Magnetyt, modelowy materiał o unikalnych właściwościach

AGH

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Magnetite team

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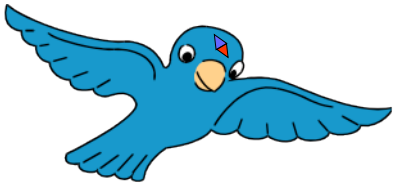
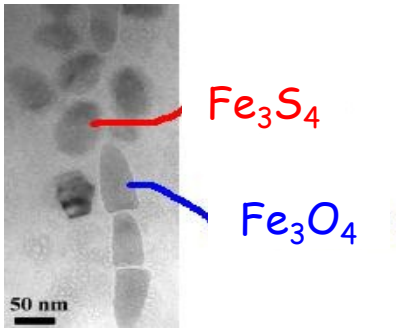
2. Manipulation of electronic order at $T<T_V$: magnetic and crystallographic axis switching (AS)
   - Magnetic observation of AS: activation process with the energy close to T_V
   - Axis Switching affects macroscopic size (magnetostriction studies)... ... and is external pressure dependent
   - AS can also be observed microscopically (NMR studies)

3. ...and is intimately linked to fast electronic processes shown in the recent Nature Materials paper

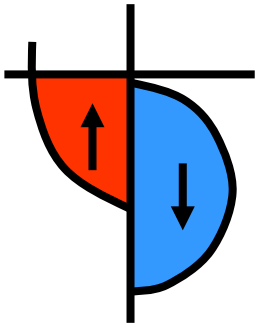
Magnetite is present in our life

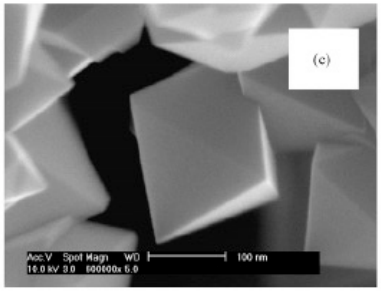




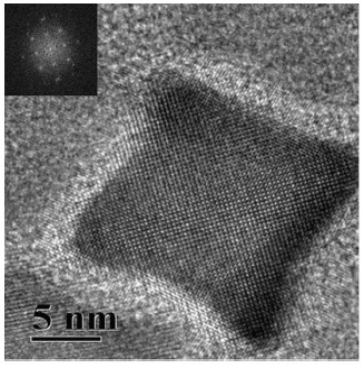
Science, 334 (2011) 1720

Magneto-bakterie



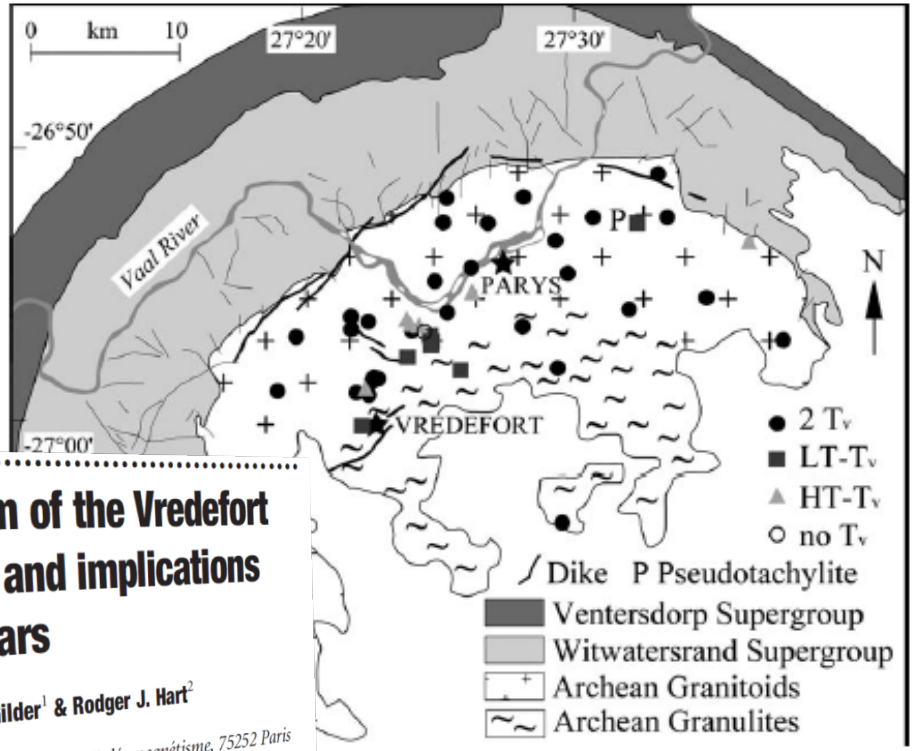


Mat. Sc. Eng. B 136 (2007) 101



J. of Cryst. Growth 296 (2006) 221

Magnetite is present in our life



Palaeomagnetism of the Vredefort meteorite crater and implications for craters on Mars

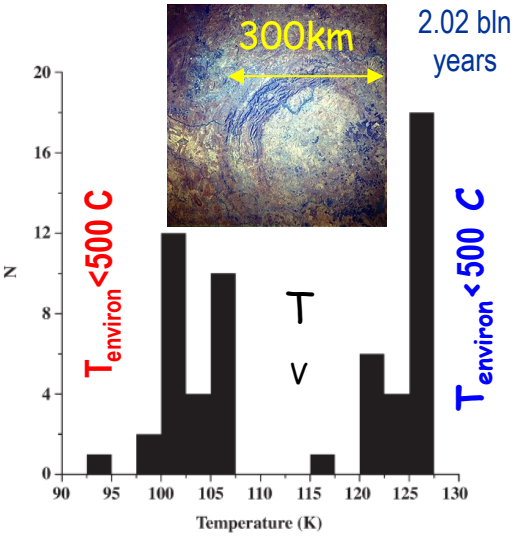
Laurent Carporzen[1], Stuart A. Gilder[1] & Rodger J. Hart[2]

[1]*Institut de Physique du Globe, Laboratoire de Paléomagnétisme, 75252 Paris Cedex 05, France*
[2]*University of the Witwatersrand, Schonland Research Center, Wits 2050, Johannesburg, South Africa*

Magnetic surveys of the martian surface have revealed significantly lower magnetic field intensities over the gigantic impact craters Hellas and Argyre than over surrounding regions[1]. The reduced fields are commonly attributed to pressure demagnetization caused by shock waves generated during meteorite impact[2,3], in the absence of a significant ambient magnetic

NATURE | VOL 435 | 12 MAY 2005 | www.nature.com/nature

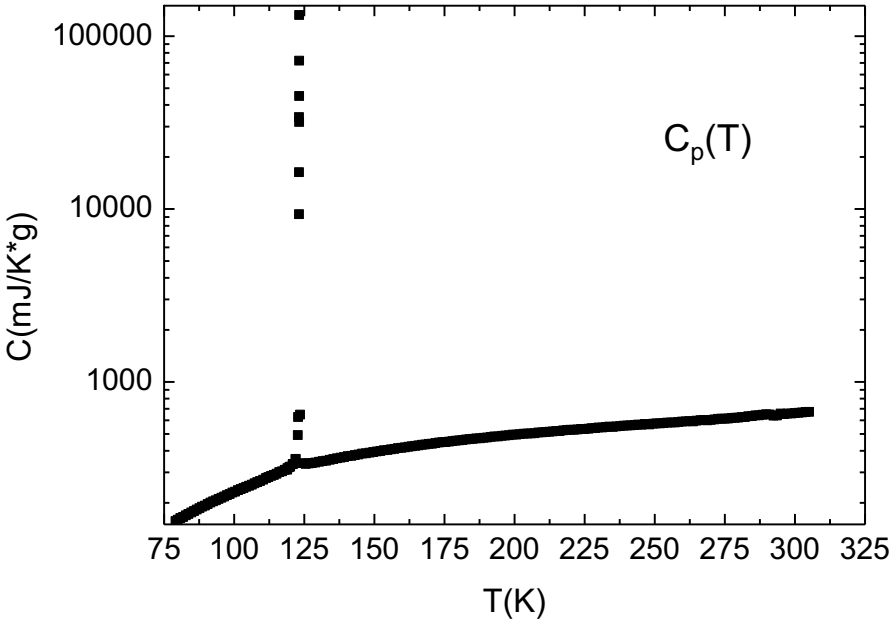
Vredeford impact crater

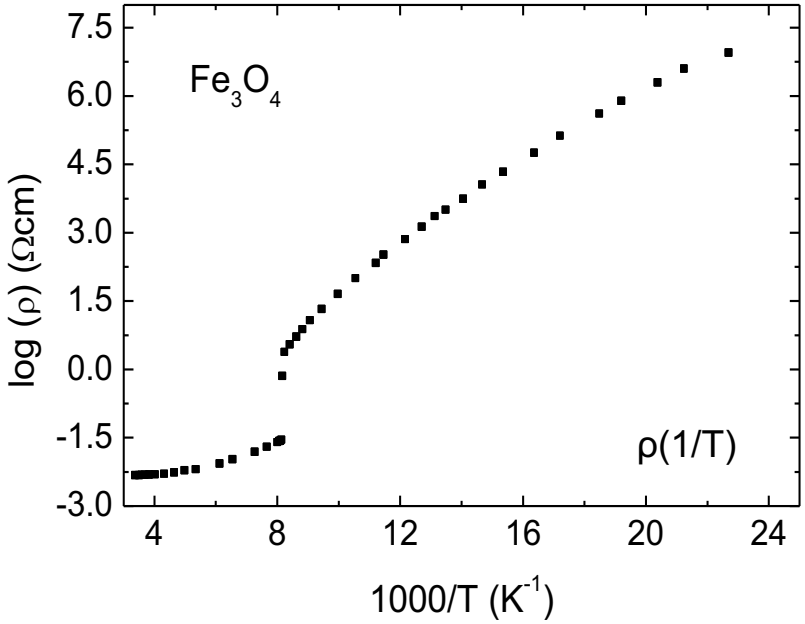


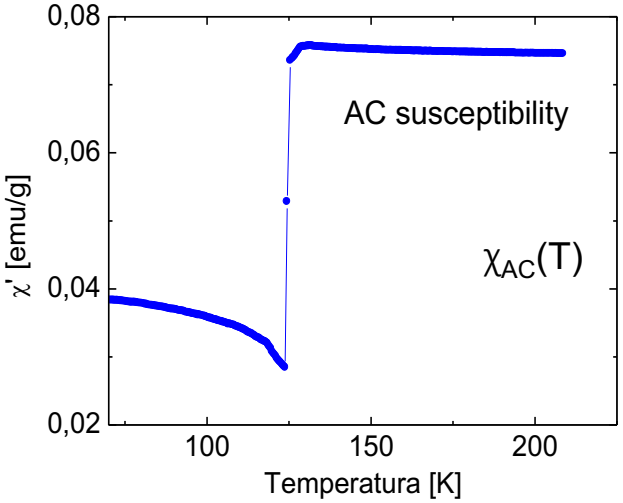
L. Carporzen, Stuart Gilder, Earth and Plan. Sci. Let. 251 (2006) 305

Verwey transition at T_V=124K: main experimental facts

Abrupt changes in many physical characteristics

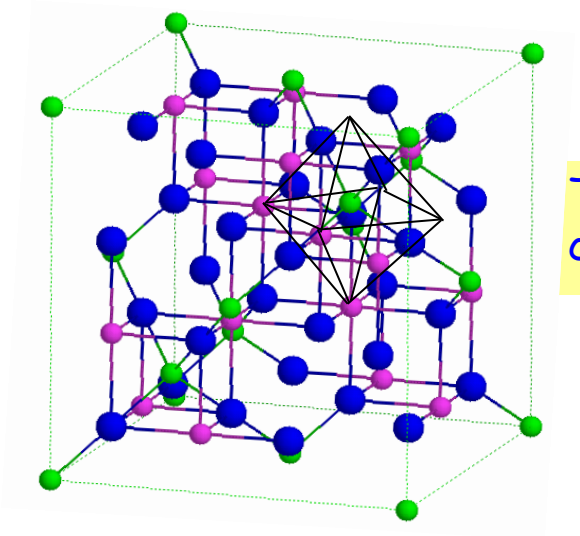






Verwey transition at T_V=124K: main experimental facts

Crystallographic Structure

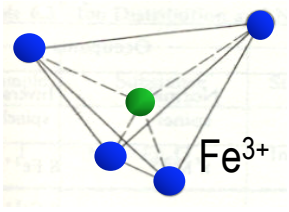


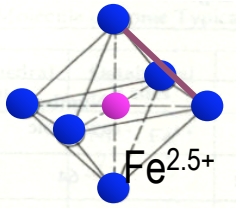
O^{2-} (Fe^{2+}, Fe^{3+}) octa Fe^{3+} tetra

