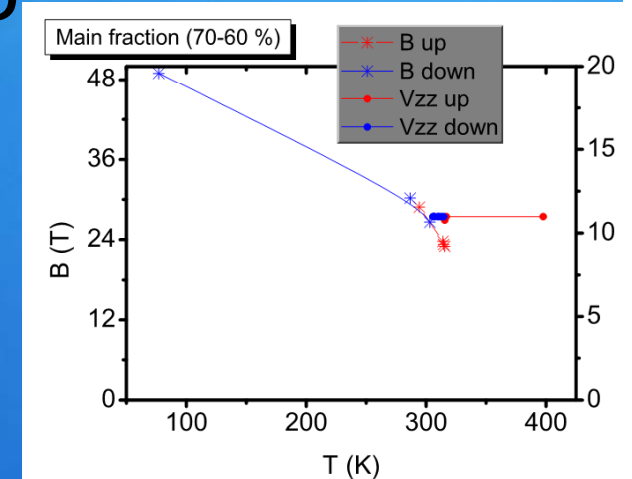
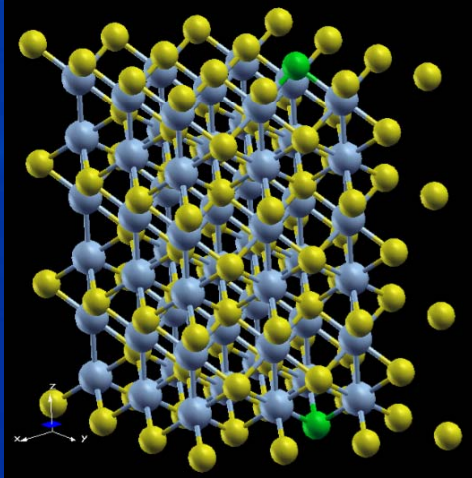
~~$B_{hf}$  total~~

~~-21.5~~



# Hyperfine Parameters

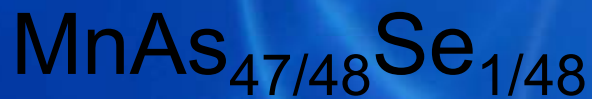
Is the concentration low enough to reproduce the diluted impurity (parts per million) experimental situation?



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

# Hyperfine Parameters

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

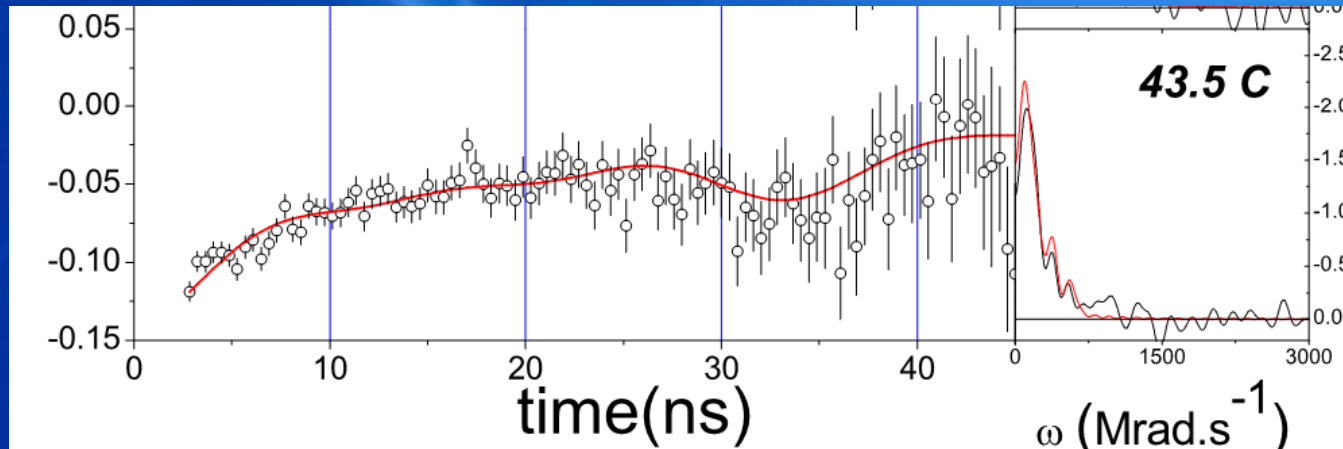


$V_{zz}$  ( $10^{21}$  V/Å<sup>2</sup>)

