Imperial College London

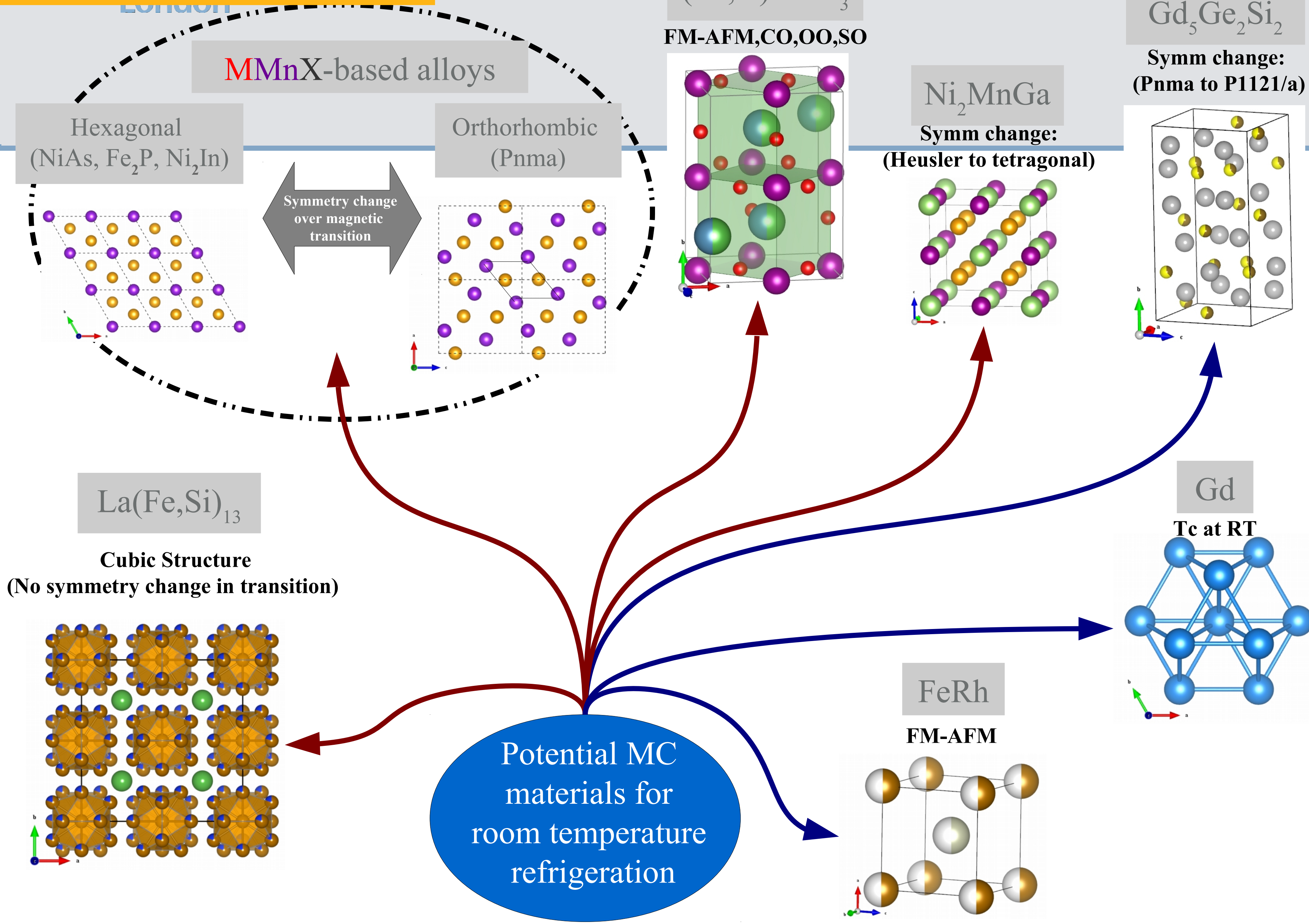
Magnetocaloric Materials Design By Density Functional Theory

Zsolt Gercsi

Dept. of Physics, Blackett Laboratory
Imperial College London
(Trinity College Dublin)

Delft Days on Magnetocalorics (DDMC) 2013

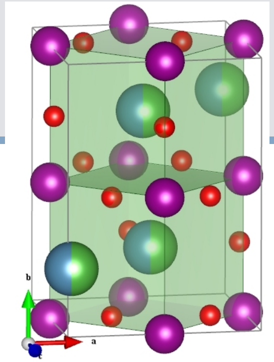
Introduction



Introduction

$(La,X)MnO_3$

FM-AFM,CO,OO,SO



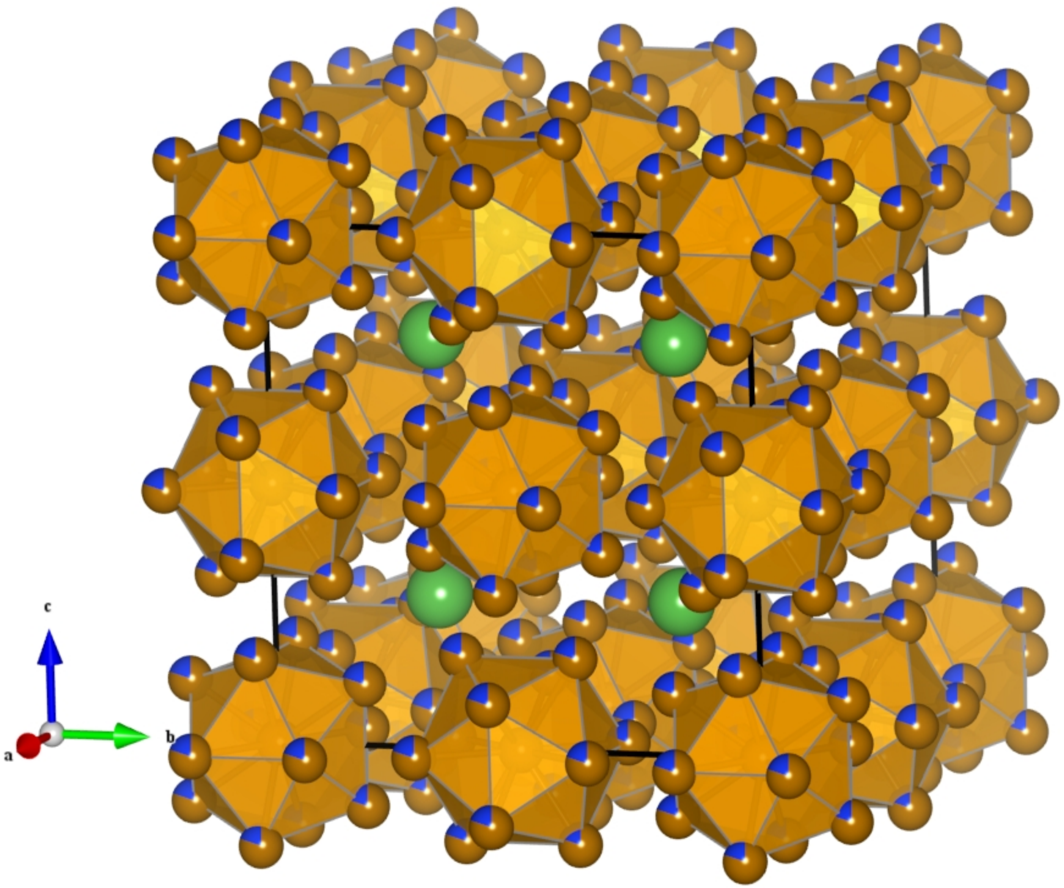
Poster session:
A Hybrid-exchange Density Functional Study of $La_{1-x}Ca_xMnO_3$
by R. Korotana

Imperial College London

$La(Fe,Si)_{13}$

Stable Cubic $NaZn_{13}$ type of structure around 10 % Si

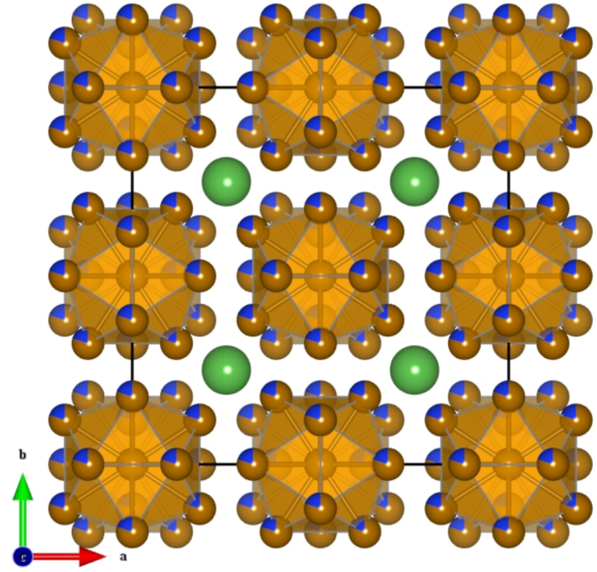
(Kripyakewich et al. 1968)



La – 8a sites

Fe (I) – 8b sites

Fe/Si (II) – 96i sites



Fe/Si clusters around La

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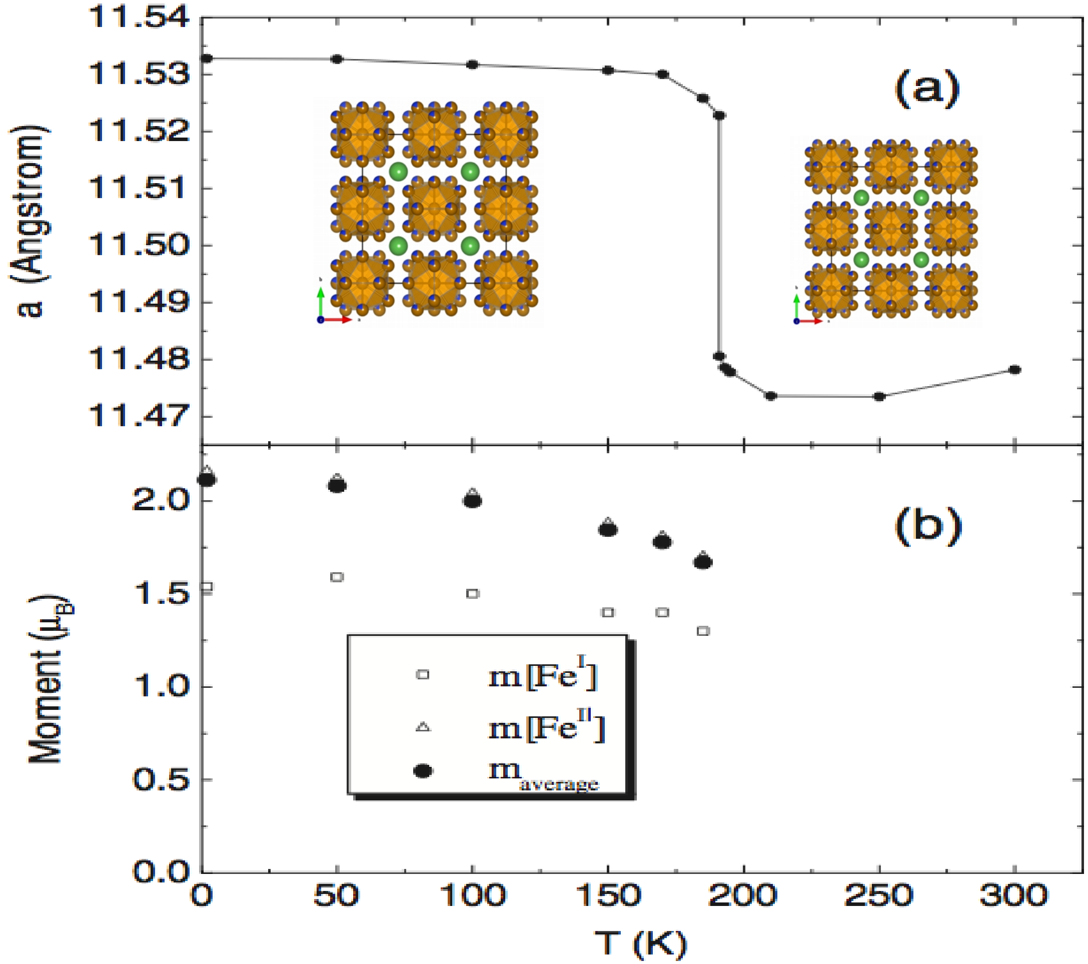
$La(Fe,Si)_{13}$ - IEM transition

Experimental

Magnetoelastic transition (no symmetry change, low volume change)

Lattice shrinkage

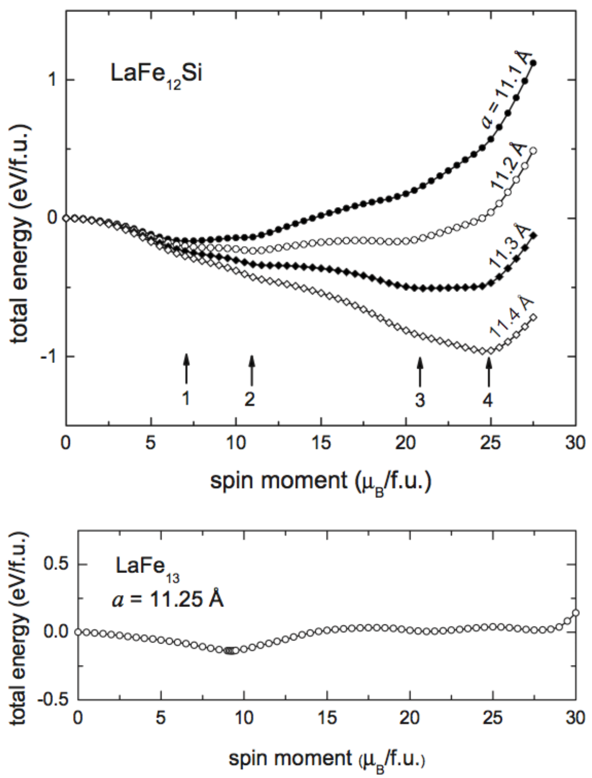


APL Zhang et al 2000

$La(Fe,Si)_{13}$ - IEM transition

Theory - FPLO-FSM

Very shallow energy plateau



M. Kuz'min and M. Richter PRB 76, 092401 (2007)

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$La(Fe,Si)_{13}$ - IEM transition

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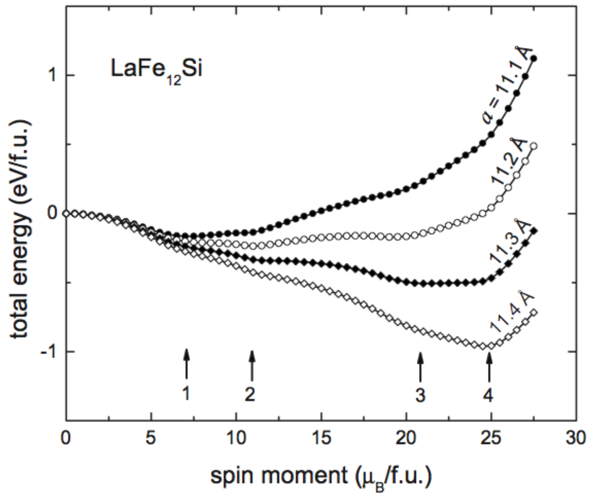
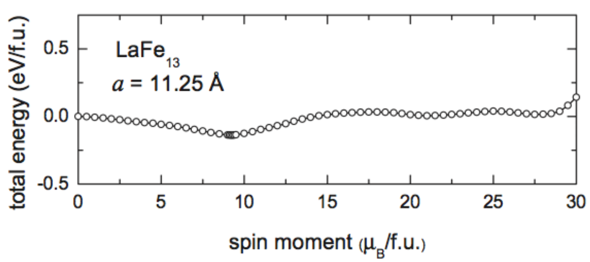
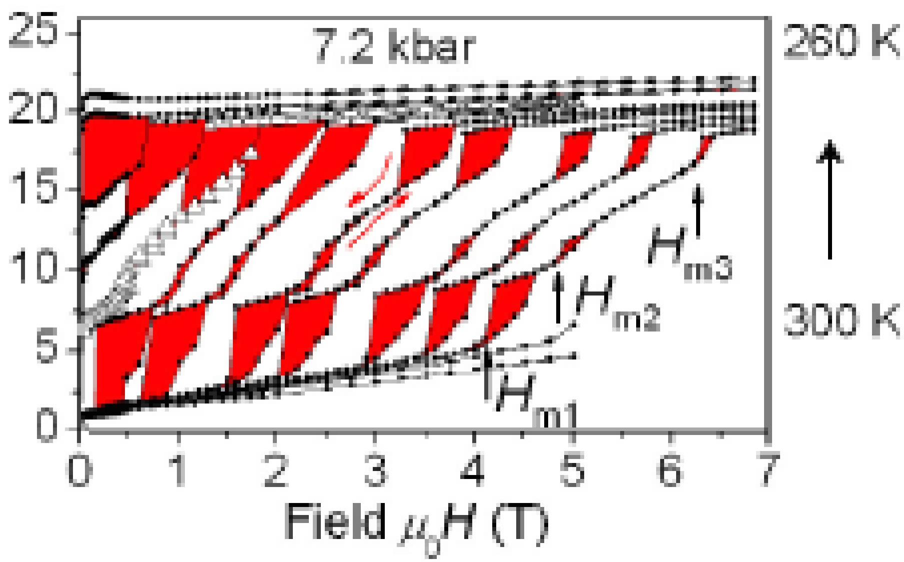