Inverse Spinel

$T > T_V$: cubic

Tetrahedral positions (A)

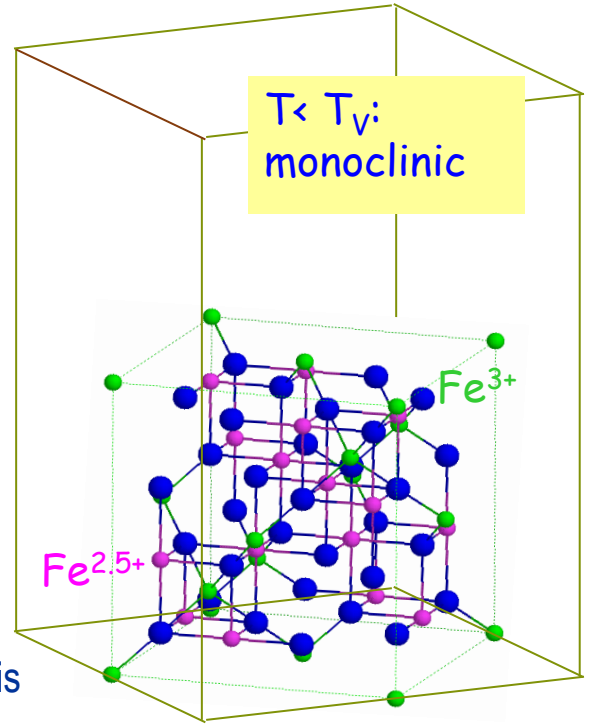




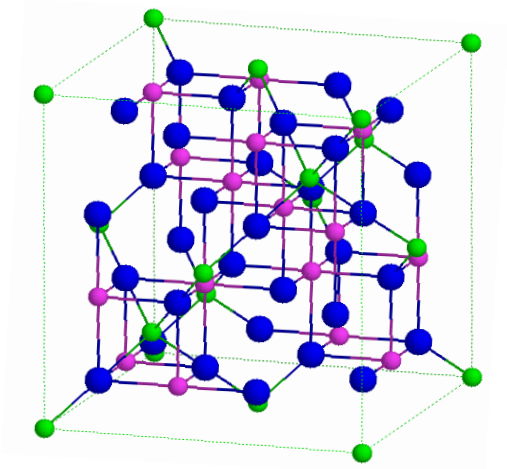
Octahedral positions (B)

c axis

$T < T_V$: monoclinic



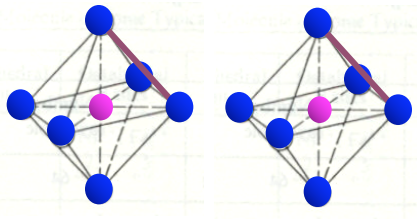
Verwey model : order-disorder transition

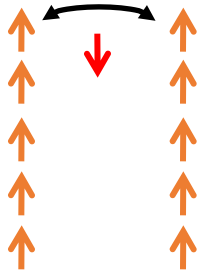


● O^{2-} ● (Fe^{2+}, Fe^{3+}) octa ● Fe^{3+} tetra

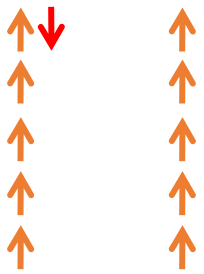
Octahedral positions=B

$T>T_V$:$Fe^{+2.5}$ | $T<T_V$:Fe^{+3}-Fe^{+2}





$Fe^{+2.5}$ $Fe^{+2.5}$

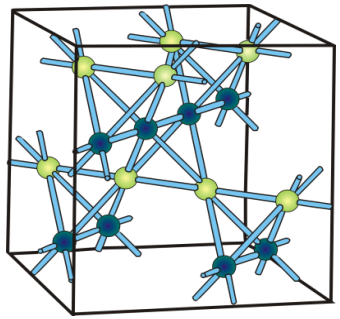


Fe^{+2} Fe^{+3}

Verwey Model :

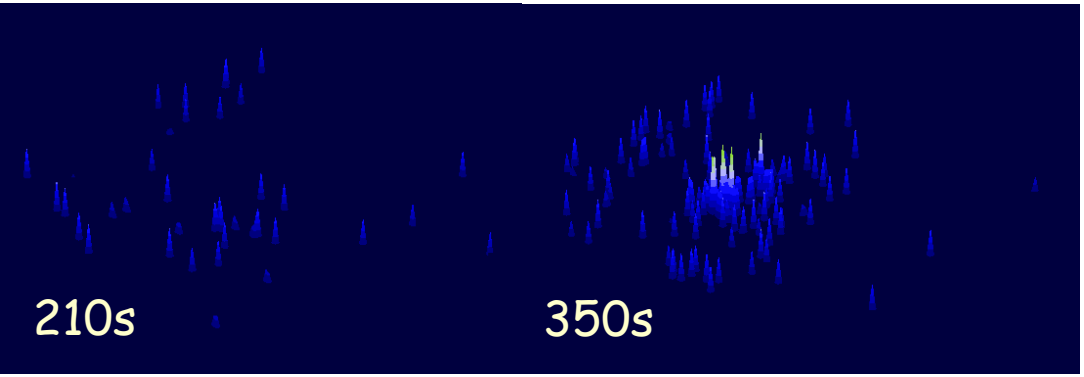
- electron repulsion on octahedral positions
- high-T electron disorder ($Fe^{+2.5}$) turns to long range order Fe^{+3}-Fe^{+2}

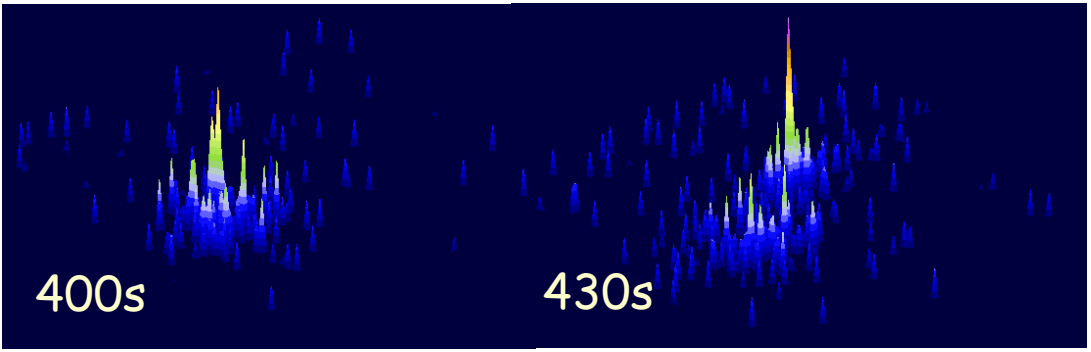
$\Delta q=1$

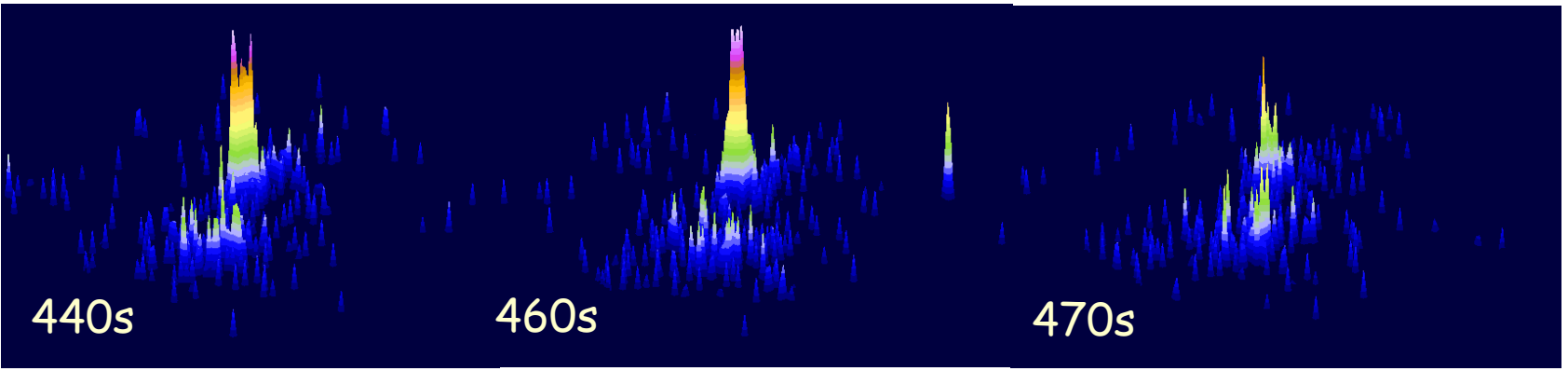


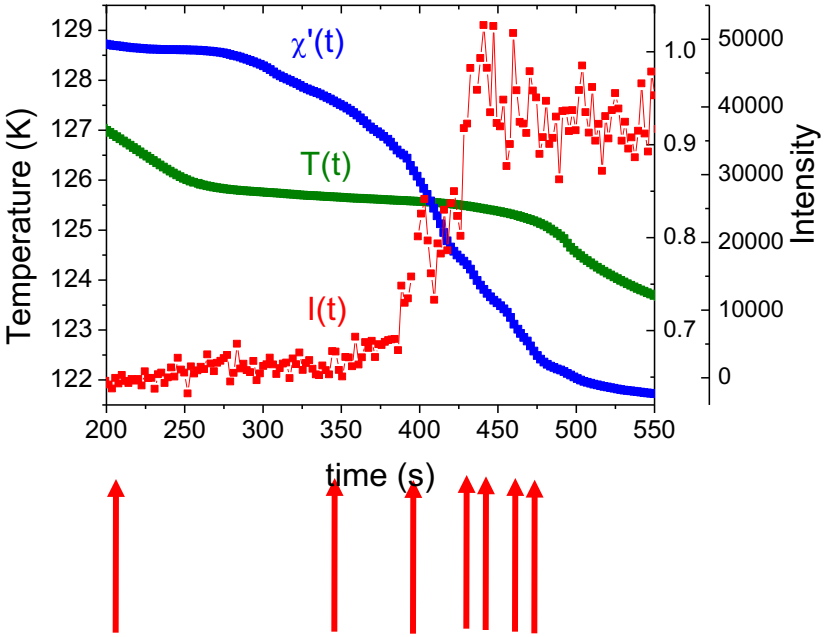
However: $\Delta q=0.2$, orbital order, different charge ordering

Verwey transition „in statu nascendi": peak (1 1½ 2)

