

**Faculty of Physics and Applied Computer Science,  
AGH University of Science and Technology  
Kraków, April, 5 2019**

# **Własności magnetyczne związków międzymetalicznych pod wysokim ciśnieniem**

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# Introduction

***I. Experiment under high pressure***

***II. Magnetostructural phase transitions in  $\text{Co}_x\text{Ni}_{1-x}\text{MnGe}$  under pressure***

***III. Magnetic properties of  $\text{MnFeP}_{1-x}\text{As}_x$  series  
–pressure, magnetic field, electronic structure***

***IV. Magnetoelastic phase transitions, pressure effect  
electronic structure***

***a)  $\text{MnRh}_{1-x}\text{As}_x$***

***b)  $\text{MnRh}_{1-x}\text{Co}_x\text{As}$***

***c)  $(\text{Mn}_{1-x}\text{Co}_x)_2\text{P}$***

***d)  $\text{MnRu}_{1-x}\text{Rh}_x\text{As}$***

# Conclusions

***I. Experiment under high pressure***



***II. Magnetostructural phase transitions in  $\text{Co}_x\text{Ni}_{1-x}\text{MnGe}$  under pressure***

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- pressure, magnetic field, electronic structure***

***IV. Magnetoelastic phase transitions, pressure effect,  
electronic structure***



## EXPERIMENTAL METHODS

- \* **X-ray diffraction**

(Philips' diffractometer, ICh UJ, Cracow, Poland)

- \* **Neutron diffraction**

(Institute Laue Langevin, Grenoble, France  
D1B spectrometer,  $\lambda=2.4*10^{-10}$  m)

- \* **Magnetization measurements**

(up to 10T, Insitute Néel, CNRS, Grenoble, France  
up to 23T, LNCI, CNRS, Grenoble, France  
up to 50T, Osaka University, Japan)

- \* **A.C. susceptibility measurements under pressure**

(up to 2 GPa, CUT, Cracow, Poland  
up to 8 GPa, Osaka University, Okayama University, Japan)

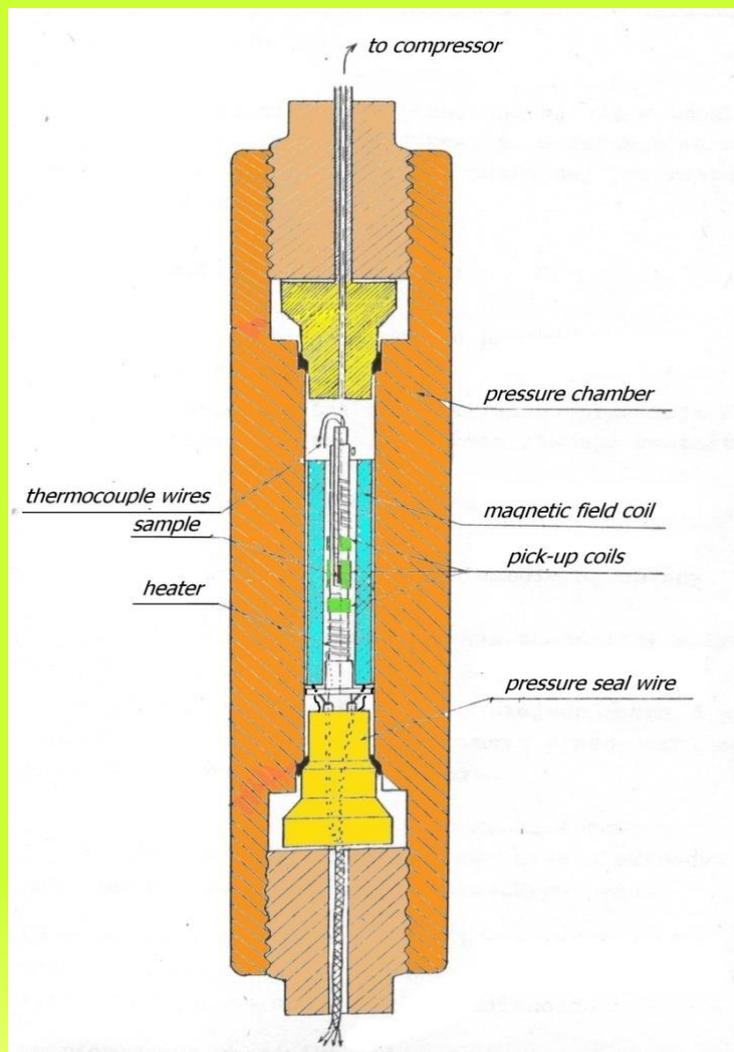
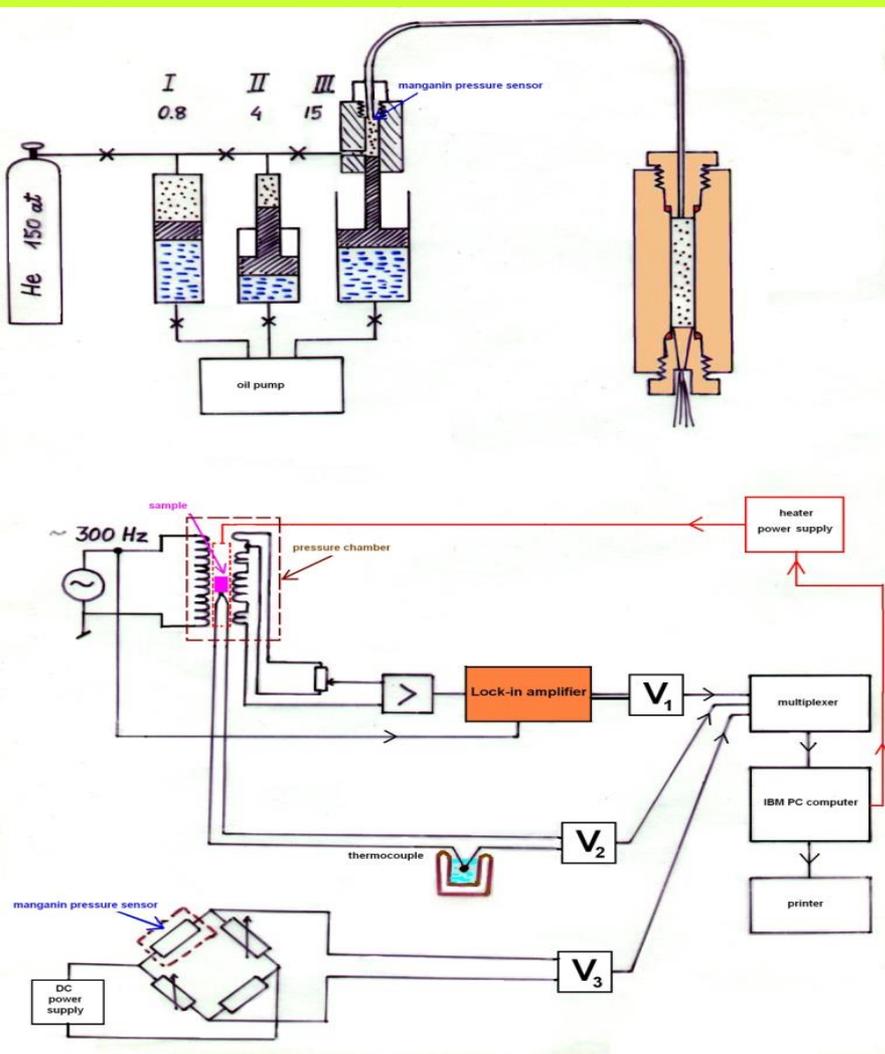
- \* **Magnetization measurements under pressure**

(up to 1.5 GPa and 17 T CUT, Cracow, Poland)

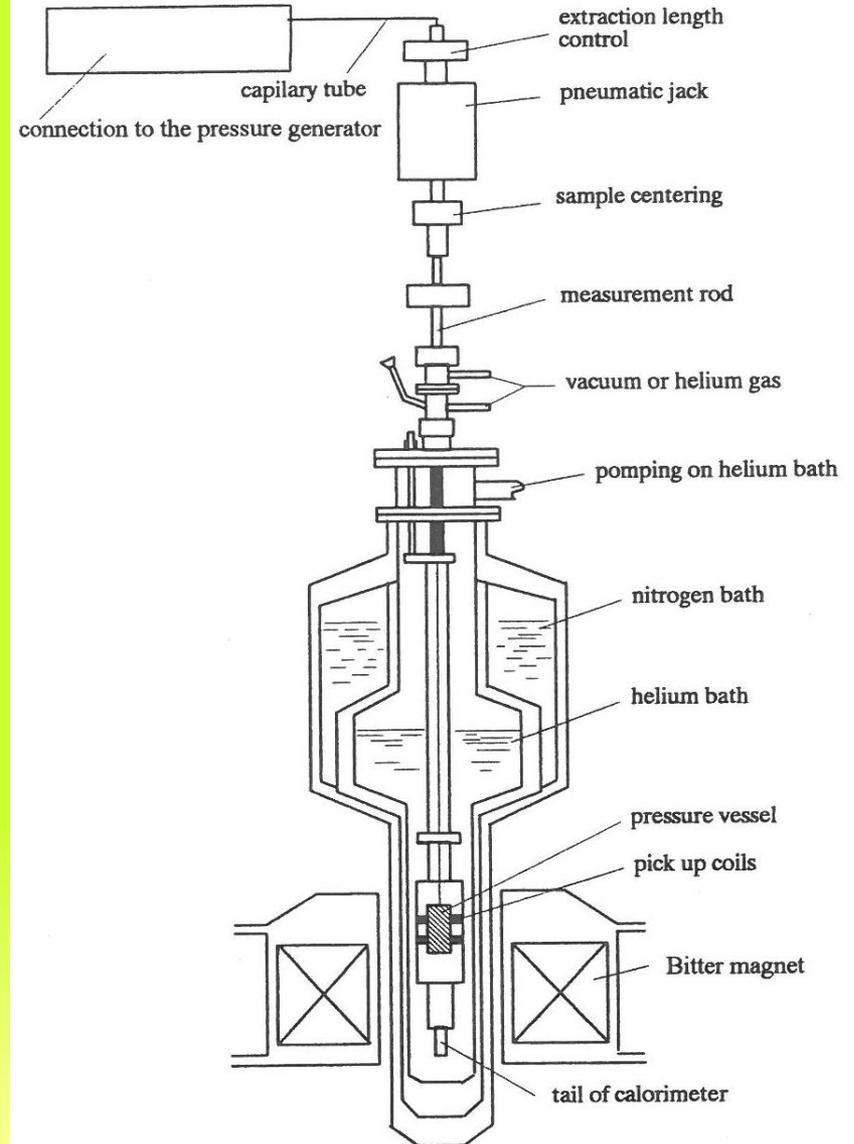
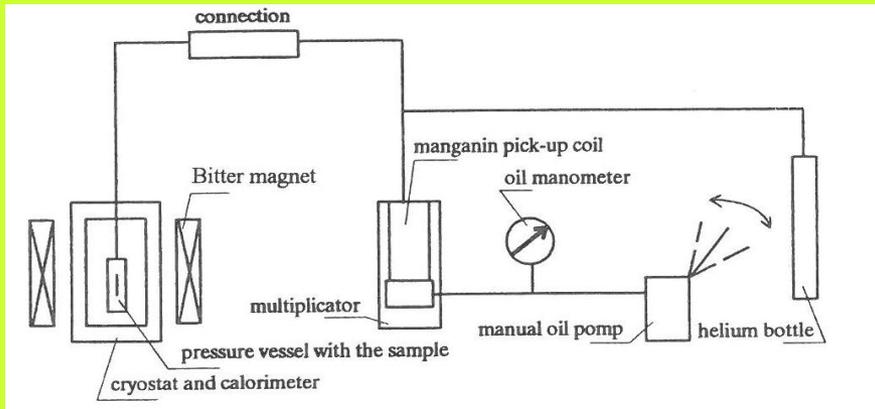
- \* **Synchrotron diffraction under high pressure**

(up to 60 GPa, Photon Factory, Tsukuba, Japan)  
Spring 8, Kobe, Japan)

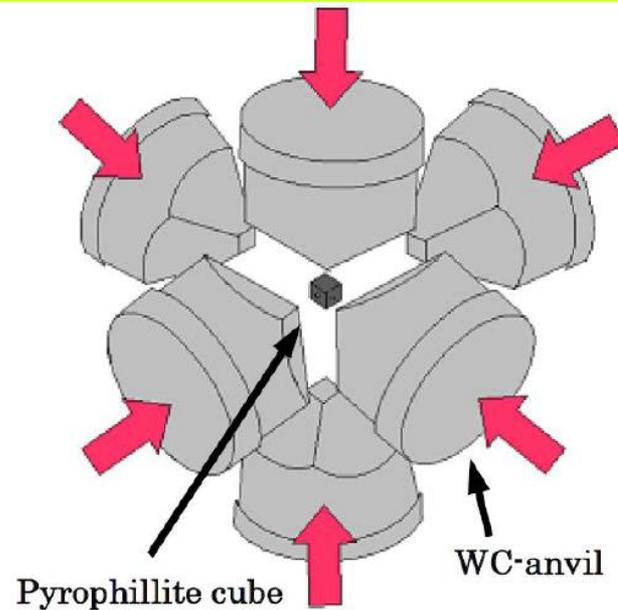
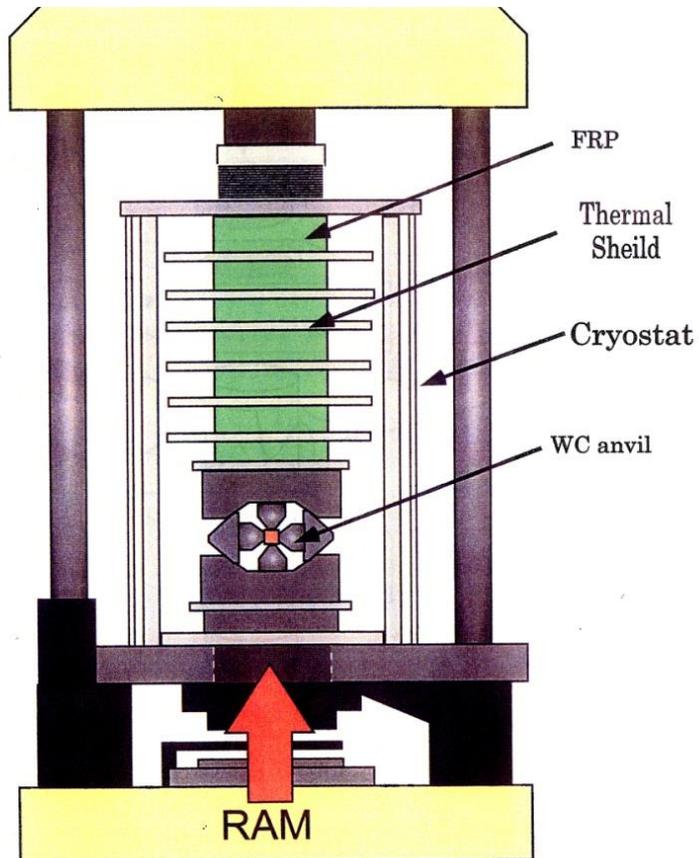
# a.c. susceptibility and magnetization measurements under pressure up to 2 GPa, temp.range 4.2 – 400 K, Cracow, Poland



# Magnetization measurements under pressure up to 2 GPa and up to 23 T, d.c. magnetic field, temp: 4.2 – 400 K, LMCI, Grenoble

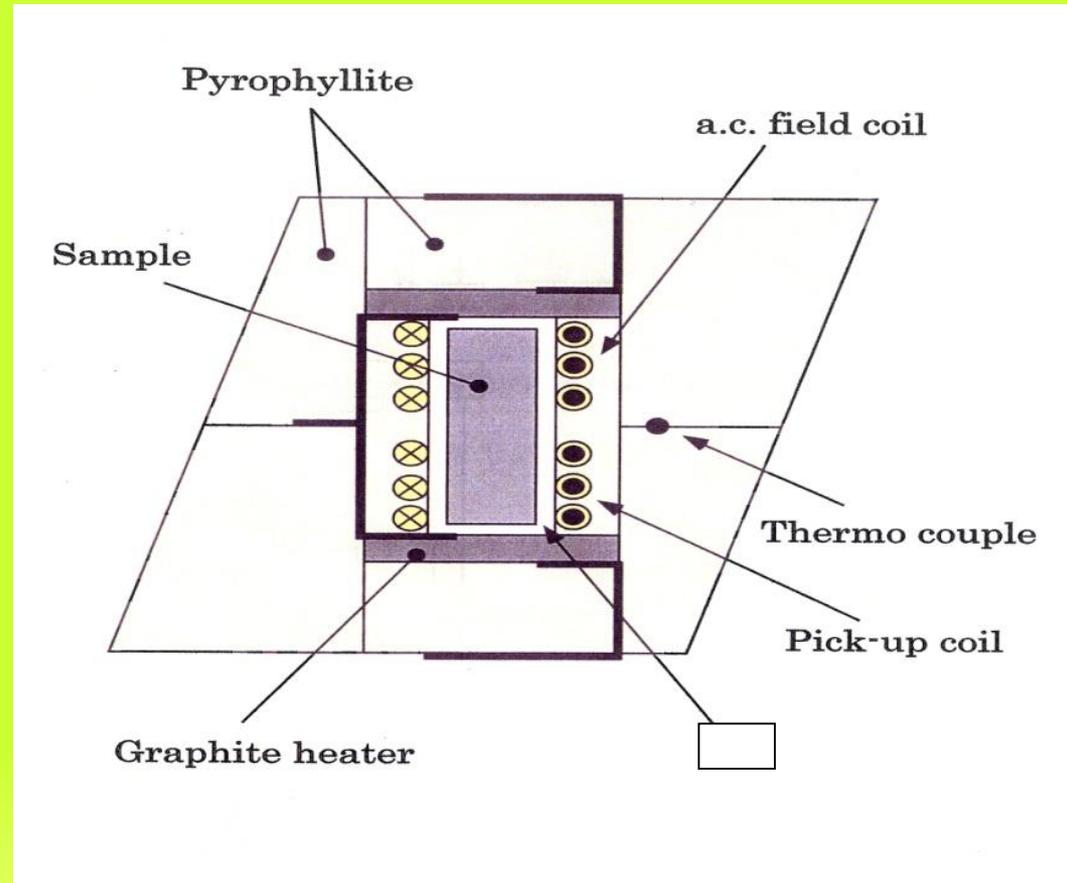
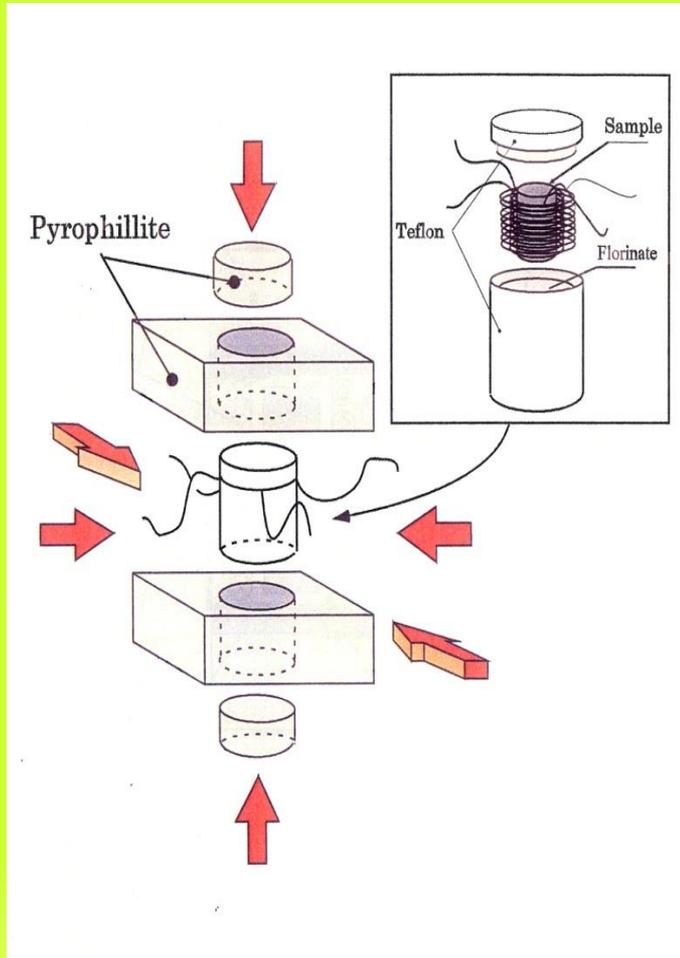


# a.c. susceptibility measurements under pressure up to 8 GPa, Osaka University, Okayama University, Japan

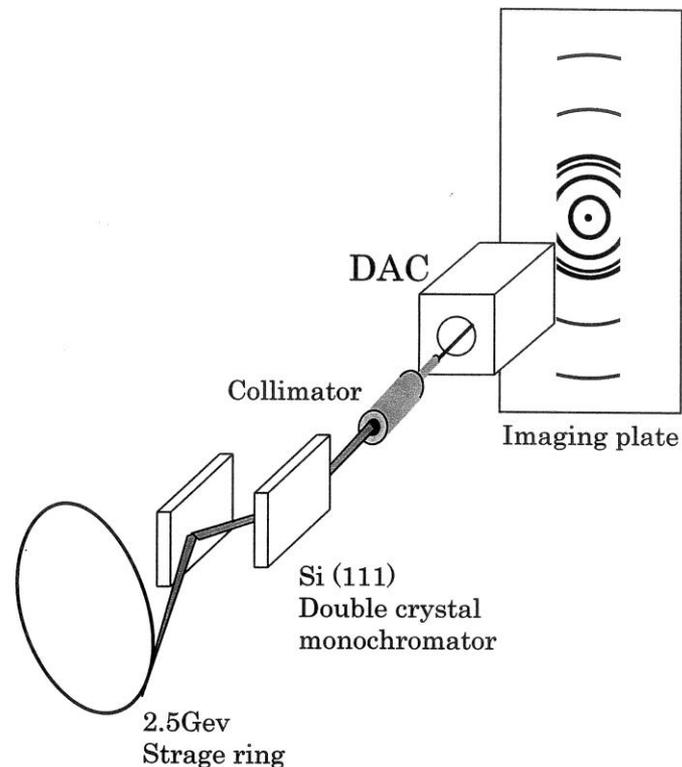
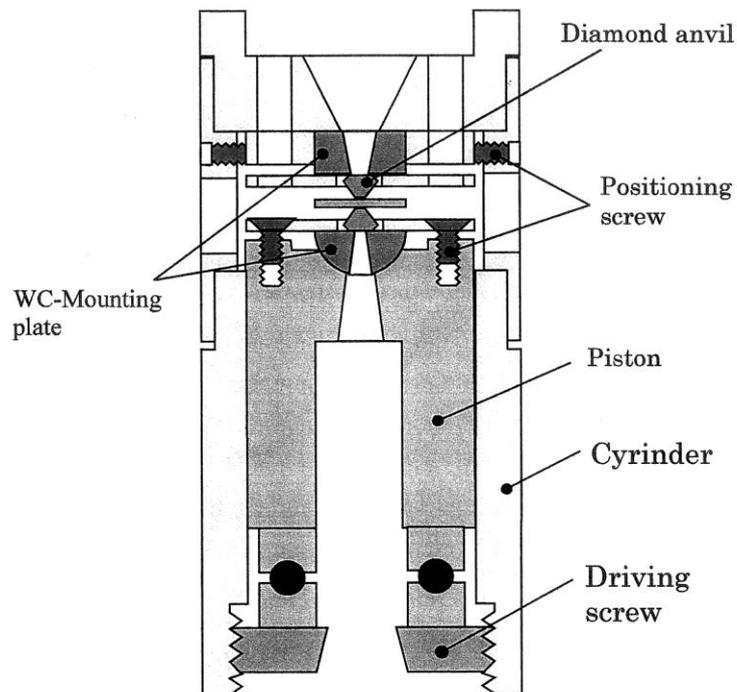


**An illustration of the six tungsten-carbide anvils compressing a pyrophyllite cube at the center of the anvils. The set of the anvils is operated by a 250-ton press.**

# a.c. susceptibility measurements under pressure up to 8 GPa, Osaka University, Okayama University, Japan



# Diffraction of synchrotron radiation under extreme pressure up to 60 GPa, Photon Factory, Tsukuba, Japan



$$\lambda = 0.6199 \text{ \AA}$$

Powder samples were filled together with a 4:1 methanol-ethanol mixture in a hole of 0.1 mm in the gasket made of stainless steel<sup>9</sup>