Experimental

Experimentally observed (??) under pressure in hydrogenated samples



M. Kuz'min and M. Richter PRB 76, 092401 (2007)

J. Lyubina et. al. PRL 101, 177203 (2008)

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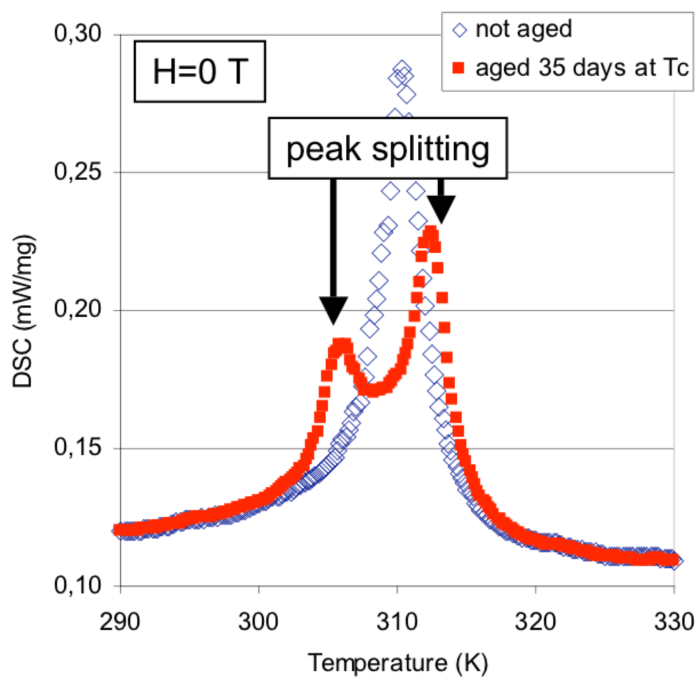
$La(Fe,Si)_{13}$ - IEM transition

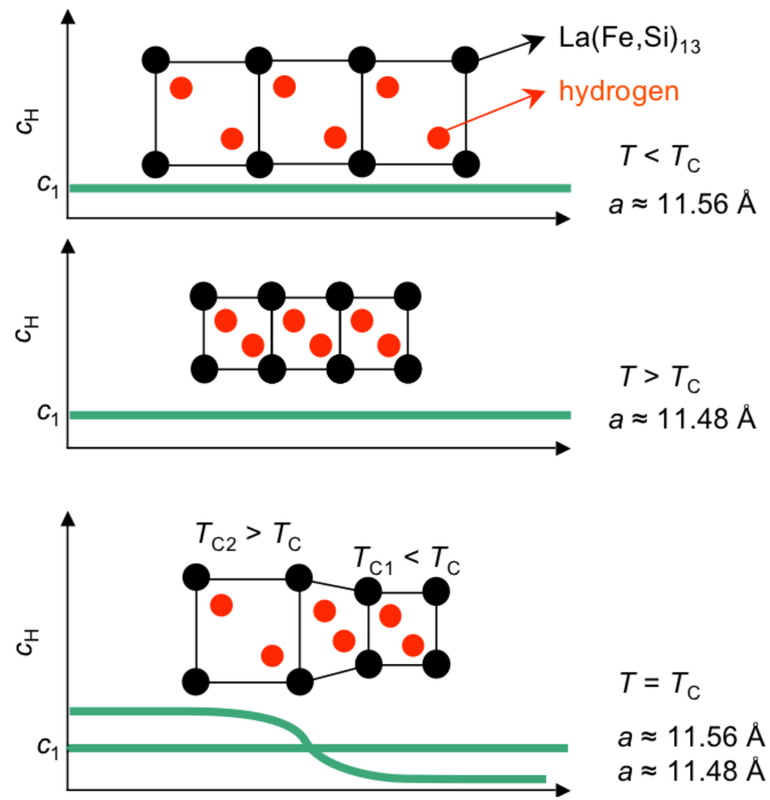
Experimental

Hydrogen disproportionation at the Curie temperature

$La_{1.04}Fe_{11.44}Si_{1.56}H_{1.35}$:

- Produced by induction melting.
- Hydrogenated at 514 K.
- Stored in air at T_C for 35 days.





A. Barcza et al. IEEE Trans Magn, **47** 10 (2011)

Also see in: M. Krautz et al. J. Appl. Phys. **112**, 083918 (2012)
C. B. Zimm et al. J. Appl. Phys. **113**, 17A908 (2013)

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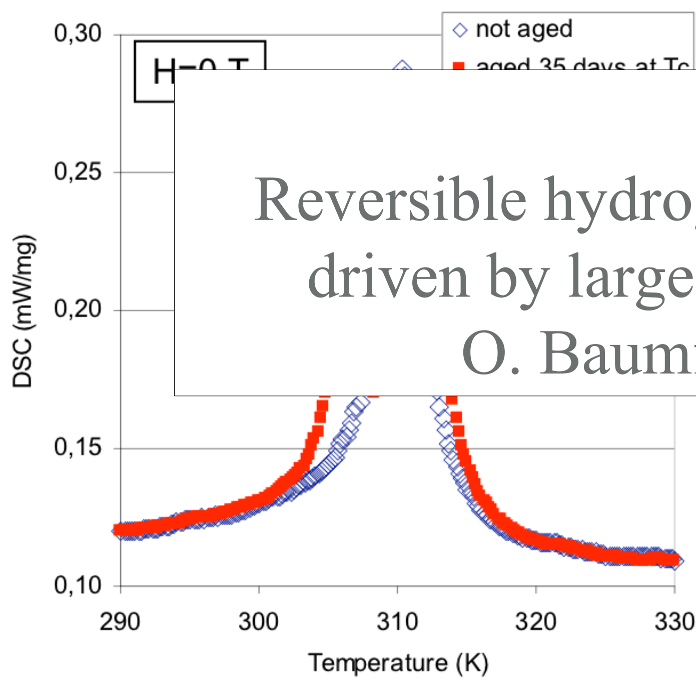

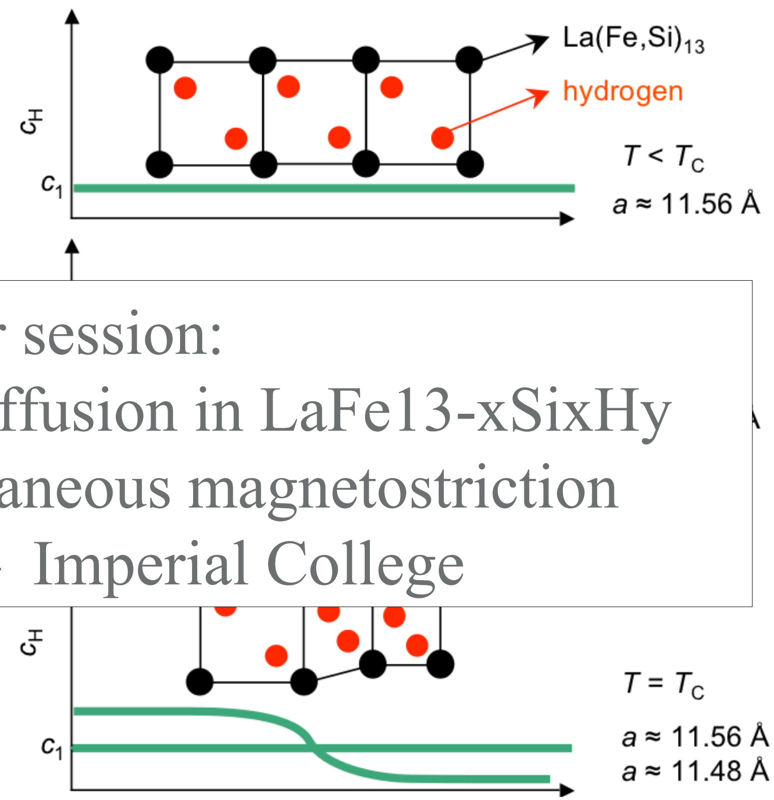

Poster session:
Reversible hydrogen diffusion in LaFe13-xSixHy driven by large spontaneous magnetostriction
O. Baumfeld – Imperial College

A. Barcza et al. IEEE Trans Magn, **47** 10 (2011)

Also see in: M. Krautz et al. J. Appl. Phys. **112**, 083918 (2012)
C. B. Zimm et al. J. Appl. Phys. **113**, 17A908 (2013)

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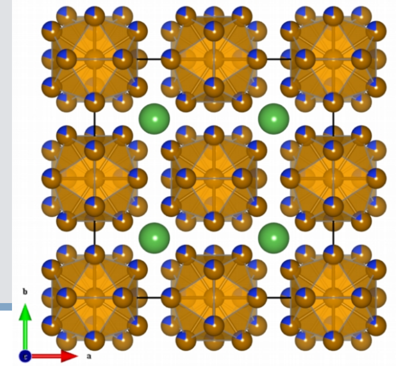
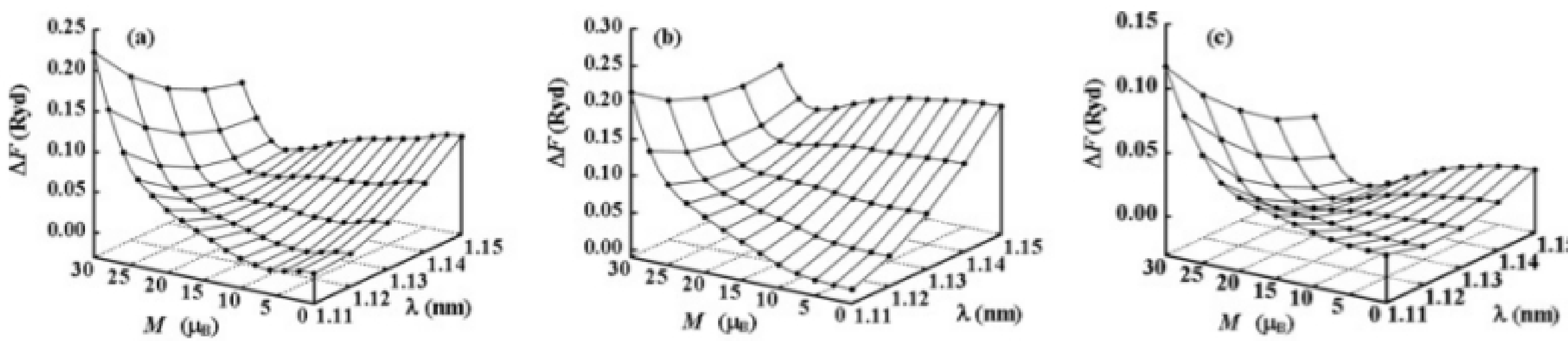
$La(Fe,Si)_{13}$ - DFT

La – 8a sites
Fe (I) – 8b sites
Fe/Si (II) – 96i sites



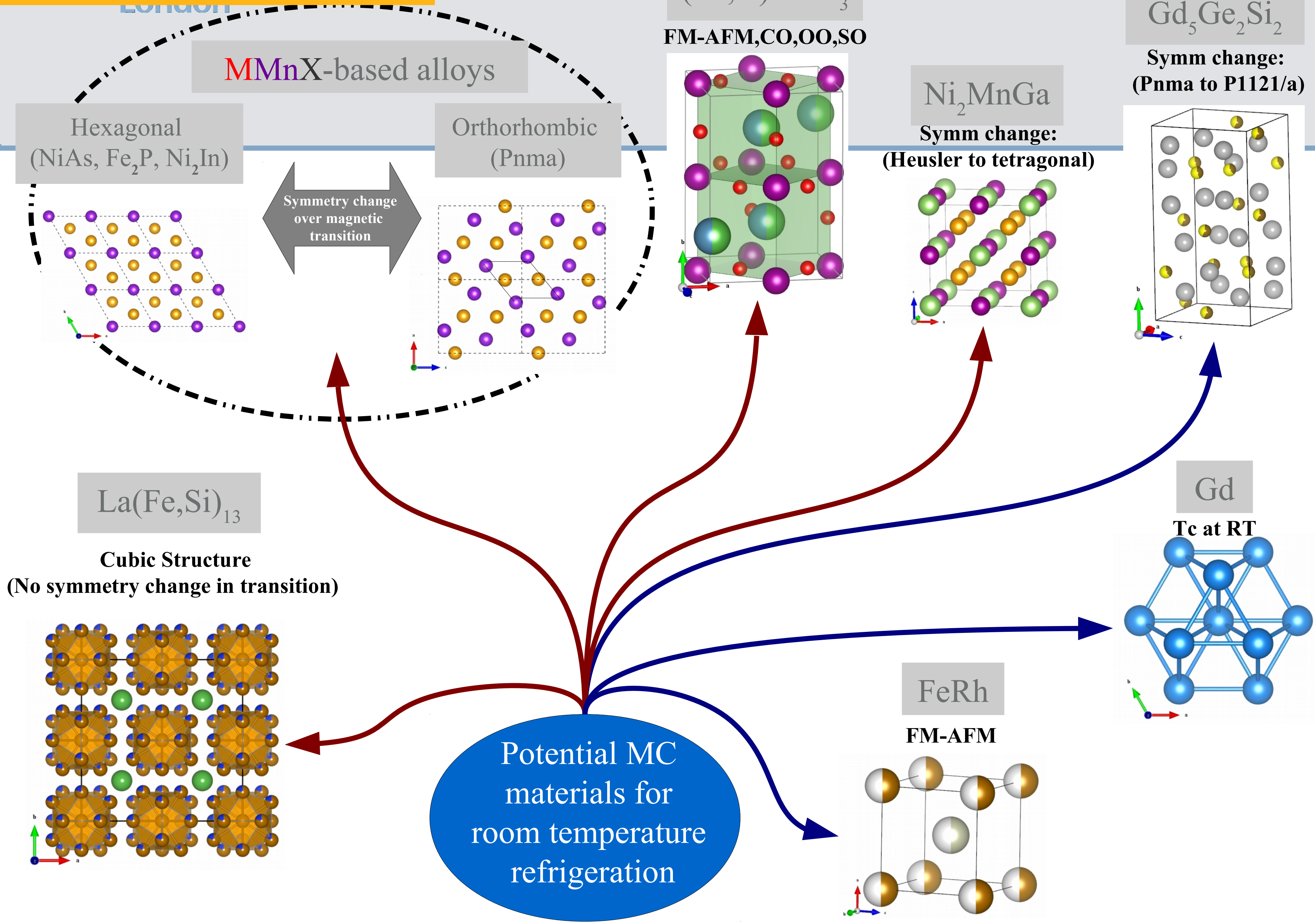
The calculated multi-minima structure depends strongly on the theory used as well as on the Si occupation considered.

A. Fujita, H. Yako / Scripta Materialia 67 (2012) 578–583



$LaFe^{II}{}_{12}Si^{I}$	$La[Fe^{II}{}_{11}Si^{II}]Fe^{I}$	$La[Fe^{II}{}_{10.5}Si^{II}{}_{1.5}]Fe^{I}$
The multiplicity of transition fades and concave–convex variation appears (M=5μ_B state is stable).	Si occupation of the 96i site show gives stable 0μ_B non-magnetic state.	CPA simulations gives the FM state most stable.

Introduction



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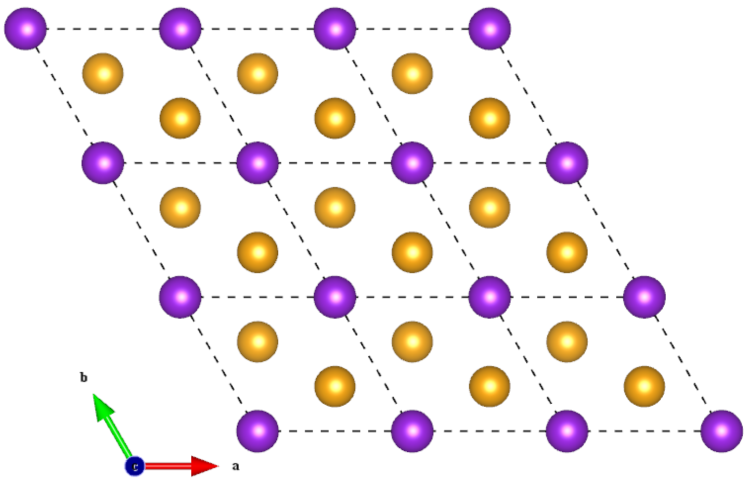
MMnX-based metallic alloys

M – void or d-block element

X – p-block element



Hexagonal
(Fe_2P, NiAs, Ni_2In)

No symmetry change

Fe_2P

$MnFeP_{1-x}As_x$

$MnFeP_{1-x}Si_x$, ...

Symmetry change over magnetic transition

MnAs

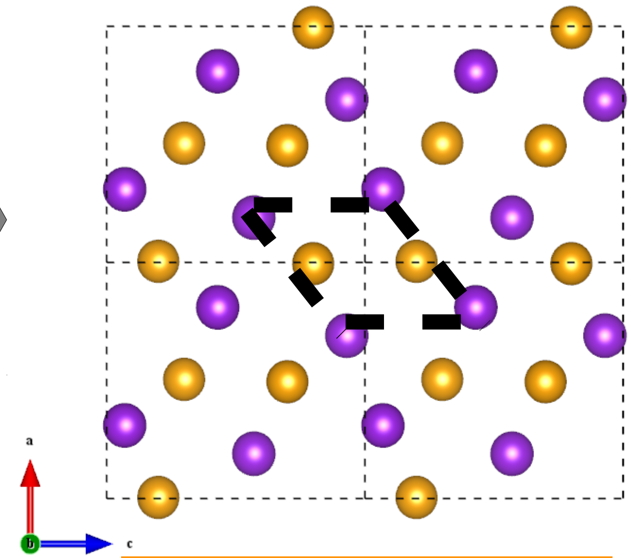
$MnAs_{1-x}Sb$

$Mn_{1-x}Fe_xAs$

$Co_{1-x}MnGe$

$CoMnGeB_x$

...



Orthorhombic
(Pnma)

No symmetry change

CoMnSi

$NiMnGe_{1-x}Si_x$

Mn_3Sn_2 , ...