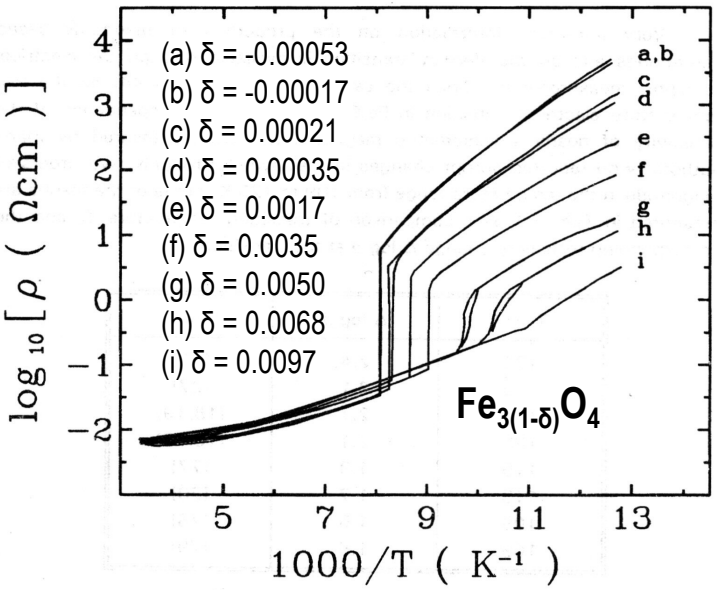


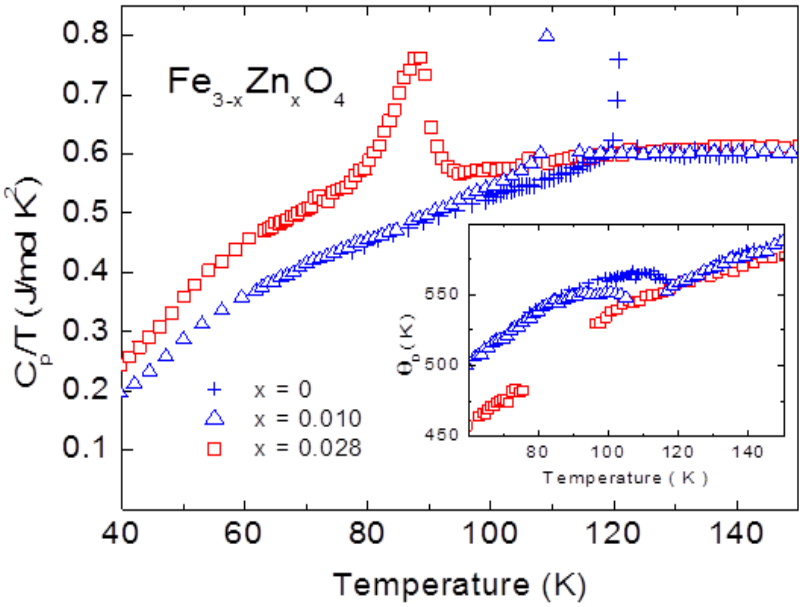






Magnetite of „first and second order"



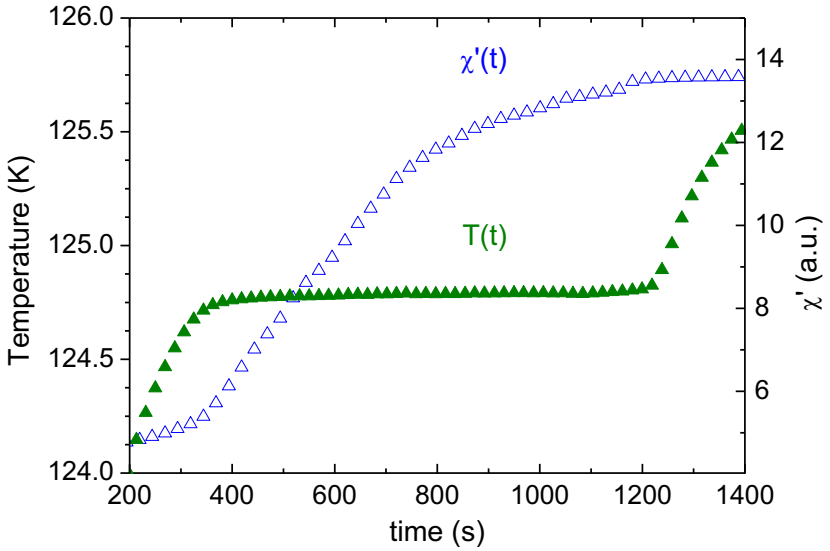


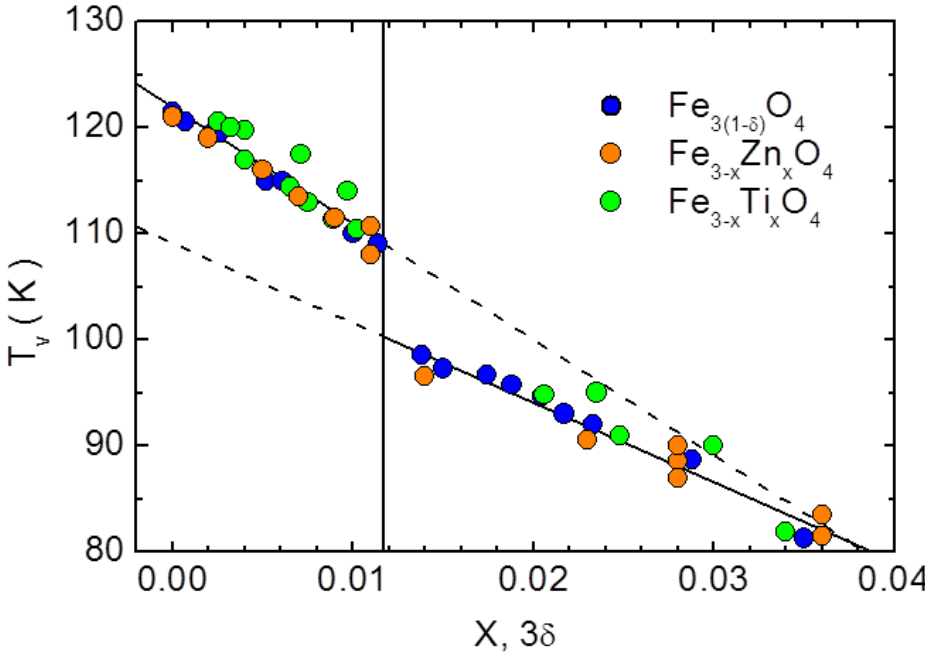
R. Aragón et. al. J. Magn. Magn. Mat. 54-57, 1335(1986)

Zn :	$Fe_{3-x}Zn_xO_4$	$Fe^{3+}_{1-x}Zn^{2+}_x$	$Fe^{3+}_{1+x}Fe^{2+}_{1-x}$	O_4 ↓ e
Ti:	$Fe_{3-x}Ti_xO_4$	Fe^{3+}	$Fe^{3+}_{1-2x}Fe^{2+}_{1+x}Ti^{4+}_x$	O_4 ↑
Nonst.	$Fe_{3(1-\delta)}O_4$	Fe^{3+}	$Fe^{3+}_{1+6\delta}Fe^{2+}_{1-9\delta}$	O_4 ↓
		Tetra (A)	Octa (B)	

The still open question: why the increasing vacancy (and dopant) concentration change the transition order

Magnetite of „first and second order"



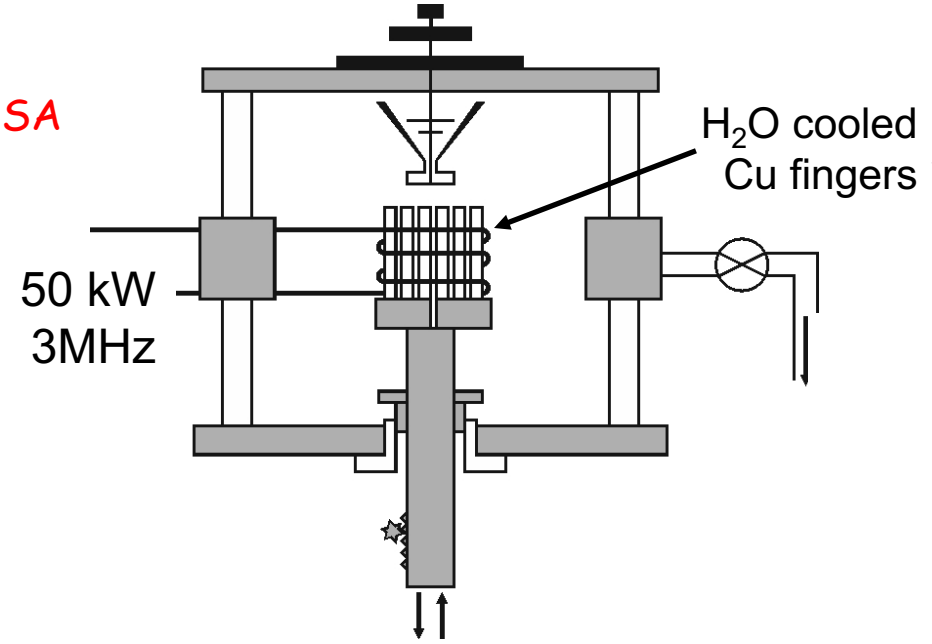


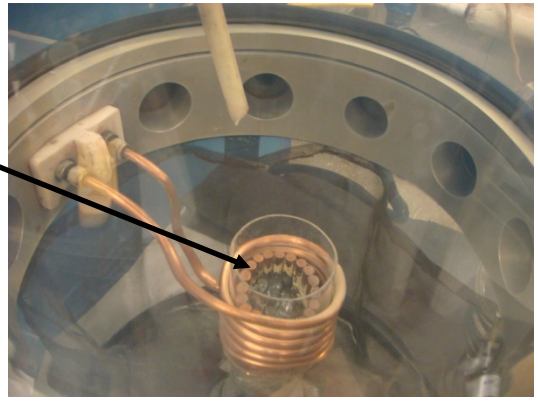
Zn :	$Fe_{3-x}Zn_xO_4$	$Fe^{3+}_{1-x}Zn^{2+}_x$	$Fe^{3+}_{1+x}Fe^{2+}_{1-x}$	O_4	e ↓
Ti:	$Fe_{3-x}Ti_xO_4$	Fe^{3+}	$Fe^{3+}_{1-2x}Fe^{2+}_{1+x}Ti^{4+}_x$	O_4	↑
Nonst.	$Fe_{3(1-\delta)}O_4$	Fe^{3+}	$Fe^{3+}_{1+6\delta}Fe^{2+}_{1-9\delta}$	O_4	↓
		Tetra (A)	Octa (B)		

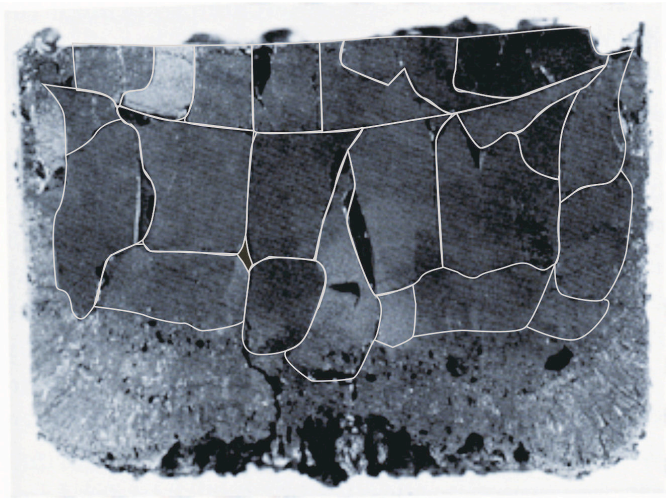
The still open question: why the increasing vacancy (and dopant) concentration change the transition order

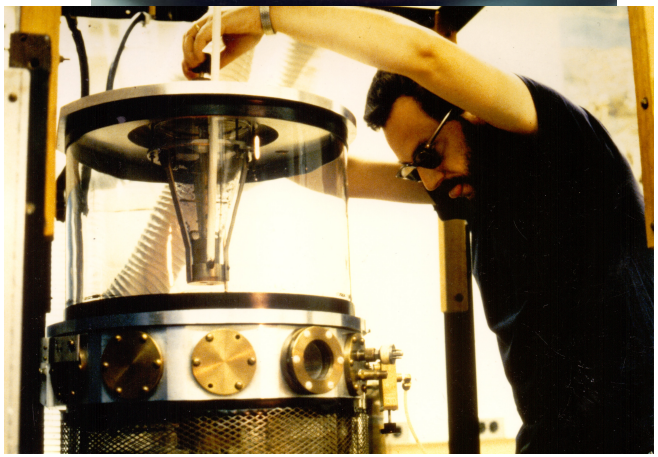
Magnetite single crystals grown in skull melter