**I. Experiment under high pressure**

**II. Magnetostructural phase transitions in  $\text{Co}_x\text{Ni}_{1-x}\text{MnGe}$  under pressure**

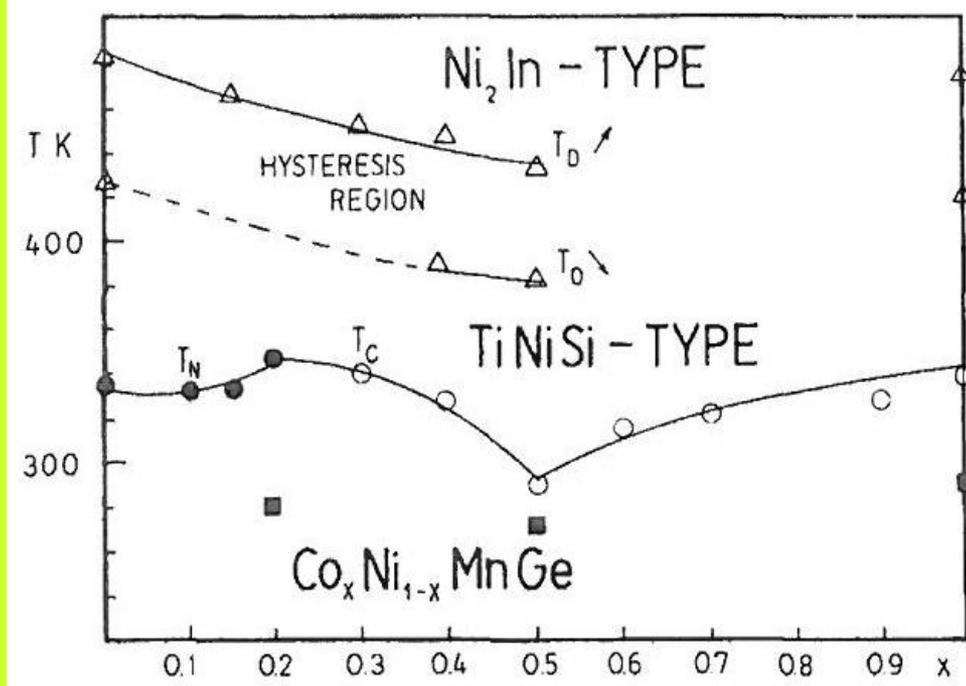
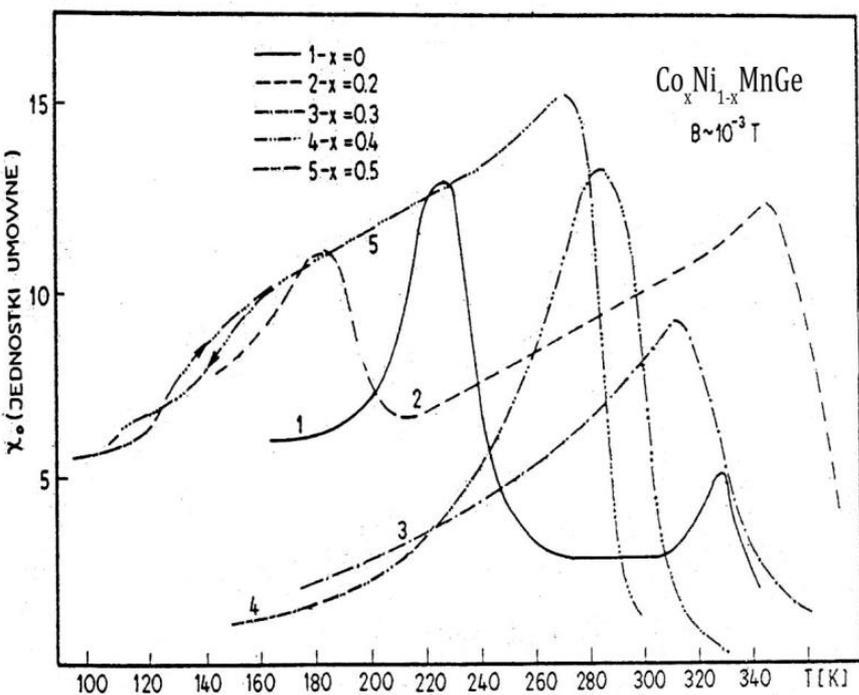


**III. Magnetic properties of  $\text{MnFeP}_{1-x}\text{As}_x$  series –pressure, magnetic field, electronic structure**

**IV. Magnetoelastic phase transitions, pressure effect, electronic structure**

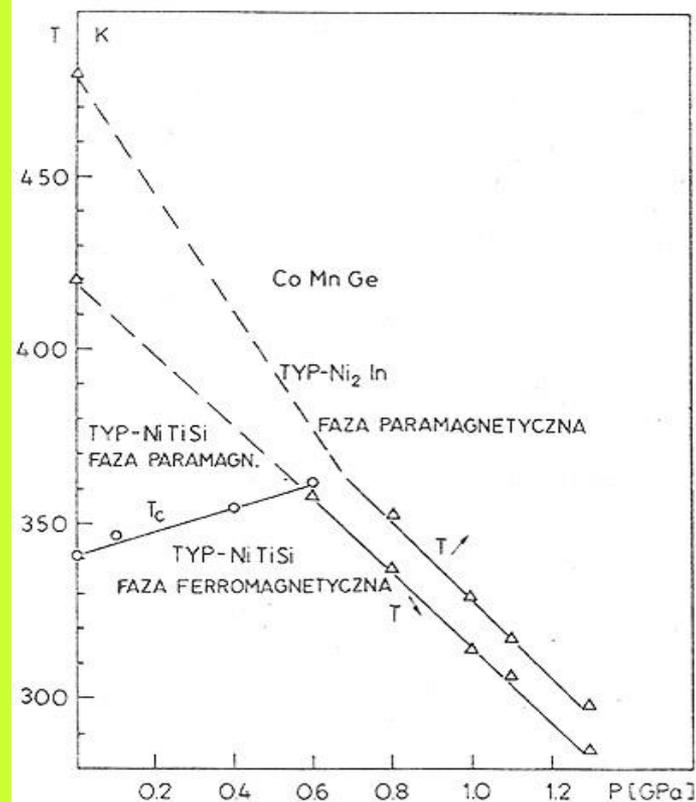
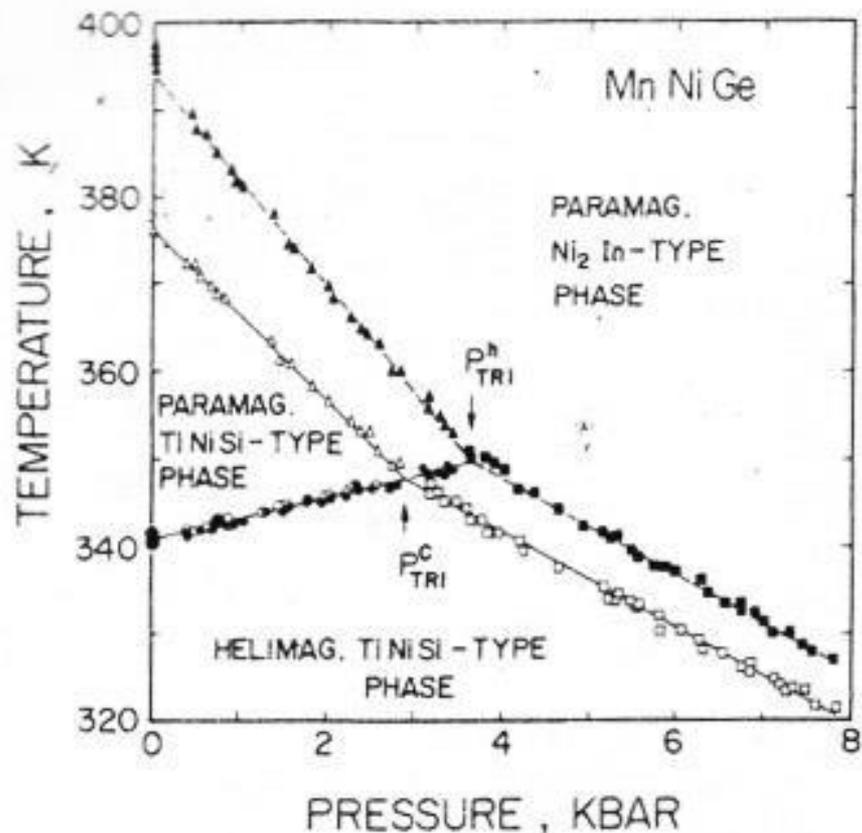
- a)  $\text{MnRhP}_{1-x}\text{As}_x$
- b)  $\text{MnRh}_{1-x}\text{Co}_x\text{As}$
- c)  $(\text{Mn}_{1-x}\text{Co}_x)_2\text{P}$
- d)  $\text{MnRu}_{1-x}\text{Rh}_x\text{As}$

# Pressure induced magnetostructural phase transitions in $\text{Co}_x\text{Ni}_{1-x}\text{MnGe}$



$\text{NiMnGe}$  and  $\text{CoMnGe}$  shows the evidence of the structural and magnetic transitions. The structural transition appears the discontinuous distortion type from the high temperature hexagonal  $\text{Ni}_2\text{In}$ -type crystal structure to the distorted orthorhombic  $\text{TiNiSi}$ -type phase.

# Pressure induced magnetostructural phase transitions in $\text{Co}_x\text{Ni}_{1-x}\text{MnGe}$



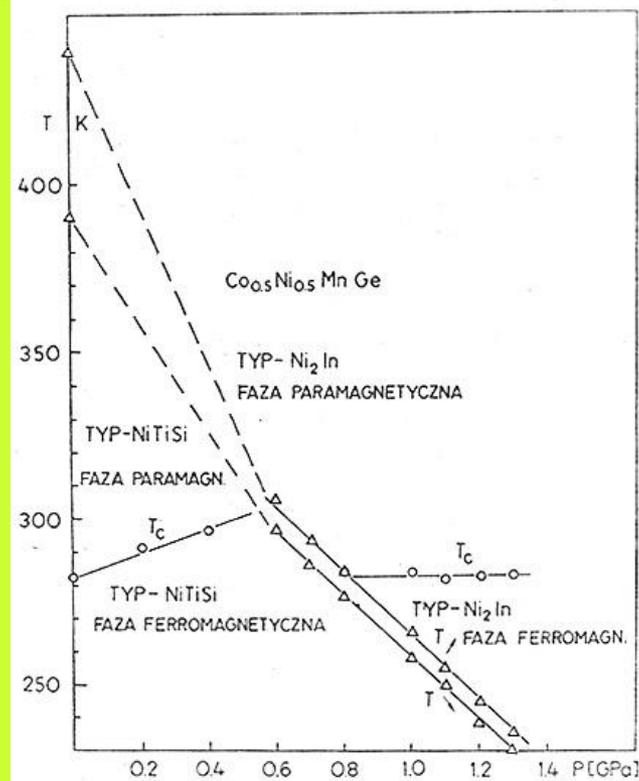
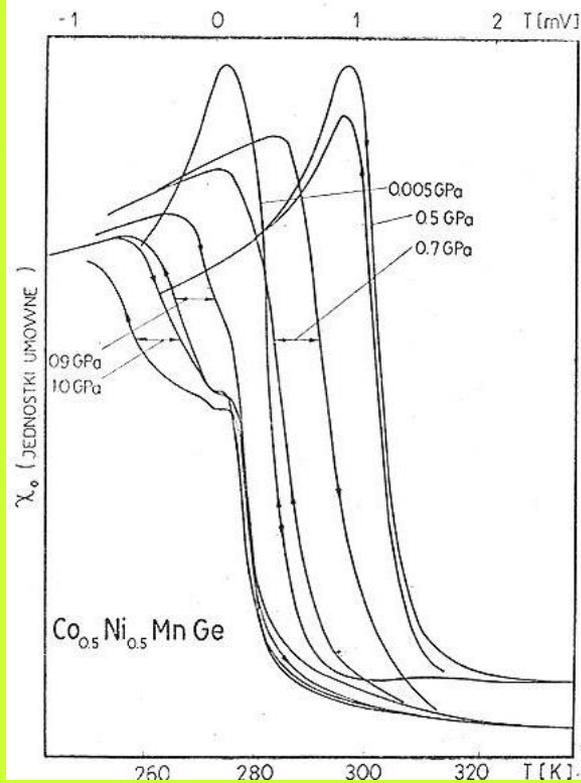
In both compounds the critical points on  $(P, T)$  phase diagrams were found

S.Anzai, K.Ozawa Phys. Rev. B 18, 2173 (1978) concerns  $\text{NiMnGe}$

S.Nizioł, A.Zięba, R.Zach, M.Baj, L.Dmowski J.Mag. Mag. Mat. 38, 205 (1983) concerns  $\text{Co}_x\text{Ni}_{1-x}\text{MnGe}$

R.Zach, R.Duraj, A. Szytuła Phys. Stat. Sol. A84 (1984) 229

# Pressure induced magnetostructural phase transitions in $\text{Co}_x\text{Ni}_{1-x}\text{MnGe}$



The interaction of magnetic ( $T_c$ ) and first-order distortion-type structural  $T_D$  transitions in  $\text{Co}_x\text{Ni}_{1-x}\text{MnGe}$  system was investigated using the ac susceptibility method under hydrostatic pressure. For all compositions  $T_c$  increases and  $T_D$  decreases versus pressure

$$G(T, P, \zeta, \eta) = a(T - \theta_D)\zeta^2 + e\zeta^4 + k\zeta^6 + b(T - \theta_C)\eta^2 + f\eta^4 + g\zeta^2\eta^2$$

# **I. Experiment under high pressure**

## **II. Magnetostructural phase transitions in $\text{Co}_x\text{Ni}_{1-x}\text{MnGe}$ under pressure**

## **III. Magnetic properties of $\text{MnFeP}_{1-x}\text{As}_x$ series –pressure, magnetic field, electronic structure**



## **IV. Magnetoelastic phase transitions, pressure effect, electronic structure**

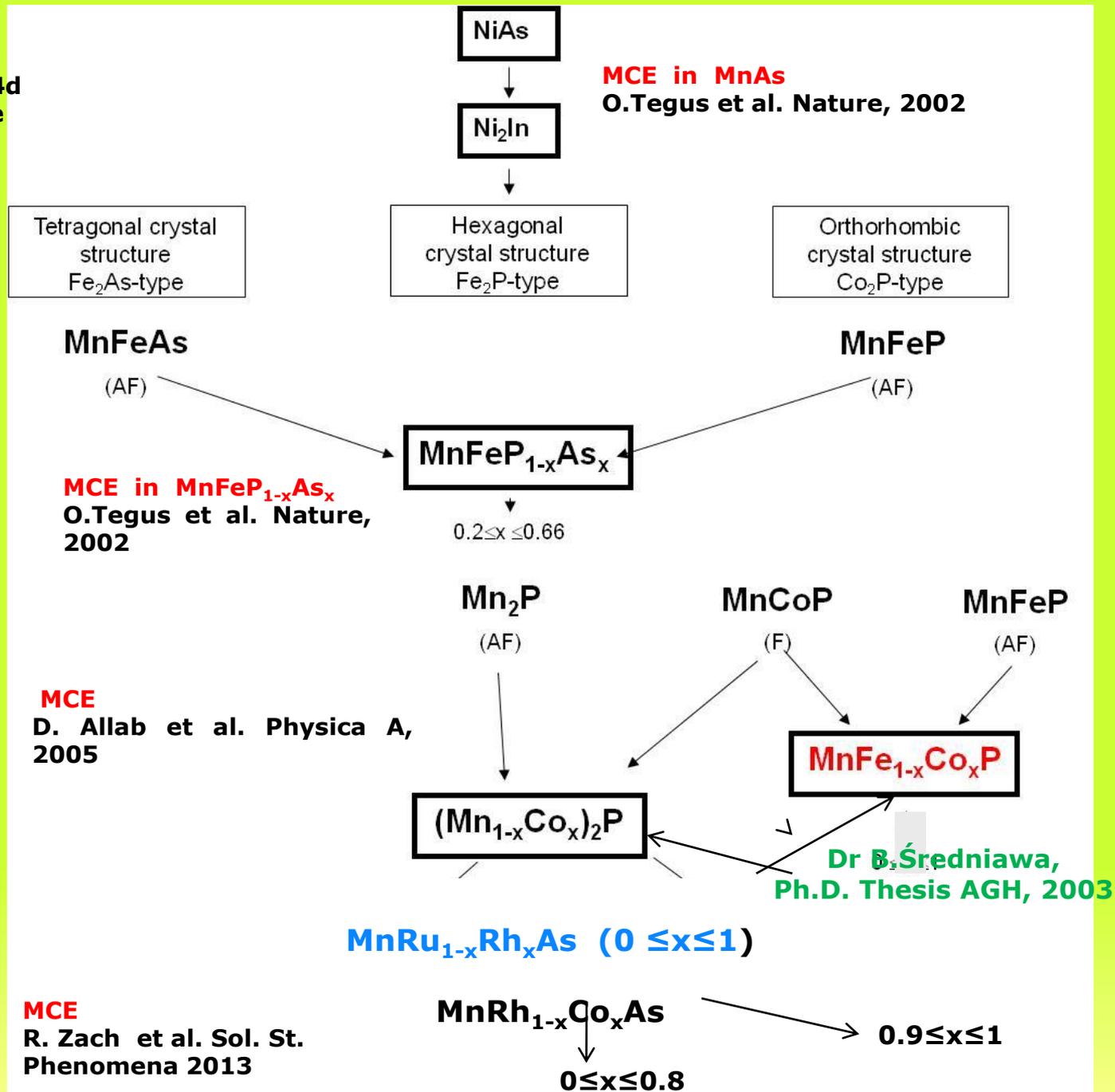
**a)  $\text{MnRhAs}$  and  $\text{MnRhP}$**

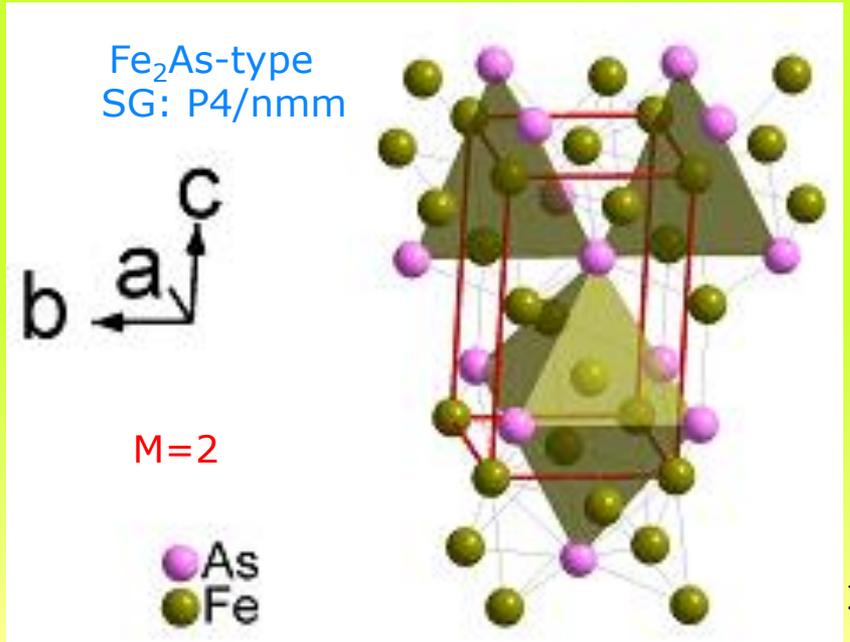
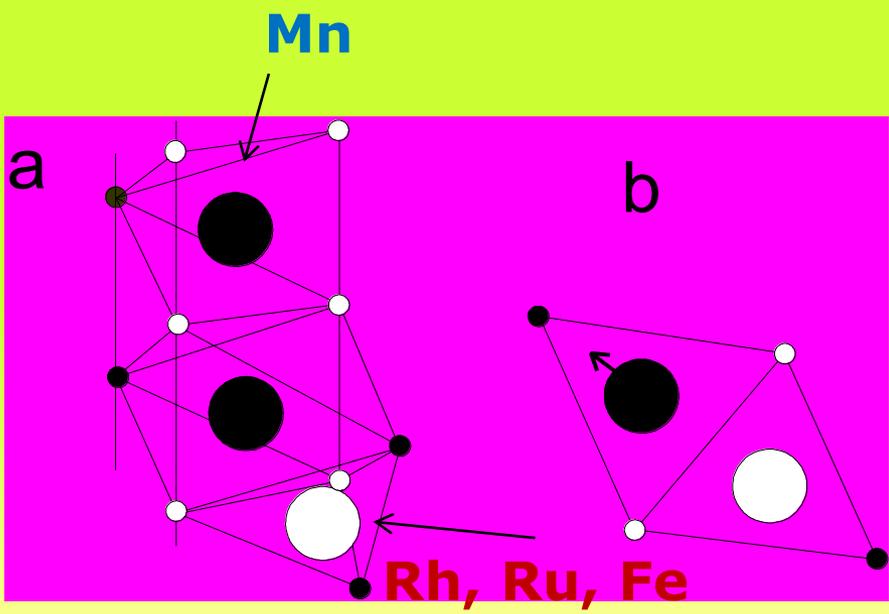
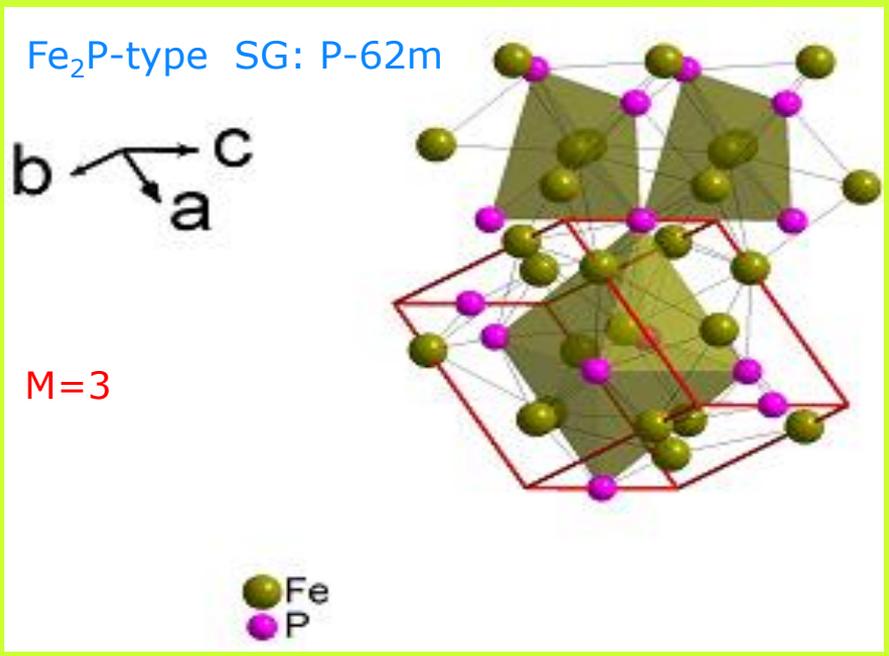
**b)  $\text{MnRh}_{1-x}\text{Co}_x\text{As}$**

**c)  $(\text{Mn}_{1-x}\text{Co}_x)_2\text{P}$**

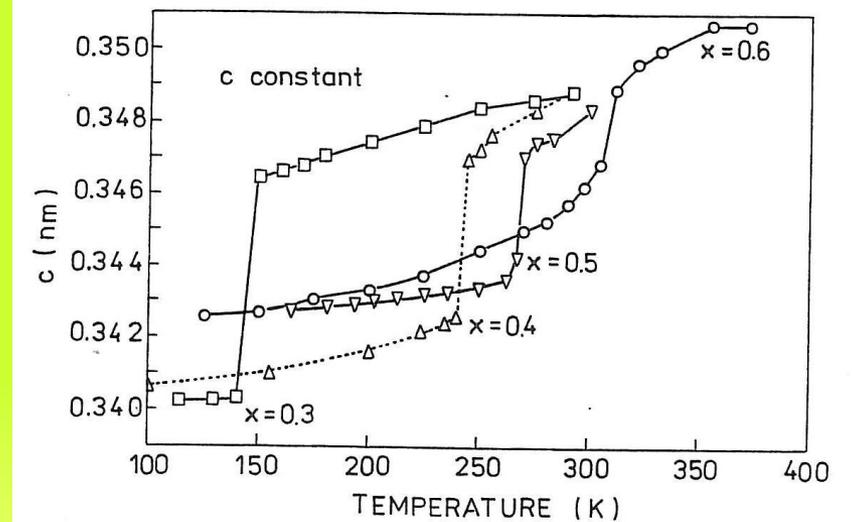
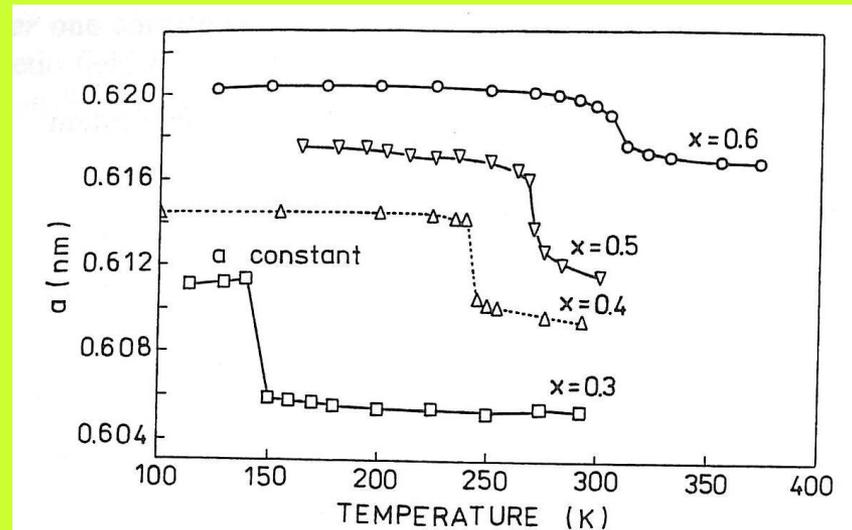
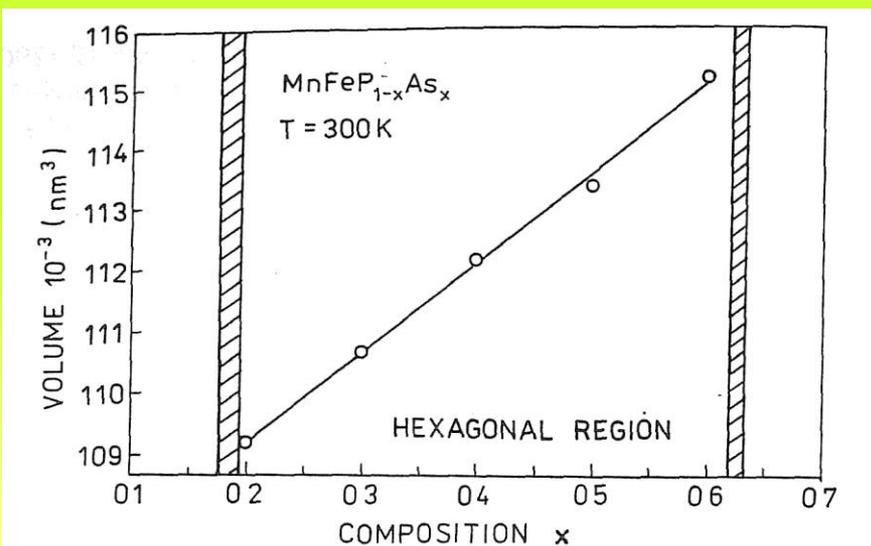
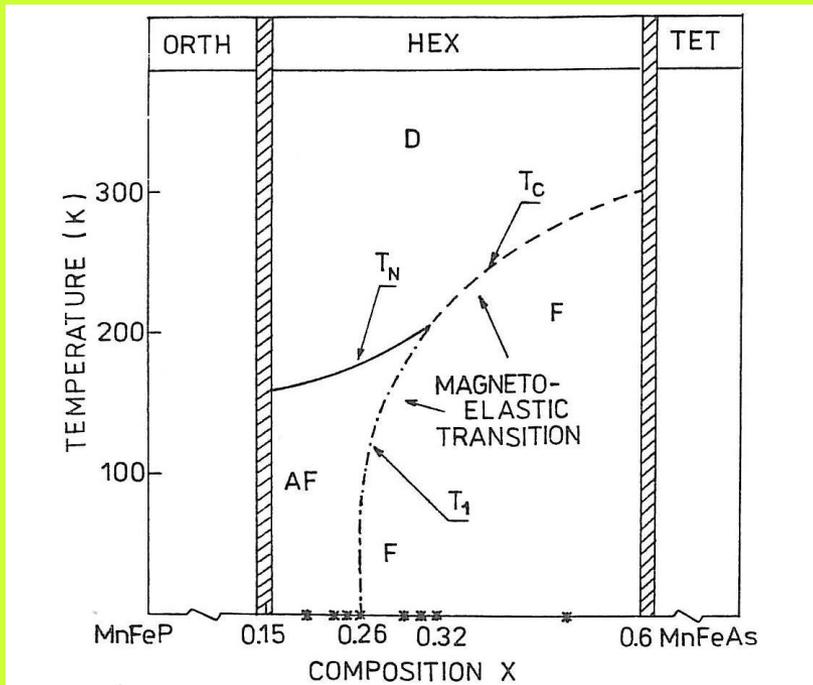
**d)  $\text{MnRu}_{1-x}\text{Rh}_x\text{As}$**