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Experimental

Magnetostructural transitions – MnAs

From NiAs to Pnma structure

- MnAs

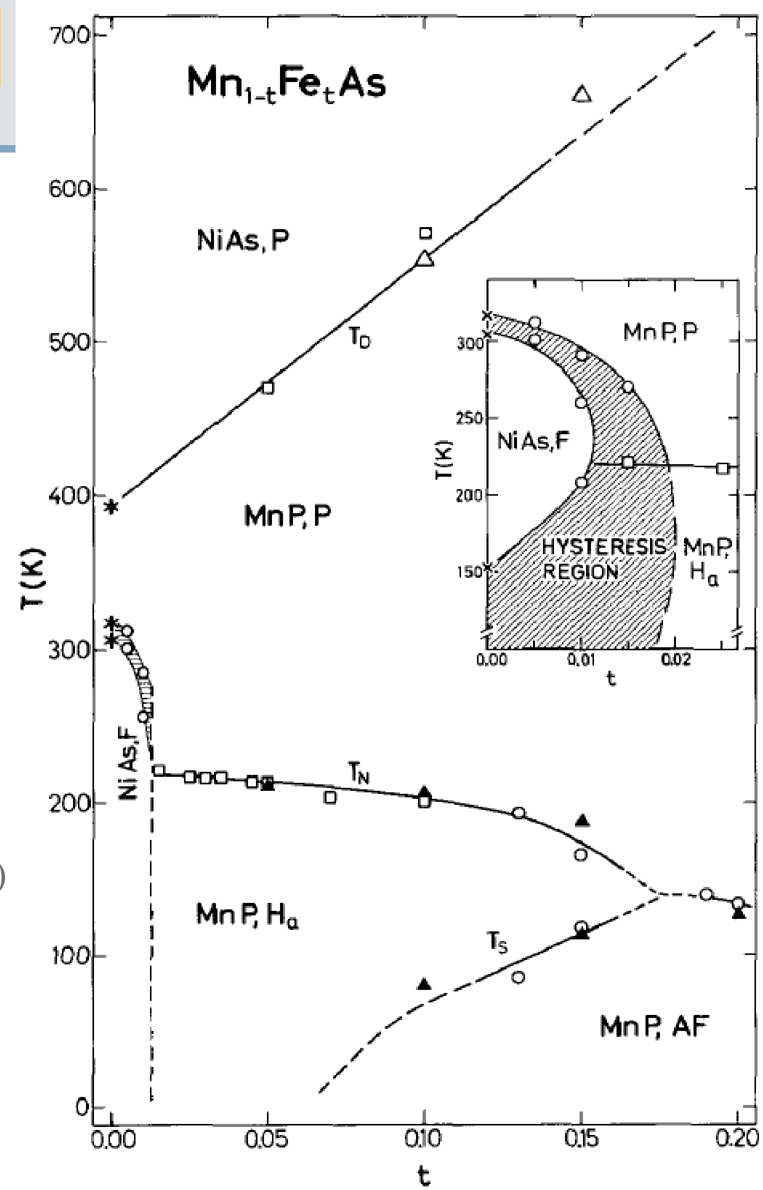
Wada et. al. Physica B: Cond. Mat. 328, 1, (2003)

Both p- and d-block type dopants have been explored

- $Mn_{1-x}Fe_xAs$, $MnAs_{1-x}Sb_x$, etc.

See for instance in De Campos et al Nature Materials 5, 802 – 804 (2006)

Relevant DFT study?



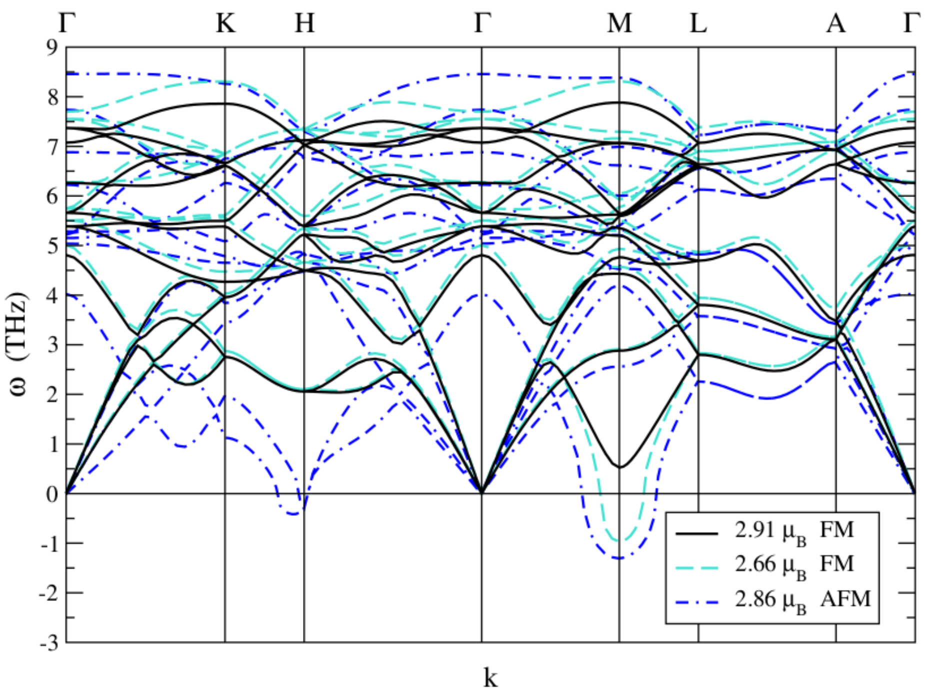
Fjellvag et. al. JMMM 46, 29, (1984)

Magnetostructural transitions – MnAs

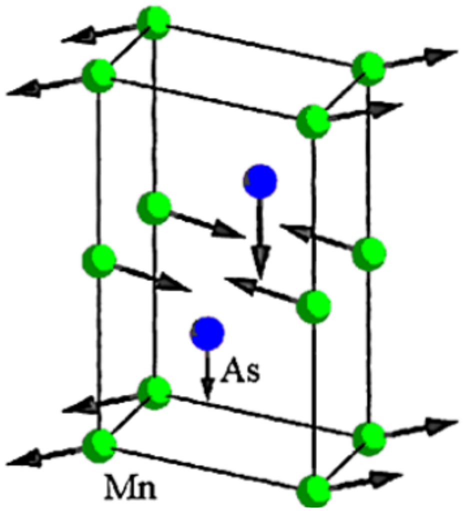
DFT

Strong (giant) coupling
between lattice and magnetic interactions

Phonon dispersion of MnAs (hexagonal)



Mn atoms move in the hexagonal a-b plane in one direction, while As atoms move along the c-direction



consistent with experimental findings
(neutron diffraction)

For more, see in
J. Łazewski et al., PRL 104, 147205 (2010)

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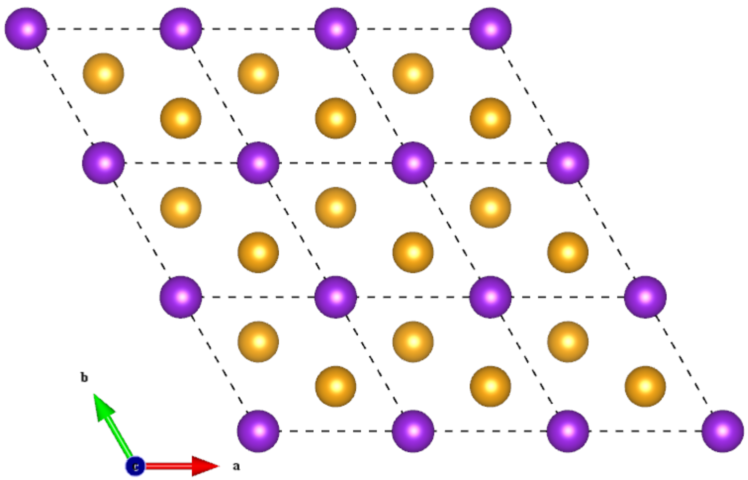
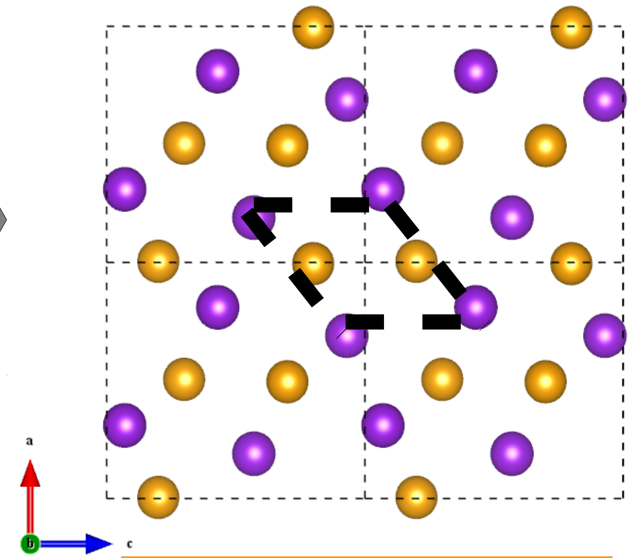
MMnX-based metallic alloys

M – void or d-block element

X – p-block element



Symmetry change over magnetic transition



Hexagonal (Fe_2P, NiAs, Ni_2In)

No symmetry change

Fe_2P

$MnFeP_{1-x}As_x$

$MnFeP_{1-x}Si_x$, ...

$MnAs$

$MnAs_{1-x}Sb$

$Mn_{1-x}Fe_xAs$

$Co_{1-x}MnGe$

$CoMnGeB_x$

...

Orthorhombic (Pnma)

No symmetry change

CoMnSi

$NiMnGe_{1-x}Si_x$

Mn_3Sn_2 , ...

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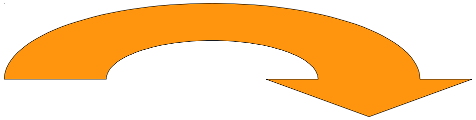
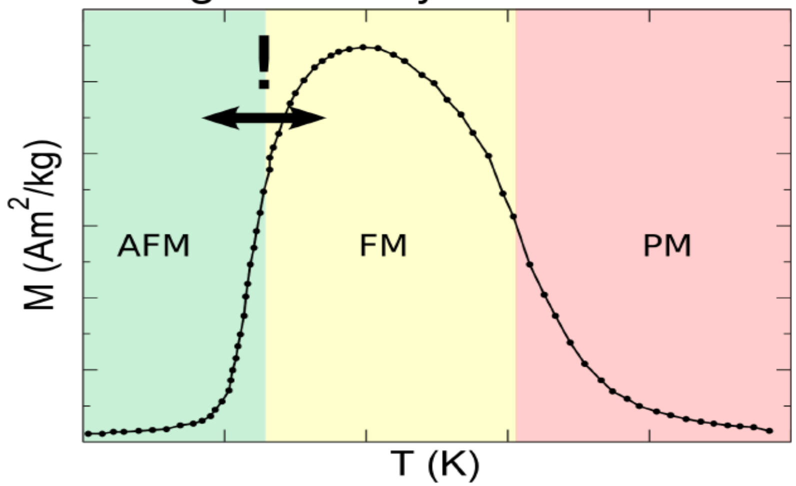
Orthorhombic (Pnma) metamagnet:

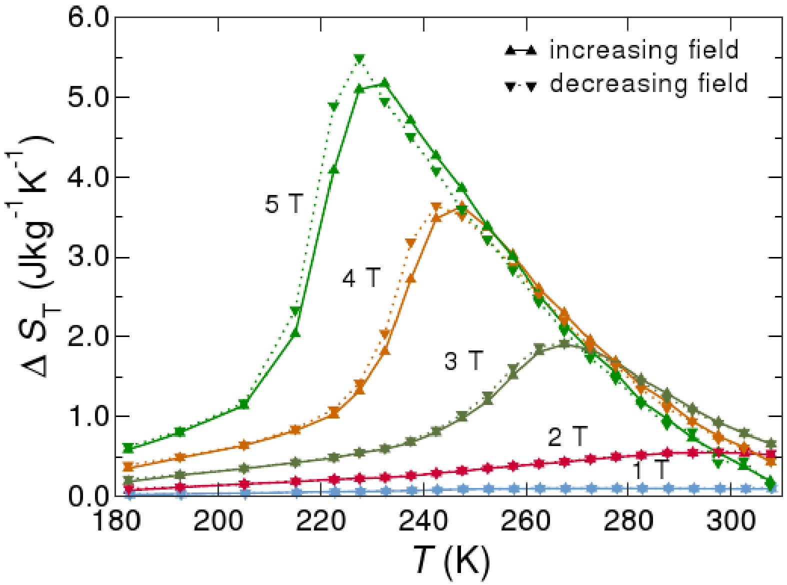
CoMnSi



Bulk magnetometry:



after H. Binczycka, A. Szytula, Phys. Stat. Sol. A, **35** K69-K72 (1976)



K.G. Sandeman et al.
Phys. Rev. B 74, 224436 (2006)

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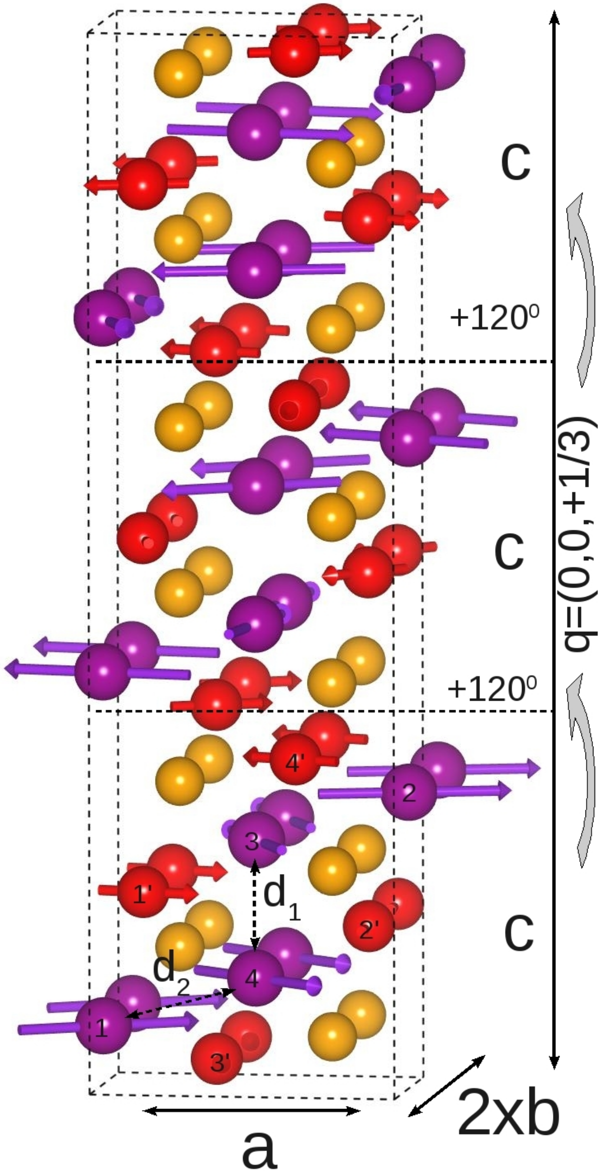
Orthorhombic (Pnma) metamagnet:

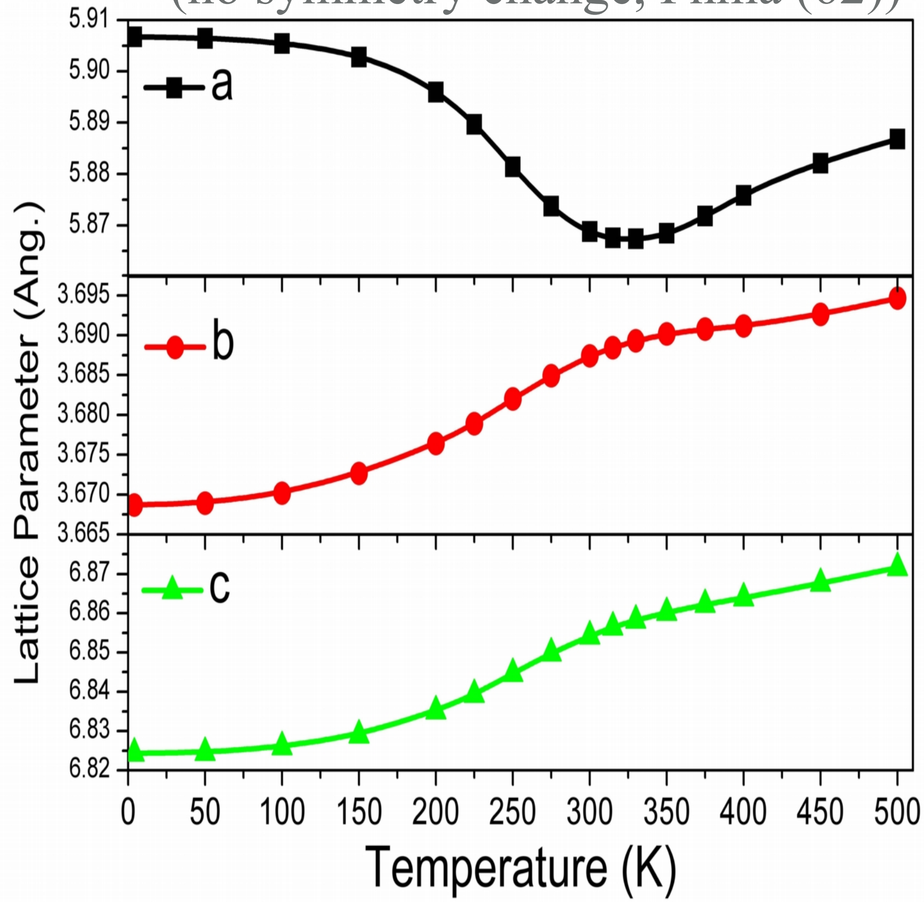
$\mu_{Mn} \approx 2.6\mu_B$, $\mu_{Co} \approx 0.3\mu_B$

CoMnSi

High Resolution Powder Diffraction (ISIS, Didcot, UK)



Negative a-lattice parameter expansion
(no symmetry change, Pnma (62))