PURDUE, USA





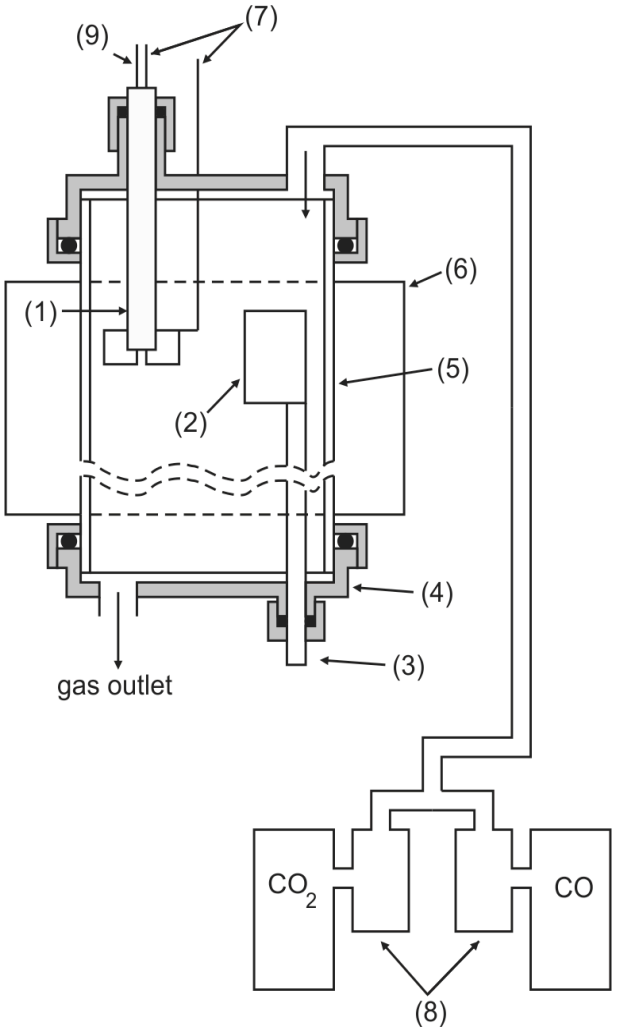




Magnetite single crystals annealing

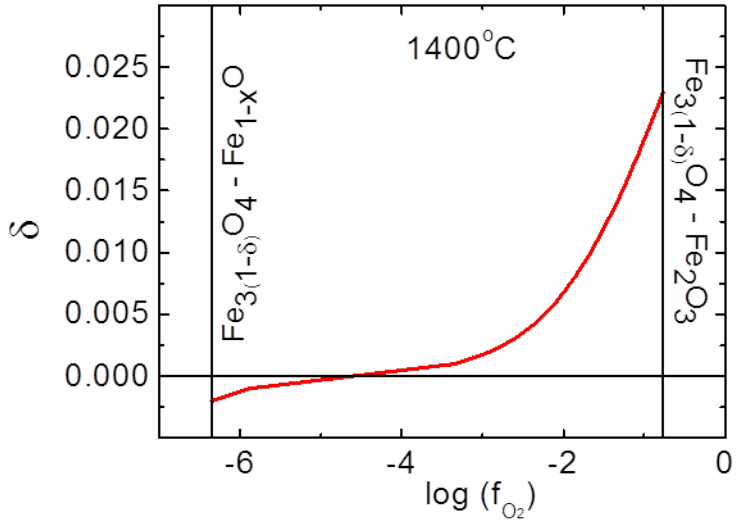
PURDUE, USA

Annealing in the controlled oxygen atmosphere



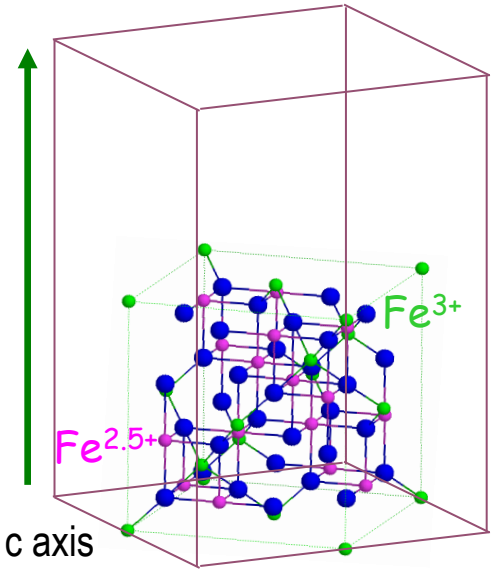
$$E = \frac{RT}{4F} \ln \frac{p_{O_2\,badany}}{p_{O_2\,odniesienia}}$$

$$\log p_{O_2} = 20.159 \frac{E(mV)}{T(K)}$$

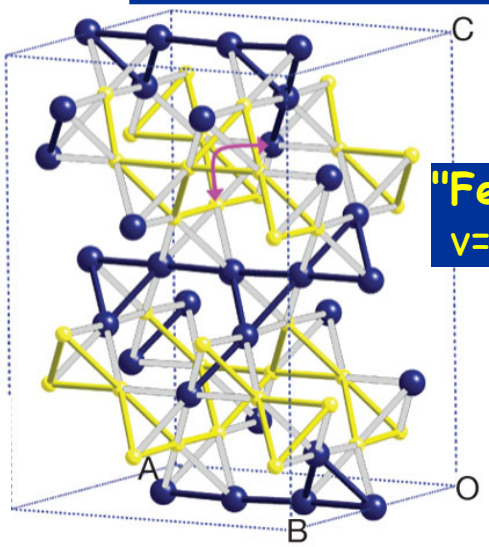


Magnetite structure at $T<T_V$, M. S. Senn et al. (Nature 2012)

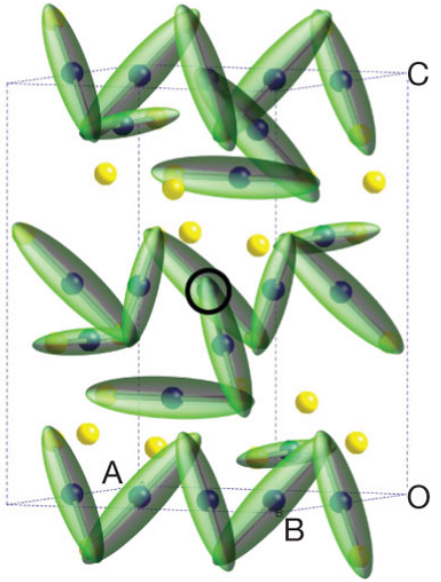
24 structural domains ⟹ Single domain material if the size < 40μm ⟹ 91433 Bragg reflections



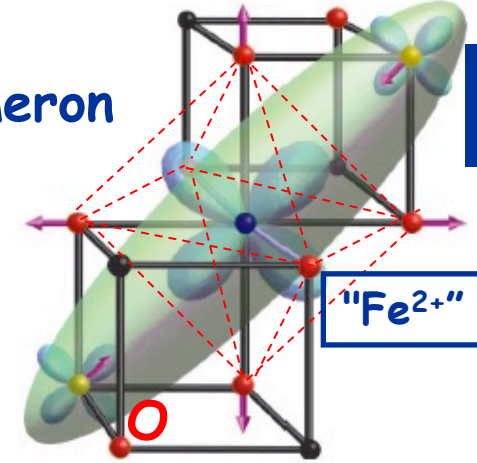
"Fe^{2+}" v=2.32-2.55



"Fe^{3+}" v=2.6-2.95



Trimeron



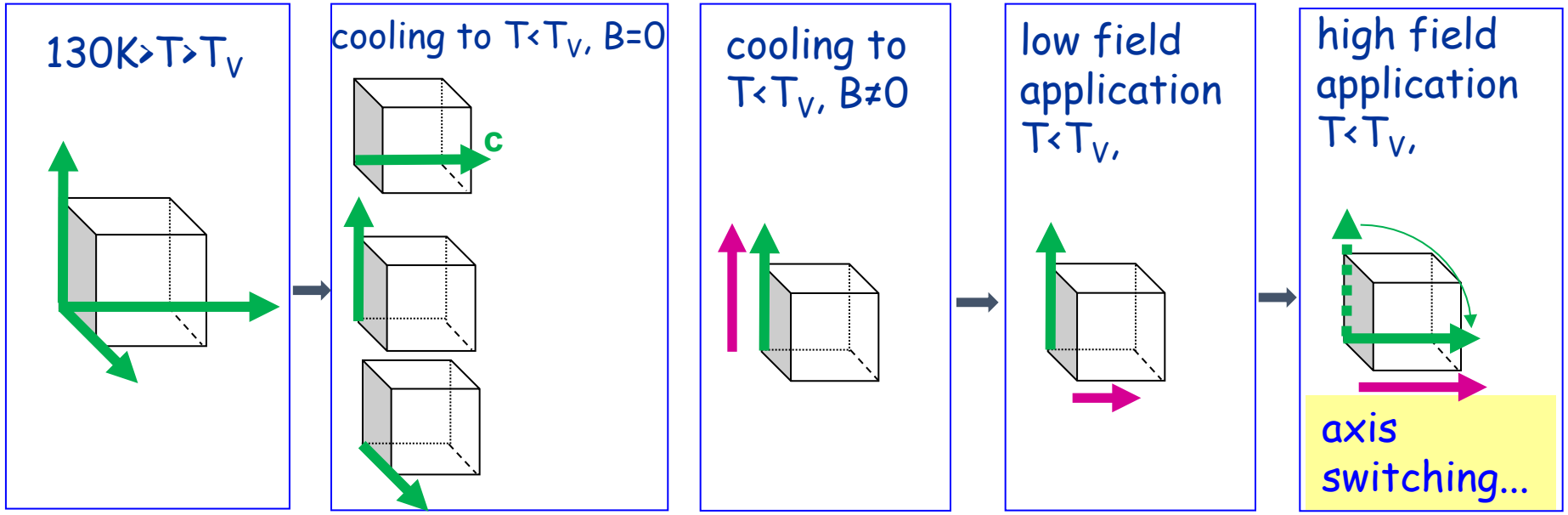
"Fe^{3+}" v=2.6-2.95

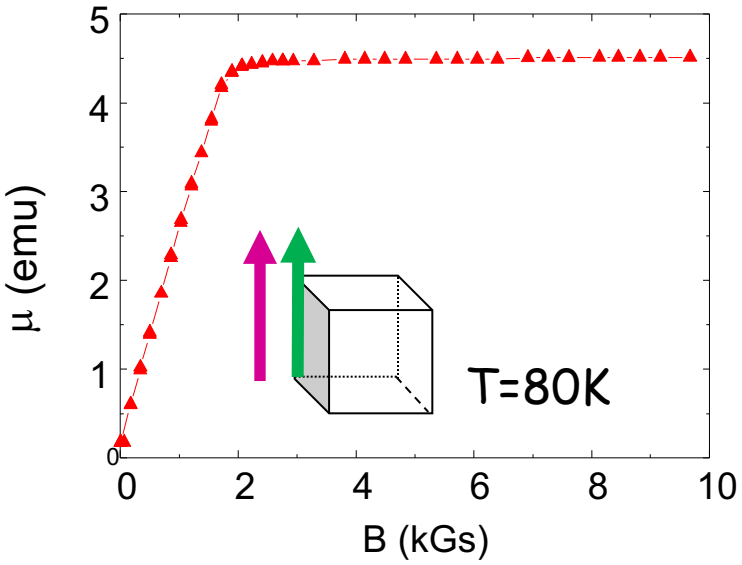
"Fe^{2+}" v=2.32-2.55

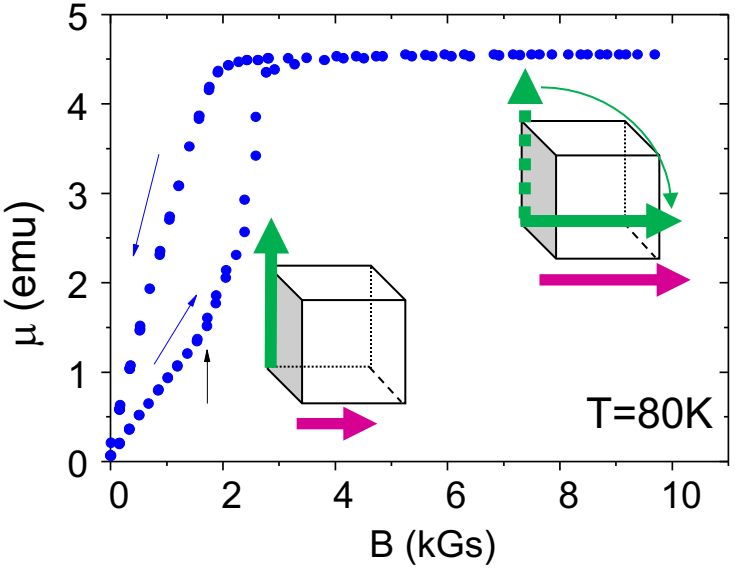
M. S. Senn et al. Nature 481, 173 (2012)