-1.0

$V_{zz}$  ( $10^{21}$  V/Å<sup>2</sup>)

15.3



$V_{zz} \sim 11$   
V/Å<sup>2</sup>

# Heat Formation Energies

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

In the hexagonal phase: 2x2x2 supercell

Se subs. Mn: 2.84 eV

**Se subs. As: 0.03 eV -> lower energy**

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

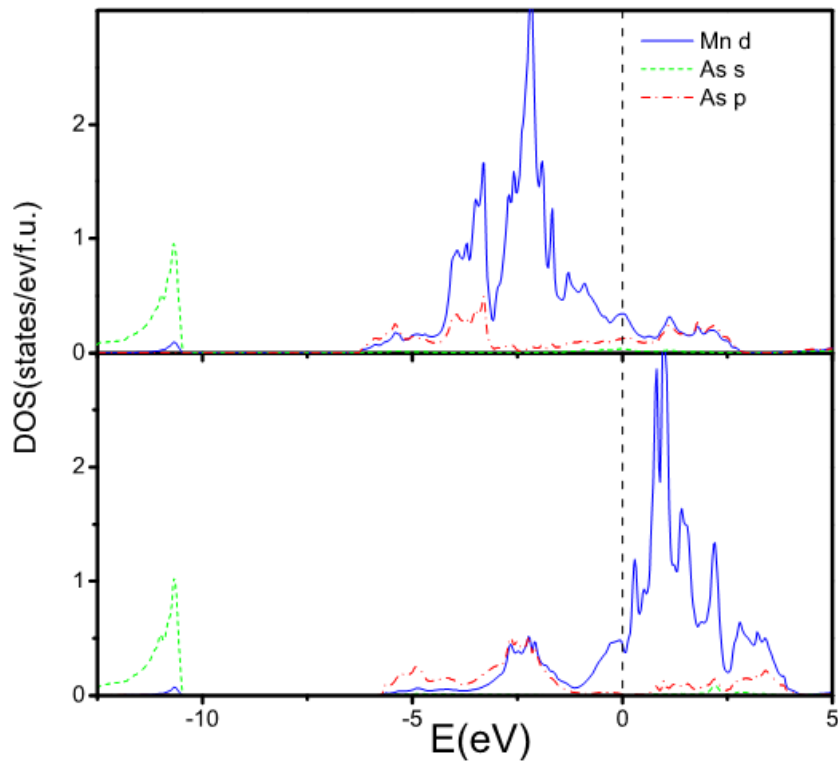
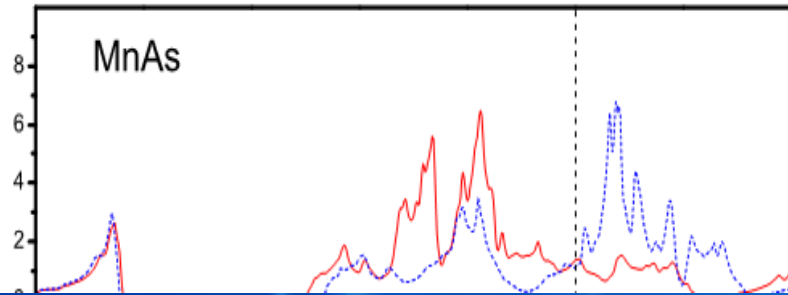
# Conclusions

- 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.

The background is a solid blue color with several white, glowing, wavy lines that create a sense of motion and depth. The lines are curved and overlap, giving the impression of light trails or energy waves.