A. Barcza, Z. Gercsi, K.S. Knight and K.G. Sandeman
Phys. Rev. Lett. 104, 247202 (2010)

Imperial College London

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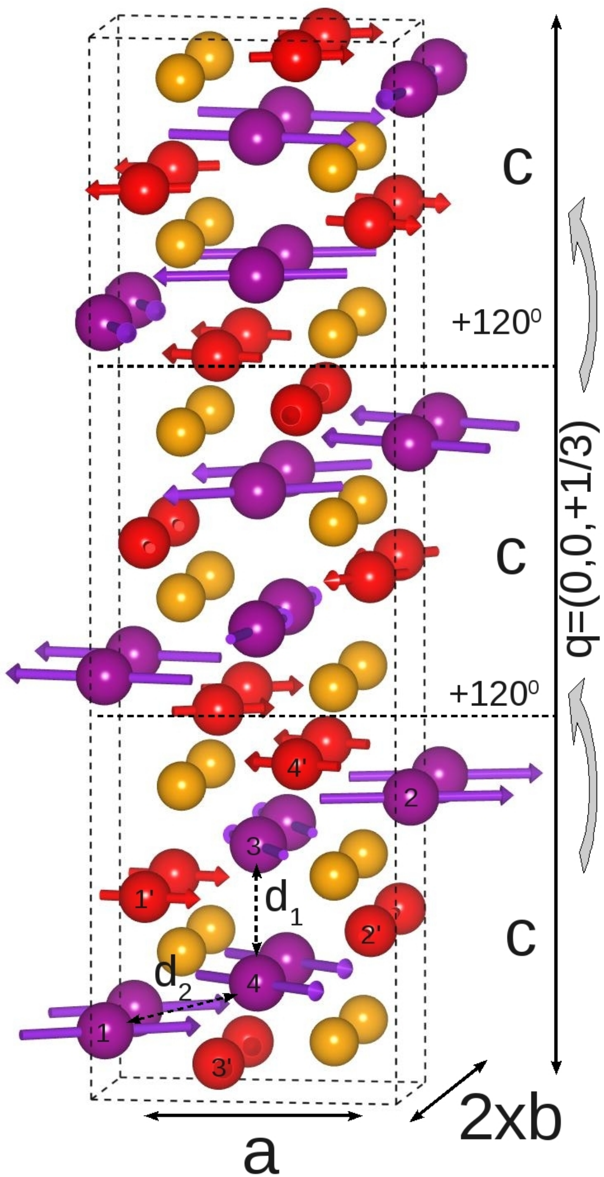
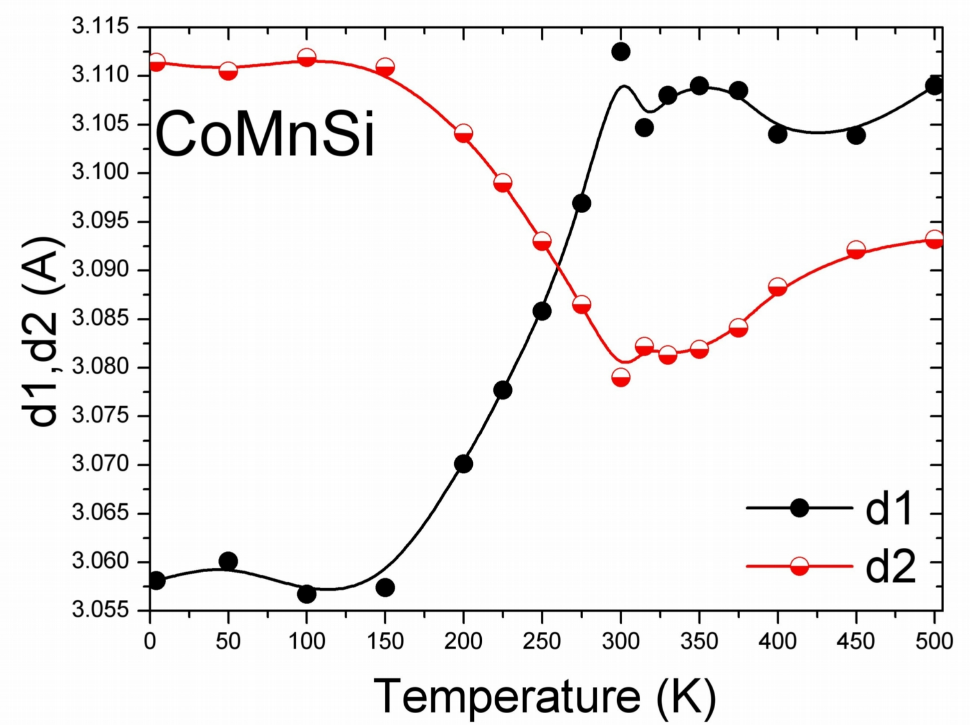
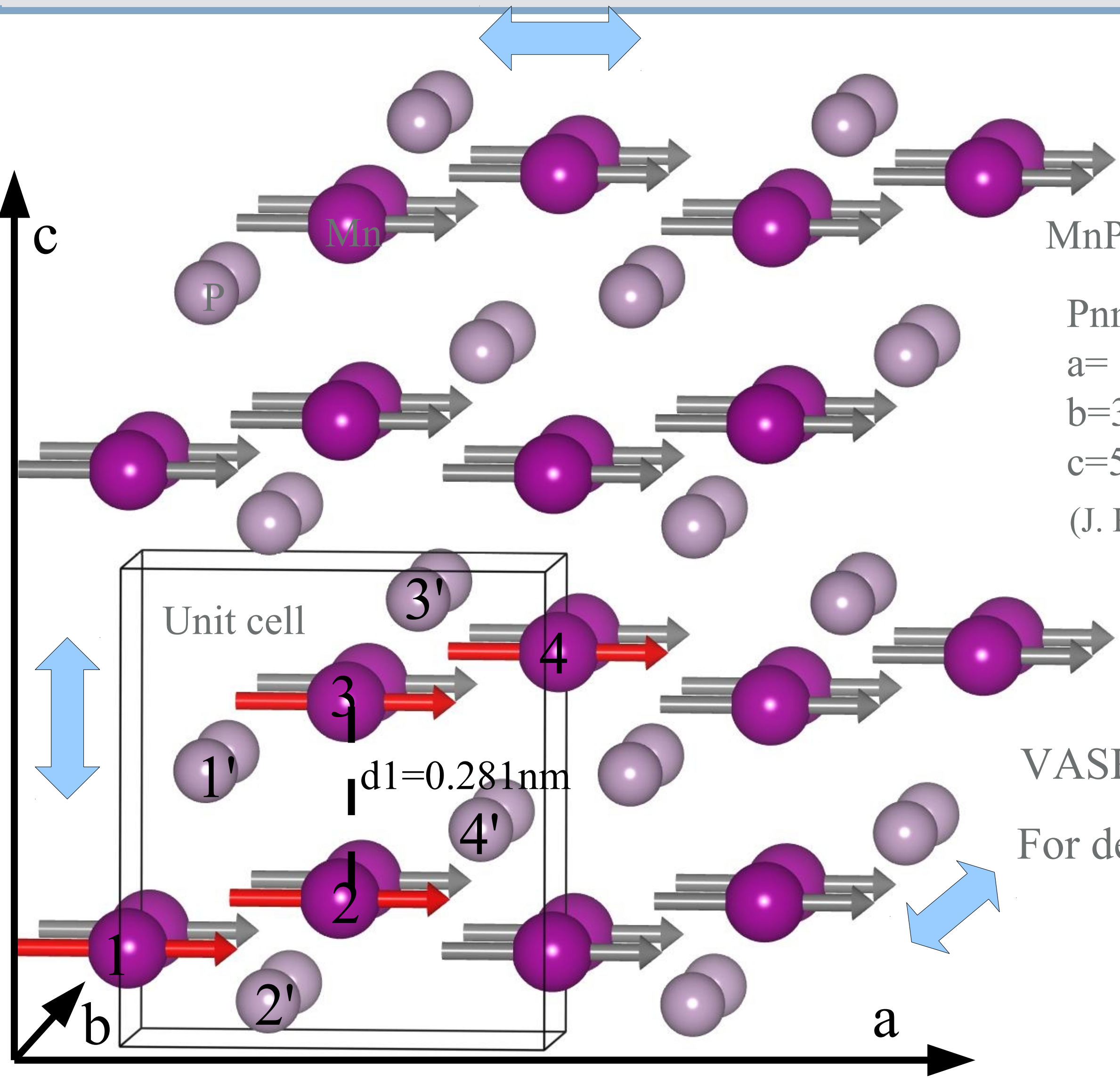


We found giant changes in Mn-Mn distances (d_1,d_2) link to the metamagnetic transition.



A. Barcza, Z. Gercsi, K.S. Knight and K.G. Sandeman Phys. Rev. Lett. 104, 247202 (2010)

DFT theory to map the magnetic phase stability vs. lattice volume using the prototype (MnP) structure



MnP Experimentally – Ferromagnetic (47K)

Pnma (62) Orthorhombic structure

a= 5.259(1) Å
b=3.173(1) Å
c=5.920(1) Å

Mn - 4c
P - 4c

(J. Phys. Soc. Jap. Vol. 47, No. 2 (1979))

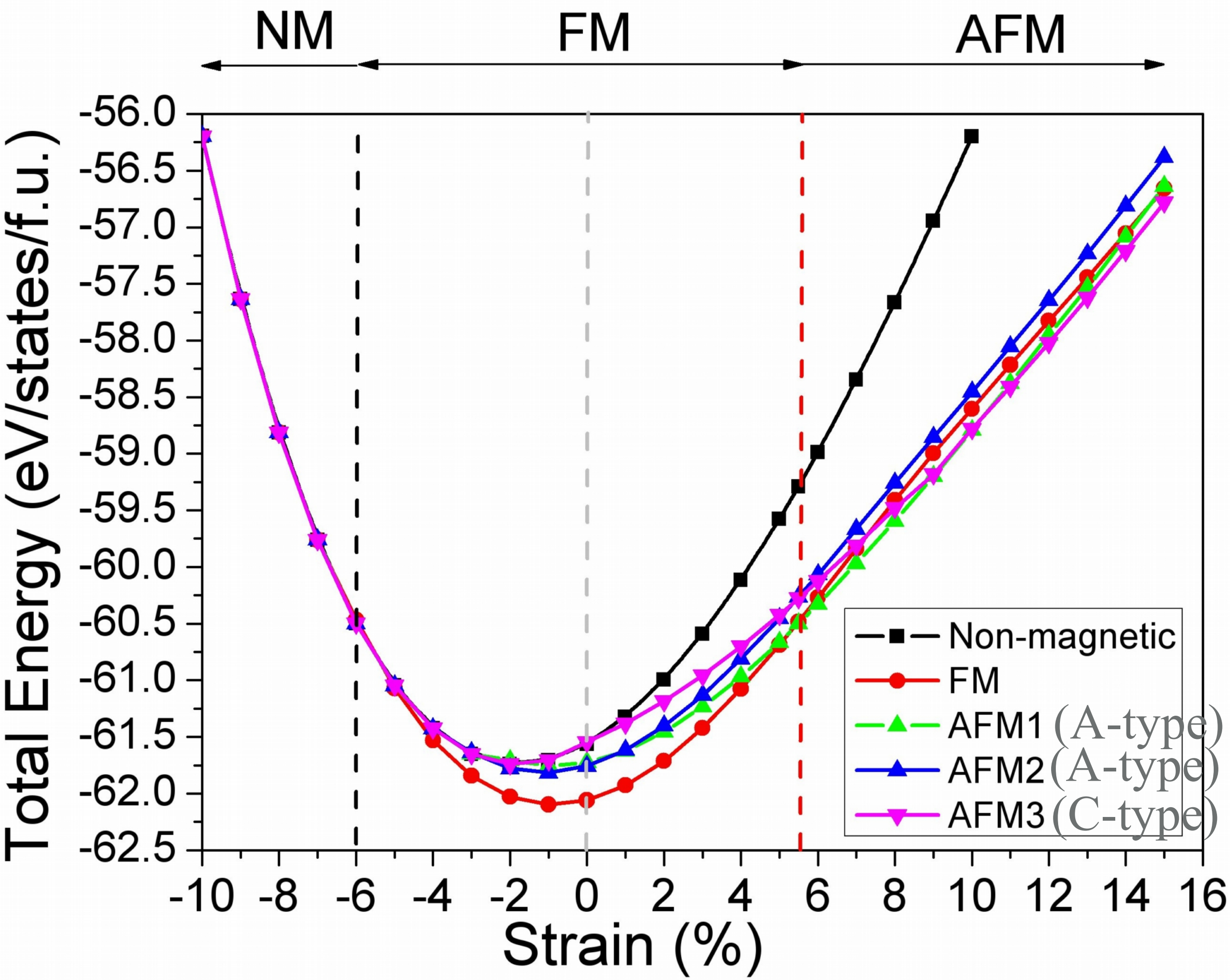
VASP code was used for the calculations.

For details, see

Z. Gercsi and K.G. Sandeman
Phys. Rev. B 81, 224426 (2010)

Imperial College London

DFT theory to map the magnetic phase stability vs. lattice volume using the prototype (MnP) structure

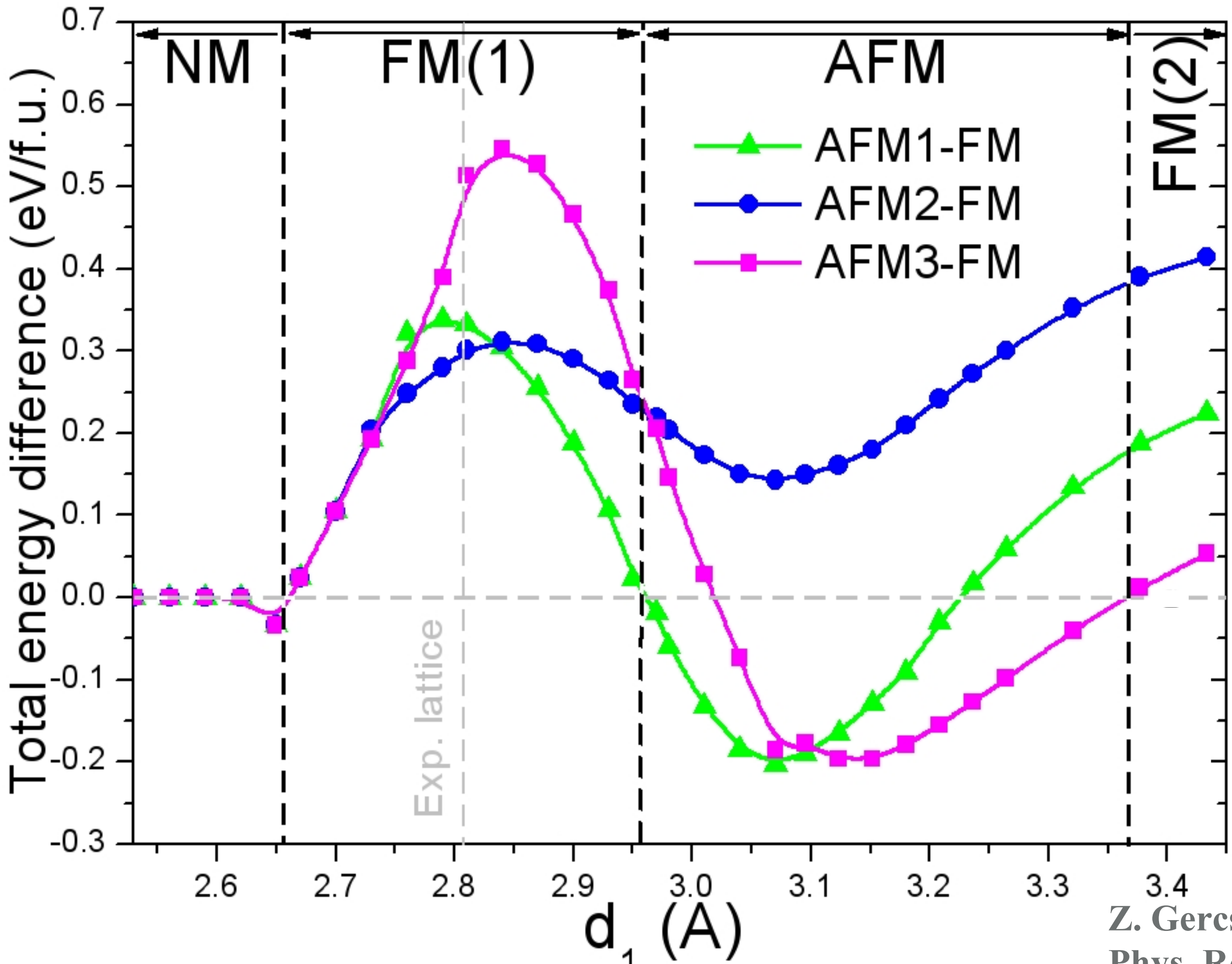


- Total energy curve predicts ferromagnetic ground state in accordance with experimental.

- These energies can also be plotted with respect to the FM phase using a more informative (Mn-Mn interatomic) scale.

New metamagnet from DFT: CoMn(GeP)

The stability plot predicts stable AFM ground state for $CoMnGe_{1-x}P_x$ with x~0.5.