Switching of magnetic easy axis

B. A. Calhoun, Phys. Rev. **94** (1954) 1577



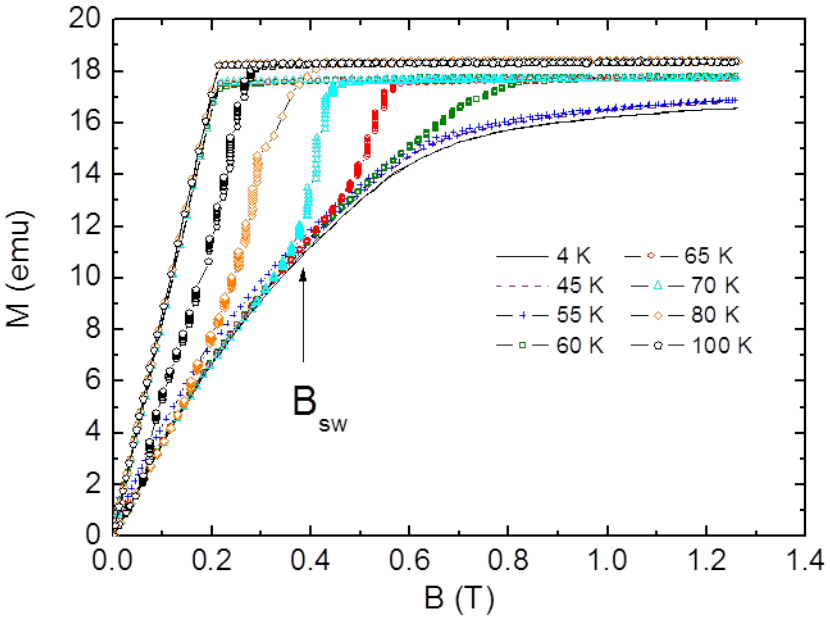


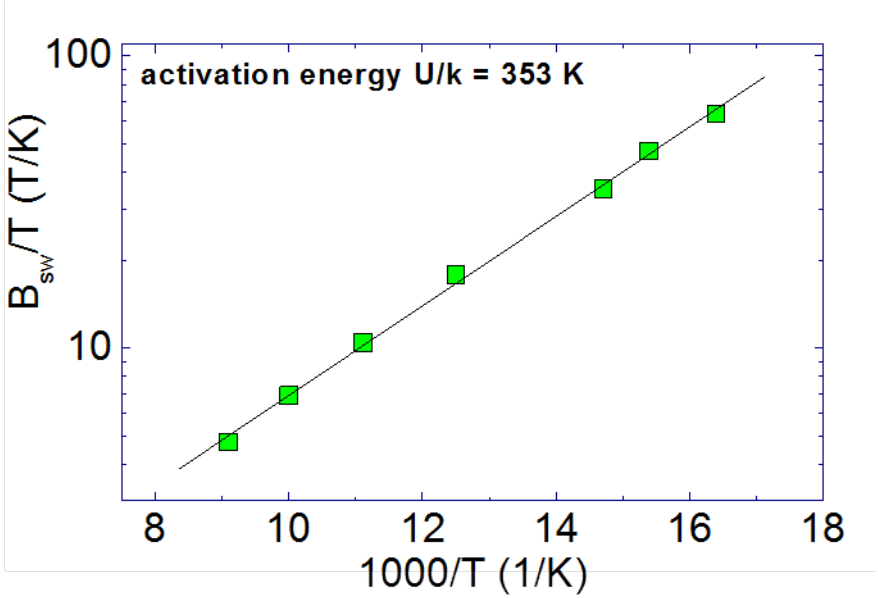


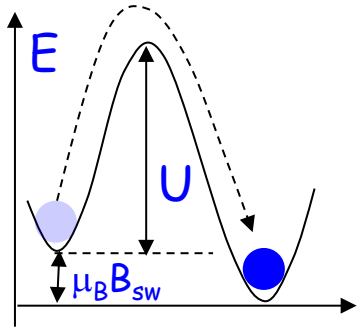
...that can be easily seen by magnetization measurements

Easy axis switching vs. Verwey transition

G. Król, et. al., J. All. Comp., 442, (2007), 83







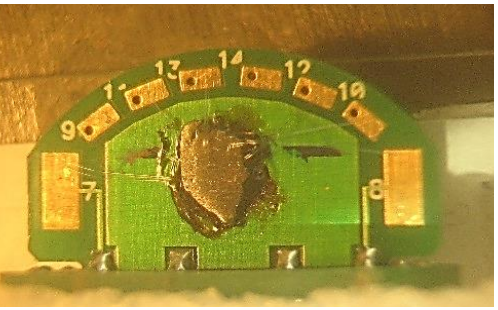
$$B_{sw} = cT\exp(U/kT)$$

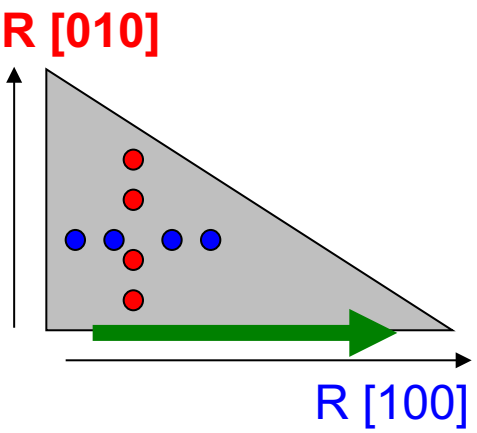
B. A. Calhoun, Phys. Rev. **94** (1954) 1577

Axis switching is the activation process with the characteristic energy close to that of the Verwey transition

Does AS affect electrical resistance?

G. Król, et. al., J. All. Comp., 480, 128 (2009)



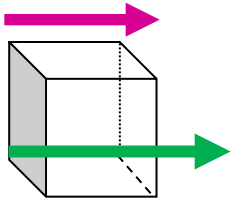


- c axis was forced by FC in 1T
- R along [100] and [010] was observed
- The axis was switched and the result on R was measured

Experiment layout

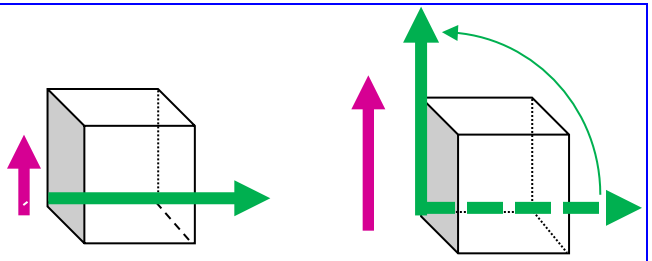
1 B=-4T to +4T

T=99K



2

T=99K

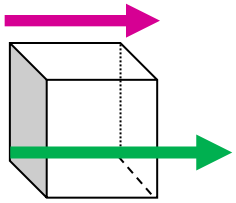


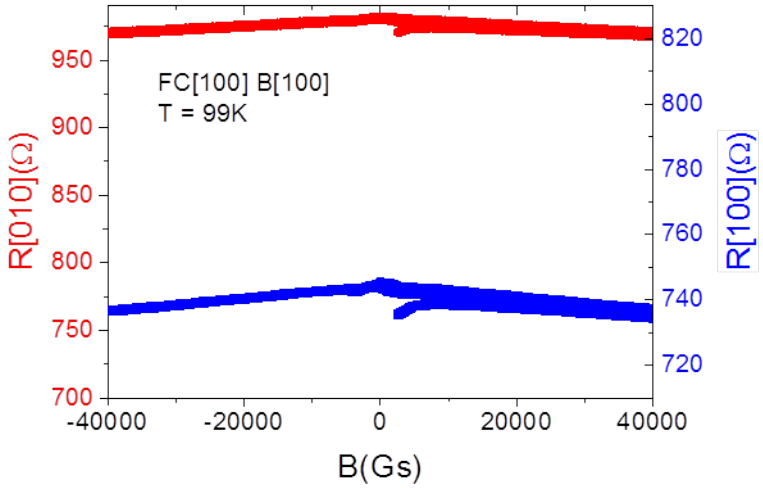
Can AS be seen in R(B)?

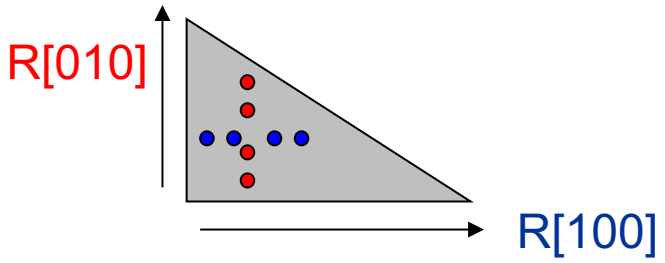
Does the resistance depend on structural disorder?

Does AS affect electrical resistance?

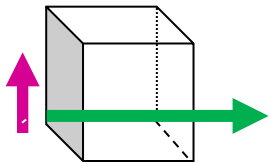
B[100]

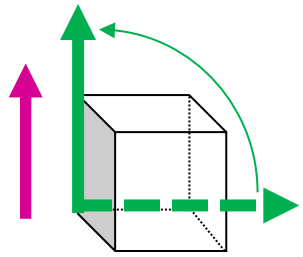


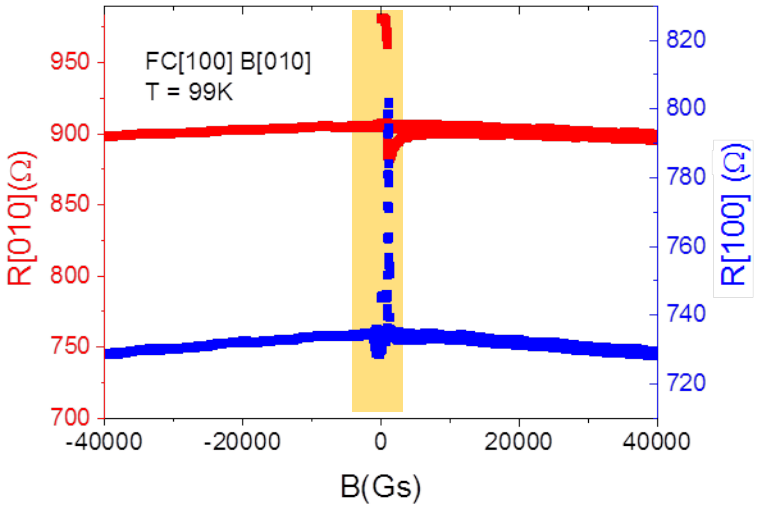


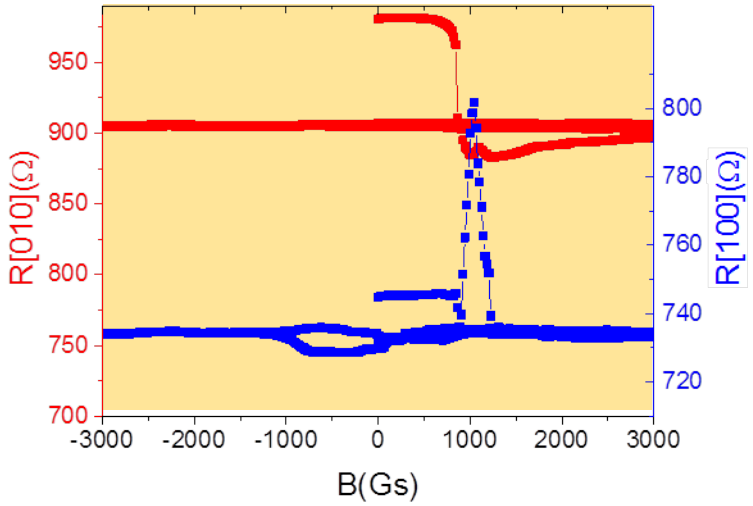


B[010]