MM'X - type  
 M -- metal 3d  
 M'-- metal 3d,4d  
 X-- As,P,Si,Ge

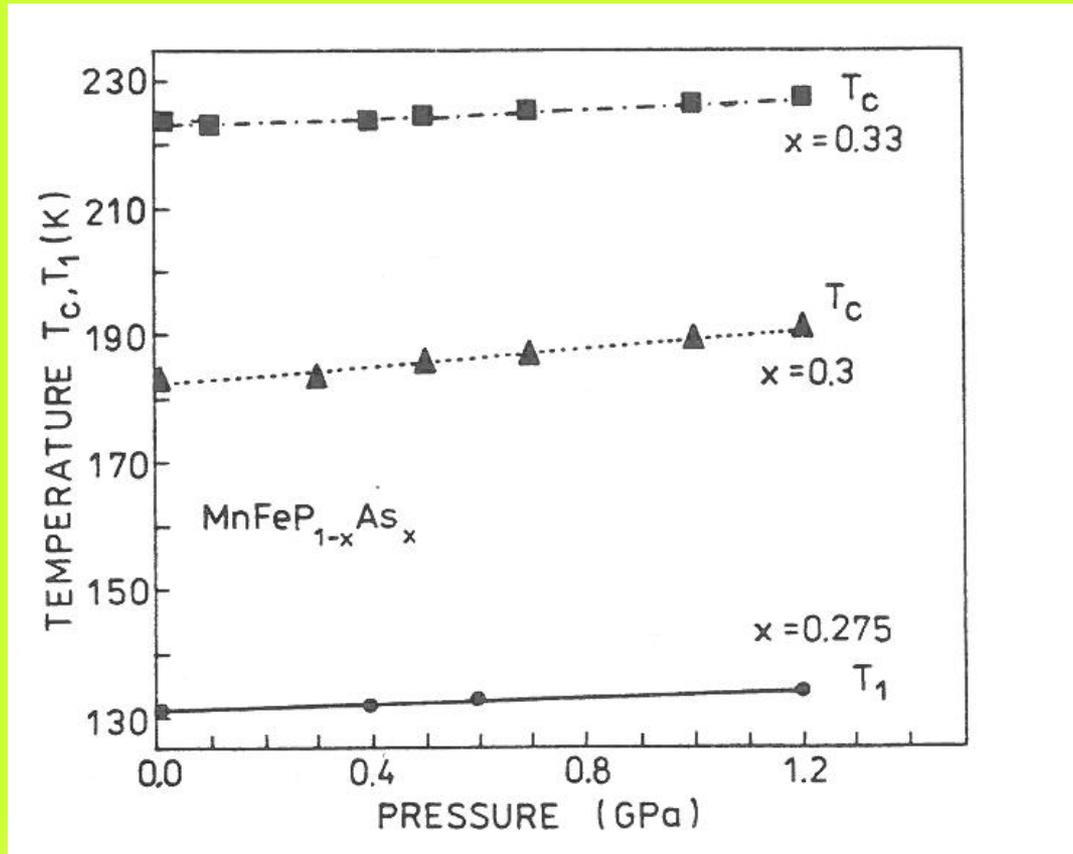




# Magnetic properties of $MnFeP_{1-x}As_x$ series



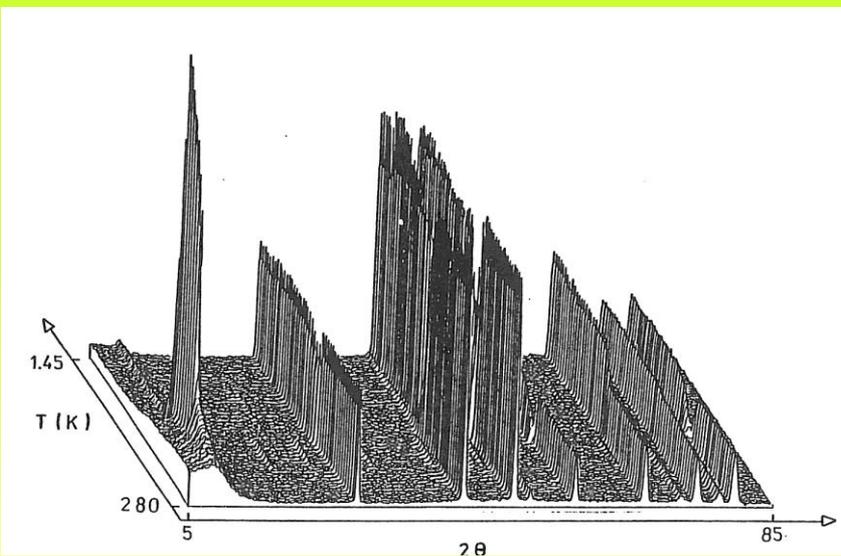
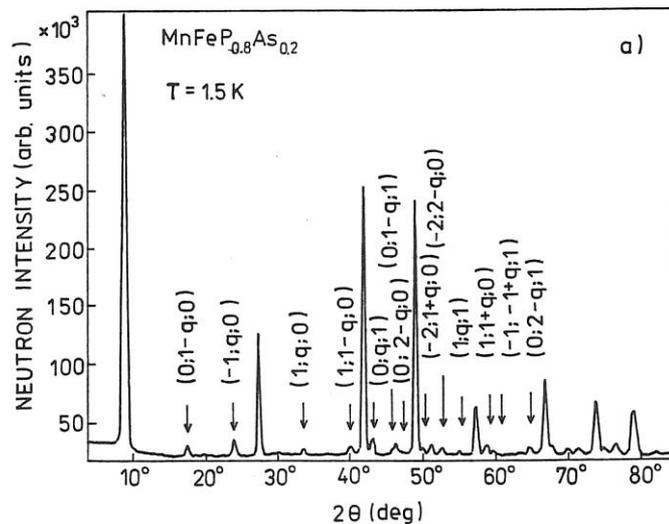
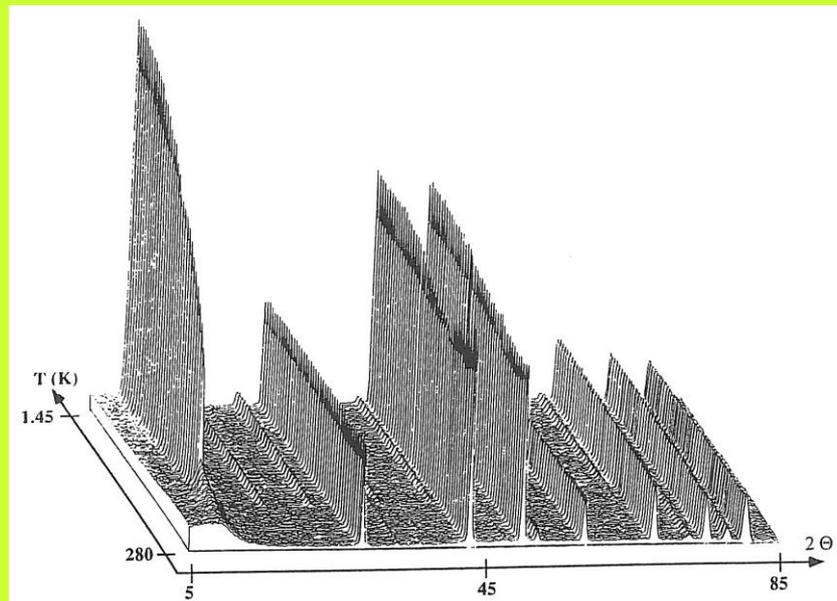
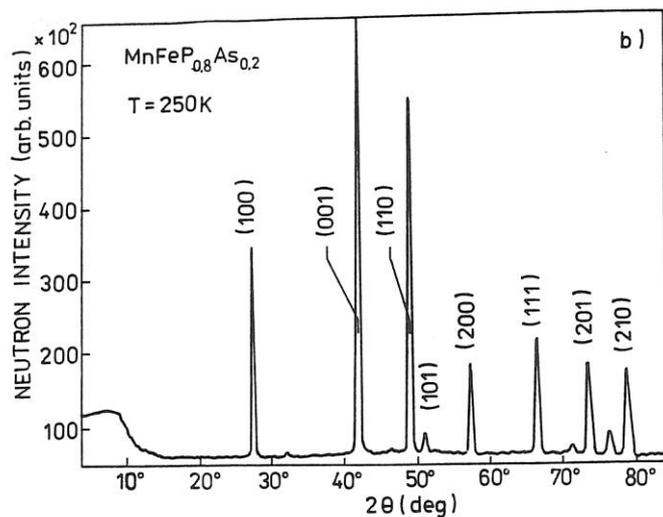
***(P,T) magnetic phase diagram for  $MnFeP_{1-x}As_x$***



No the unit cell volume change at the transitions at  $T_C$  and  $T_1$

# Magnetic properties of $MnFeP_{1-x}As_x$ series

## X=0.2



## X=0.2

## X=0.275

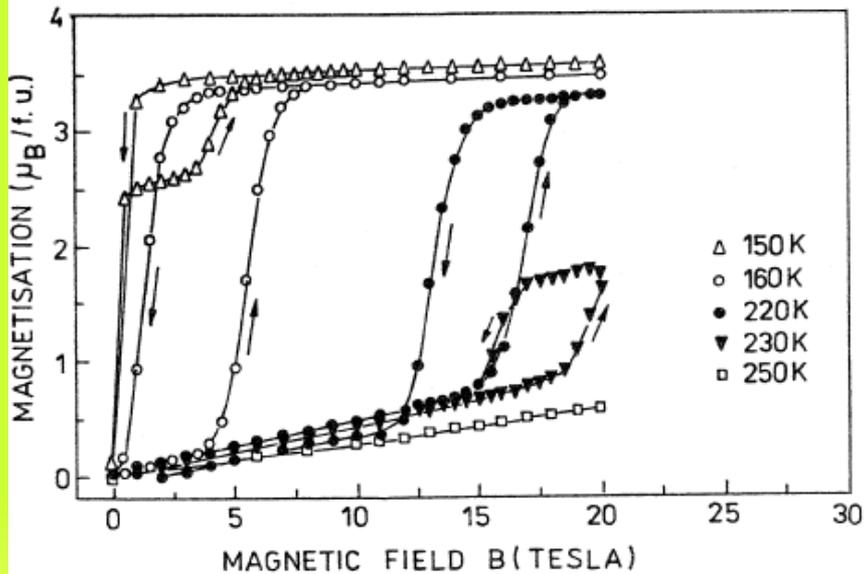
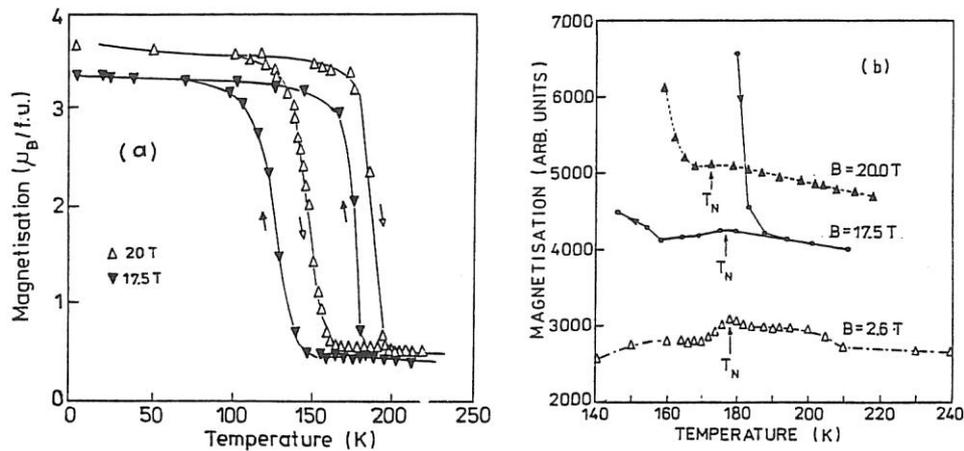
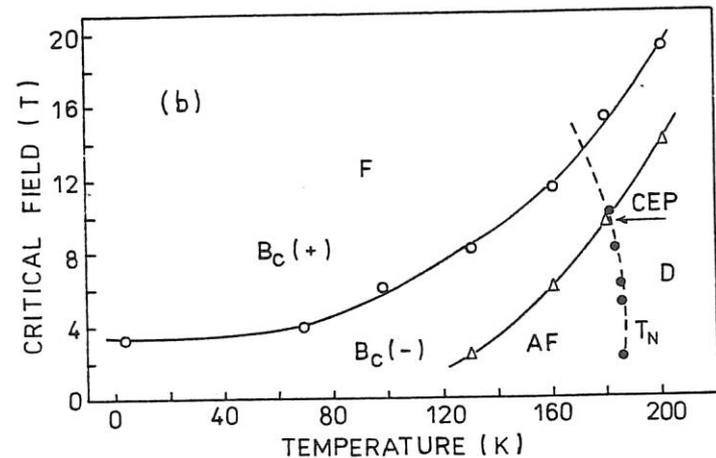
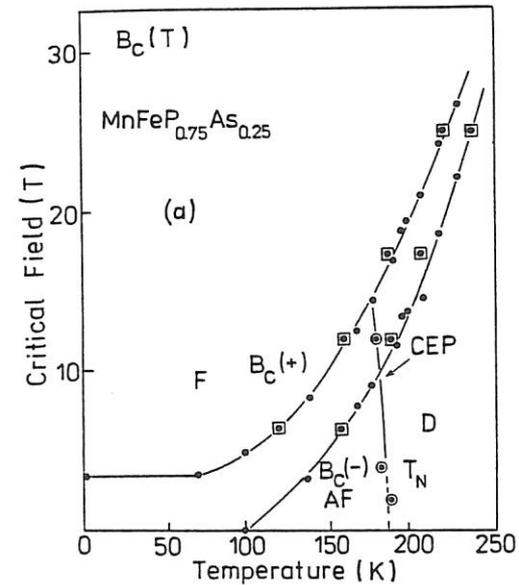
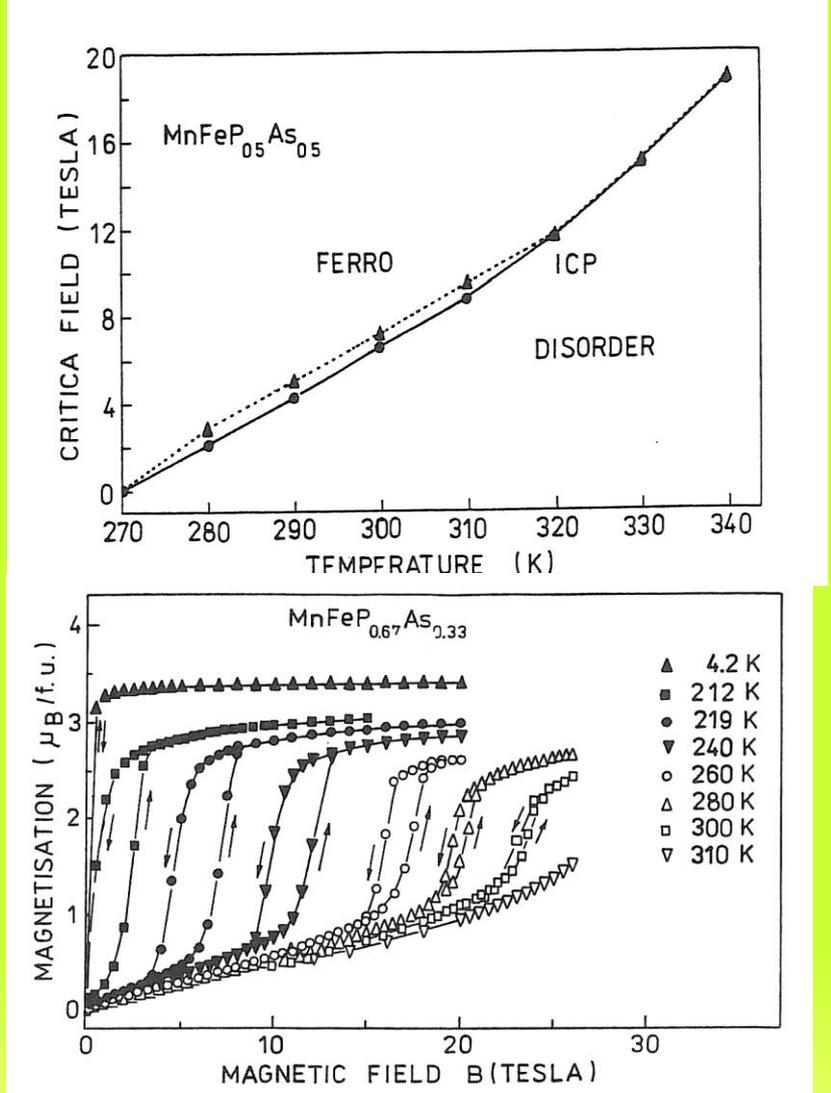
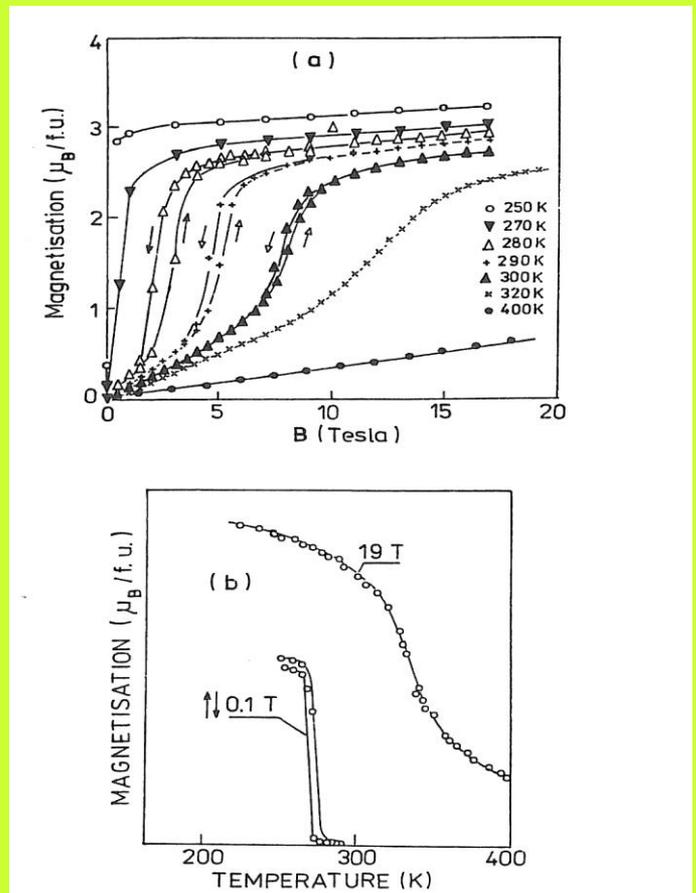


Fig. 3.14. Magnetisation of  $MnFeP_{0.725}As_{0.275}$  at various temperatures



Critical end point – the critical point where the line of the second order phase transition terminates in the line of the discontinuous phase boundary. The discontinuous phase boundaries are tangent one to each other at the CEP

# Magnetic properties of $MnFeP_{1-x}As_x$ series

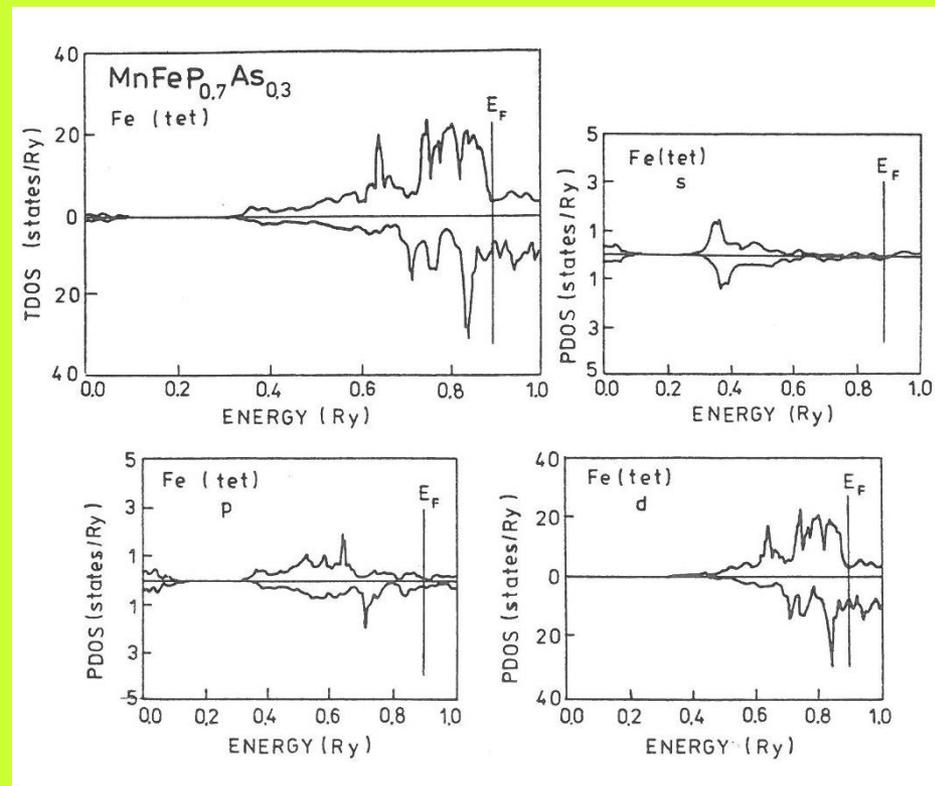
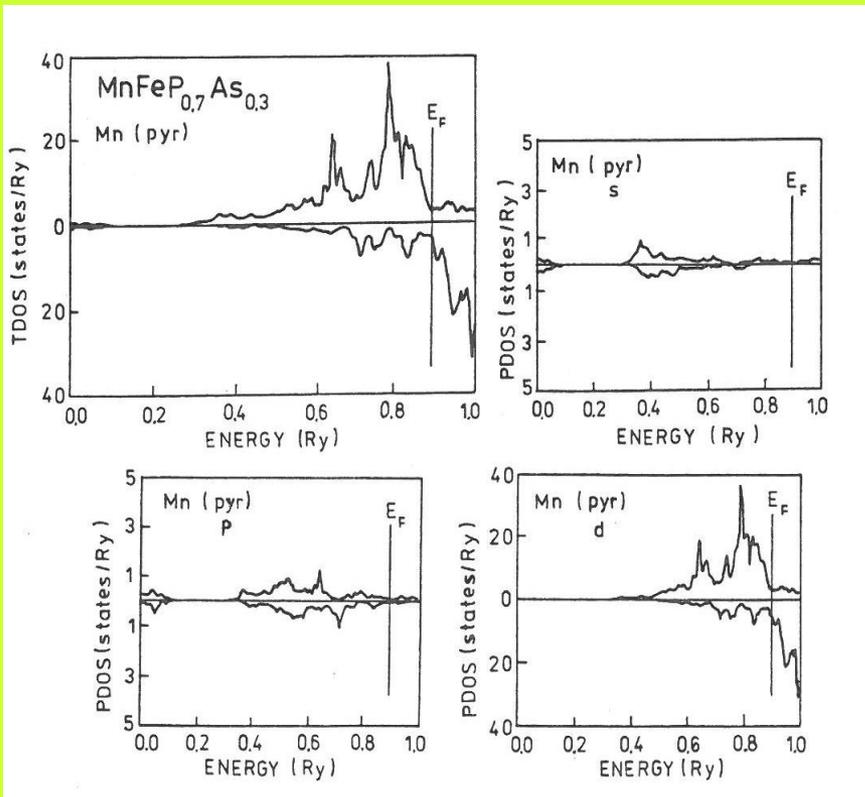


## Isolated Critical Point –

The critical point where the first order phase transition between the state and the ordered one terminates. The critical line separates two different phases having the same symmetry.