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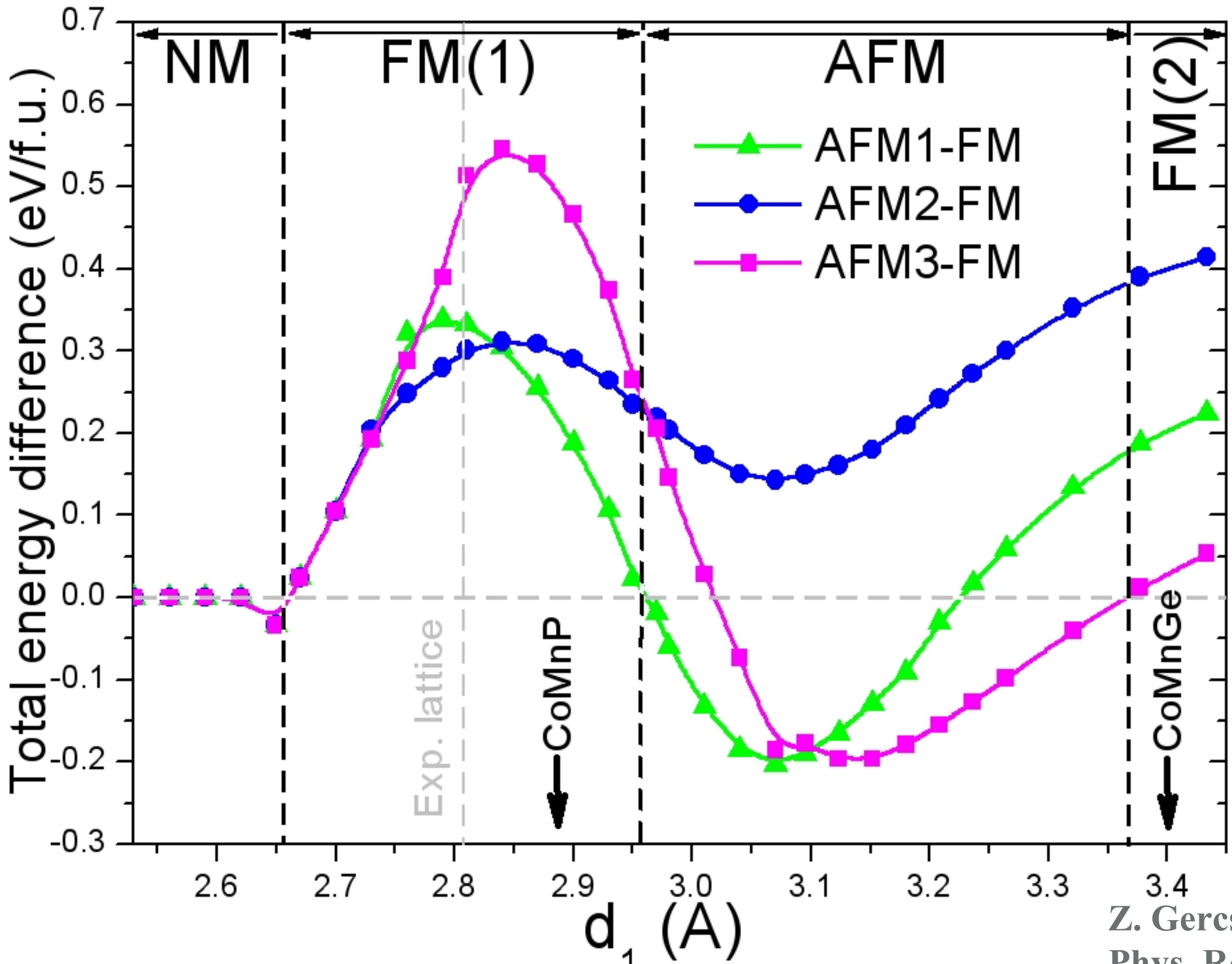
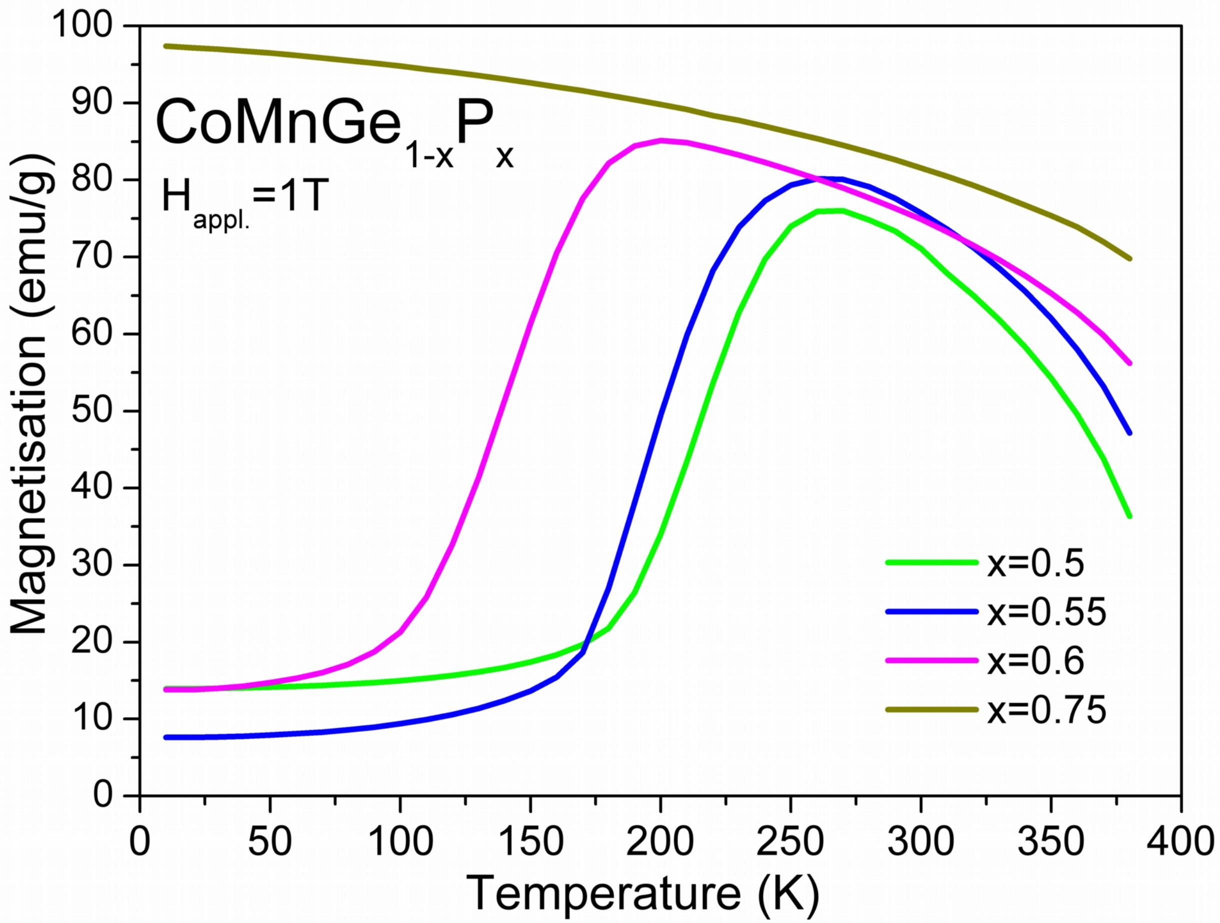


Z. Gercsi and K.G. Sandeman
Phys. Rev. B 81, 224426 (2010)

Imperial College London

New metamagnet from DFT: CoMn(GeP)

AFM ground state with metamagnetism for x=0.5,0.55, 0.6 as predicted!



Z. Gercsi, K. Hono and K.G. Sandeman Phys. Rev. B 83, 174403 (2011)

Imperial College London

Orthorhombic (Pnma) metamagnet:

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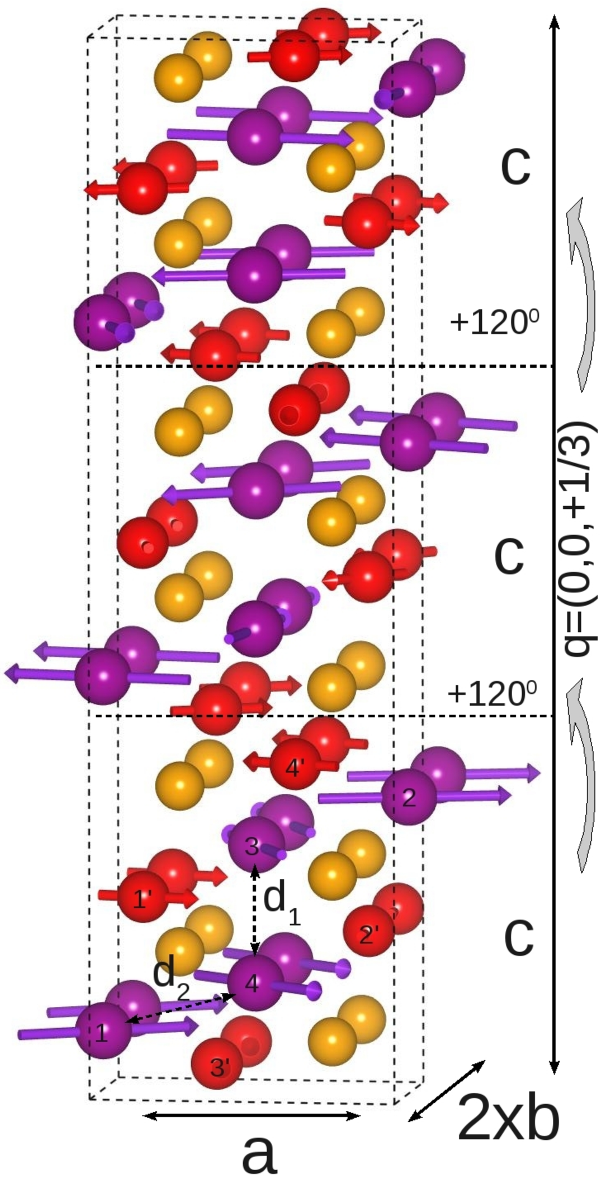

Our recent works on these materials:

A. Barcza, Z. Gercsi, et al. Phys. Rev. Lett. **104**, 247202 (2010)
Z. Gercsi and K.G. Sandeman Phys. Rev. B **81**, 224426 (2010)
Z. Gercsi, K. Hono and K.G. Sandeman Phys. Rev. B **83**, 174403 (2011)
A. Barcza, Z. Gercsi et al. Phys. Rev. B **87**, 064410 (2013)
Q. Recour, V. Ban, Z. Gercsi et al. Phys. Rev. B **88**, 054429 (2013)
J. B. Staunton, M. dos Santos Dias, J. Peace, Z. Gercsi, and K. G. Sandeman Phys. Rev. B **87**, 060404 (2013)

09:30 – 10:00
Tuning the metamagnetism of an antiferromagnetic metal
J. Staunton – Warwick University

MMnX-based metallic alloys

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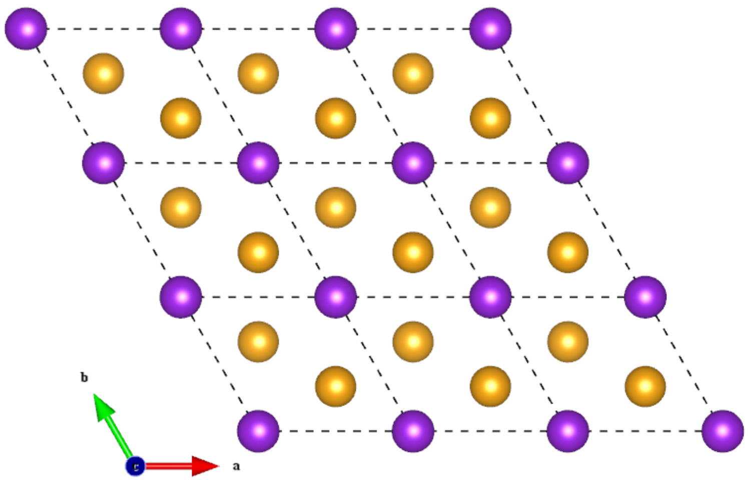
X – p-block element



Hexagonal
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No symmetry change

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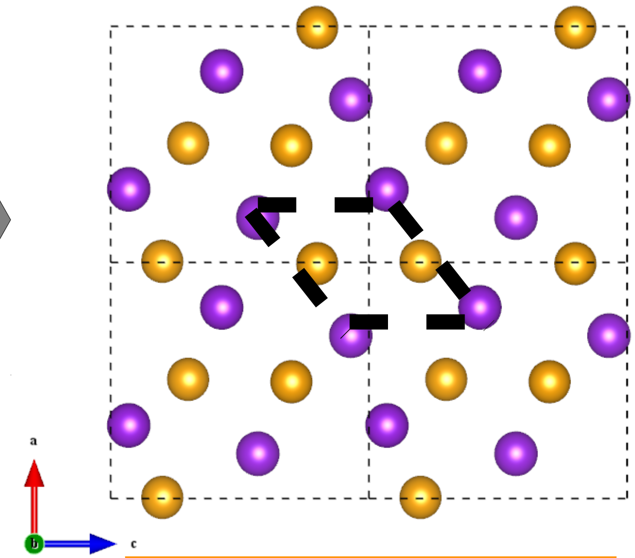

Orthorhombic
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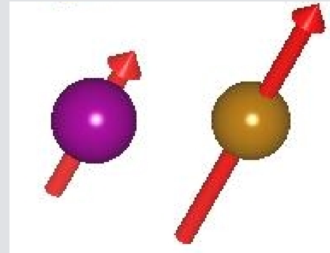
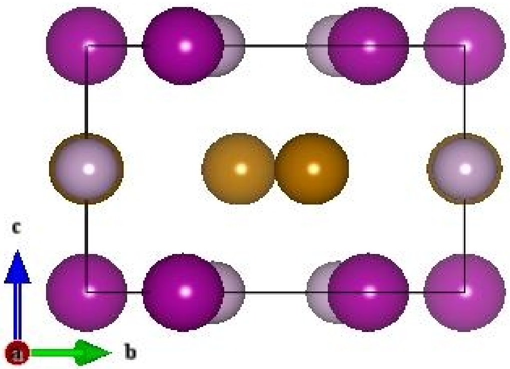
Mn_3Sn_2 , ...

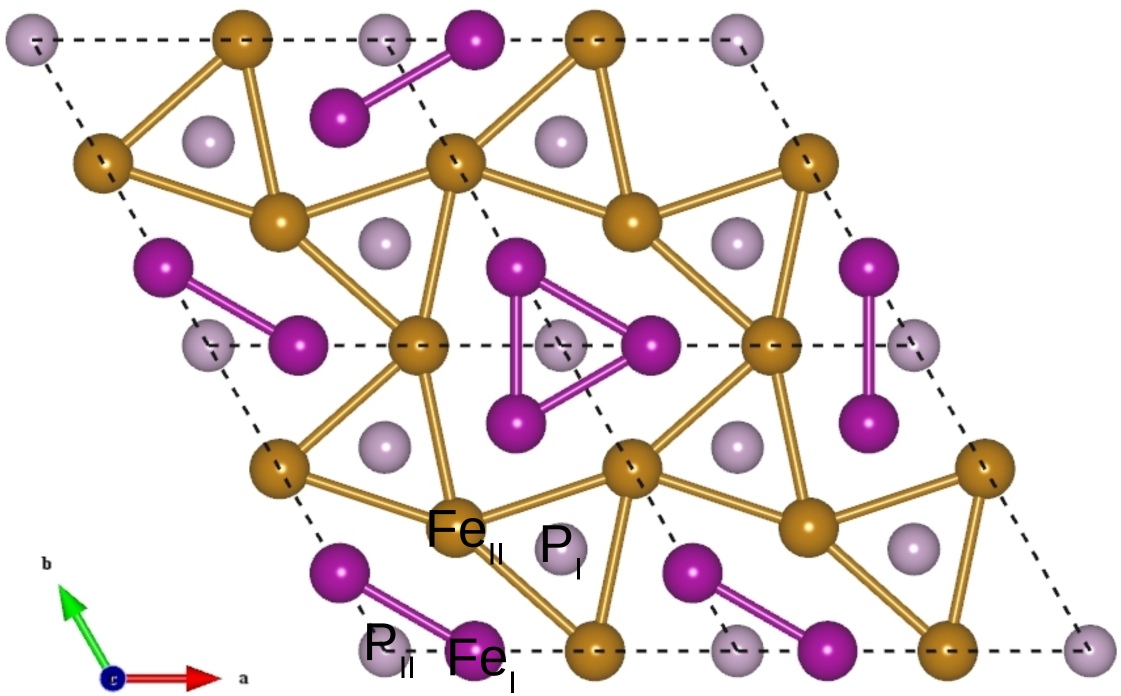
Parent → Fe_2P

P-62m (189)



Fe_I	3f sites ~$0.8\mu_B$
Fe_{II}	3g sites ~$2.4\mu_B$
P	1b&2c sites

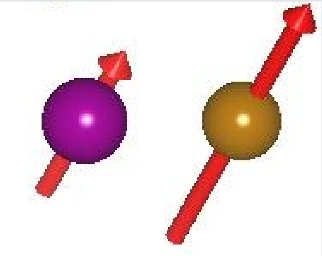




Fe_2P is the prototype of the space group with unusual magnetic properties.