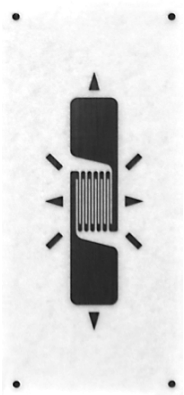




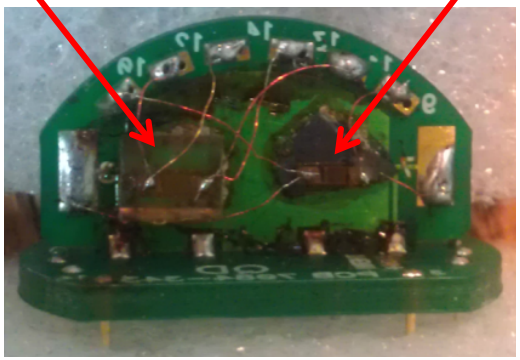


Rapid changes of R at B_{sw}

Does AS affect macroscopic size?



strain gauge...

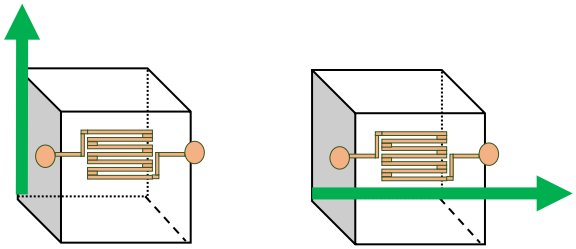


... glued to the surface

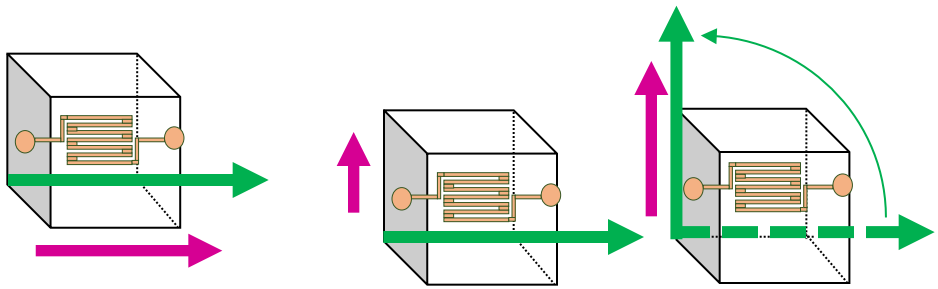
- c axis was forced by FC in 1T
- size along [100] and [010] was observed
- The axis was switched and the result on size was measured

Experiment layout

1 Heating from 10K to 300K



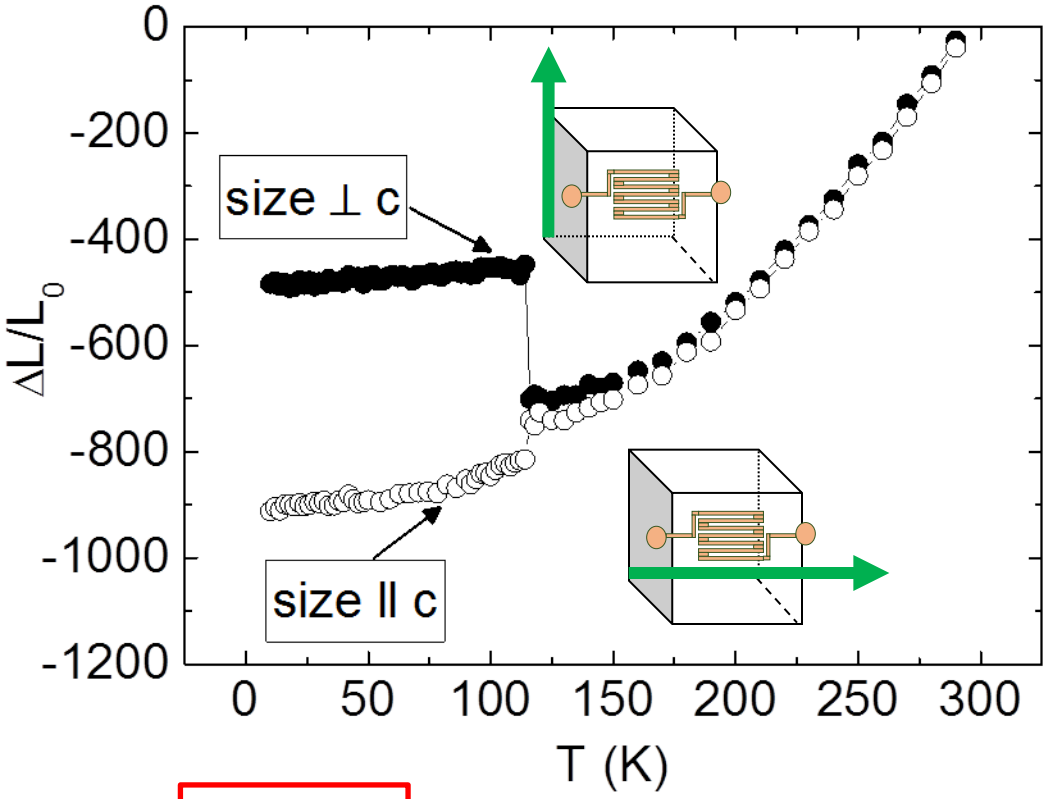
2 T=90K



Does AS affect the size?

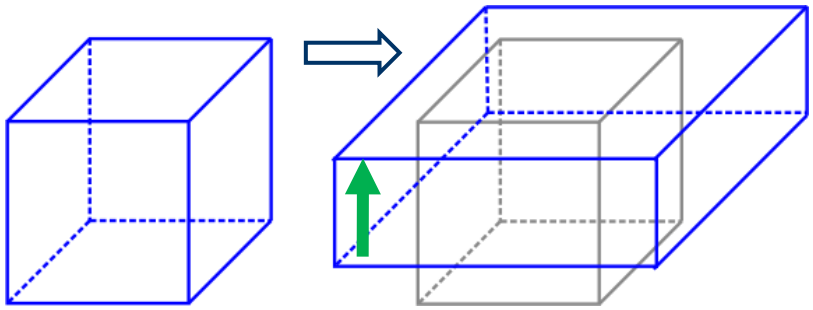
Does AS affect macroscopic size?

A. Britwum, et. al., Solid State Phenomena Vol. 194 (2013) pp 120-123



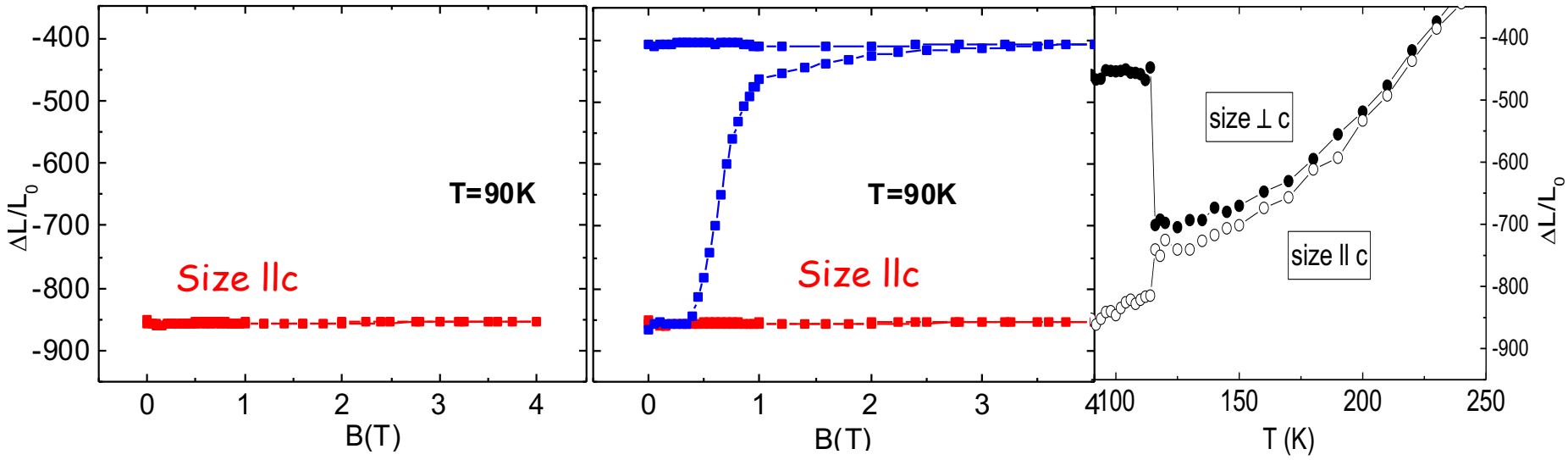
T = 130K

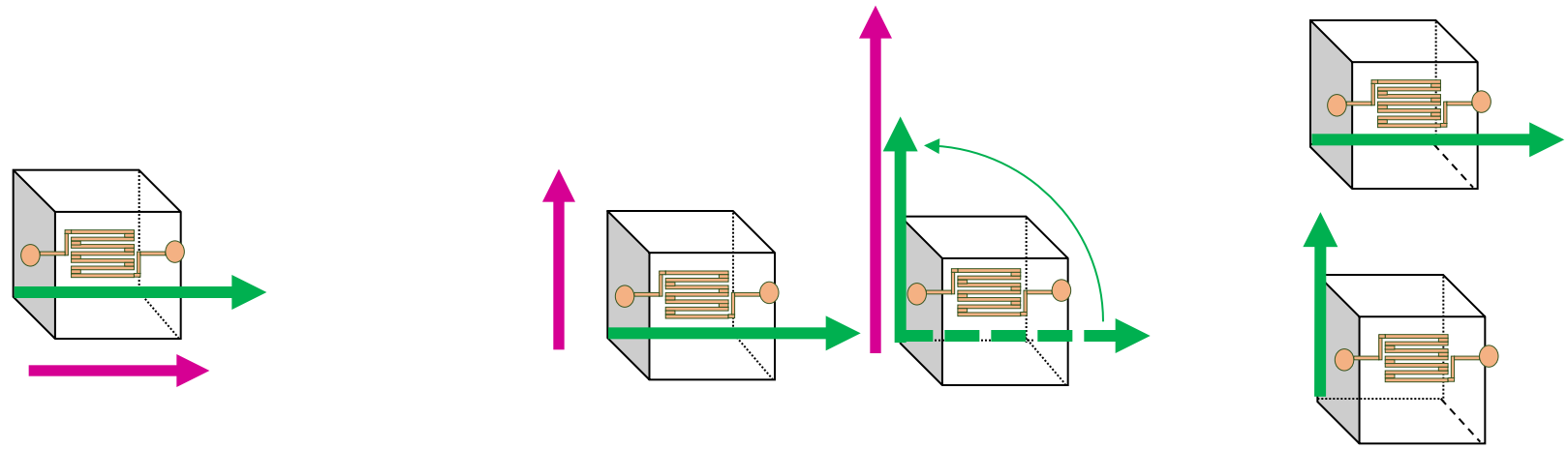
T = 90K



Sample shrinks along c but expands ⊥ c

Does AS affect macroscopic size?