# KKR-CPA electronic band structure calculations – $\text{MnFeP}_{1-x}\text{As}_x$

$x=0.3$



# MnFe(As,P)

## Measured and calculated magnetic moments KKR-CPA

	Magnetic moment [ $\mu_B$ ]		Hyperfine field [T]	
	<i>Measured</i>	<i>Calculated</i>	<i>Measured</i>	<i>Calculated</i>
<b>MnFeP<sub>0.7</sub>As<sub>0.3</sub></b>				
Mn	2.55 (0.2)	3.02	-----	18,6
Fe	1.25 (0.2)	1.25	19.1	15,3
<b>MnFeP<sub>0.5</sub>As<sub>0.5</sub></b>				
Mn	2.02 (0.3)	3.01	-----	18,2
Fe	1.48 (0.3)	1.20	18.1	15,6
<b>MnRhAs</b>				
Mn	3.5 + 3.6	3.42		
Rh	0 + 0.2	0.0		
<b>MnRhP</b>				
Mn	3.13 (0.1)	2.99		
Rh	0.02 (0.1)	0		
<b>MnRhP<sub>0.8</sub>As<sub>0.2</sub></b>				
Mn	3.14(0.1)	3.2		
Rh	-----	0		

**I. Experiment under high pressure**

**II. Magnetostructural phase transitions in  $\text{Co}_x\text{Ni}_{1-x}\text{MnGe}$  series of compounds under pressure**

**III. Magnetic properties of  $\text{MnFeP}_{1-x}\text{As}_x$  series pressure, magnetic field, electronic structure**

**IV. Magnetoelastic phase transitions, pressure effect, electronic structure**



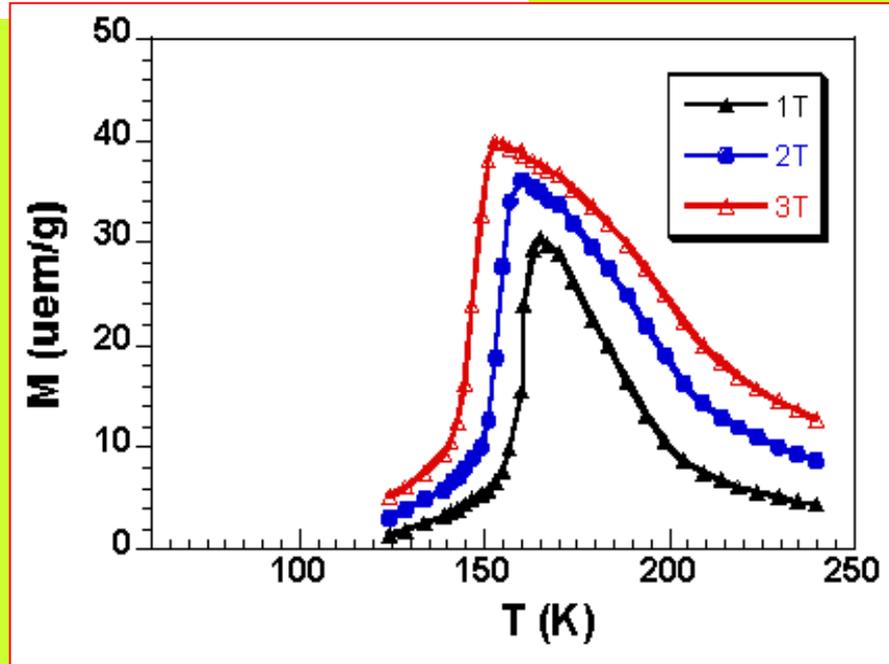
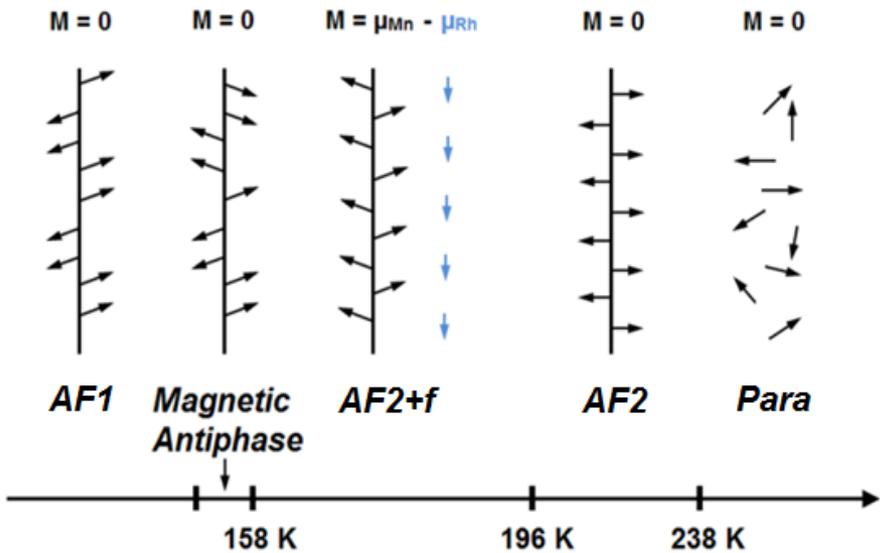
**a)  $\text{MnRhP}_{1-x}\text{As}_x$**

**b)  $\text{MnRh}_{1-x}\text{Co}_x\text{As}$**

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**d)  $\text{MnRu}_{1-x}\text{Rh}_x\text{As}$**

# Magnetic structures of MnRhAs



**Crystal structure: hexagonal  $Fe_2P$ -type,**  
 **$T_t = 158 K$  and  $T_c = 196 K$  magnetoelastic phase transitions**  
 **$T_N = 238 K$  Néel temperature**

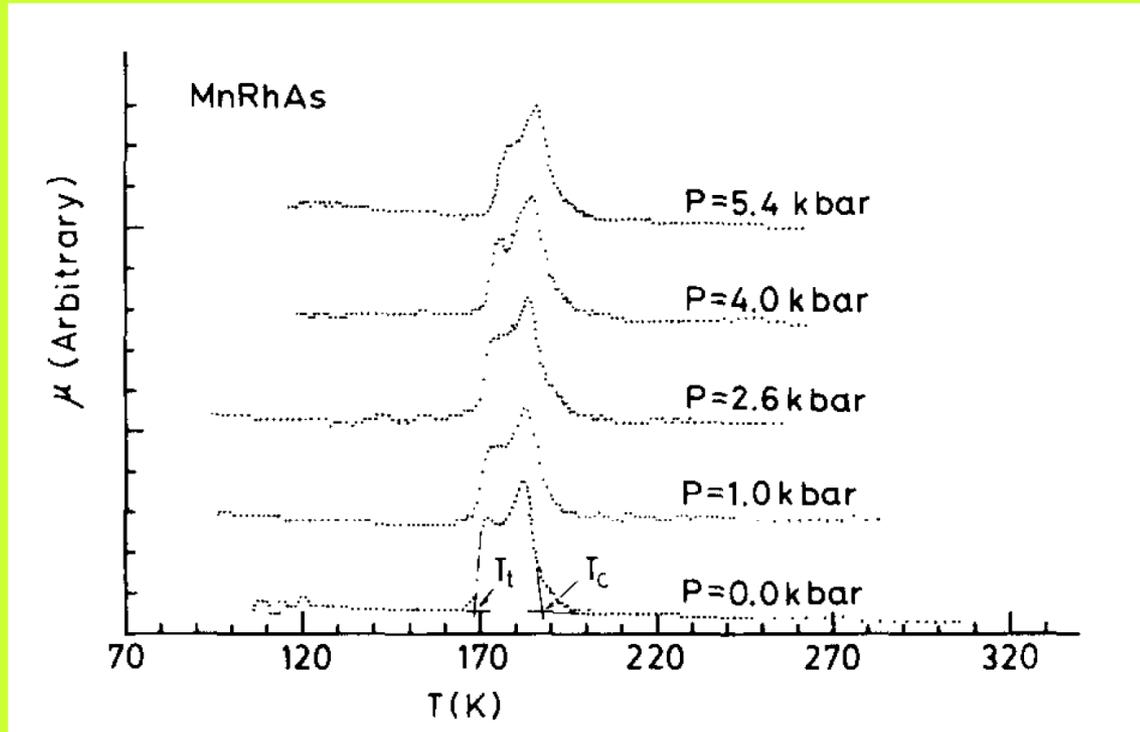
- AF1** – non-collinear antiferromagnetic phase,
- Magnetic Antiphase boundaries (ab)** ranging between the **AF1** and **AF2+f** configuration,
- AF2 + f** – complex antiferromagnetic + ferromagnetic ordering,
- AF2** – collinear antiferromagnetic phase,
- Para** - paramagnetic state

B. Chenevier, PhD Thesis UJF Grenoble, France (1990).  
 B. Chenevier, M. Bacmann, D. Fruchart, J.P. Sénateur, R. Fruchart, Phys. Stat. Sol. (a) 90(1) (1985) 331.  
 M. Balli, D. Fruchart, R. Zach, J. Appl. Phys. 115 (2014) 2039091.

# MnRhAs under pressure up to 1.5 GPa

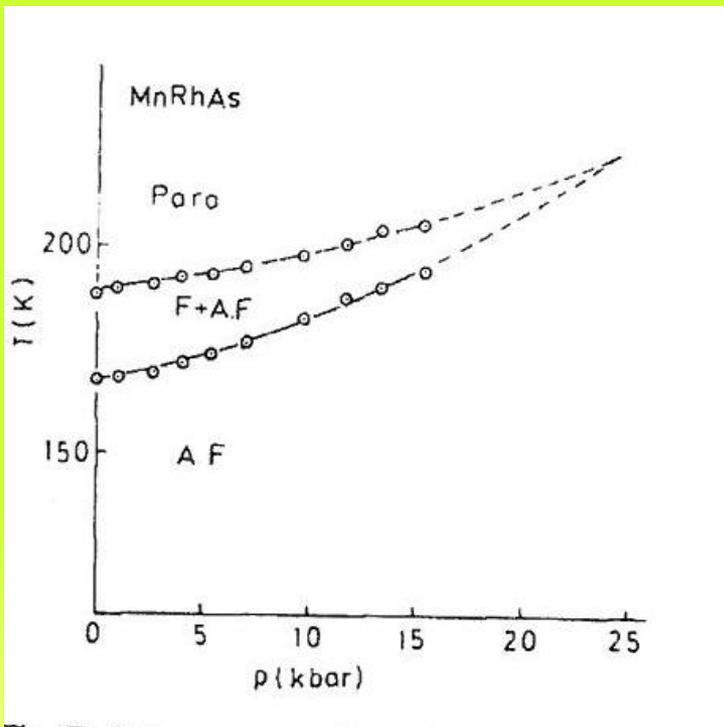
Magnetisation vs. T recorded at constant pressure

(P,T) magnetic phase diagram

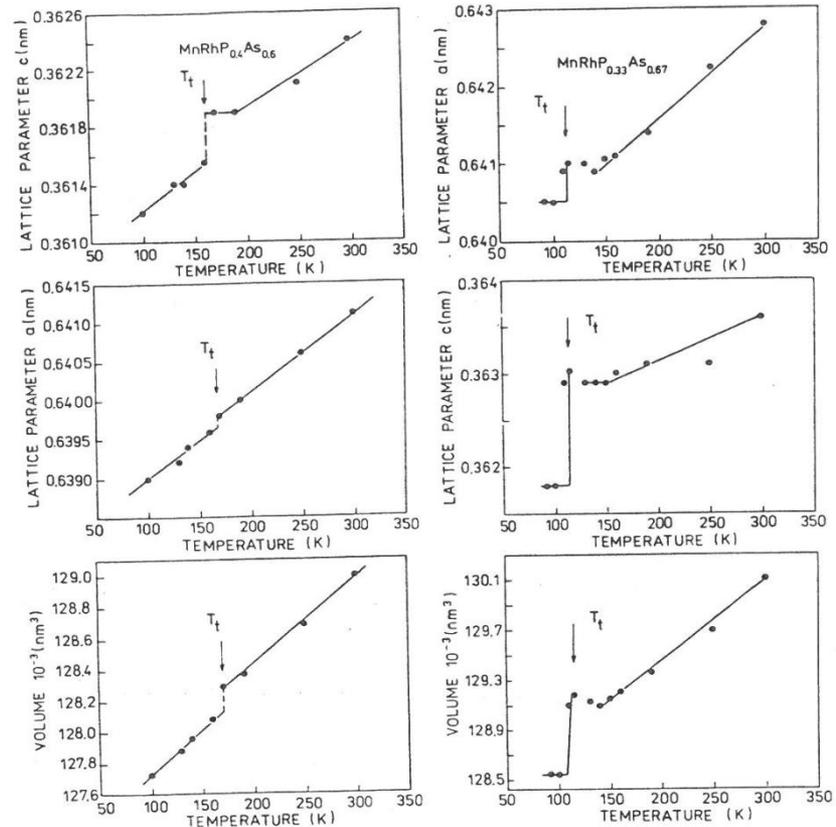
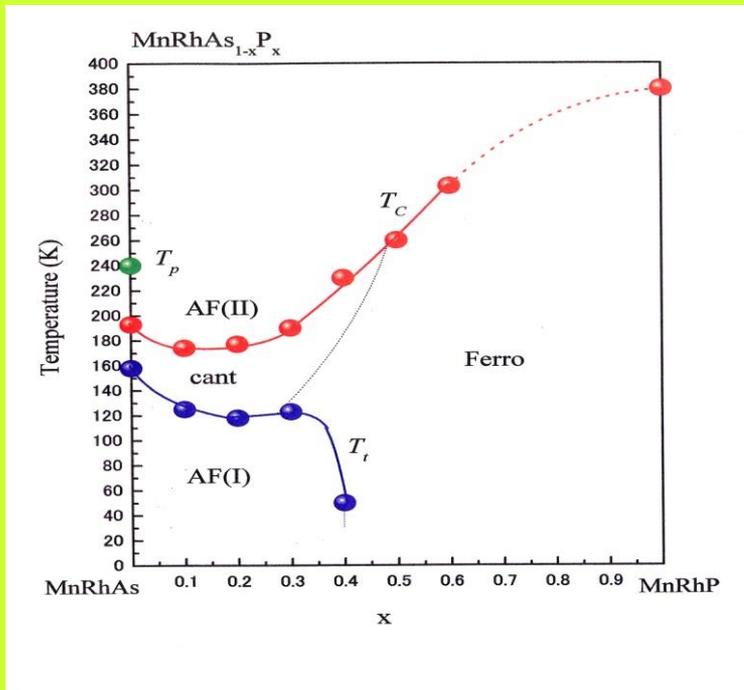


It is found that  $T_C$  and  $T_t$  increases vs. applied pressure and the pressure dependence of  $T_C$  and  $T_t$  is nonlinear. Kanomata et al. suggested critical point at  $P=2.45$  GPa and  $T=224$  K

T. Kanomata et al. J.Mag. Mag. Mat. 68, 286 (1987)



# Magnetic and crystal structure properties of $\text{MnRhP}_{1-x}\text{As}_x$

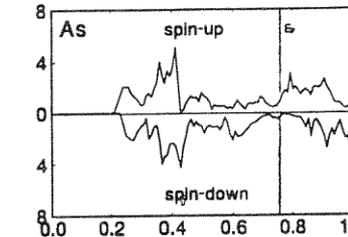
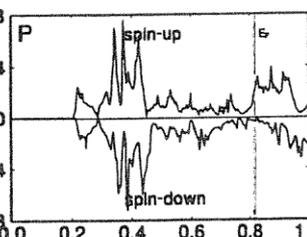
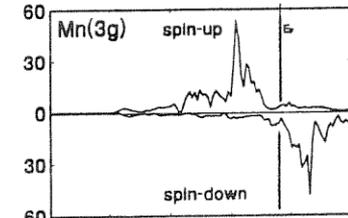
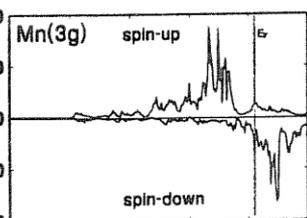
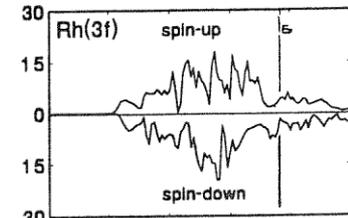
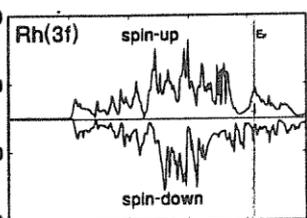
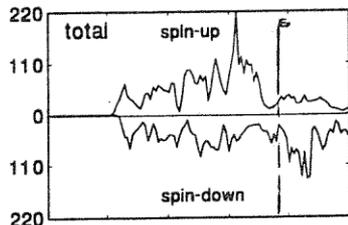
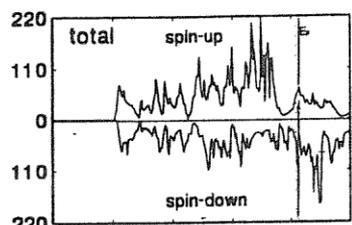


A. Roger, Thesis, Paris 1970  
 B. N. Fuji Thesis Osaka 2002

**Crystal structure: hexagonal  $\text{Fe}_2\text{P}$ -type**  
**Volume of elementary cell linearly decreases with the increase of the phosphorus content**  
**Transitions at  $T_t$ : magnetoelastic phase transition**  
**The abrupt volume change is found for two studied contents.**

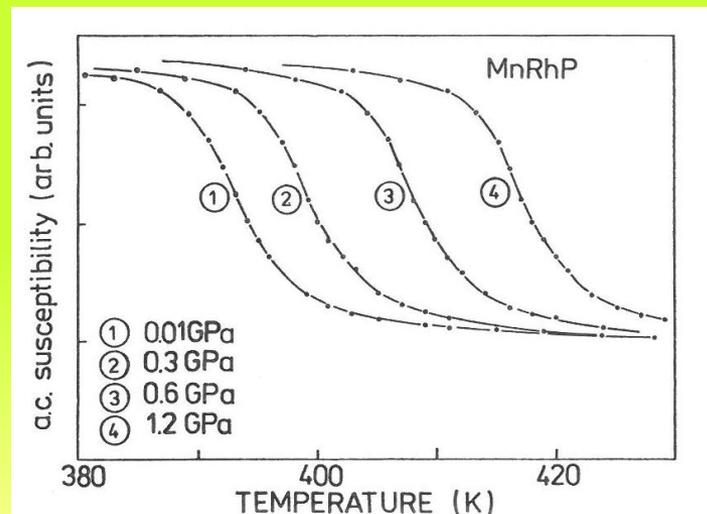
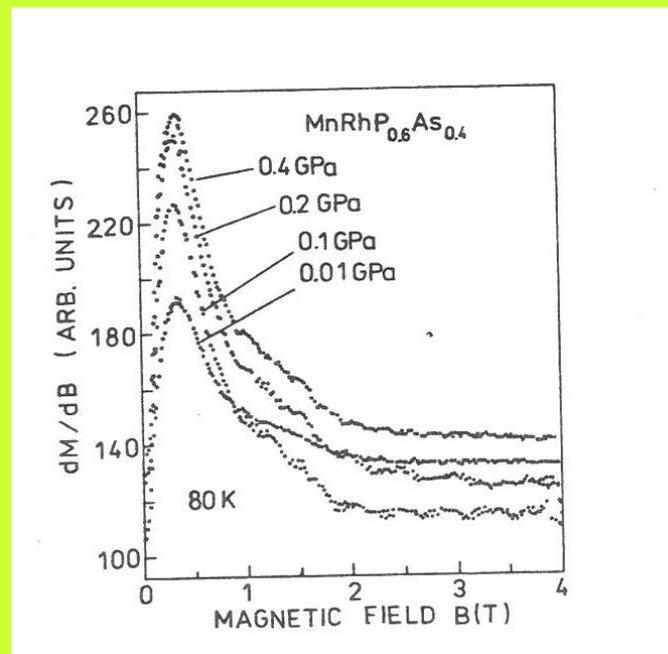
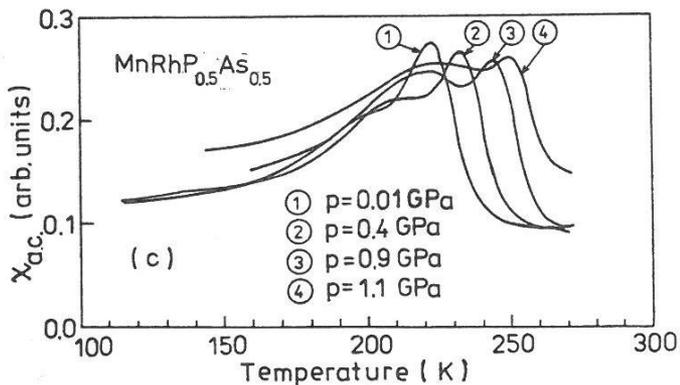
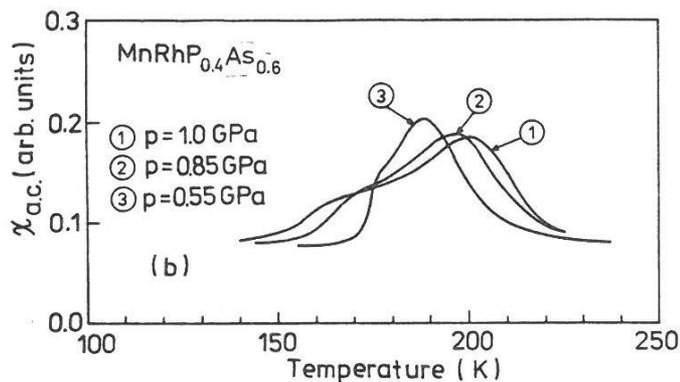
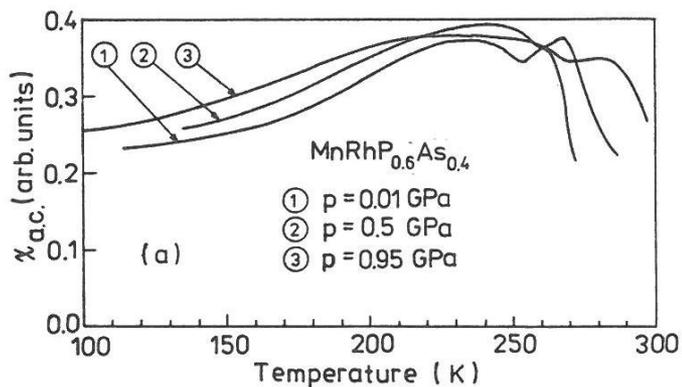
# Electronic band structure calculations KKR (KKR\_CPA)