Parent → Fe_2P

P-62m (189)



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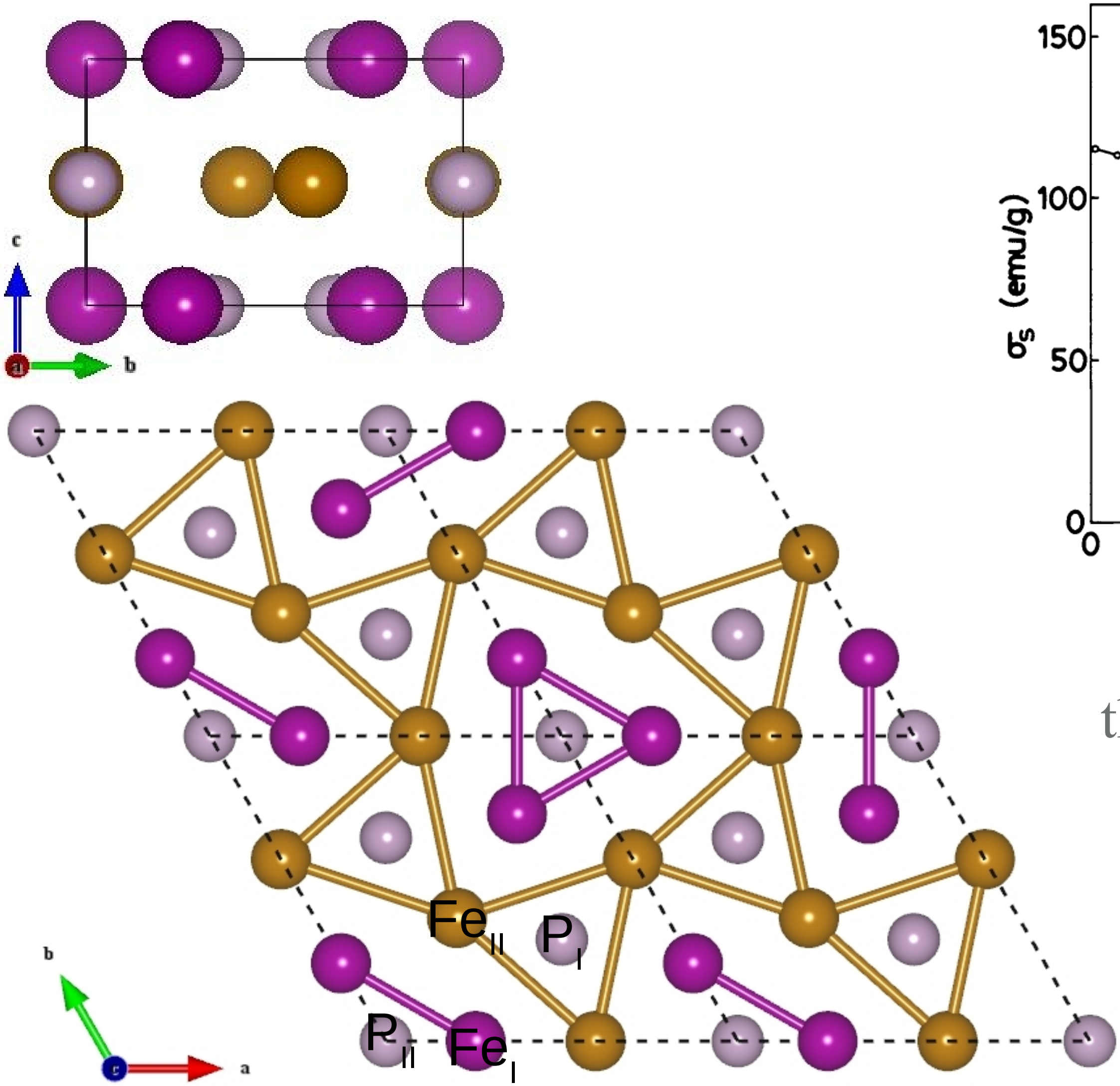
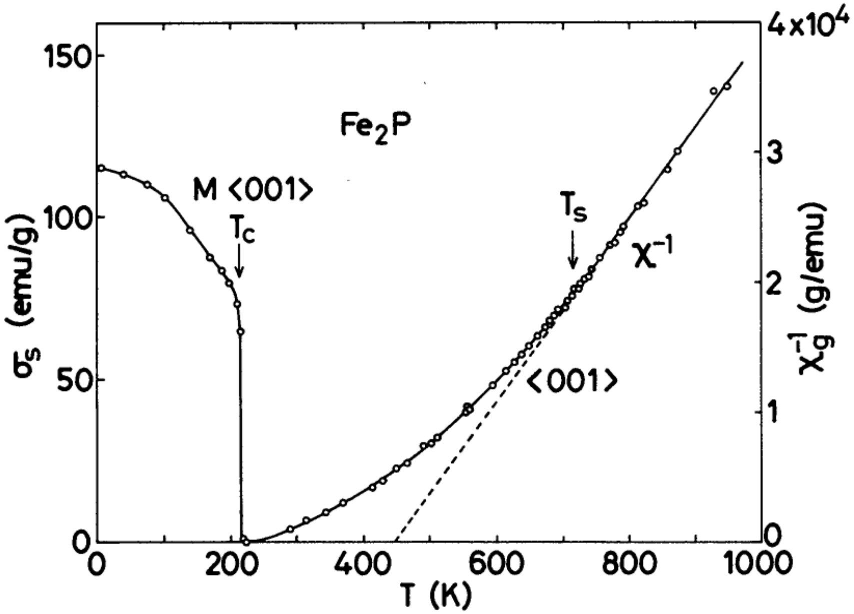




Only above ~700K
the Curie-Weiss law is followed

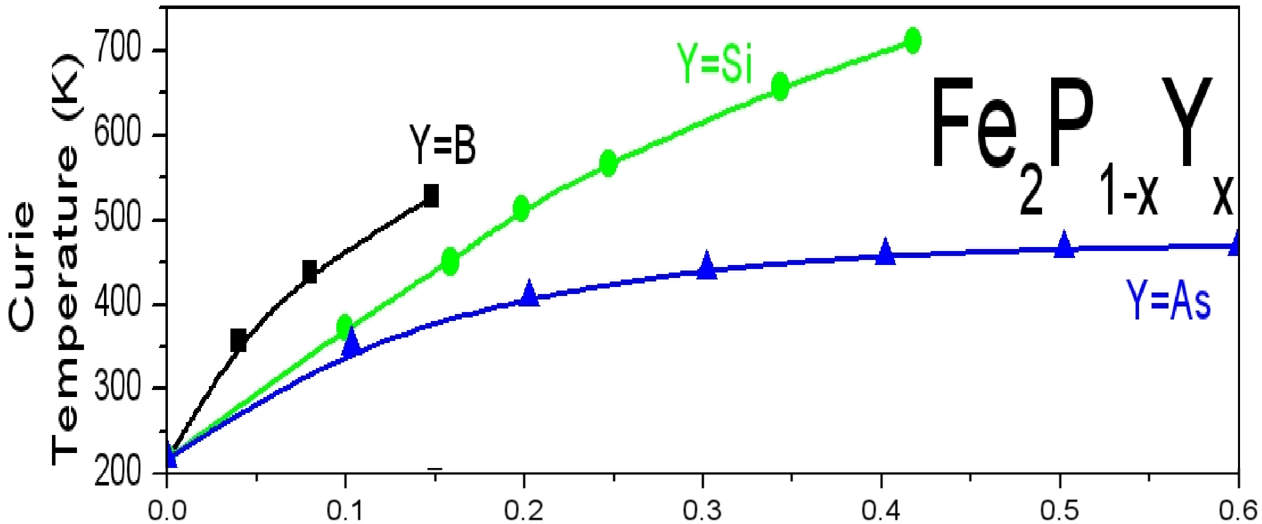
↓

local magnetic order above Tc!

H. Fujii et al. JPSJ 43, 1 (1977)

Magneto-elastic coupling in doped Fe_2P

Strong dependence of magnetic ordering temperature with doping



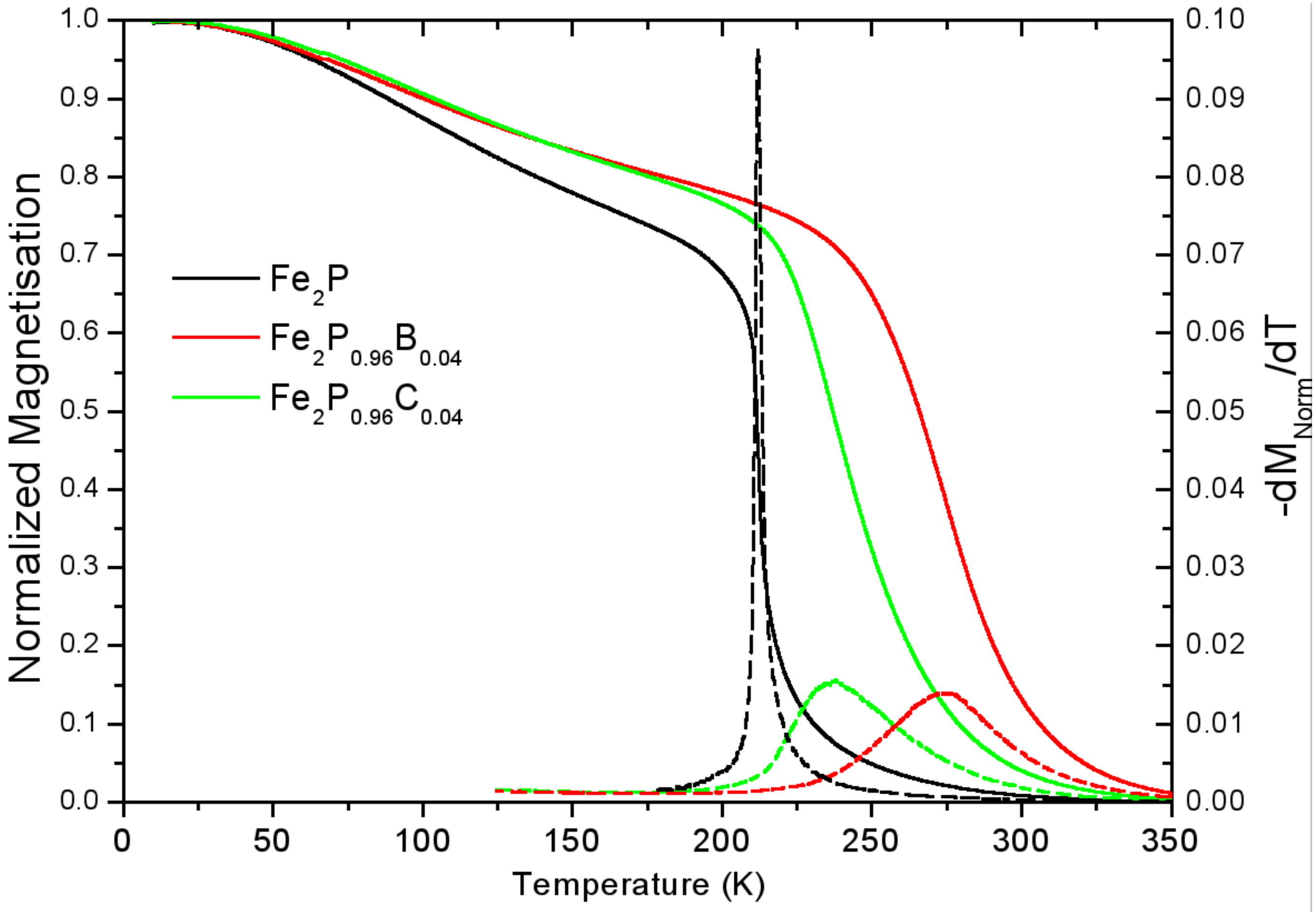
x

Data combined from:

P. Jernberg et al. J. Sol. State Chem. 53 (1984)
R. Chandra et al. J. Sol. State Chem. 34 (1980)
A. Catalano et al. J. Sol. State Chem. 7 (1973)

Magnetic properties

Strong influence on doping with broadening transition



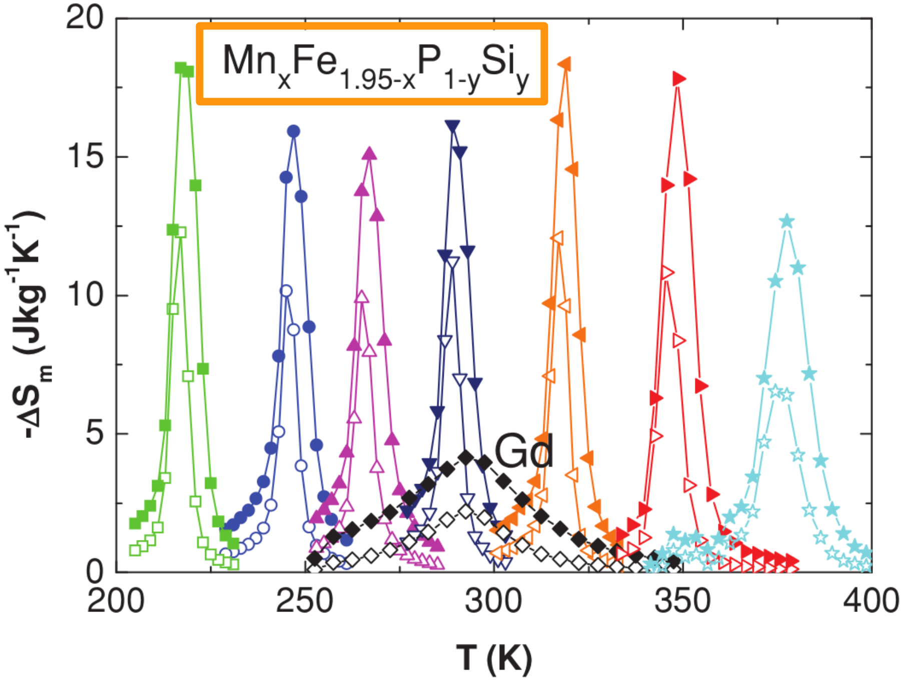
Magnetoelastic effects in doped Fe2P
Z. Gercsi et al. Phys. Rev. B **88**, 024417 (2013)

MCE of Fe2P single crystal
L. Caron et al.
PRB **88**, 094440 (2013)

Introduction

Metamagnetic transition in Fe_2P-based alloys

Tunable, field-dependent magnetic transition with large accompanying MCE



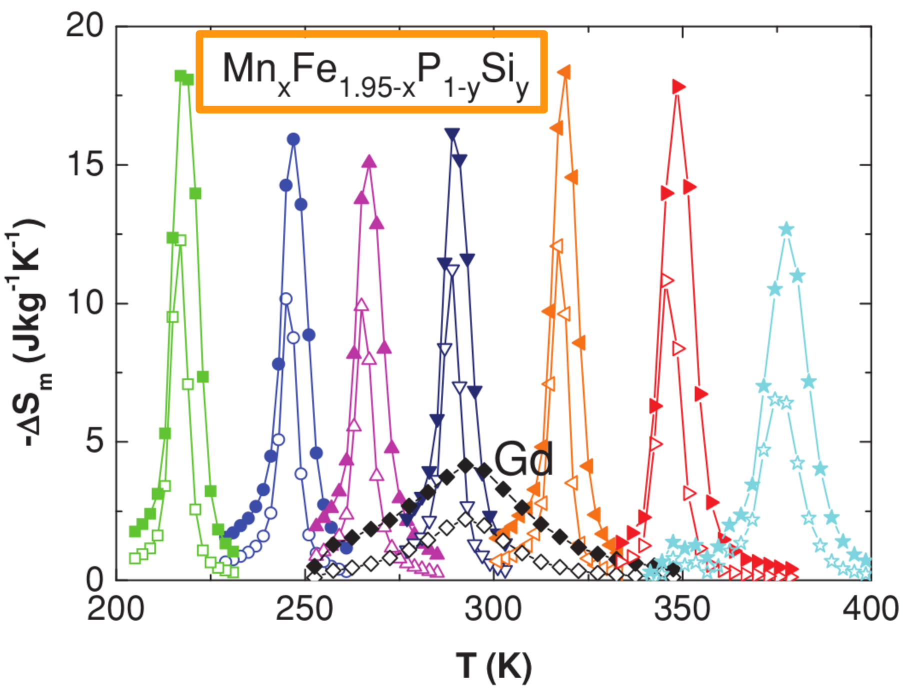
N. Dung et al.
Adv. Energy Mater. **1** 1215–1219 (2011)

Introduction

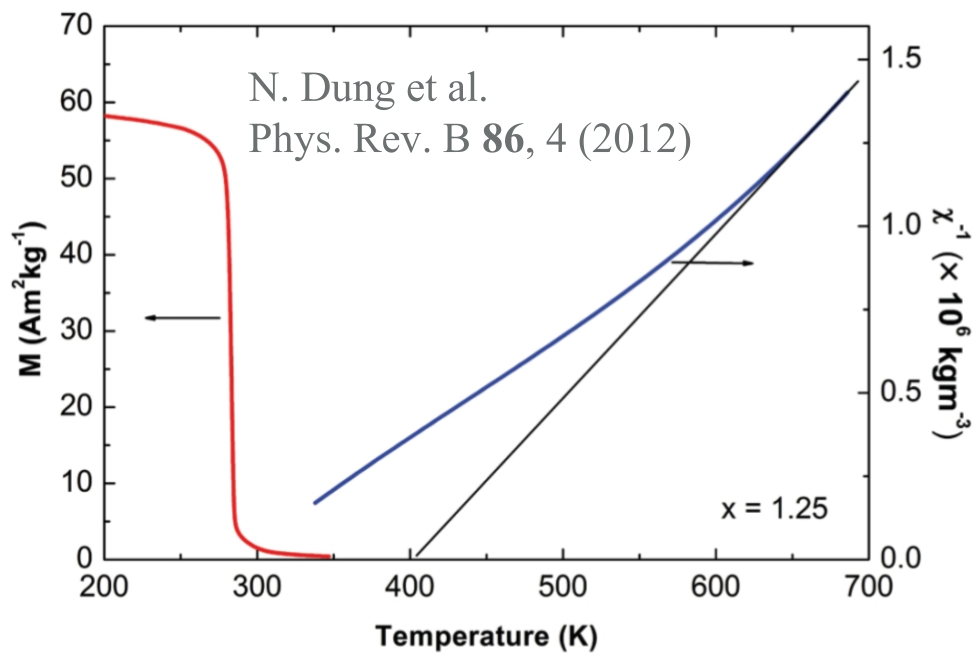
Metamagnetic transition in Fe_2P-based alloys

Tunable, field-dependent magnetic transition with large accompanying MCE

Similarly to parent alloy, short range magnetic order exist above Tc



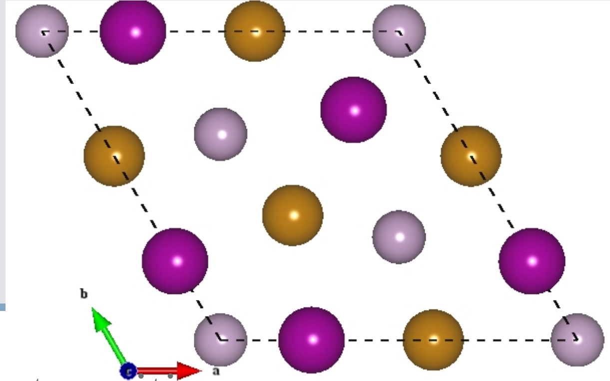
N. Dung et al.
Adv. Energy Mater. **1** 1215–1219 (2011)