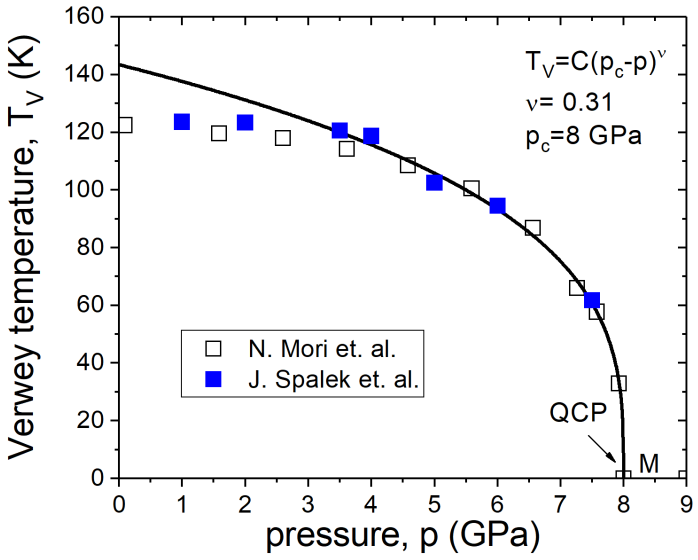




Macroscopic size is affected by the axis switching

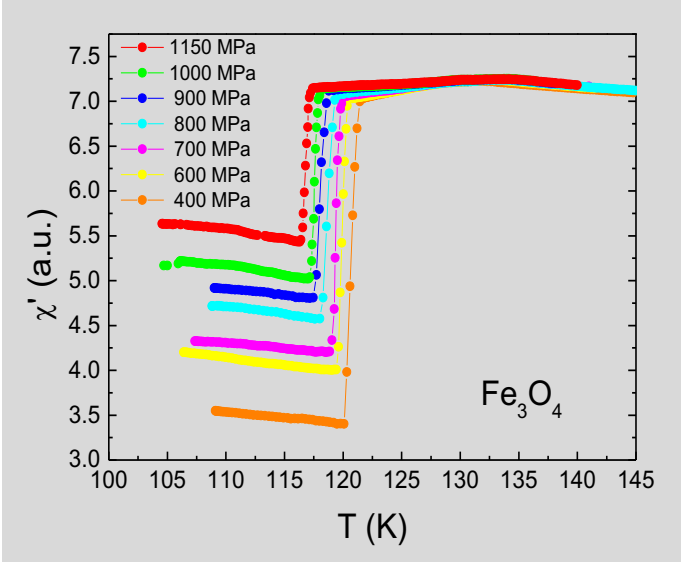
Does AS depend on pressure?

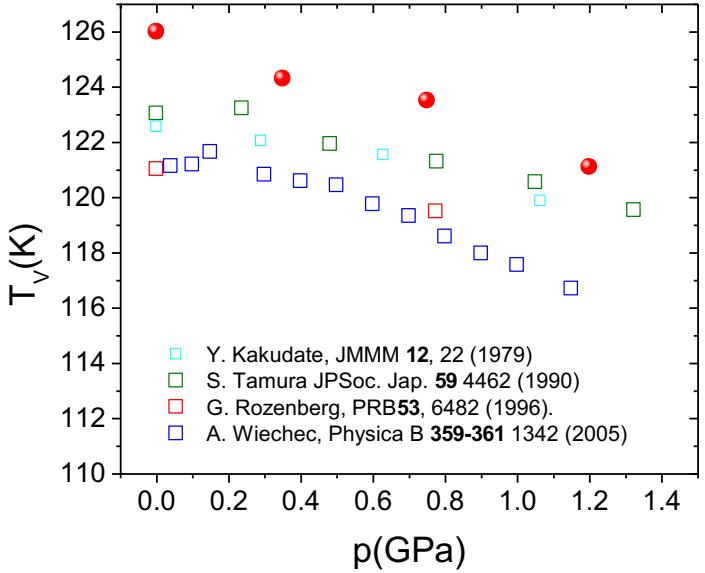
J. Spałek, et. al. PRB 78, 100401R (2008)



N.Mori et. al.,PhysicaB312–313(2002) 686;
S. Todo et. al., J.Appl.Phys.89(2001) 7347.

A. Wiecheć, et. al., Physica B 359-361, 1342 (2005)

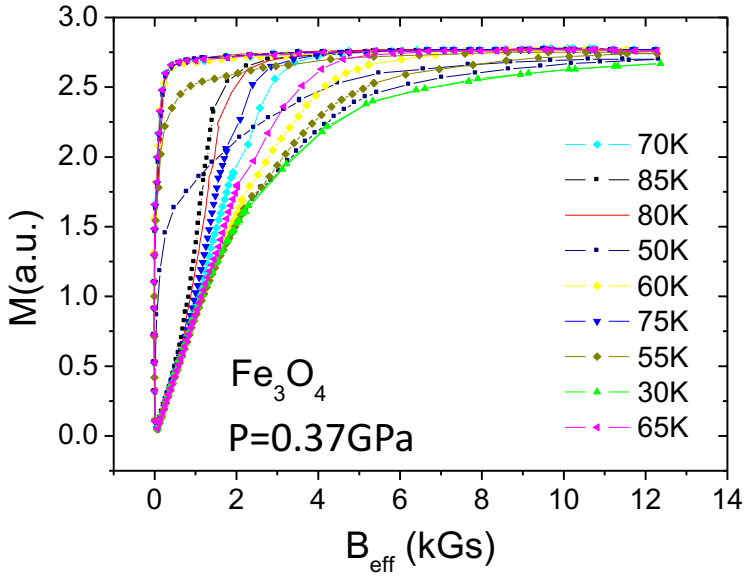


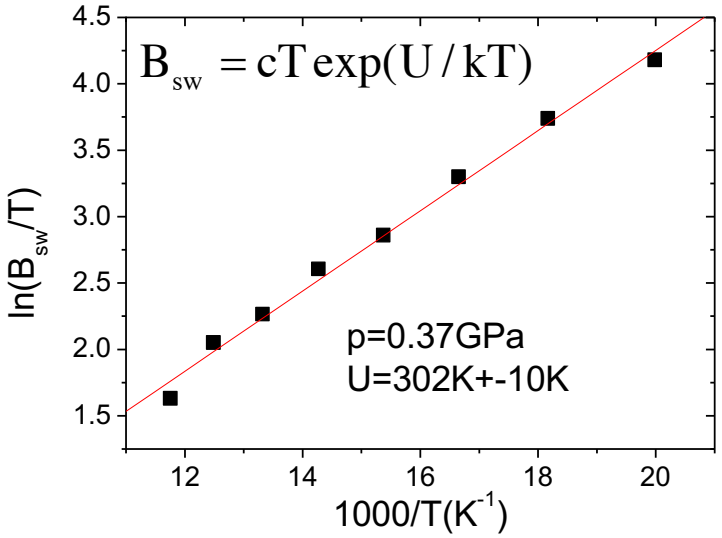


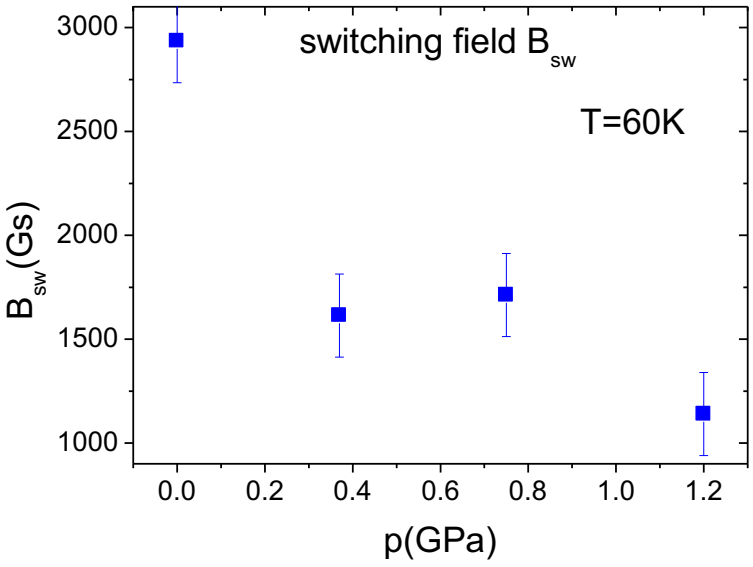
Experiment layout

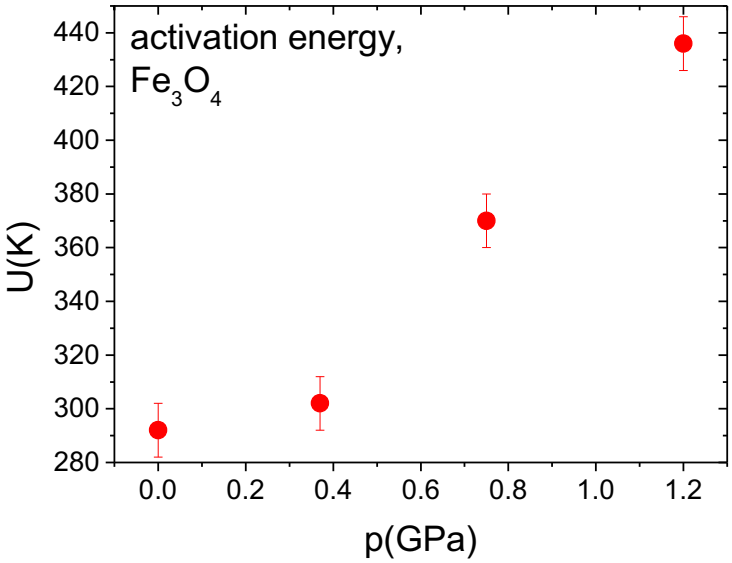
- Magnetization on VSM
- p=0-1.2GPa

Does AS depend on pressure?