## MnRhP and MnRhAs<sub>0.4</sub>P<sub>0.6</sub>

**MnRhP**
**MnRhAs<sub>0.4</sub>P<sub>0.6</sub>**

**ENERGY (Ry)**
**MnFe(As,P)**

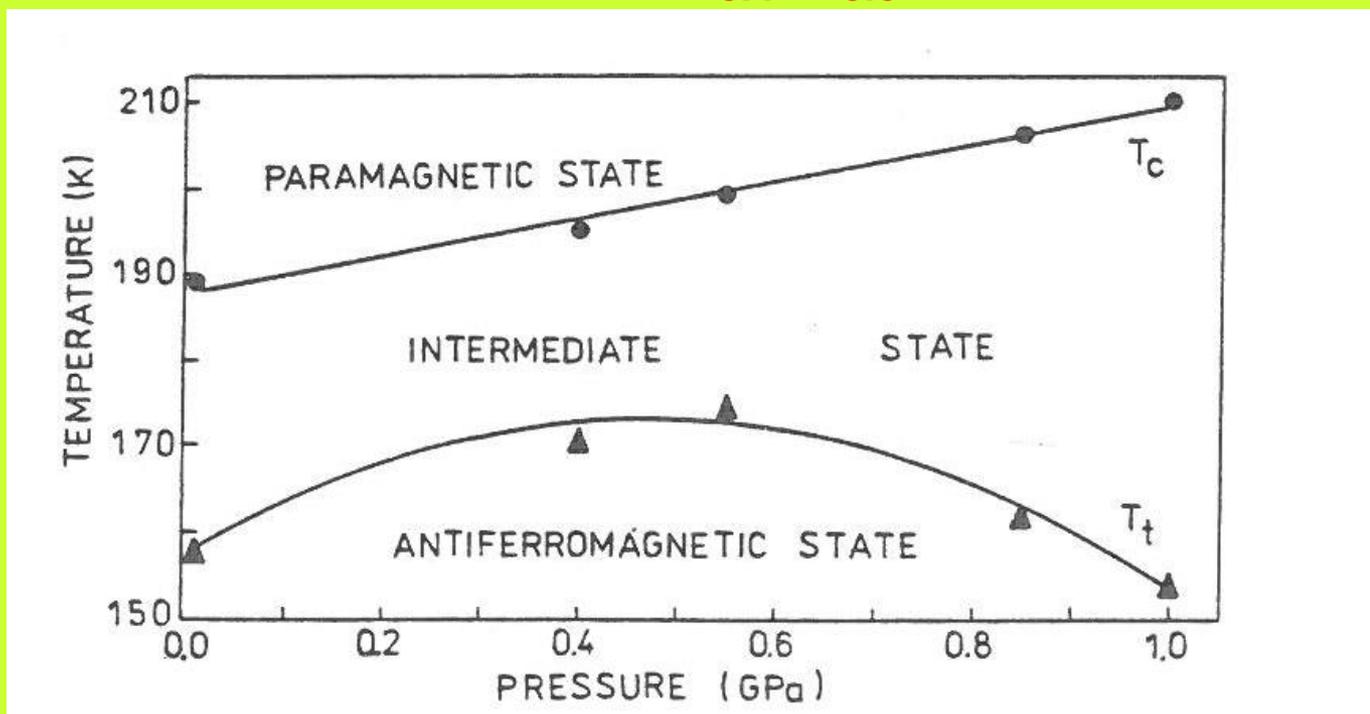
	Magnetic moment [ $\mu_B$ ]		Hyperfine field [T]	
	Measured	Calculated	Measured	Calculated
<b>MnFeP<sub>0.7</sub>As<sub>0.3</sub></b>				
Mn	2.55 (0.2)	3.02	-----	18,6
Fe	1.25 (0.2)	1.25	19.1	15,3
<b>MnFeP<sub>0.5</sub>As<sub>0.5</sub></b>				
Mn	2.02 (0.3)	3.01	-----	18,2
Fe	1.48 (0.3)	1.20	18.1	15,6
<b>MnRhAs</b>				
Mn	3.5 + 3.6	3.42		
Rh	0 + 0.2	0.0		
<b>MnRhP</b>				
Mn	3.13 (0.1)	2.99		
Rh	0.02 (0.1)	0		
<b>MnRhP<sub>0.8</sub>As<sub>0.2</sub></b>				
Mn	3.14(0.1)	3.2		
Rh	-----	0		

# MnRhP<sub>1-x</sub>As<sub>x</sub> under pressure up to 1.5 GPa



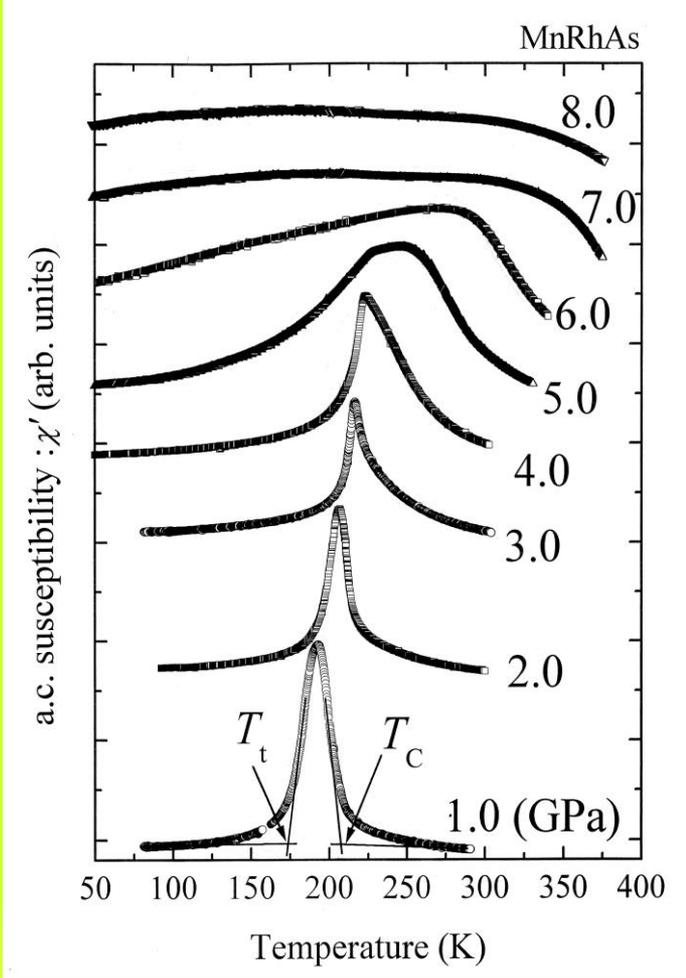
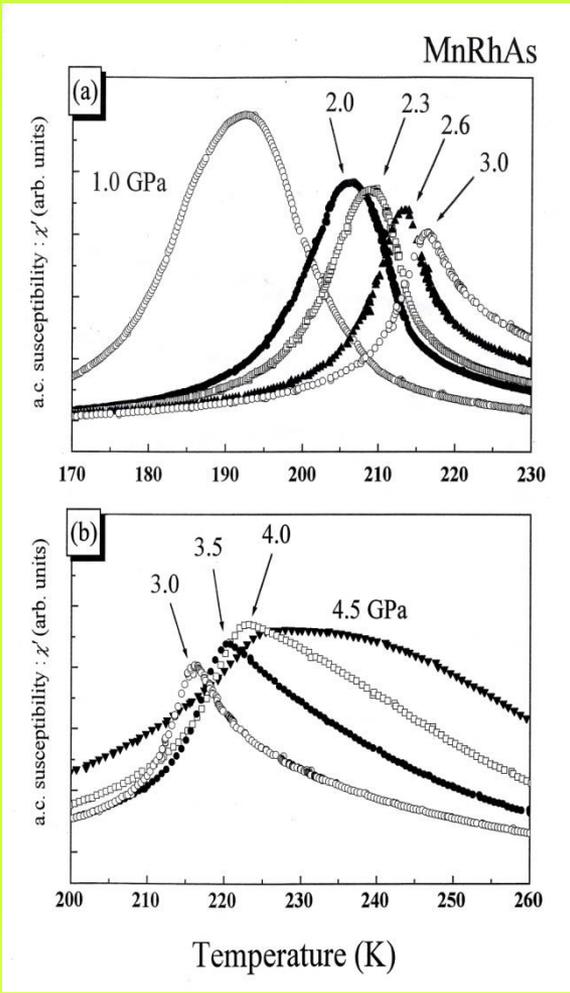
# MnRhAs<sub>1-x</sub>P<sub>x</sub> under pressure up to 1.5 GPa

## MnRhP<sub>0.4</sub>As<sub>0.6</sub>

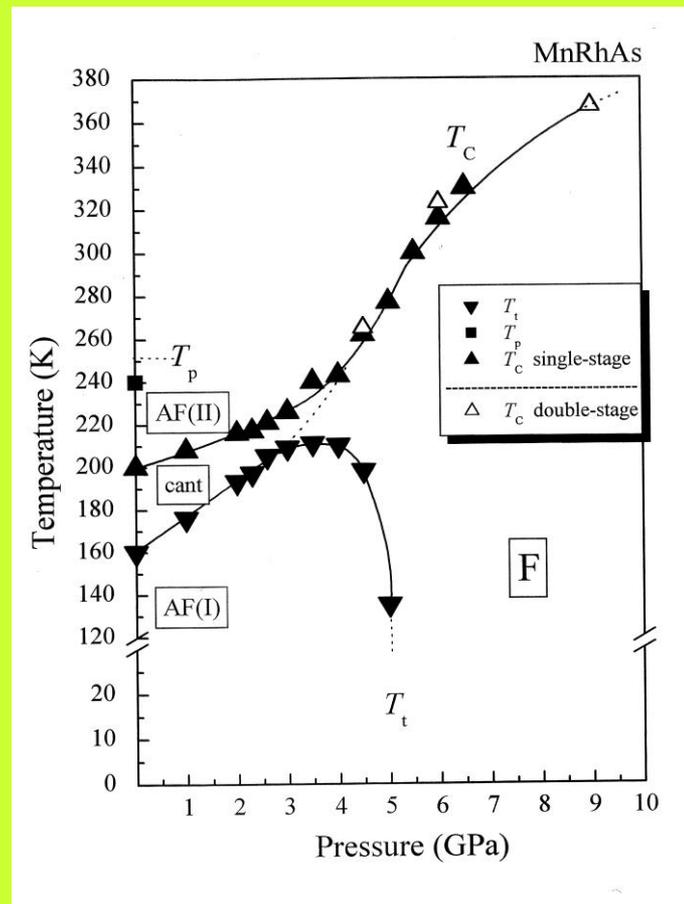
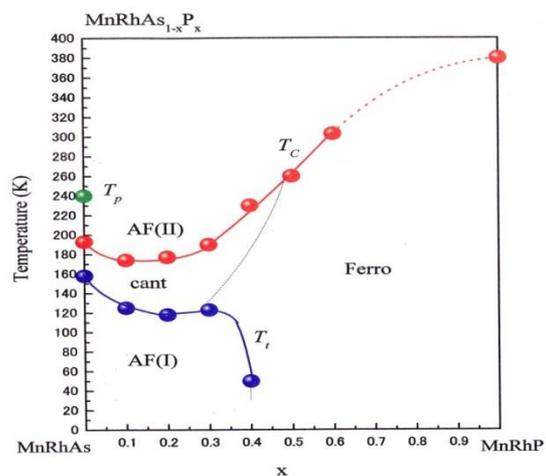
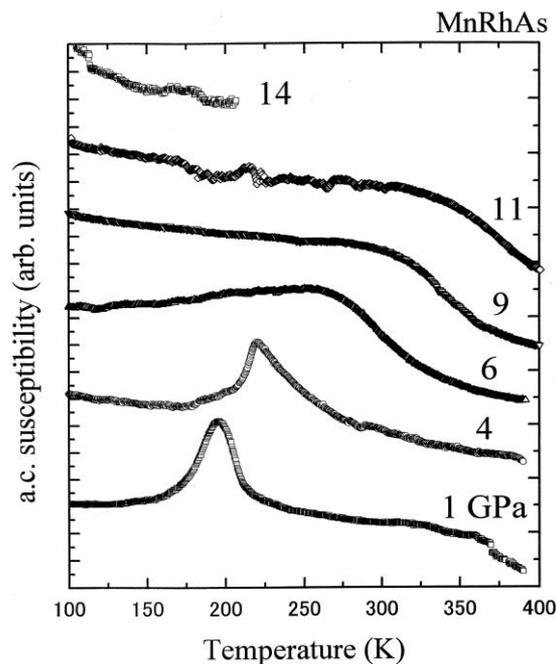


- \* The (P,T) magnetic phase diagrams were determined.
- \* The Curie temperature increases vs. pressure for all specimens.
- \* The pressure variation of the T<sub>t</sub> critical temperature depends on composition.
- \* In the case of MnRhP<sub>0.4</sub>As<sub>0.6</sub> the T<sub>t</sub> variation versus external pressure P and versus chemical substitution x presents the same nonlinear character. The ferromagnetic state is stabilised under higher pressure.

# MnRhAs under pressure a.c. susceptibility measurements up to 8 GPa



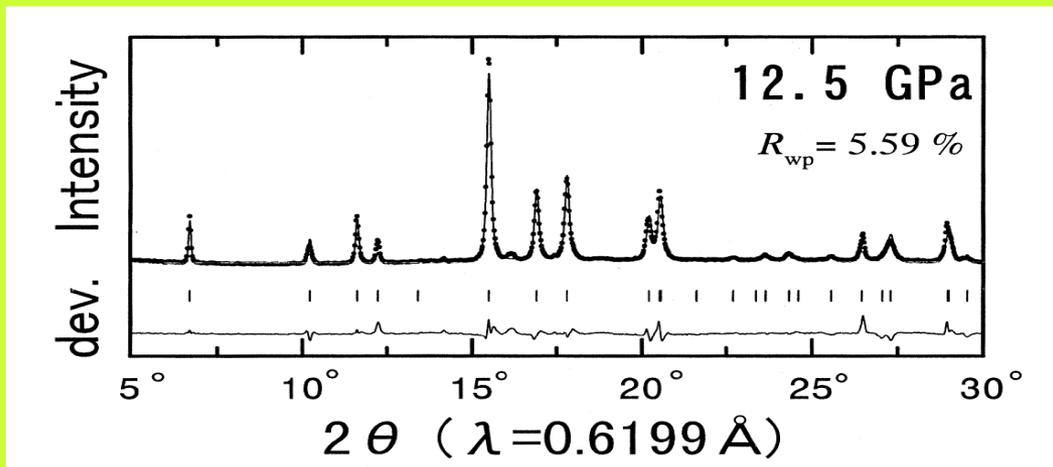
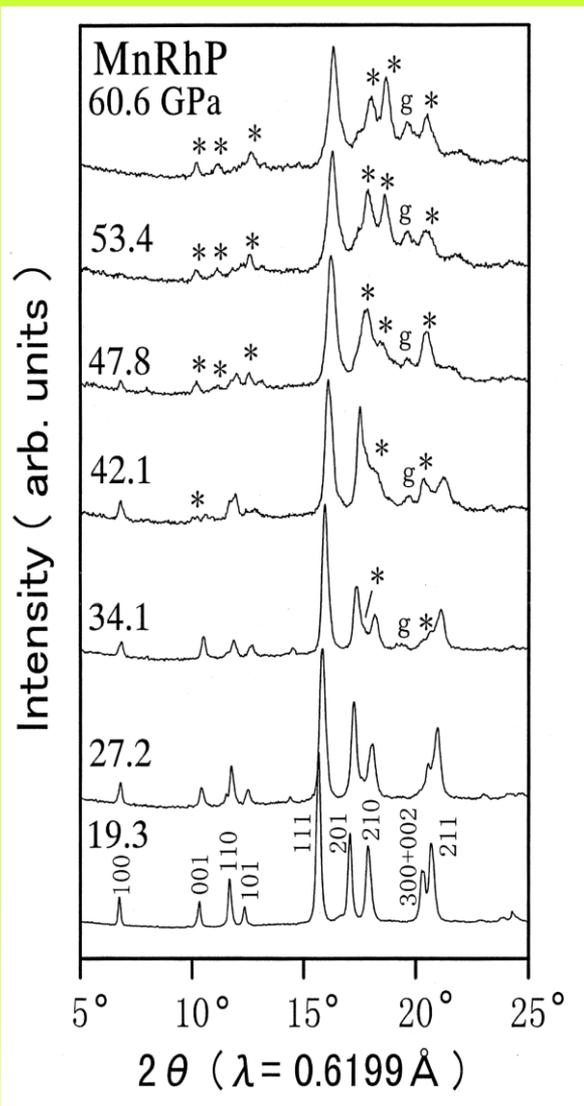
# (P,T) magnetic phase diagram of MnRhAs



**Pressure induced ferromagnetic state above 5 GPa in MnRhAs**

N.Fujii, R.Zach, M.Ishizuka, S.Endo, F.Ono, T. Kanomata  
J.Magn.Magn.Mat. 224, (2001) 12

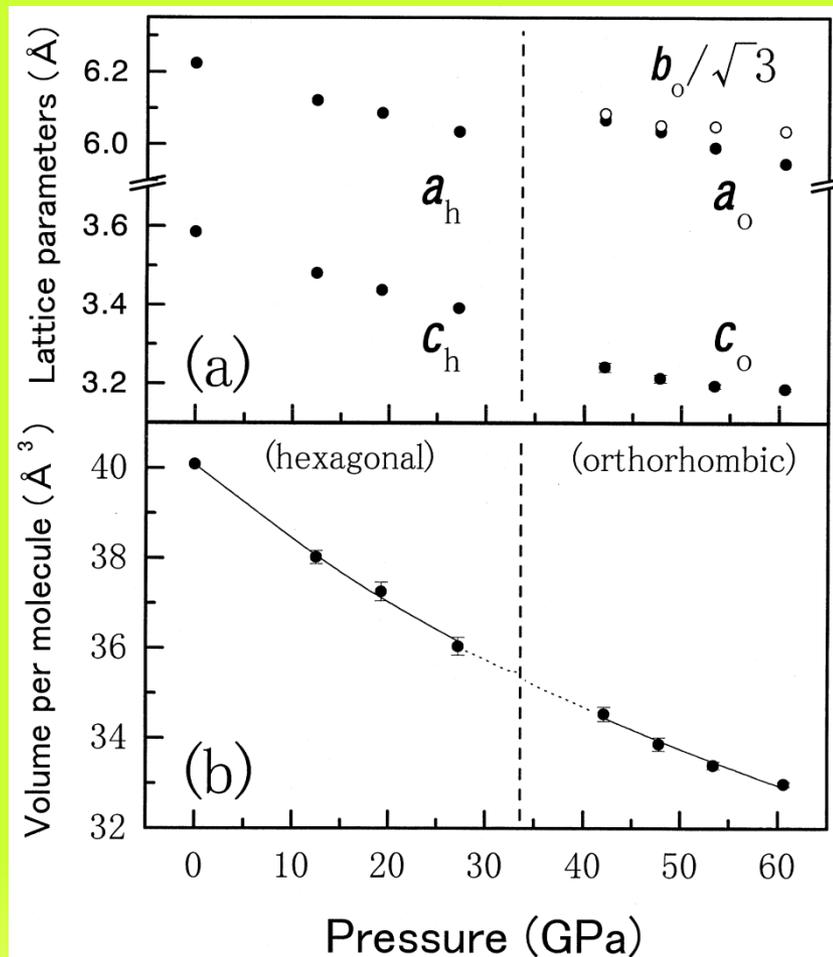
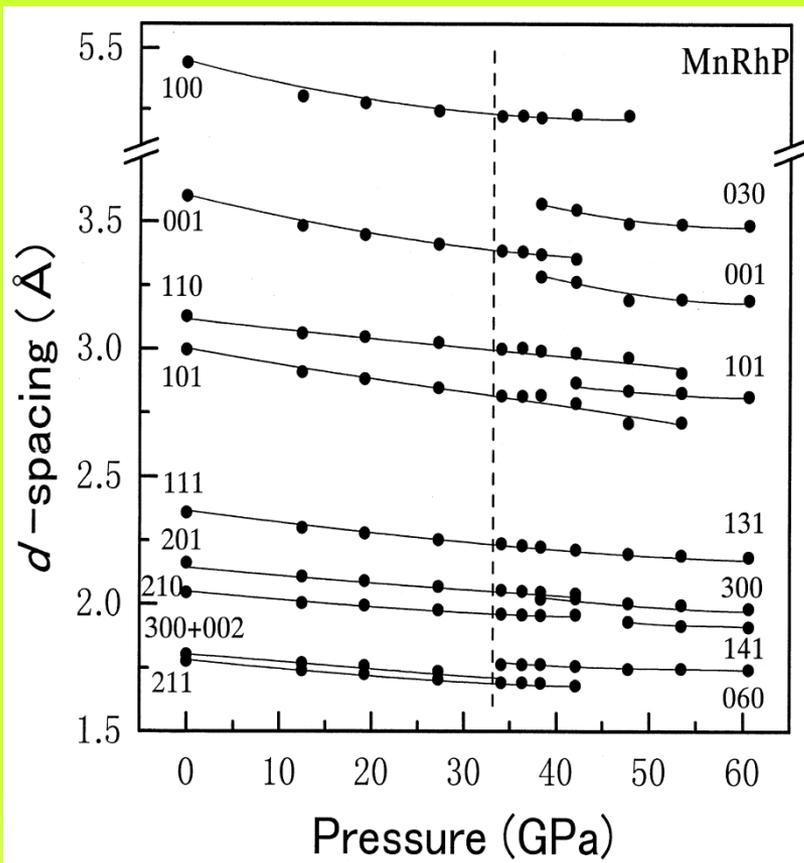
## Pressure induced structural transition in MnRhP



**Results of Rietveld analysis for low pressure phase of MnRhP.  
Observed pattern is indicated by dots**

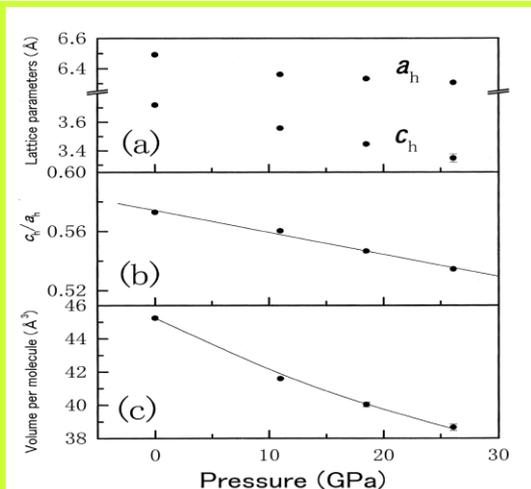
**A transition from the hexagonal  $\text{Fe}_2\text{P}$ -type structure to an orthorhombic one was observed in MnRhP at a pressure of approximately 34 GPa**

# Pressure induced structural transition in MnRhP

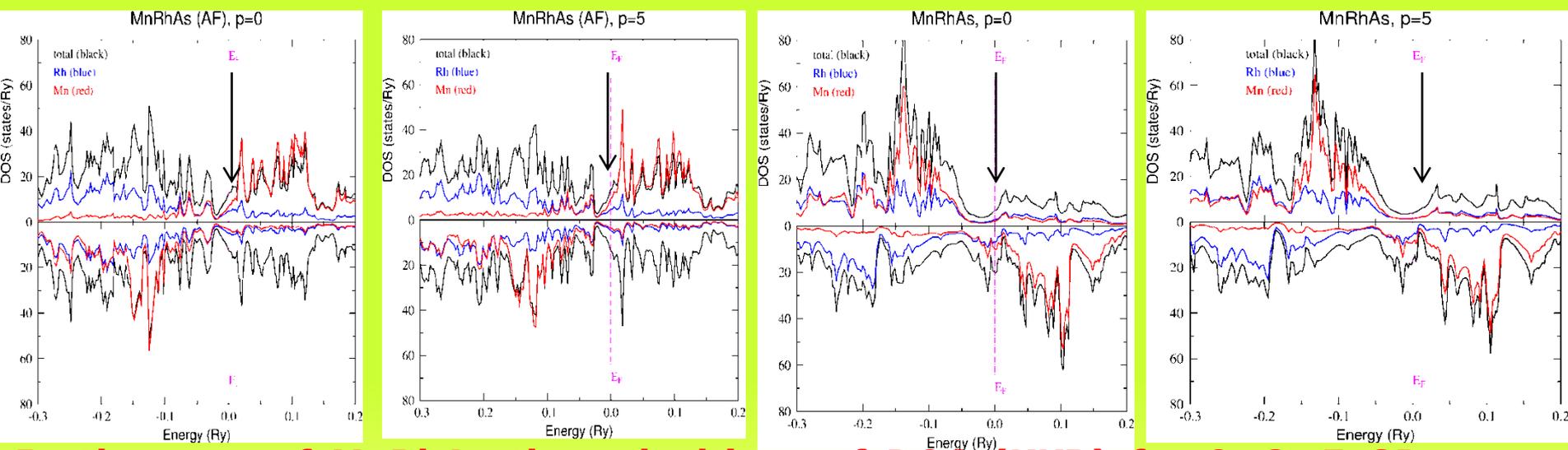


T.Eto, M.Yamagishi, M.Ishizuka, S.Endo, T.Asida, T.Kanomata, T.Kikegawa R.Zach JALCOM 307, p.96 (2000)