**Thank you**

# Hyperfine Parameters – pure MnAs



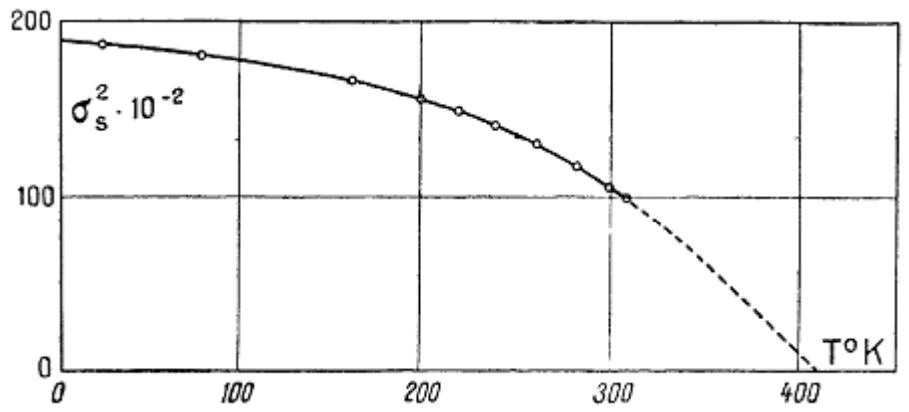
Compound	Atom	$V_{zz}(10^{21} \text{V/m}^2)$	$V_{zz}^{p-p}$	$V_{zz}^{d-d}$
MnAs	Mn	-3.63	-1.45	-1.70
	As	1.53	1.27	0.06



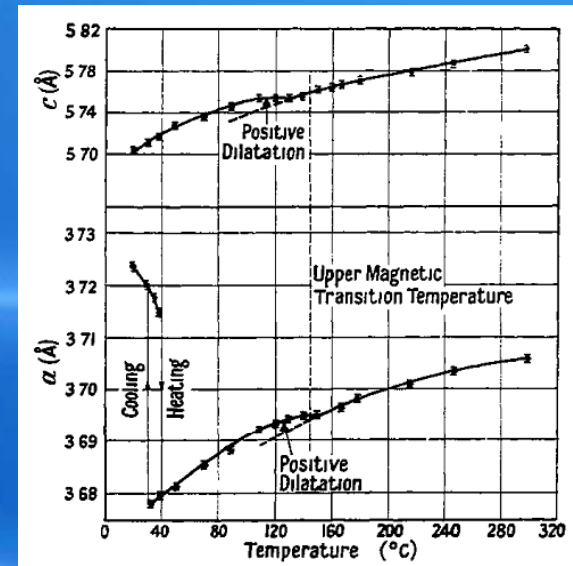
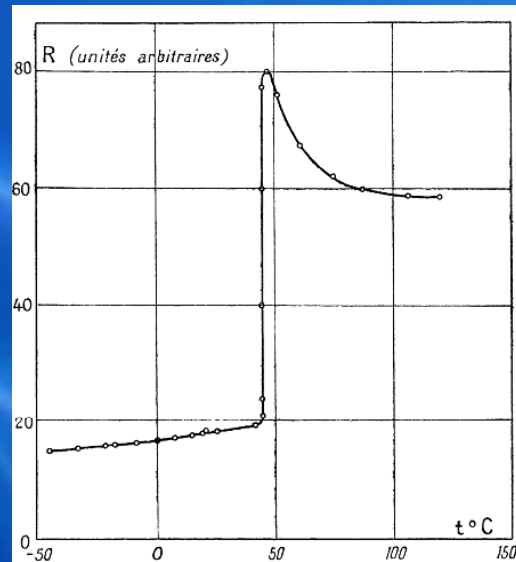
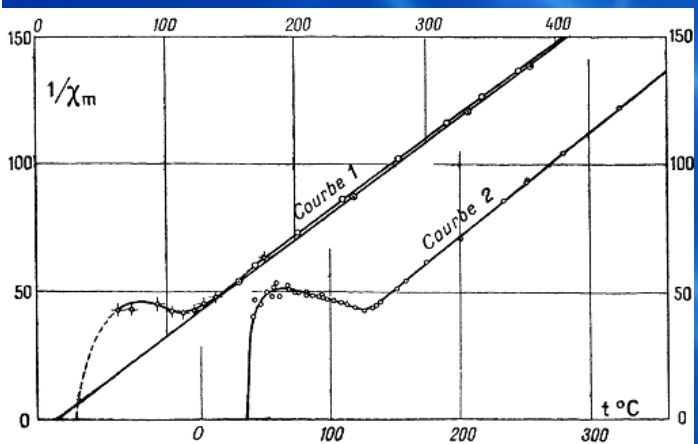
- In this case the hyperfine field masks the electric field gradient. The EFG is very low, due to the low quadrupole moment of the probe at the high symmetry of the position.

Other isotopes:  $^{172}\text{Lu}$





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



Why is it still studied?