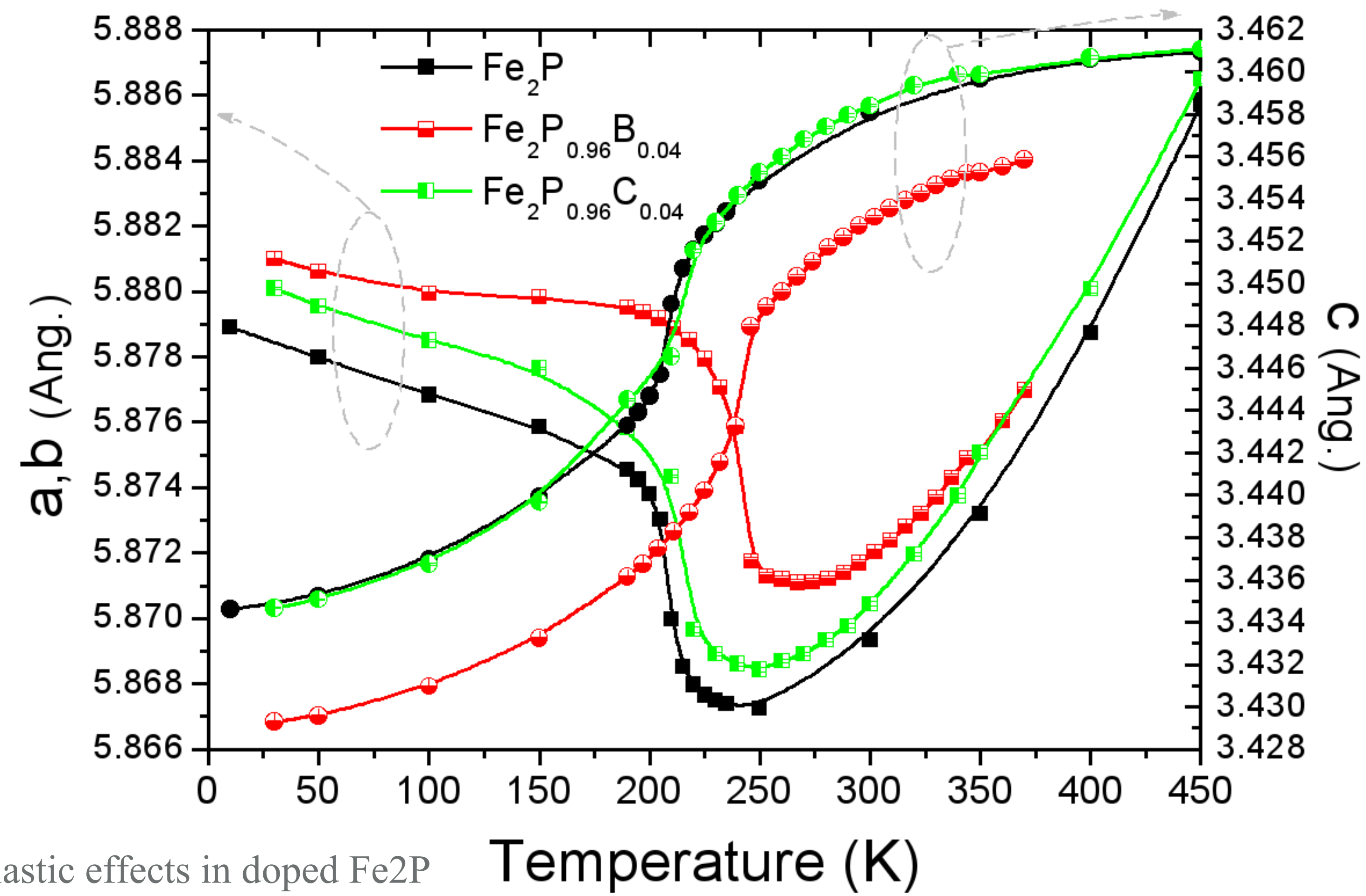
Also, Mn has a strong 3g-site preference as found experimentally.

Magneto-elastic response

Neutron diffraction (HRPD-ISIS)



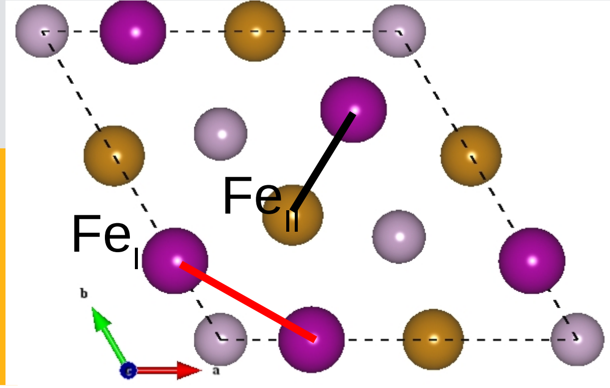
“Counteracting” change in lattice parameters over the transition.

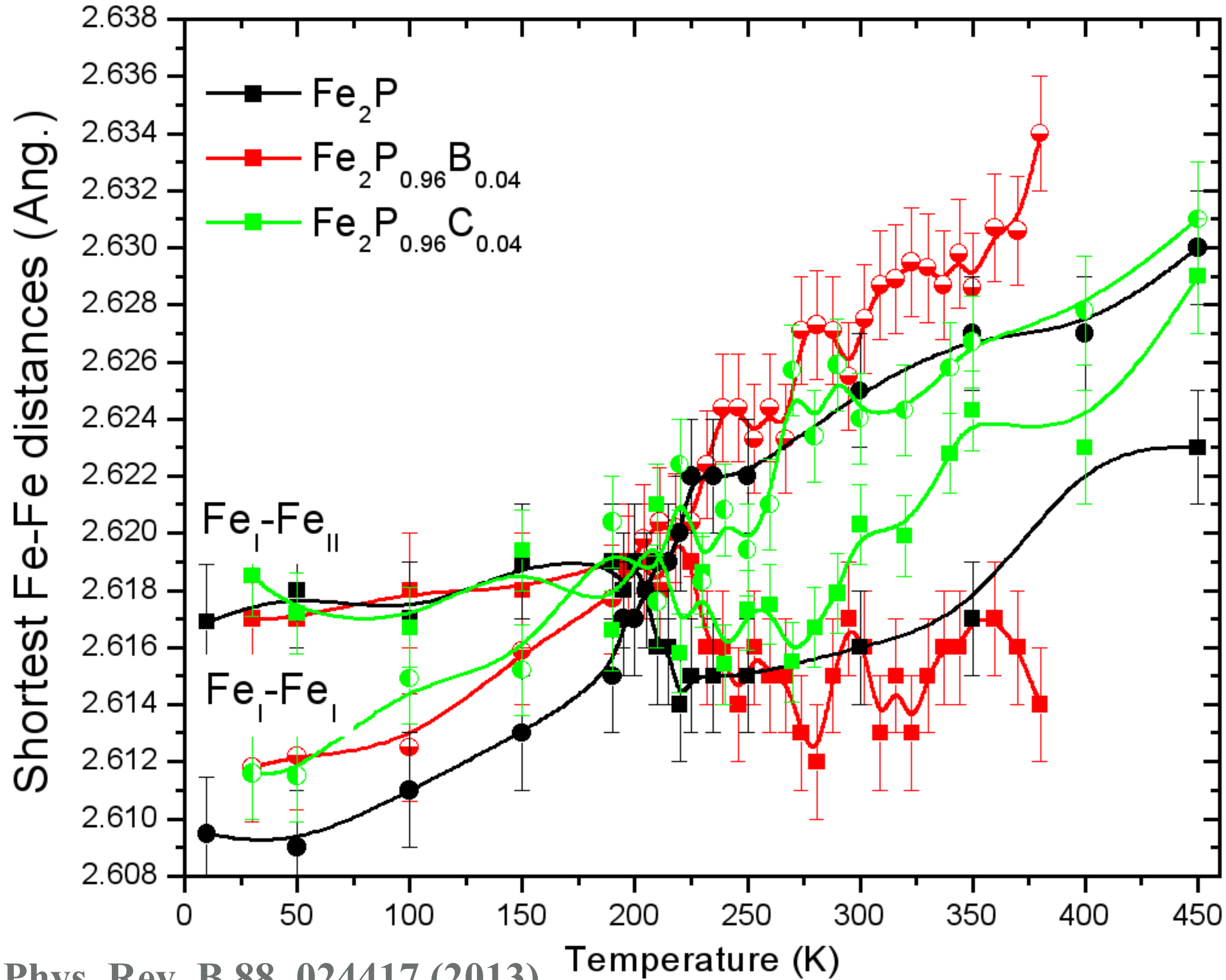


Magnetoelastic effects in doped Fe2P
Z. Gercsi et al. **Phys. Rev. B 88, 024417 (2013)**

Magneto-elastic response

We observed an increase in the shortest Fe_I-Fe_I distance and simultaneously a drop in the second shortest metal-metal distance (Fe_I-Fe_{II}) at the transition temperature.

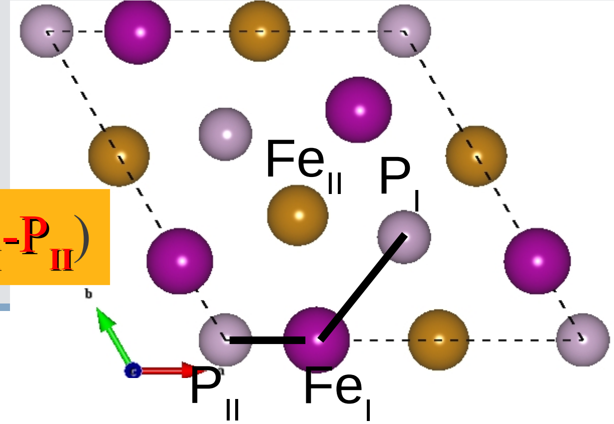


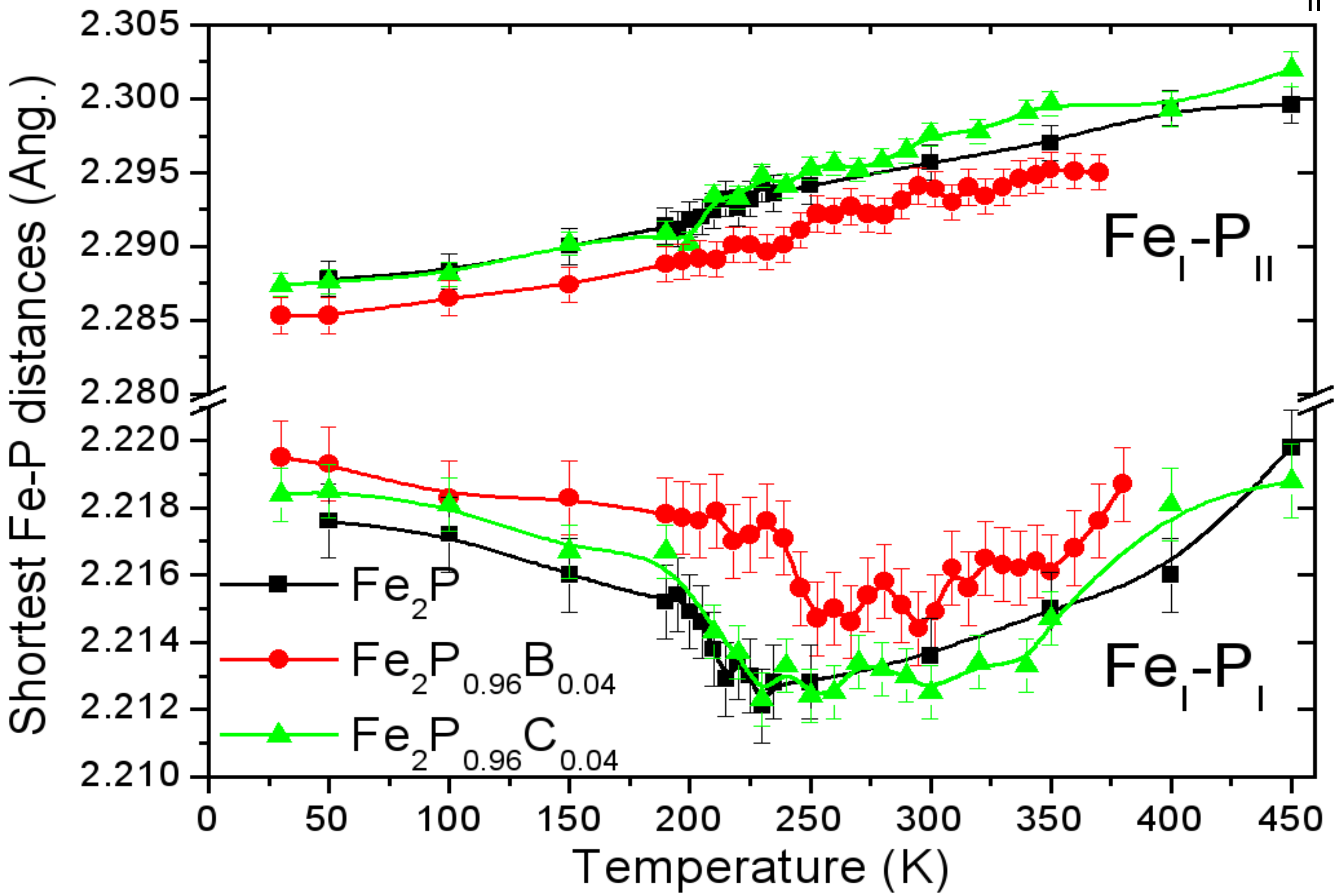


Z. Gercsi et al. **Phys. Rev. B 88, 024417 (2013)**

Magneto-elastic response

Change in the shortest metal-metalloid distances (Fe_I-P_I, Fe_I-P_{II})



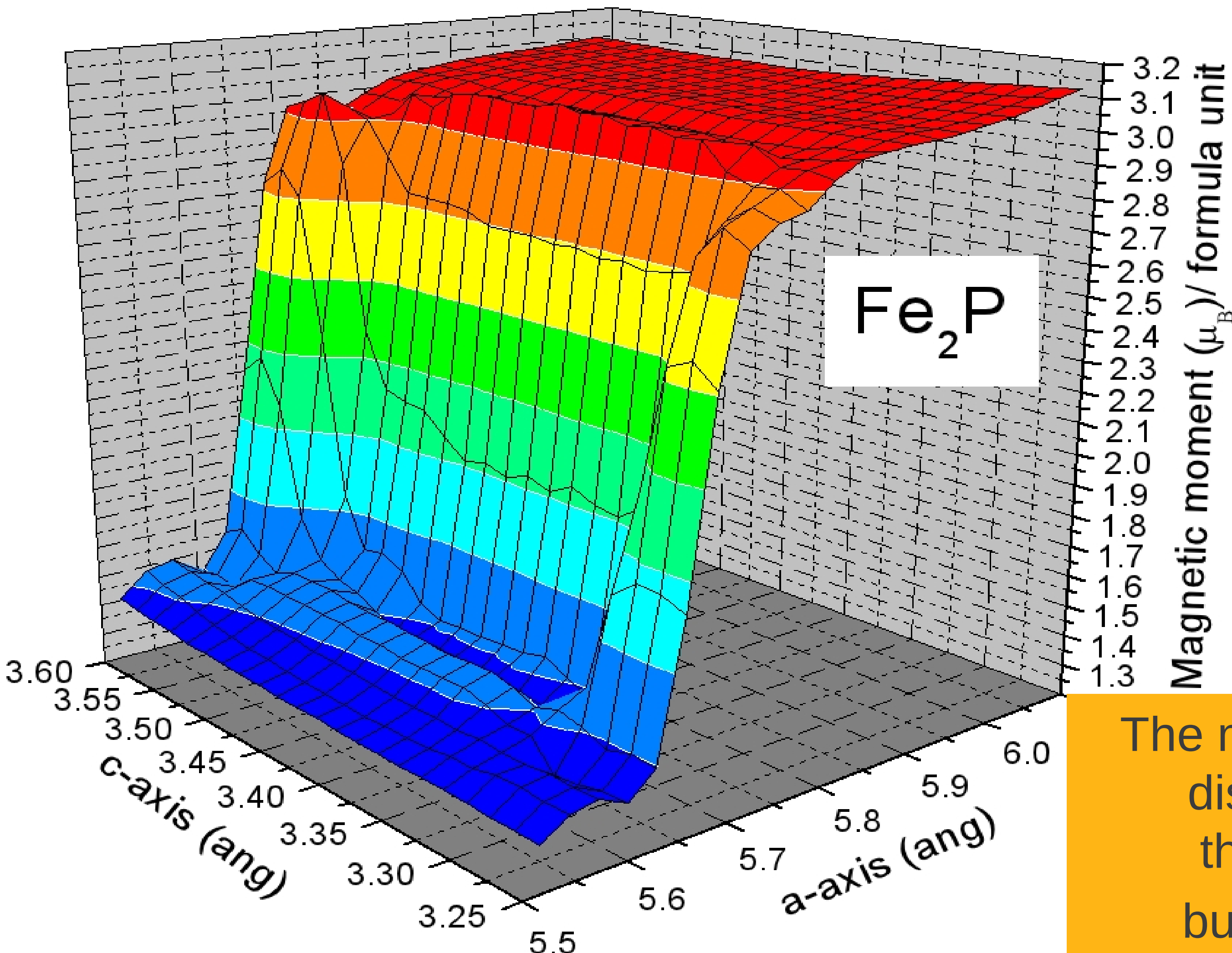


Z. Gercsi et al. **Phys. Rev. B 88, 024417 (2013)**

Density Functional Theory

VASP-GGA

The calculations revealed → the basal plane is sensitive to the magnetic properties.



The magnetic moment disappears from the 3f-site (Fe_I) but only reduced on the 3g-site (Fe_{II})≈1.4μ_B.