# Electronic band structure calculations for MnRhAs „under pressure” KKR



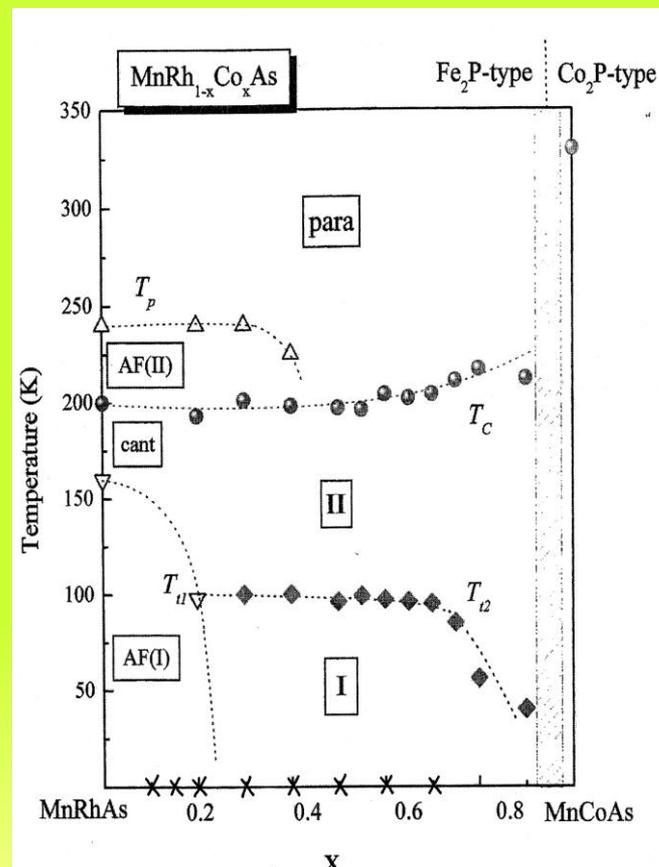
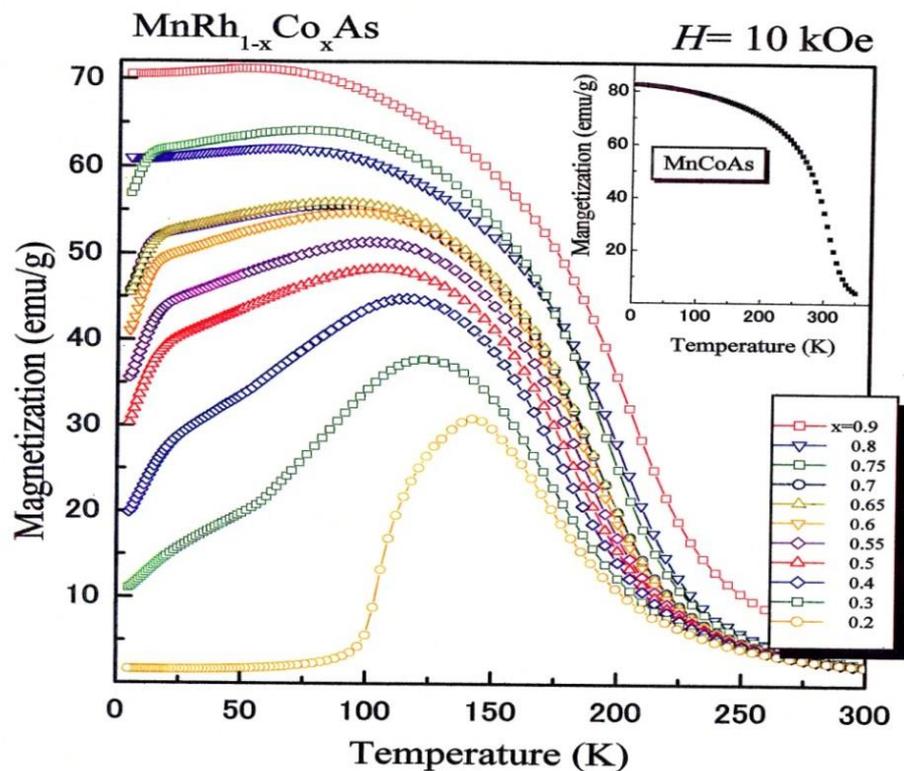
<b>P</b> <b>[GPa]</b>	<b>DOS at E<sub>F</sub></b> <b>in <i>Ferro</i> state</b> <b>[states/Ry]</b>	<b>DOS at E<sub>F</sub></b> <b>in <i>AF</i> state</b> <b>[states/Ry]</b>
<b>0</b>	27.0	24.8
<b>3</b>	23.5	26.5
<b>5</b>	20.7	27.1



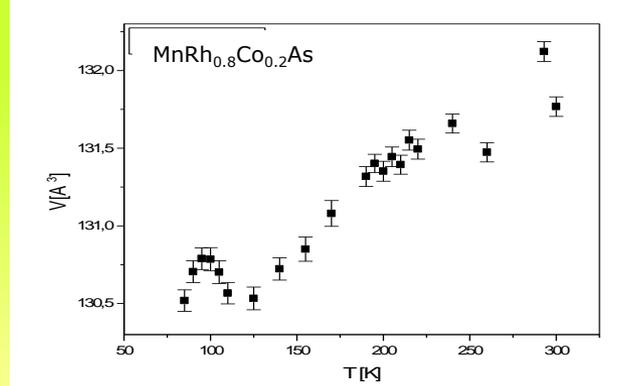
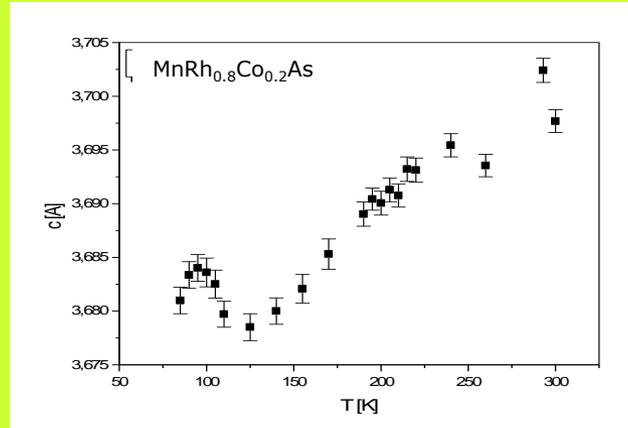
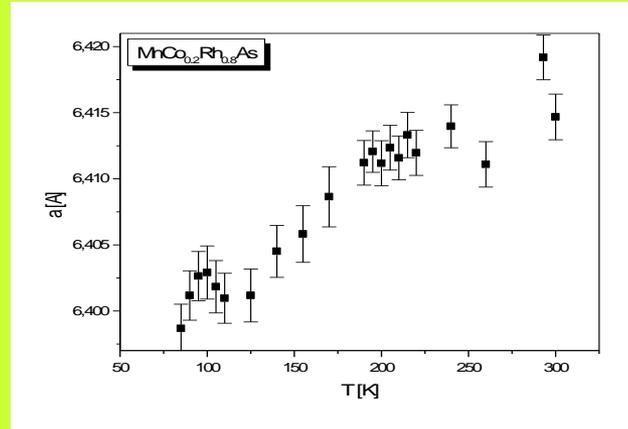
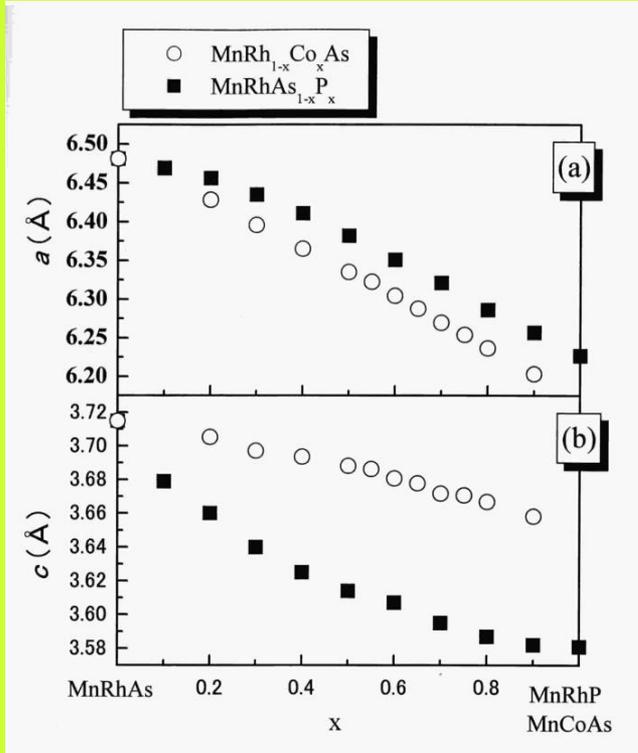
In the case of MnRhAs the calculations of DOS (KKR) for 0, 3, 5 GPa were performed. It was concluded, that in the atmospheric pressure the AF state was more favored, however under pressures 3 GPa and 5 GPa the F state was found as the most stable (it remains in good agreement with experiments)

# Magnetoelastic phase transitions in $\text{MnRh}_{1-x}\text{Co}_x\text{As}$

The  $\text{MnRh}_{1-x}\text{Co}_x\text{As}$  isoelectronic system of solid solutions has a complex  $(x, T)$  magnetic phase diagram caused by the substitution in the metal sublattice. The crystal structure of the  $\text{MnRh}_{1-x}\text{Co}_x\text{As}$  system is a hexagonal one of the  $\text{Fe}_2\text{P}$ -type except for the samples with the composition in the close vicinity of  $\text{MnCoAs}$ , which exhibits orthorhombic crystal structure of the  $\text{Co}_2\text{P}$ -type.

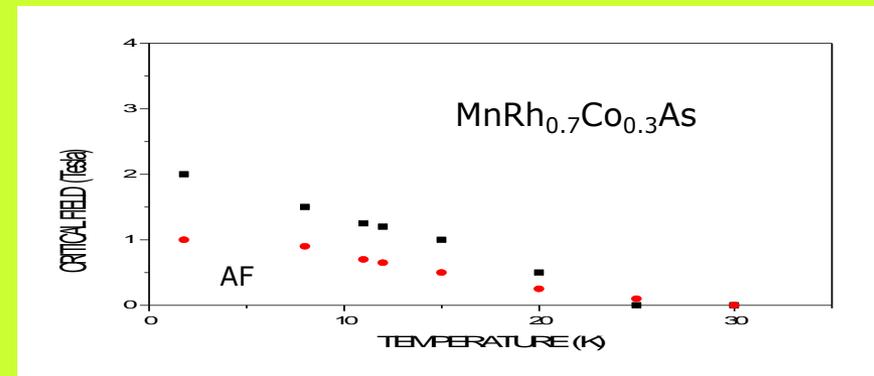
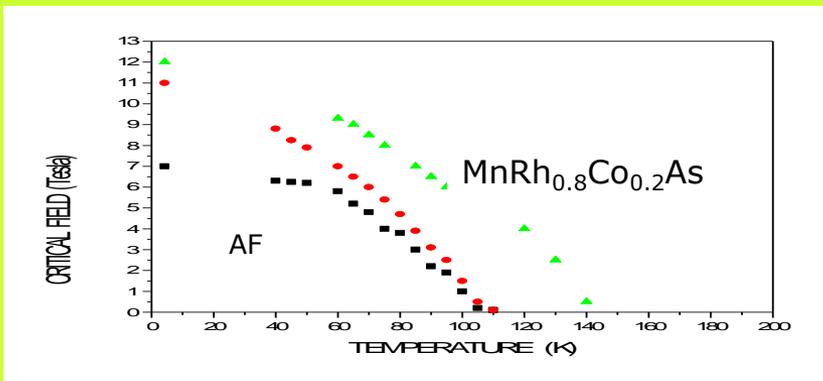
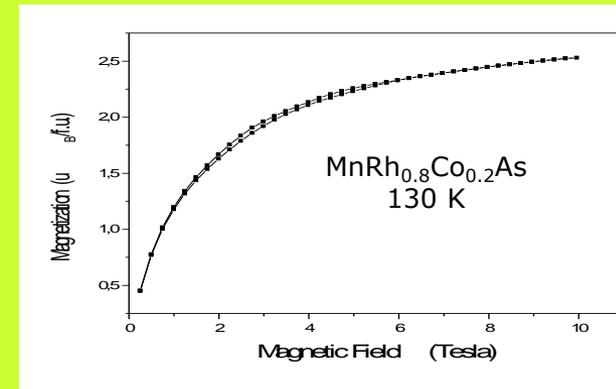
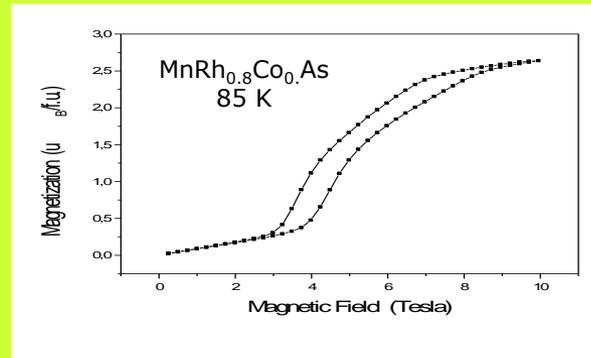
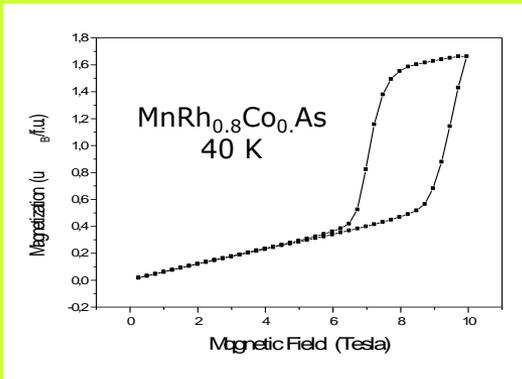


# X ray diffraction studies $\text{MnRh}_{1-x}\text{Co}_x\text{As}$



- \* it was found that with the increase of cobalt content  $x$  the elementary cell volume linearly decreases,
- \*\* the jump in both lattice parameters and in the unit cell volume associated with the phase transition was found,
- \*\*\* interatomic distances mainly Mn-Mn and Mn-Rh change at the phase transitions,
- \*\*\*\* lattice and atomic parameters determined by means of X-ray diffraction were used in the KKR-CPA electronic structure calculations.

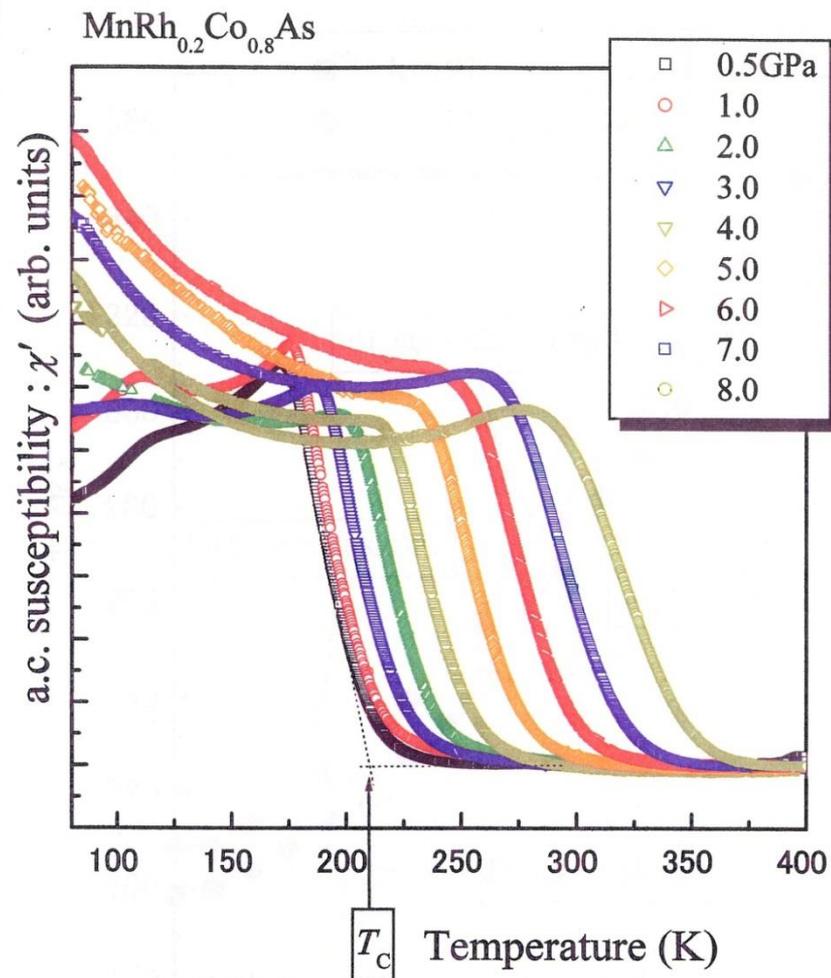
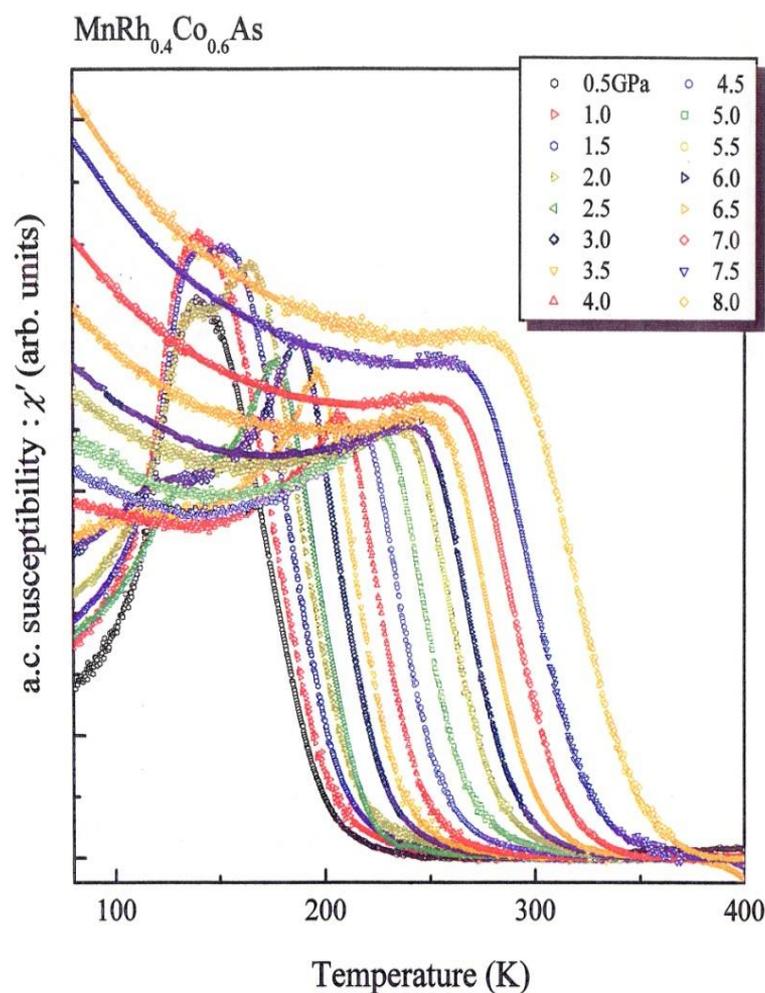
# High d.c. field magnetization studies $\text{MnRh}_{1-x}\text{Co}_x\text{As}$



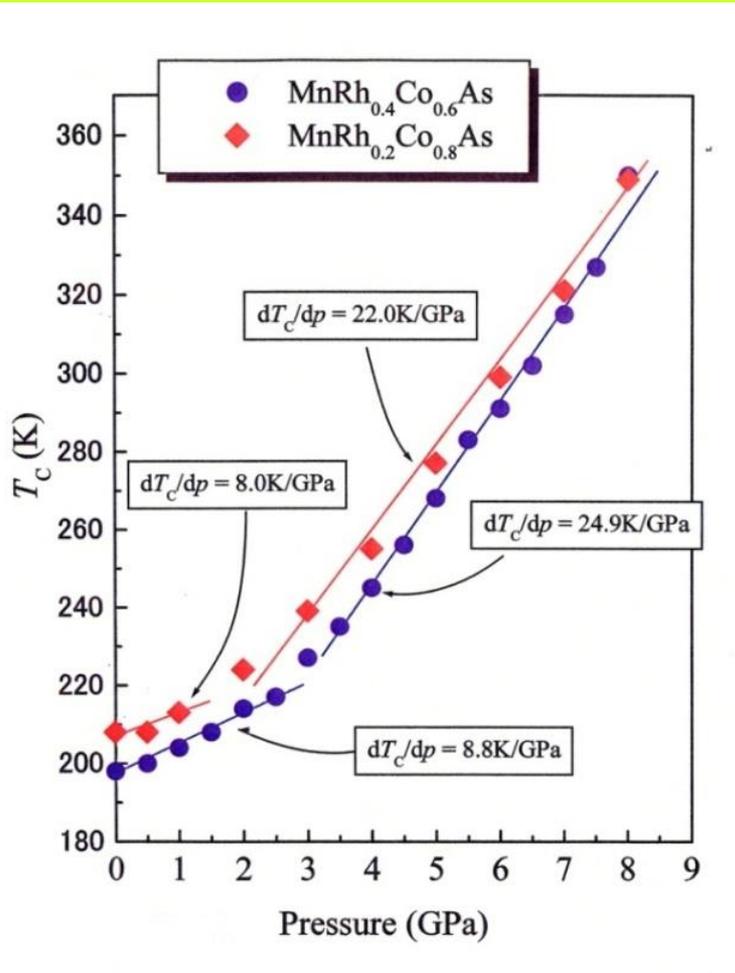
To summarize the experimental results the  $(B, T)$  magnetic phase diagrams were proposed. The following conclusions could be drawn:

- i) the field induced discontinuous phase transitions were discovered,
- ii) the critical fields decrease with temperature for both studied compounds,
- iii) the critical field values and the width of the hysteresis vanish to zero for both samples, however at markedly different temperatures.

# High pressure a.c. susceptibility studies of $\text{MnRh}_{1-x}\text{Co}_x\text{As}$



# High pressure a.c. susceptibility studies of $\text{MnRh}_{1-x}\text{Co}_x\text{As}$

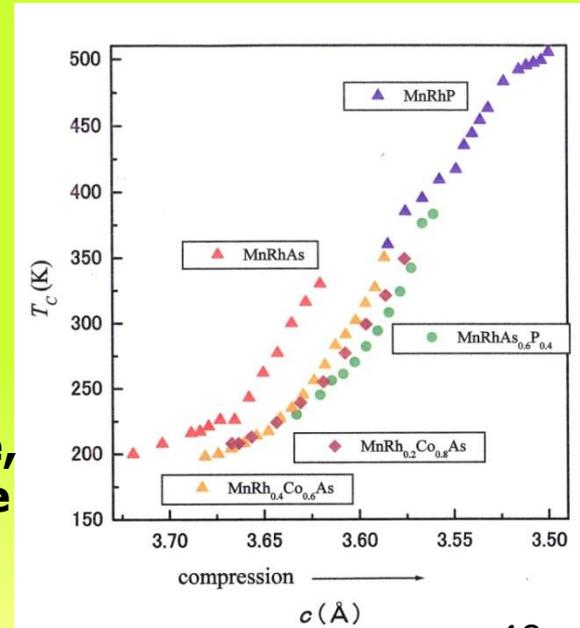
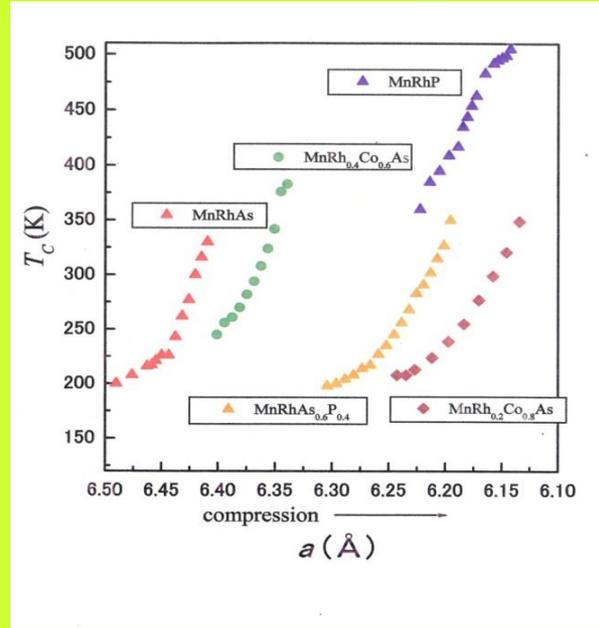


$T_C$  is widely scattered, which suggests that  $T_C$  is not directly related to the  $a$ -value

$T_C$  is plotted against the  $c$ -value

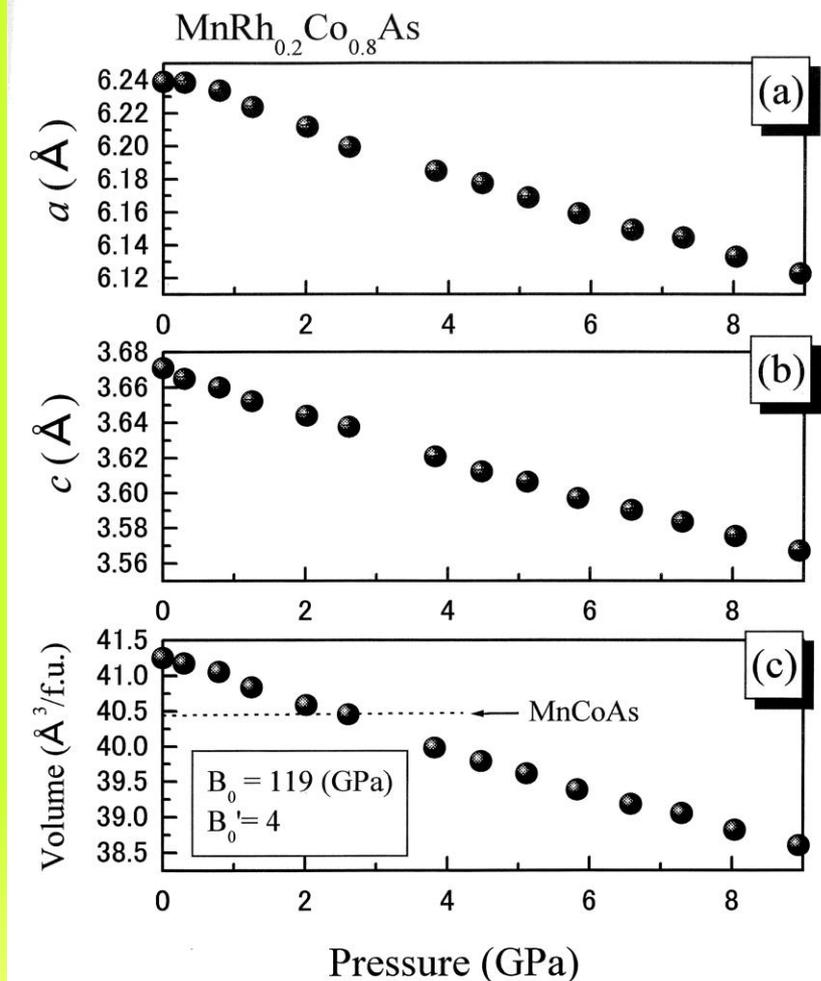
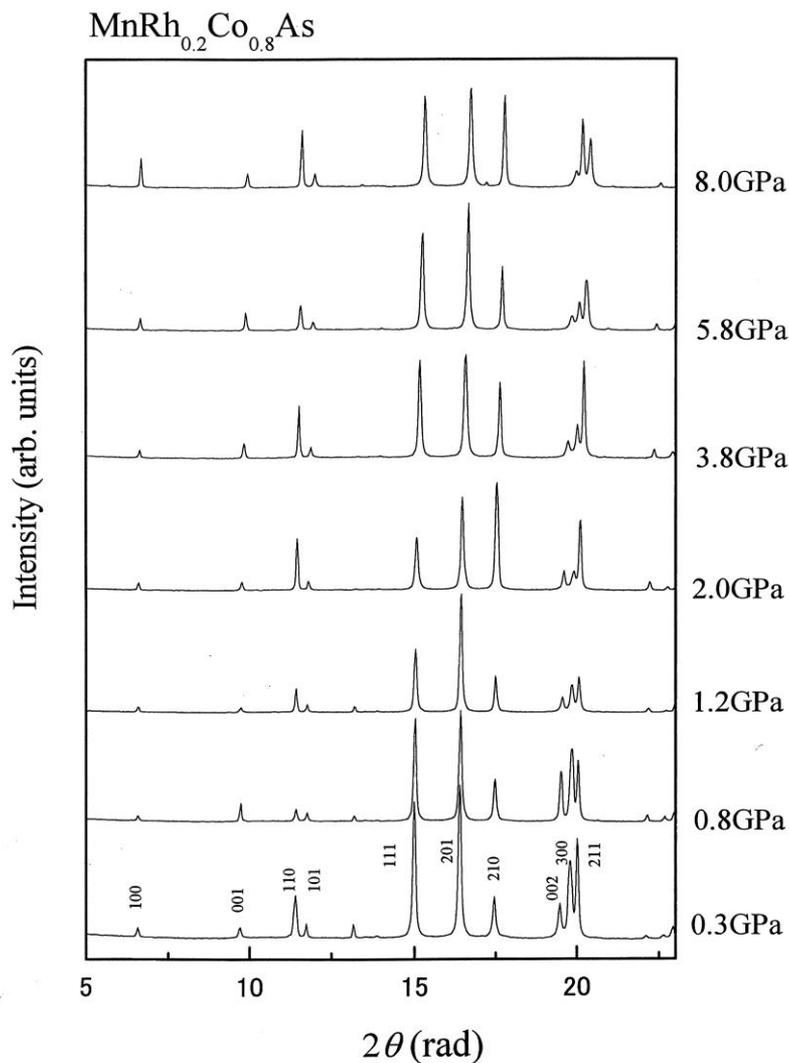
all the points concentrate on an almost single  $T_C$  line versus  $c$  curve.

**Thus, the pressure effect on  $T_C$  strongly depend on the  $c$ -value, but not on the  $a$ -value**

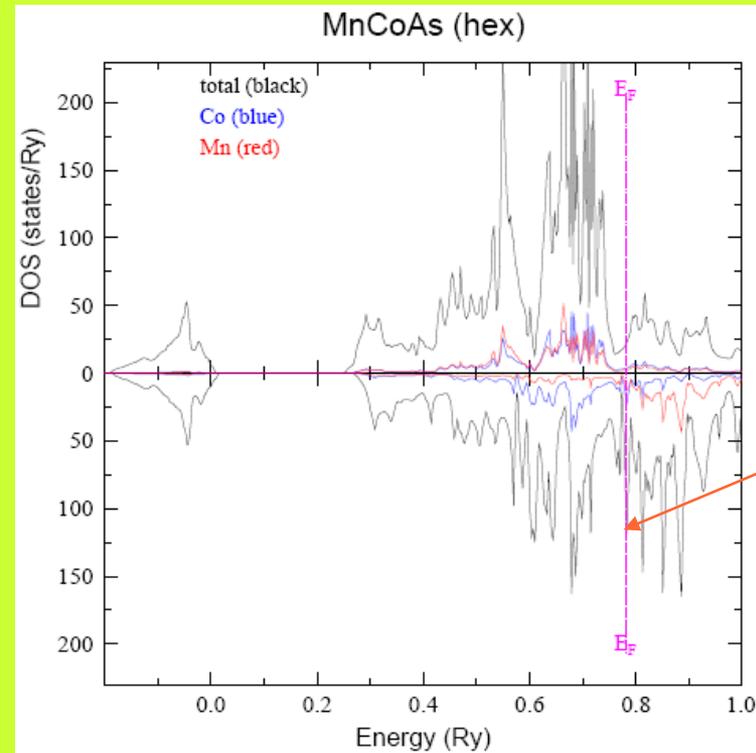
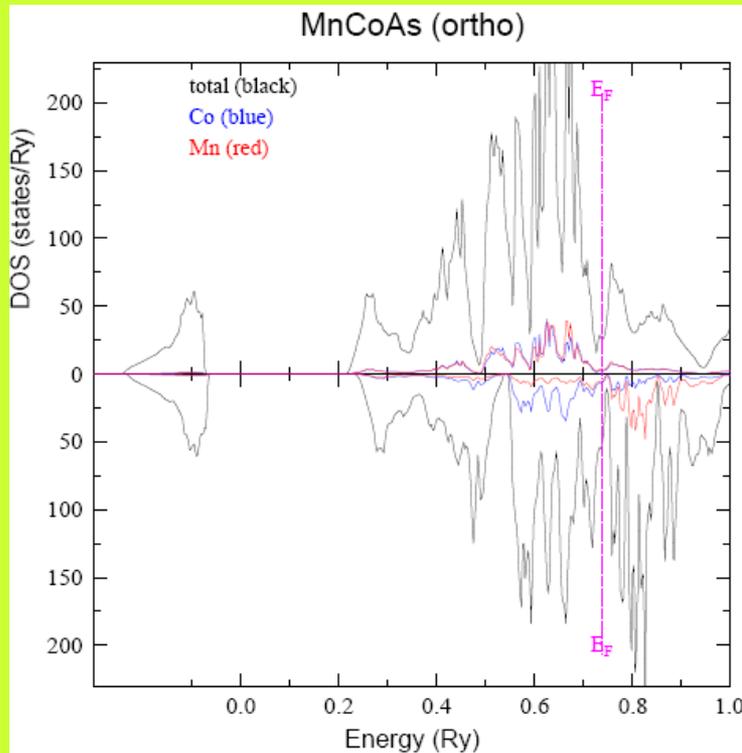


$T_C$  versus the lattice parameter  $a$  and  $c$  of  $\text{Mn}(\text{Rh},\text{Co})\text{As}$ .

# Crystal structure under pressure in $\text{MnRh}_{1-x}\text{Co}_x\text{As}$



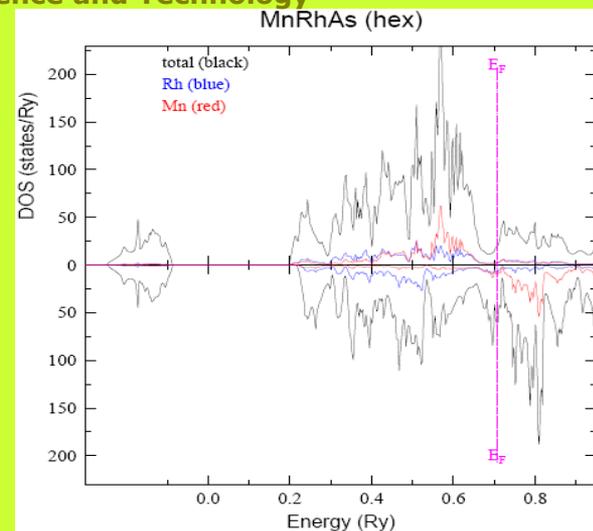
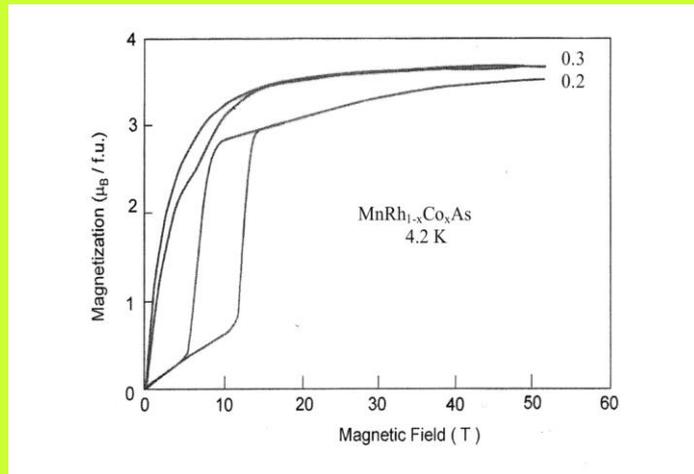
# MnCoAs (ortho) and MnCoAs (hex)



In MnCoAs the electronic band structure calculations were carried not only in the case of **the real orthorhombic** crystal structure but also in the case of **the hypothetical hexagonal** one.

The crystal structure parameters by extrapolations of those  $a$  and  $c$  lattice parameters from the hexagonal domain of the  $\text{MnRh}_{1-x}\text{Co}_x\text{As}$  ( $x < 0.9$ ) system were used.

A very interesting property was established for the hexagonal crystal structure: the Fermi level for **the spin down subbands in the maximum of DOS** is placed. This fact may be the reason why no hexagonal crystal structure of MnCoAs is observed. Contrary, in **the orthorhombic crystal structure for both spin directions the Fermi level close to deep DOS valley** is located.

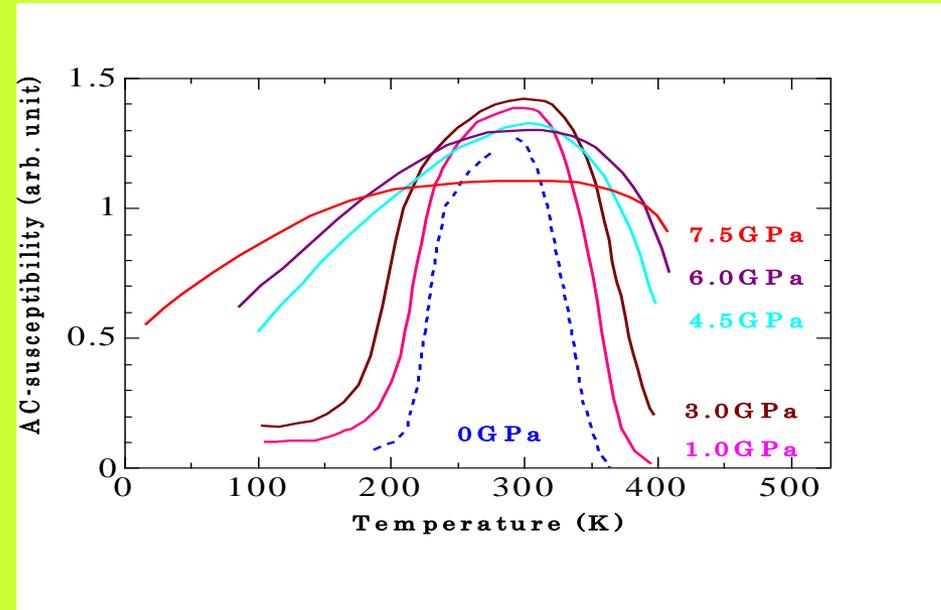
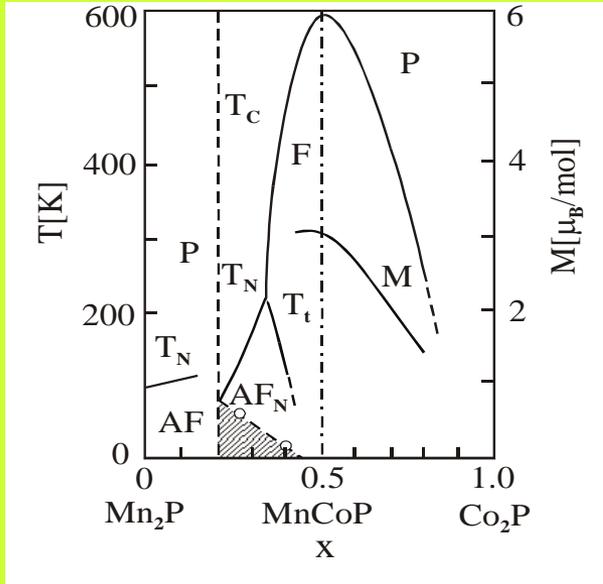


## Magnetic moments calculated for $\text{MnRh}_{1-x}\text{Co}_x\text{As}$

Compound	Tot [ $\mu_B/\text{f.u.}$ ]	Mn [ $\mu_B$ ]	Rh [ $\mu_B$ ]	Co [ $\mu_B$ ]	Tot [ $\mu_B/\text{f.u.}$ ] - exp
<b>MnRhAs</b>	<b>3.31</b>	3.45	0.02	—	<b>3.5</b>
MnRh <sub>0.7</sub> Co <sub>0.3</sub> As	<b>3.27</b>	3.17	0.03	0.26	<b>3.5</b>
MnCoAs (hex)	<b>3.21</b>	3.02	—	0.25	—
MnCoAs (ort)	<b>3.15</b>	3.14	—	0.13	<b>3.0</b>

The DOS plots obtained for Mn, Co and Rh atoms indicate strong *s*, *p* and *d* hybridization of the electron states observed for all the studied samples. It may be concluded that the covalent character of chemical bonds is also present. **A fair agreement between calculated and experimental values of magnetic moments was established.**

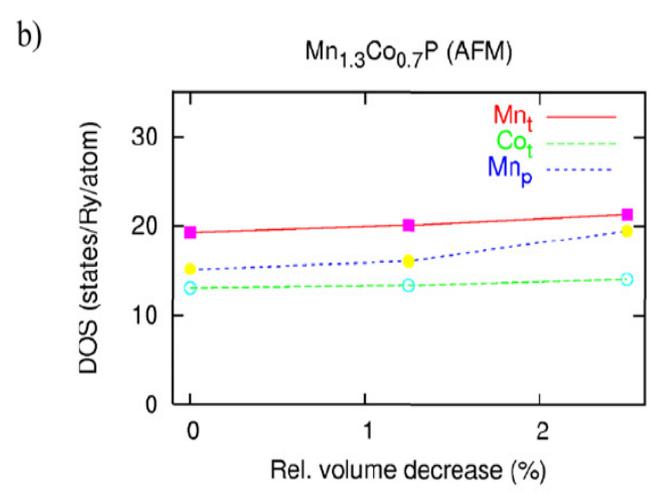
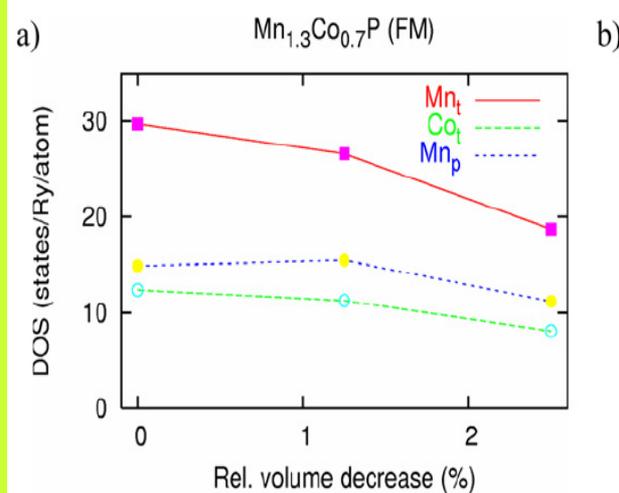
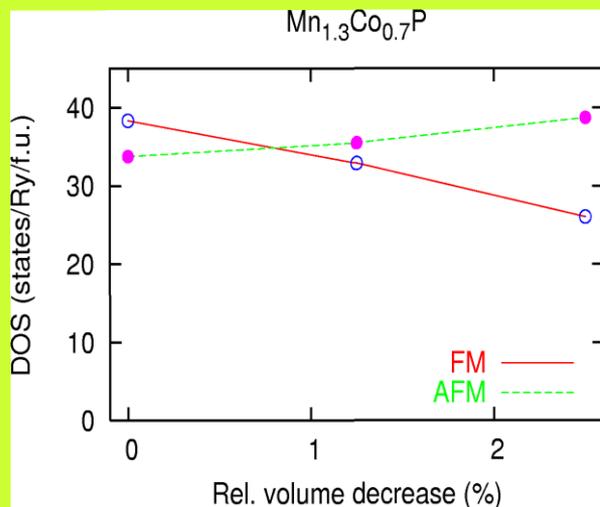
# Pressure induced magnetic phase transitions in $(\text{Mn}_{1-x}\text{Co}_x)_2\text{P}$ with $x=0.35$



To summarize the ac susceptibility behavior under high pressure it may be concluded that:

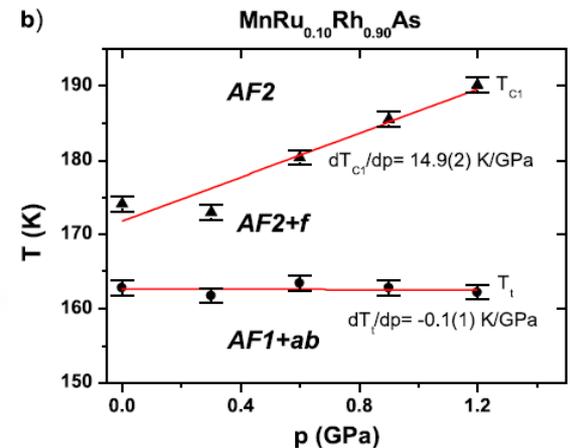
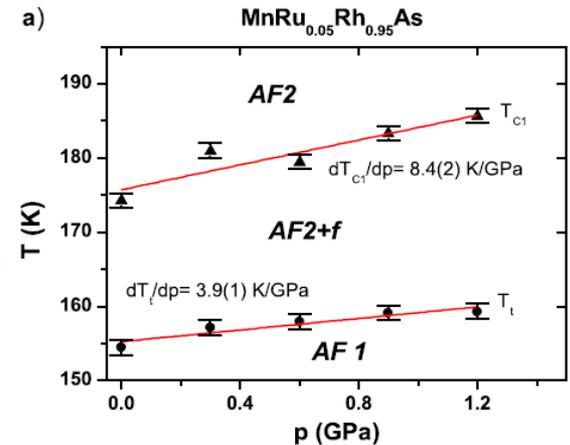
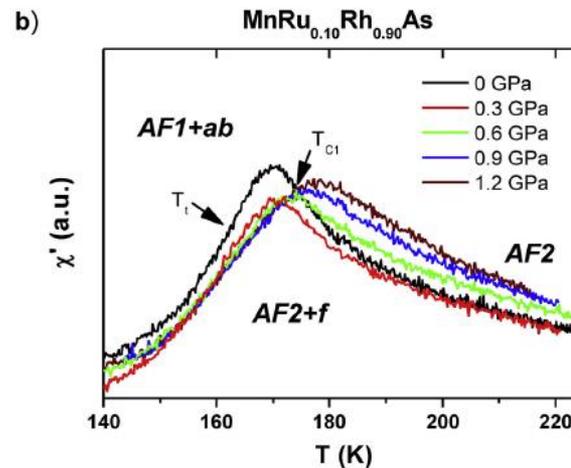
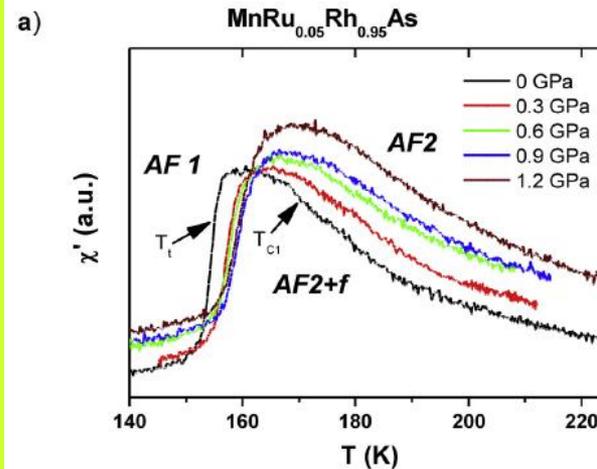
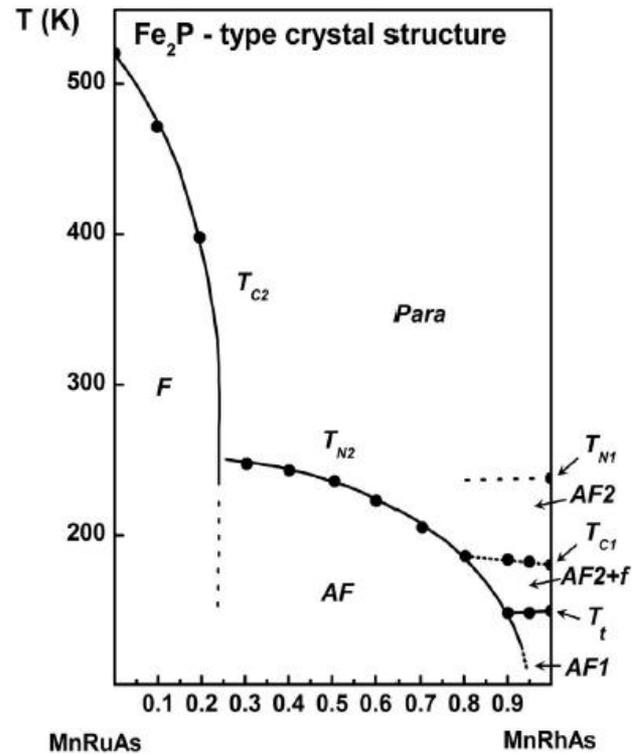
- i) the Curie temperature increases with pressure;
- ii) the  $AF_N$ -F phase transition temperature  $T_t$  strongly decreases with pressure;
- iii) the **pressure induced** ferromagnetic state was established **at low temperatures (4.2.K – 80 K) and at 6 – 8 GPa pressure range.**

# Electronic band structure calculations for $(\text{Mn}_{0.65}\text{Co}_{0.35})_2\text{P}$ with $x=0.35$ under pressure (KKR-CPA)

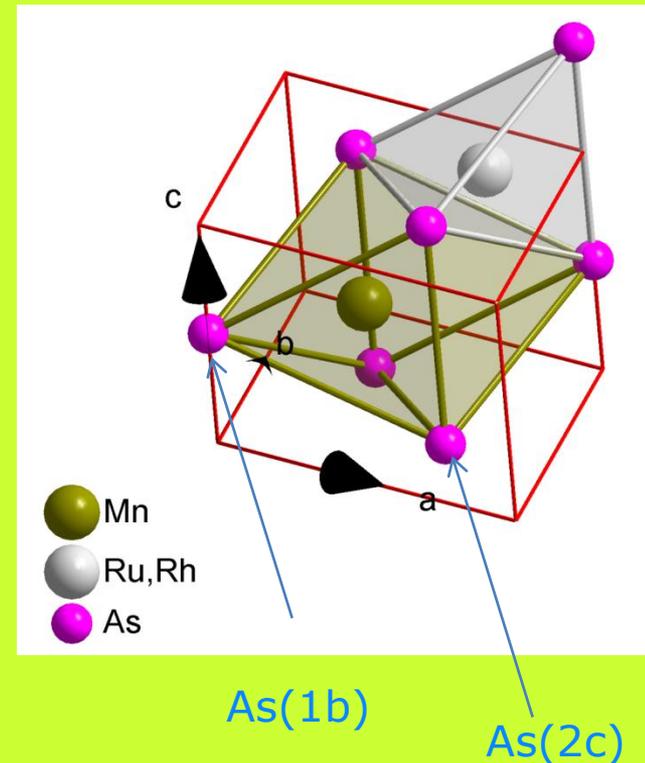
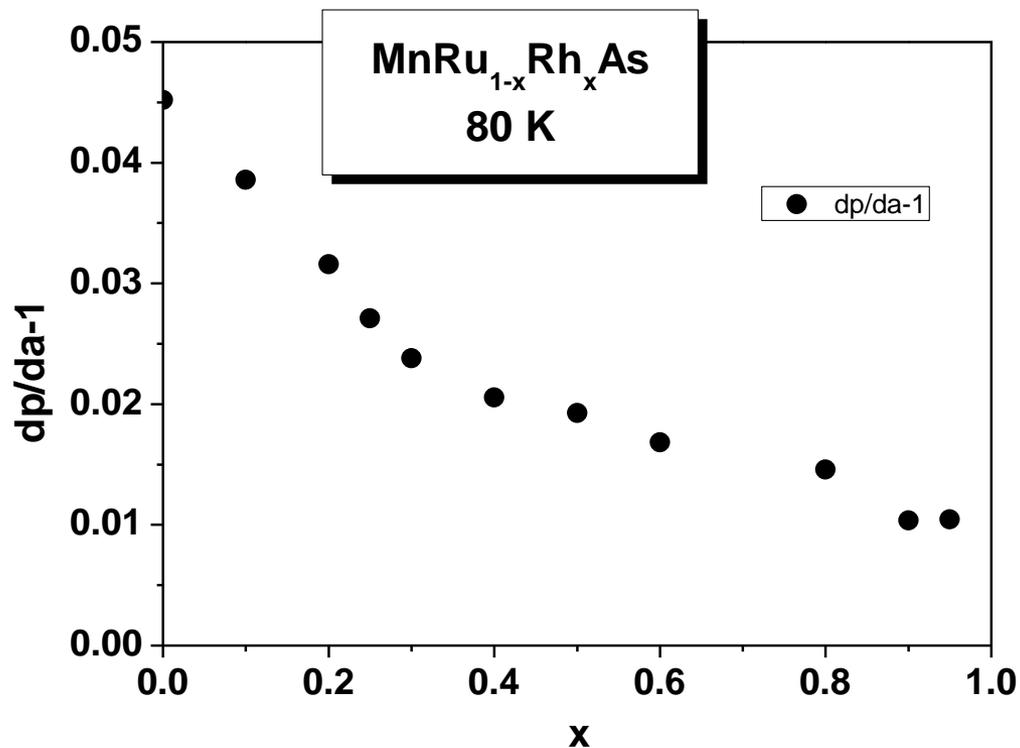


- i) The DOS at the Fermi level decreases with pressure applied along any axis. The highest decrease of DOS was found in the case of c-axis applied pressure.
- ii) The computed local magnetic moments in  $x=0.35$  decrease versus pressure (particularly for large magnetic moment on the pyramidal Mn atoms) and are comparable in F and AF states
- iii) The magnetic moments on Mn atoms on tetrahedral sites are sensitive to the volume decrease and practically disappear with c axes compression while they decreases only slightly on the Co atoms. This type of behavior may be responsible for pressure induced AF-F phase transition.
- iv) For the c-axis compression in  $x=0.35$  the total DOS at the Fermi level behaves in the opposite way i.e. it rapidly decreases in the Ferro state, whereas it slightly increases in the AF state.