Z. Gercsi et al. **Phys. Rev. B 88, 024417 (2013)**

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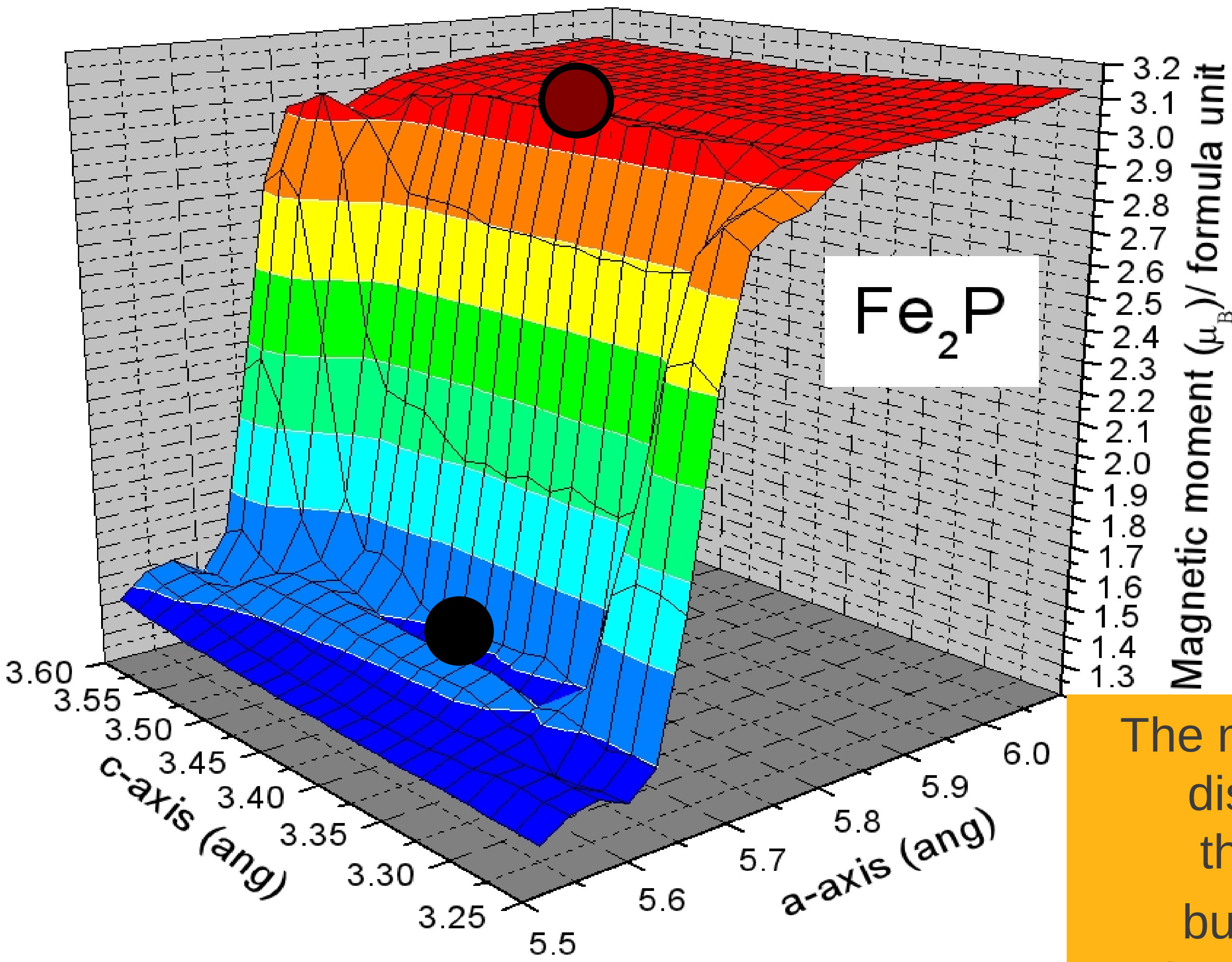

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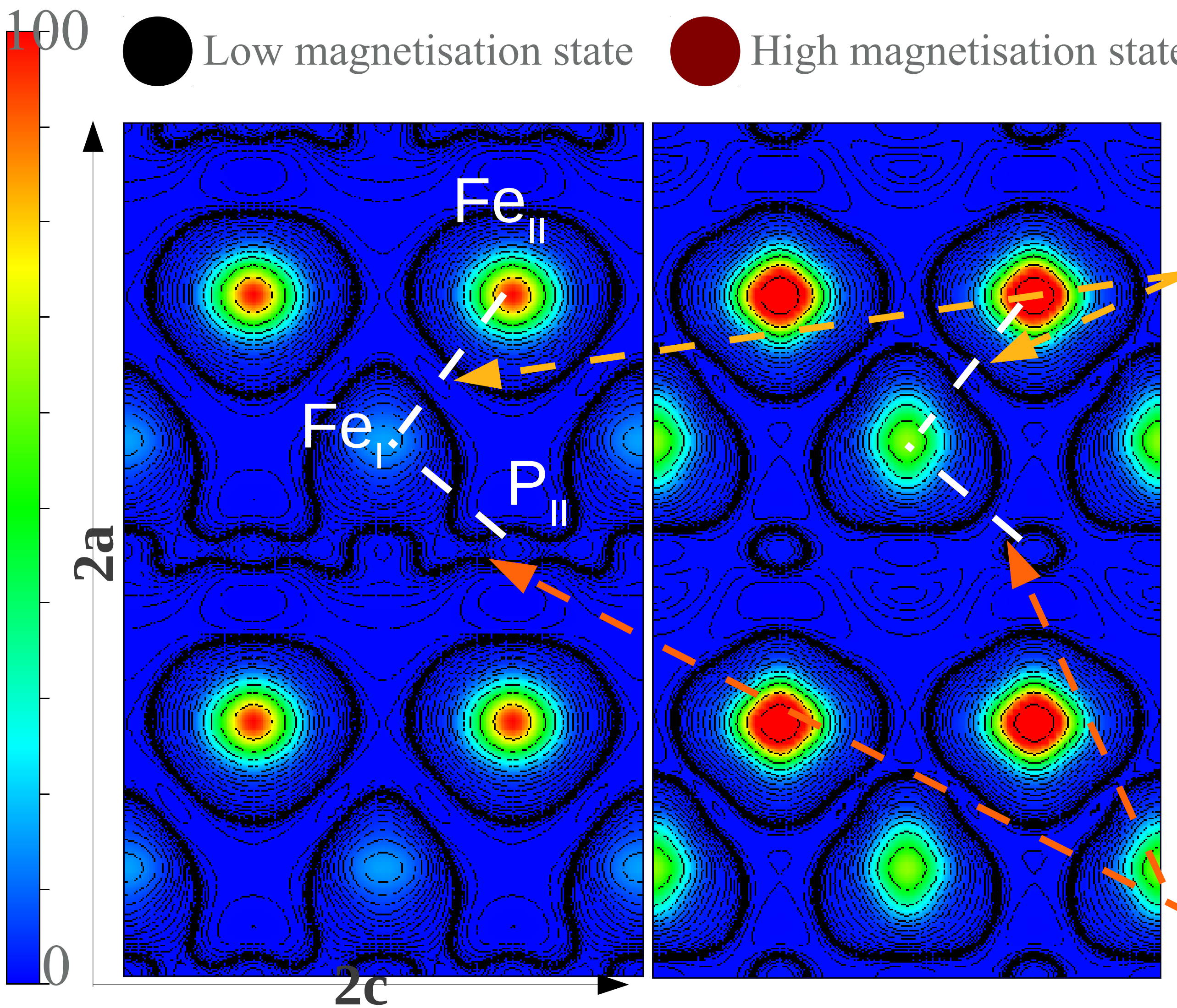
Z. Gercsi et al. **Phys. Rev. B 88, 024417 (2013)**

Density Functional Theory

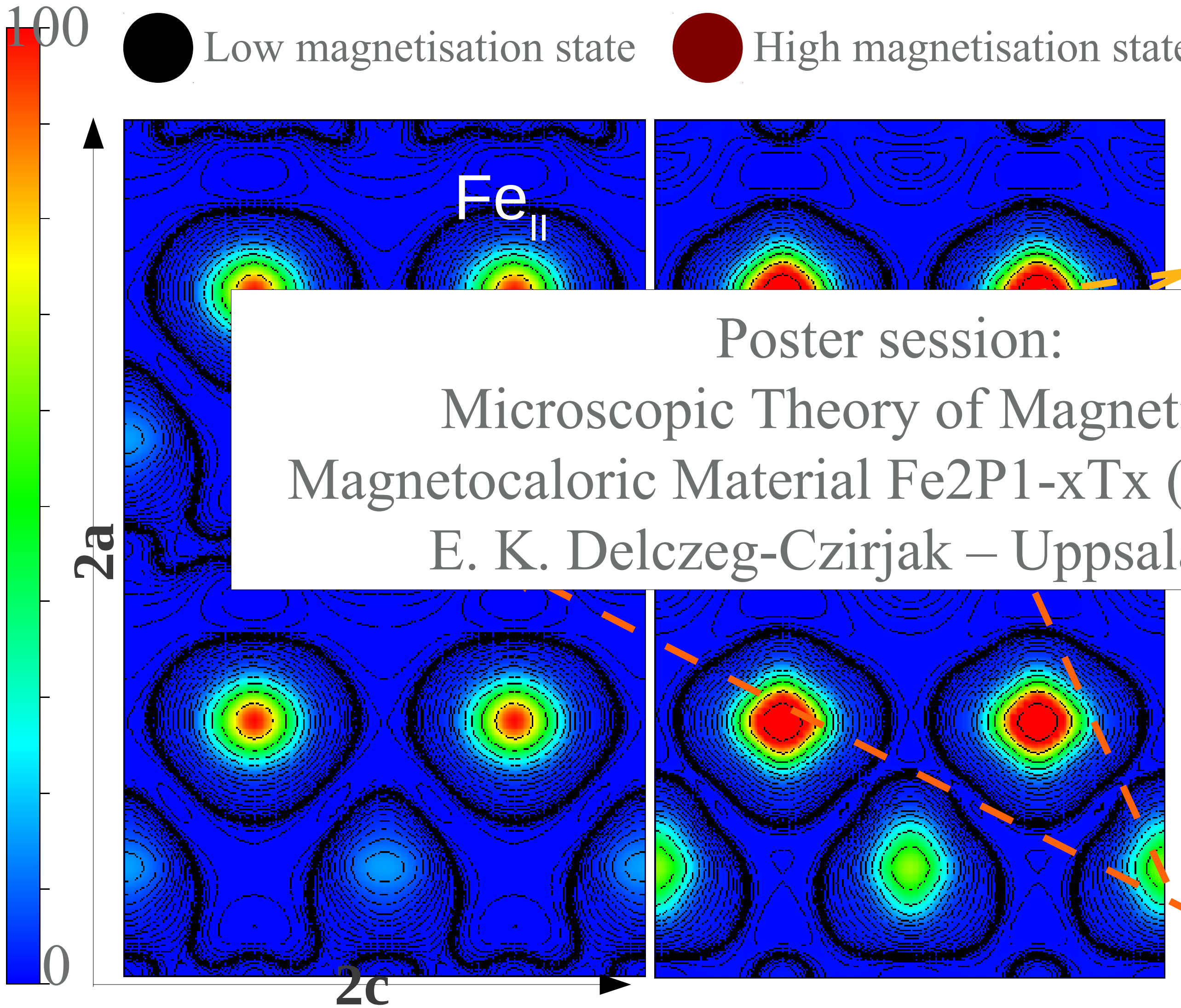
Magnetisation density plot in the *a*-*c* plane of Fe_2P



The closest metal-metal and metal-metalloid distances—the latter also linked to the metamagnetic 3f site—are strongly altered by both the d-d and p-d hybridization energies at the transition. As a result, the delocalization of the magnetization from the 3f site along the FeI -PII chains in the c-axis direction occurs, implying its strong influence on bonding.

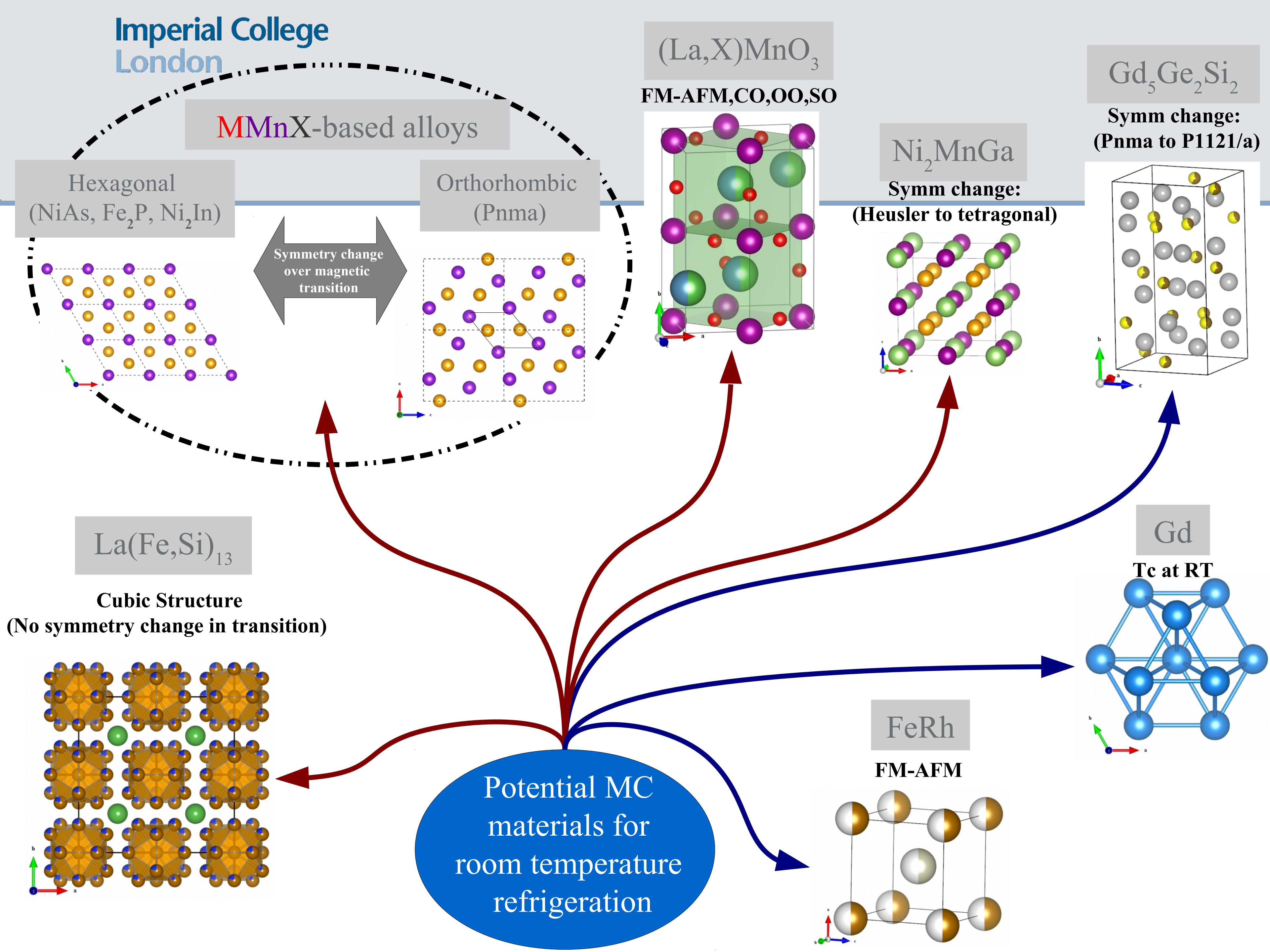
Density Functional Theory

Magnetisation density plot in the *a*-*c* plane of Fe_2P



The closest metal-metal and metal-metalloid ... ter also ... ne ... ite—are ... both the ... dization energies at the transition. As a result, the delocalization of the magnetization from the 3f site along the FeI -PII chains in the c-axis direction occurs, implying its strong influence on bonding.

Poster session:
Microscopic Theory of Magnetism in Magnetocaloric Material Fe2P1-xTx (T= B and Si)
E. K. Delczeg-Czirjak – Uppsala Univ.



Imperial College London
MMnX-based alloys
Hexagonal
(NiAs, Fe_2P, Ni_2In)
Symmetry change over magnetic transition
Orthorhombic
(Pnma)
(La,X)MnO_3
FM-AFM,CO,OO,SO
Ni_2MnGa
Symm change:
(Heusler to tetragonal)
$Gd_5Ge_2Si_2$
Symm change:
(Pnma to P1121/a)
La(Fe,Si)$_{13}$
Cubic Structure
(No symmetry change in transition)
Gd
Tc at RT
FeRh
FM-AFM
Potential MC materials for room temperature refrigeration

Imperial College London

Thank you for your attention!

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- E. K. Delczeg-Czirjak, L. Vitos, UU - KTH, Sweden
- Kevin Knight, A. Daoud-Aladine, ISIS, UK
- K. Hono, NIMS, Japan

For further details, please see in

Z. Gercsi, E. K. Delczeg-Czirjak et al. Phys. Rev. B **88**, 024417 (2013)
E. K. Delczeg-Czirjak, Z. Gercsi et al. Phys. Rev. B **85**, 224435 (2012)
E. K. Delczeg-Czirjak, L. Bergqvist, O. Eriksson, Z. Gercsi et al. Phys. Rev. B **86**, 045126 (2012)

CoMnSi related works:

J. B. Staunton, M. dos Santos Dias, J. Peace, Z. Gercsi, and K. G. Sandeman Phys. Rev. B **87**, 060404 (2013)
A. Barcza, Z. Gercsi et al. Phys. Rev. B **87**, 064410 (2013)
Q. Recour, V. Ban, Z. Gercsi et al. Phys. Rev. B **88**, 054429 (2013)
Z. Gercsi, K. Hono and K.G. Sandeman Phys. Rev. B **83**, 174403 (2011)
Z. Gercsi and K.G. Sandeman Phys. Rev. B **81**, 224426 (2010)
A. Barcza, Z. Gercsi, K.S. Knight and K.G. Sandeman Phys. Rev. Lett. **104**, 247202 (2010)

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