# Magnetic properties of $\text{MnRh}_{1-x}\text{Ru}_x\text{As}$



From pressure measurements we may conclude that the ferromagnetic orderings become more favorable under higher pressure. This tendency was also discussed on the basis of electronic structure KKR calculations suggesting a ferromagnetic state in  $\text{MnRhAs}$  to be more favorable with unit cell contractions. Similarly, substitution of Ru to Rh leads to a stability of the ferromagnetic state in agreement with the  $(x, T)$  diagram.



$$\delta = \frac{dp}{da} - 1 = \frac{d_{\text{As}(2c)-\text{As}(2c)}}{c} - 1$$

Distortion of the tetrahedral site  $\delta$  (%)

MnRuAs	4.07 %
MnRhAs	0.73 %



dp -- the edge of the rectangle defined by the two atoms in the As-2 position of the ab plane

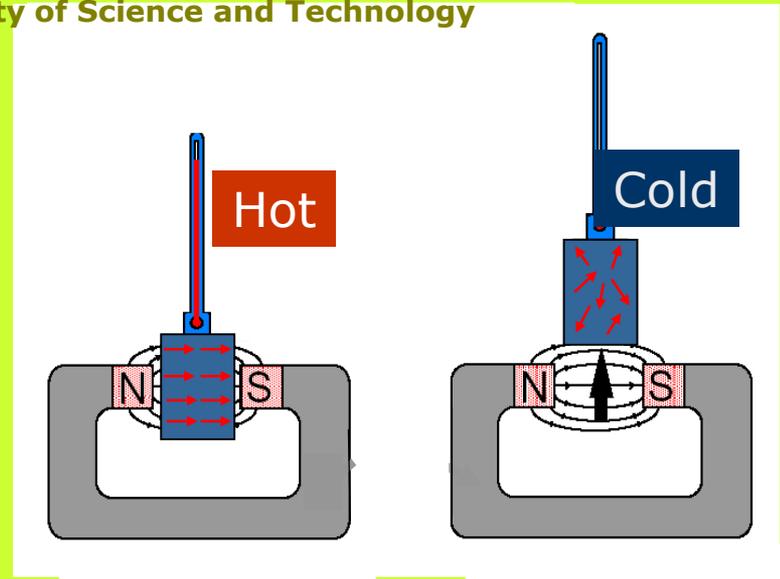
da=c: -- short parameter of the hexagonal unit cell

# MAGNETOCALORIC EFFECT

Intrinsic property of a material

The concept of magnetic fridge is based on the **magneto-caloric effect**.

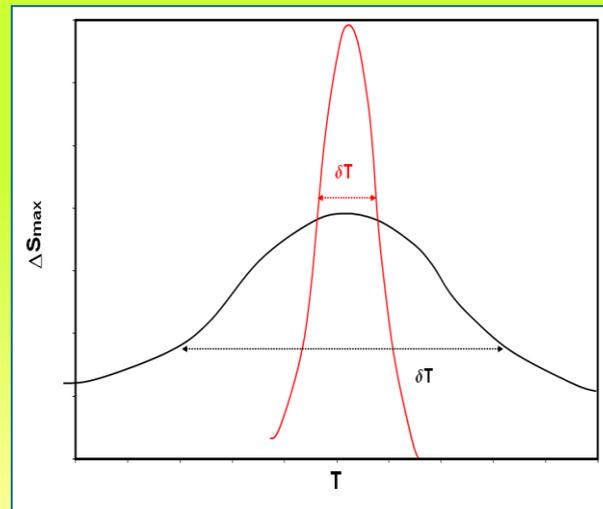
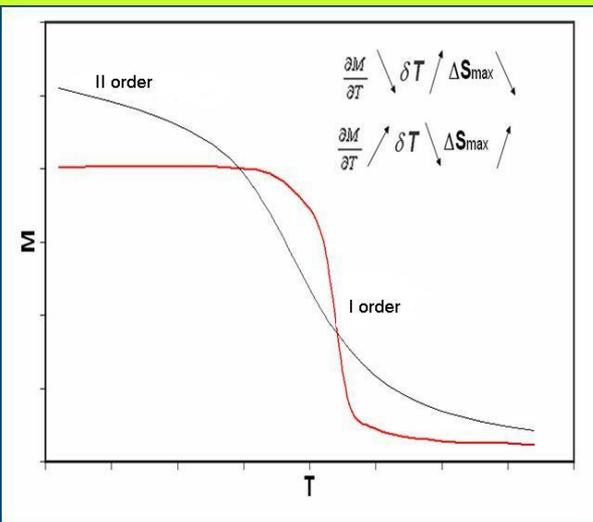
It involves a process in which reversible **heating** or **cooling down** of specific magnetic materials result from the **application** or **suppression** of an external magnetic field.



Adiabatic

Magnetisation / Demagnetisation

**Ferromagnet, Ferrimagnet, Antiferromagnet, Inhomogeneous Ferromagnet, Amorphous, Superparamagnet....**



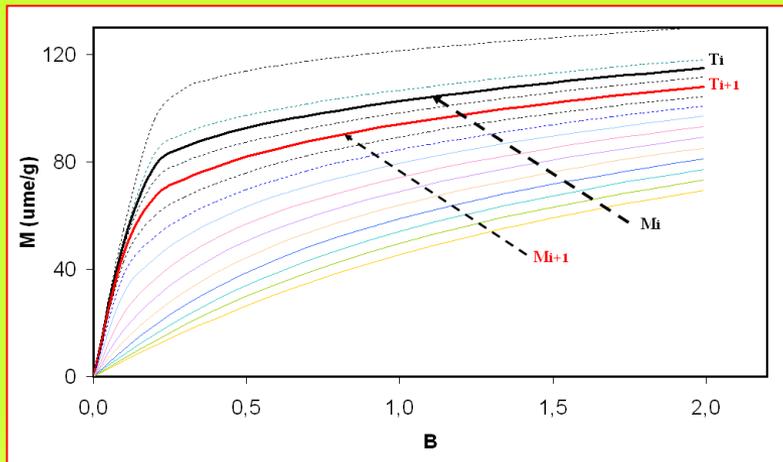
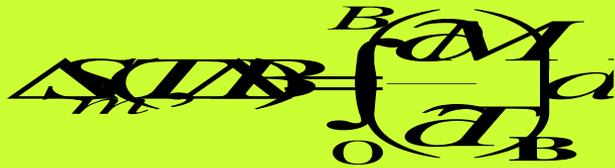
**Conditions for giant MCE**  
**What model to apply for ?**

It depends on:  
the nature of the transition,  
the type of magnetic ordering,  
the nature of the material....

# MAGNETOCALORIC EFFECT

Integration from isothermal magnetization curves

Magnetization measurements



Analysis of the data

Magnetic measurements

$$M(T, B)$$

Correction of demagnetising field

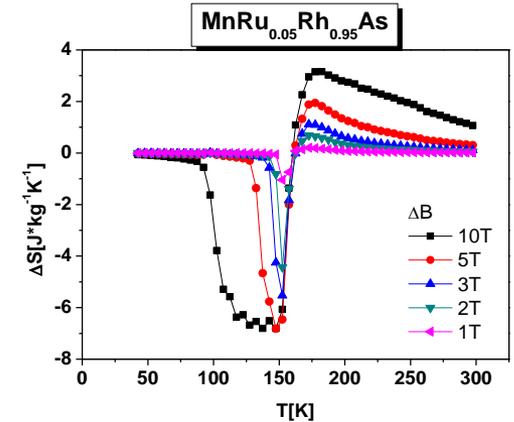
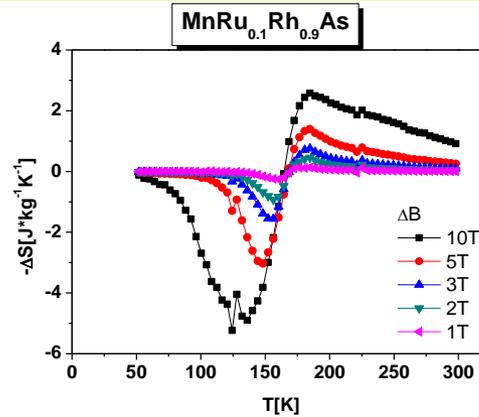
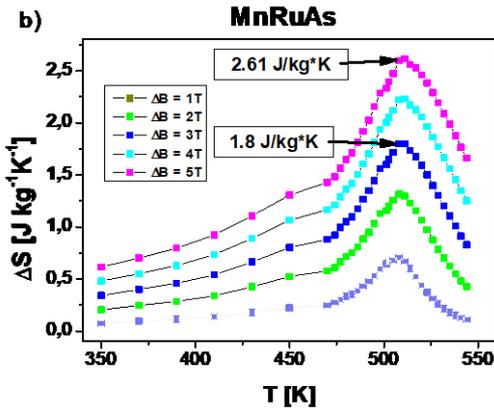
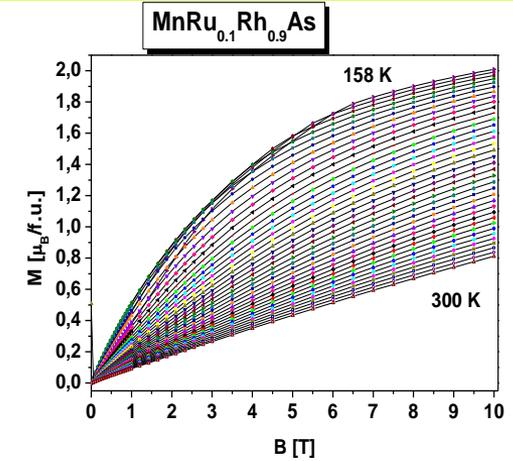
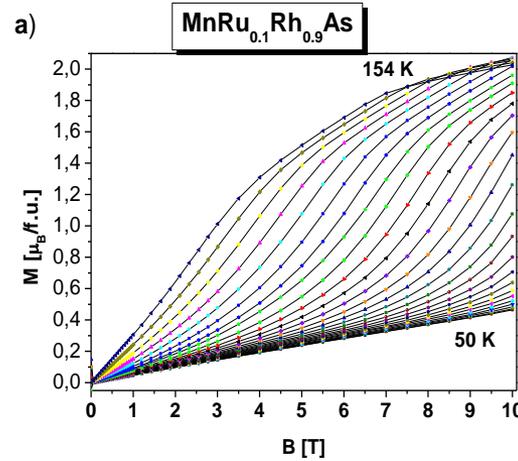
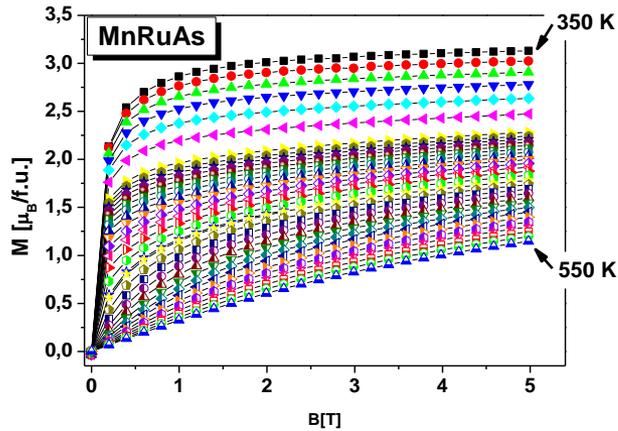
$$(-N_d M)$$

$$\Delta S_m = \sum_i \frac{1}{T_{i+1} - T_i} (M_{i+1} - M_i) \Delta B_i$$

$$\Delta T_{ad}(T, B) = - \int_0^B \frac{T}{C(T, B')} \left( \frac{\partial M}{\partial T} \right)_B dB'$$

Directly measured or computed from specific heat measurements

# MAGNETIZATION AND MAGNETOCALORIC EFFECT

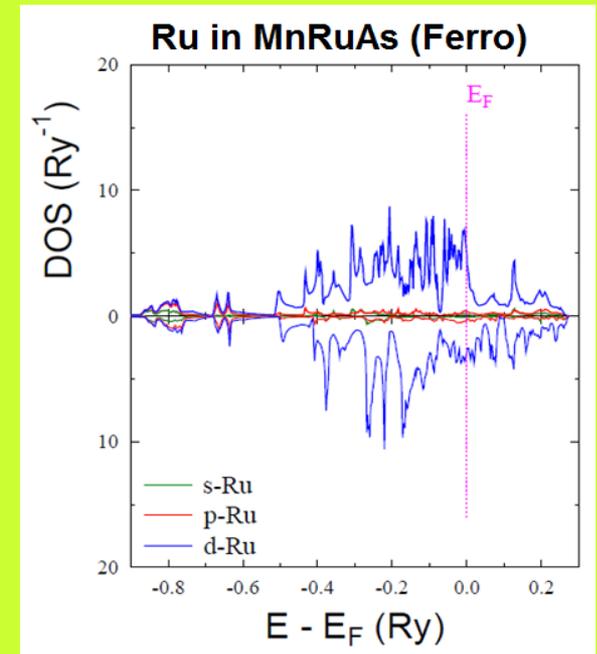
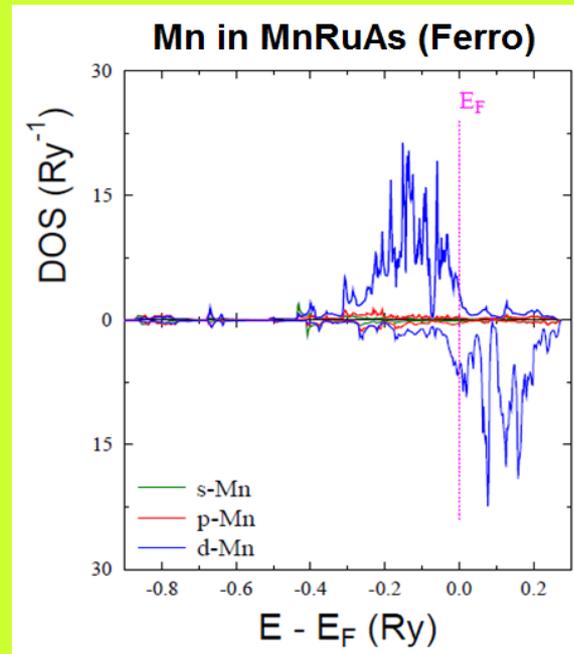
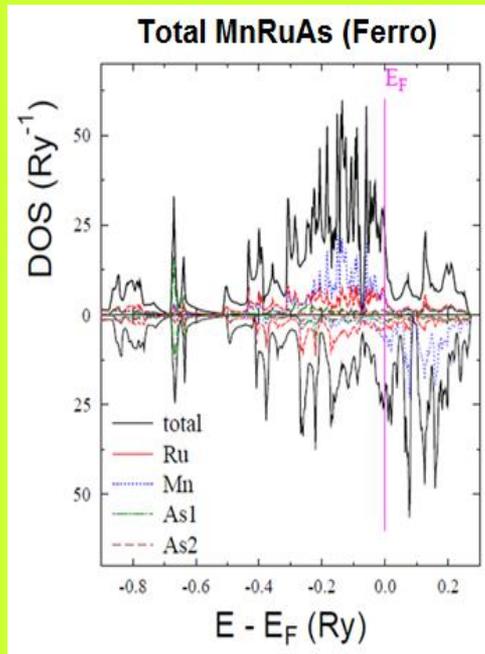


## Conventional and Negative MCE

Mn <sub>3</sub> GaC	15 [J/Kkg]
CoMn(SiGe)	1 [J/Kkg]
MnRhAs	4 [J/Kkg] (single crystal)
MnRh <sub>0.95</sub> Ru <sub>0.05</sub> As	2 [J/Kkg]

## Electronic band structure calculations

The electronic band structure calculations have been performed for  $x = 0, 0.2, 0.5, 0.95$  in  $F$  and  $AF$  states (KKR-CPA, full potential). Our experimental values of the cell parameters and the atomic positions (X-ray data, this work) were used for computations.

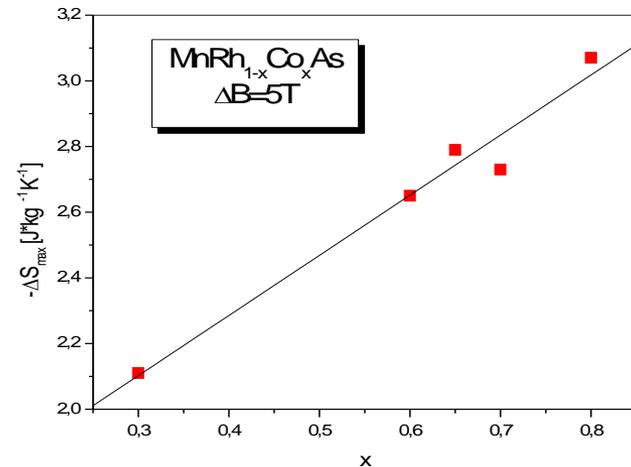
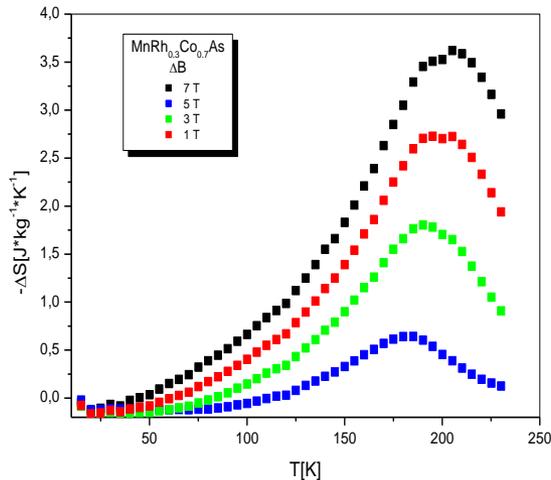
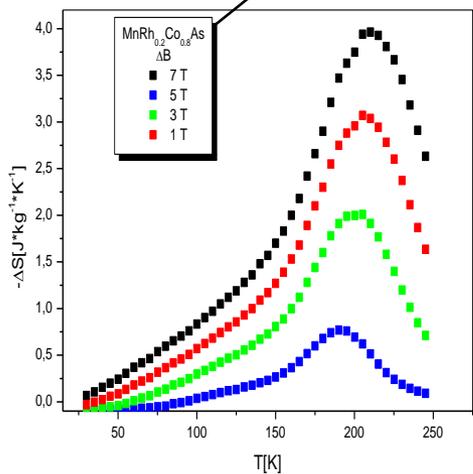
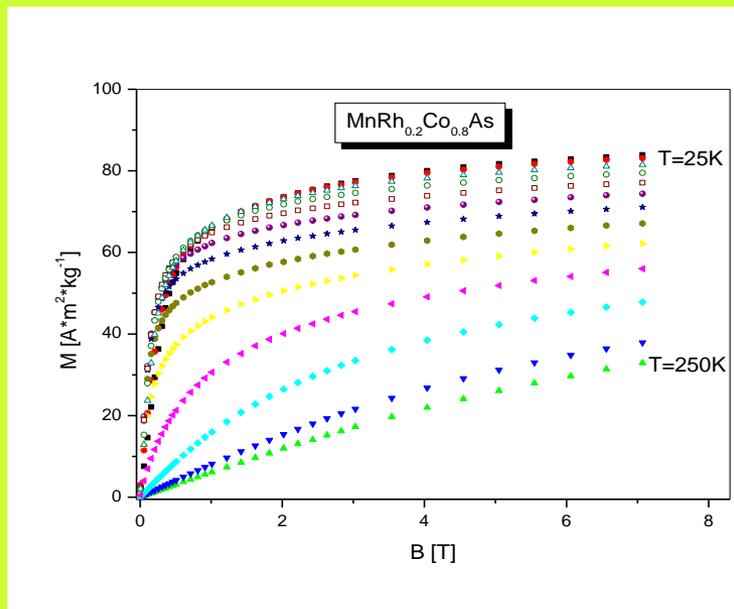
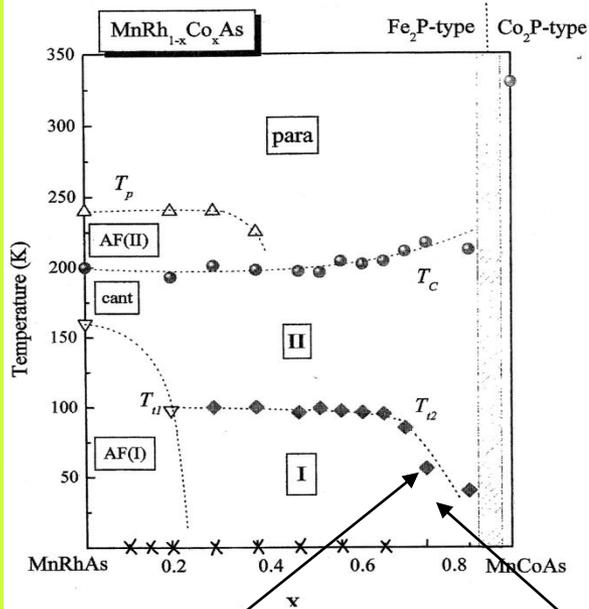


**Density of states in for  $x = 0, 0.2, 0.5, 0.95, 1.0$  exhibits a strong spin polarization arising mainly from a splitting of the Mn states in both ( $F$ ) and ( $AF$ ) states.**

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*J.Alloys Comp.* 776 (2019) 59-70

Przewód doktorski mgra D.Szymańskiego, IFJ PAN, 2019

# MCE w układzie $\text{MnRh}_{1-x}\text{Co}_x\text{As}$



## CONCLUSIONS

- \* Magnetostructural phase transitions induced by external pressure in  $\text{Co}_x\text{Ni}_{1-x}\text{MnGe}$ ,
- \* Critical behavior under magnetic field in  $\text{MnFeP}_{1-x}\text{As}_x$  series
- \* New crystal structure in  $\text{MnRhAs}$ ,  $\text{MnRhP}$  and  $\text{MnRuP}$  under extreme pressure,
- \* Pressure induced ferromagnetic state in  $\text{MnRhAs}$  and in  $\text{MnRh}_{1-x}\text{Co}_x\text{As}$  and  $(\text{Mn}_{1-x}\text{Co}_x)_2\text{P}$ ,
- \* Magnetoelastic character of AF-F, AF-P and F-P phase transitions in studied series of compounds was established
- \* Magnetic entropy change  $\Delta S_M$  was determined for several (Rh,Ru) contents. Conventional and negative MCE was reported.
- \* Electronic band structure calculations performed „under pressure“ confirmed stability of the pressure induced ferromagnetic state in  $\text{MnRhAs}$  and  $(\text{Mn}_{1-x}\text{Co}_x)_2\text{P}$
- \* Electronic band structure was calculated both in ferromagnetic and antiferromagnetic state. Good agreement between calculated and experimental values of magnetic moments was found.

1. Grant KBN nr 2 P 302 10307, główny wykonawca 1996-1997.
2. Projekt polsko-francuski: **Action Thematique Programme**, (ATP S15) 1995.
3. Projekt polsko-francuski: **Action Integreé No 5242**.
4. Projekt polsko-francuski **TEMPRA Rhone Alpes 2001 - 2002**, Uniwersytet Joseph Fourier Grenoble.
5. Projekt polsko-francuski **ECO-NET /lata: 2004-2005/**, grant międzynarodowy, Nr 08133RA, kierownik projektu ze strony polskiej.
6. Program Ramowy Akademiczne Centrum Technologii \_ Małopolska, **AKCENT 2004-2006**; (UJ, AGH, PK) (Nr WKP\_1/1.4.3/1/2004/22/22/73) finansowany przez Europejskie Fundusze Strukturalne oraz MNiI (KBN)
7. Grant MNiI – nr P 03 B 113 29, **2005-2007**; kierownictwo grantu.
8. Projekt polsko-francuski **POLONIUM 2006-2007**, kierownictwo projektu
9. Grant MNiI – nr 1P03 B01530, wykonawca grantu  
Badanie przemiany Verveya w związkach magnetytu

## Acknowledgements

**Prof. D. Fruchart, CNRS, Grenoble. France**

**Prof. J. Toboła, AGH, Cracow, Poland**

**Prof. Stanisław Nizioł AGH, Cracow, Poland**

**Prof. Stanisław Kaprzyk AGH, Cracow, Poland**

**Prof. A. Zięba, AGH, Cracow, Poland**

**Prof. A. Szytuła, IF UJ, Cracow**

**Prof. F. Ono, Okayama University of Science, Japan**

**Prof. S. Endo, Osaka University. Japan**

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**Thank you very much for your attention!!!!**