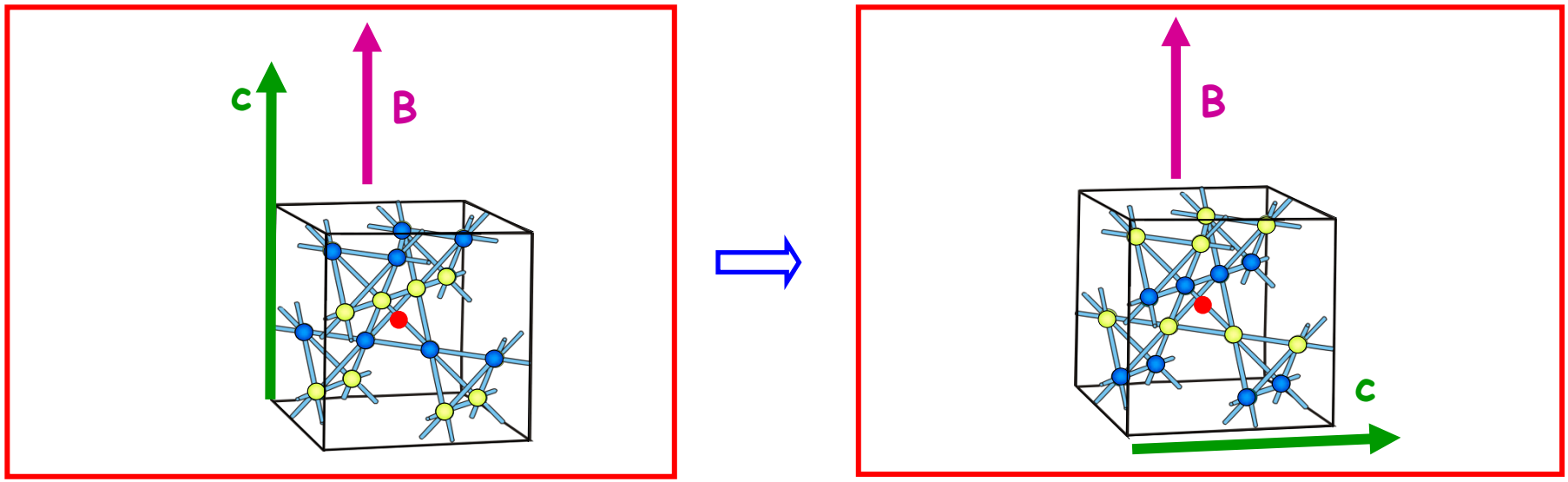




B_{sw} gets lower with p

Activation energy increases with p

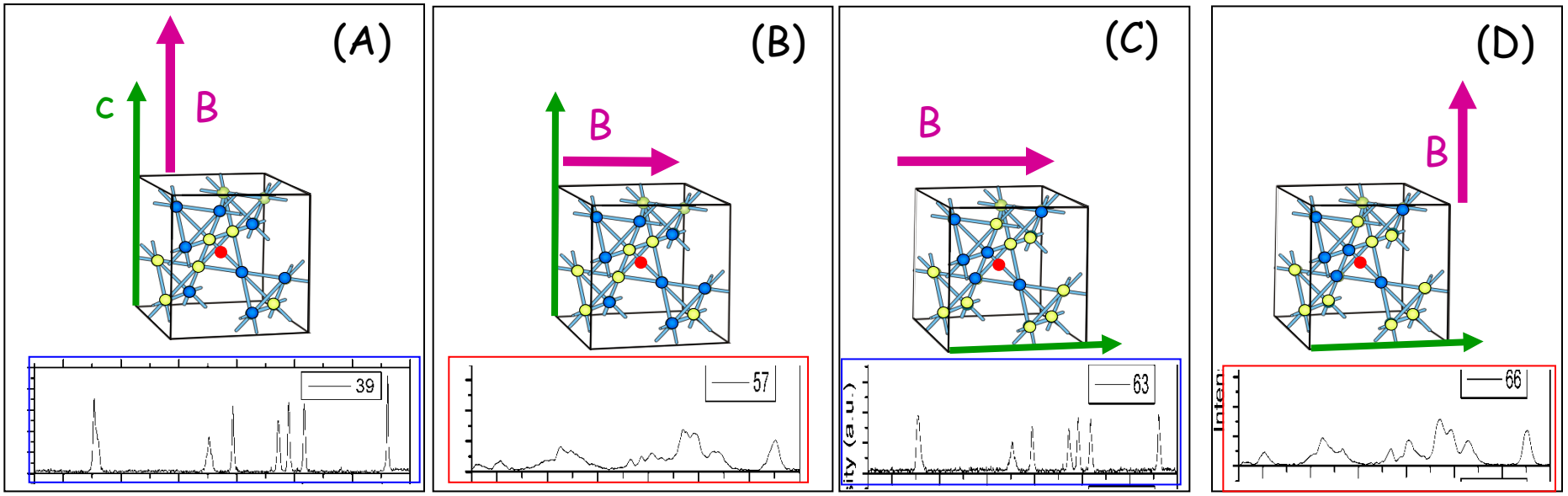
Can easy axis switching be observed by microscopic techniques?



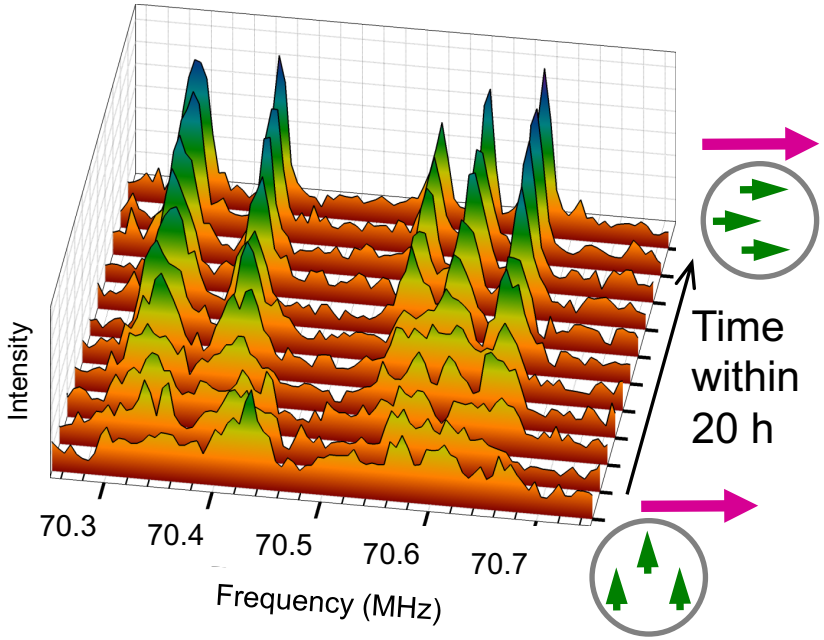
We would like to check if the change of charge order caused by axis switching can be observed by microscopic techniques

- We want to see the changes in the signal prior and after AS.
- We also would like to observe what iron positions have changed to cause AS.

Can easy axis switching be observed by microscopic techniques?



V. Chlan, et.al., Journal of Applied Physics **108**, 083914 (2010)



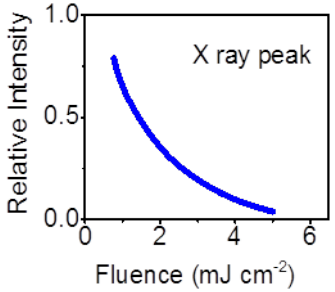
AS is clearly observed

Charge arrangement changes
(A and C are identical)

Temporal observation of the process may say what octahedral Fe positions have changed

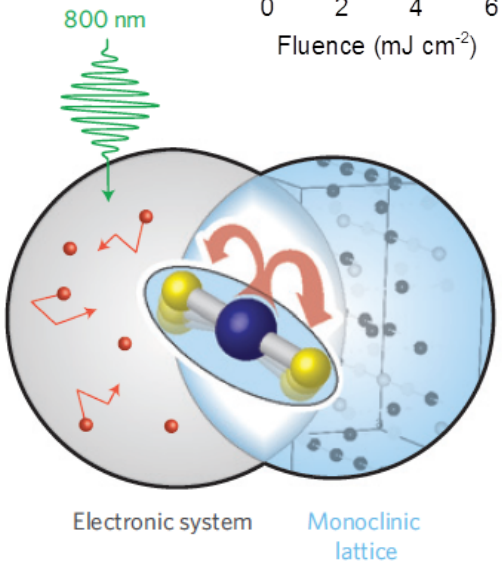
AS is a fast electronic process

S. de Jong et. al, Speed limit of the insulator–metal transition in magnetite . Nature Materials 2013



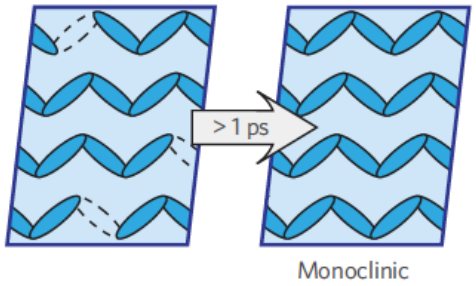
Low fluence: a few trimeron holes formation (peak lowering) that quickly recovers

strong optical pumping below T_V



<1.3 mJ cm^{-2}

<300 fs



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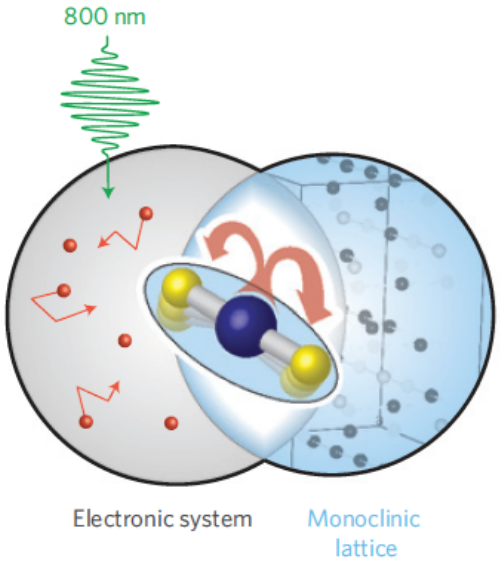
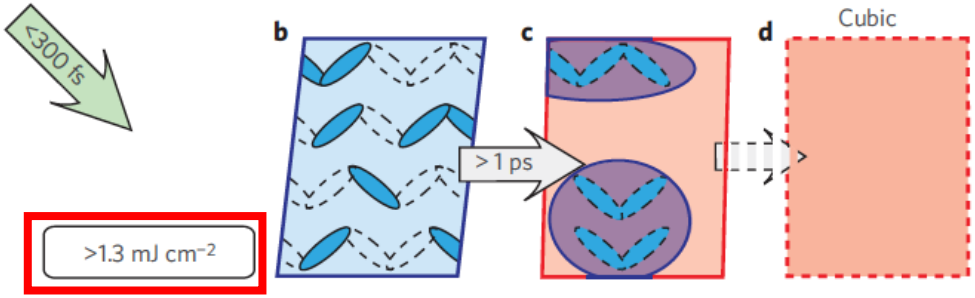
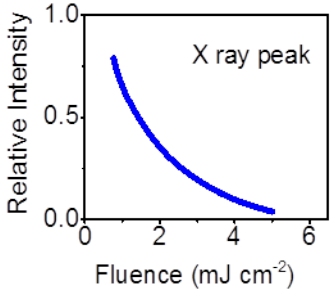
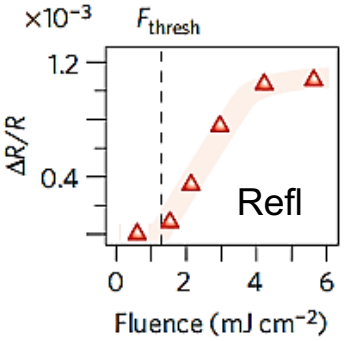
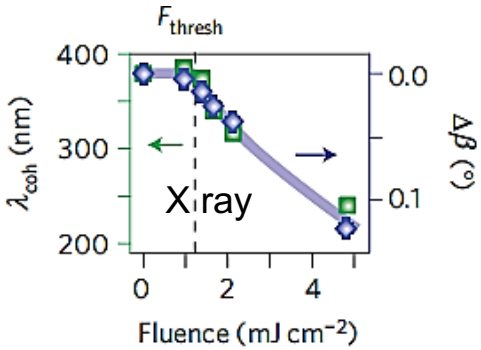






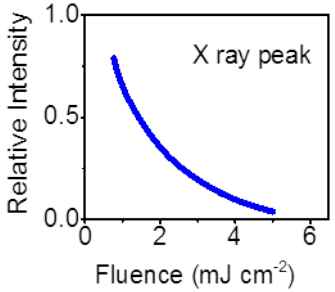




Large fluence: <u>many</u> trimeron holes formation + lattice metallic-like phase formation + metallic reflectivity

AS is a fast electronic process

S. de Jong et. al, Speed limit of the insulator–metal transition in magnetite . Nature Materials 2013



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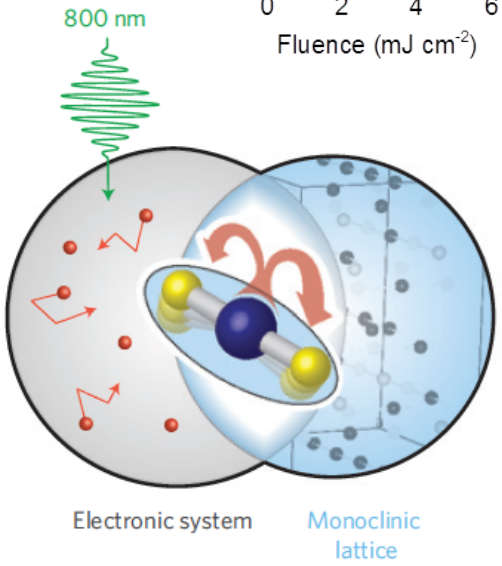
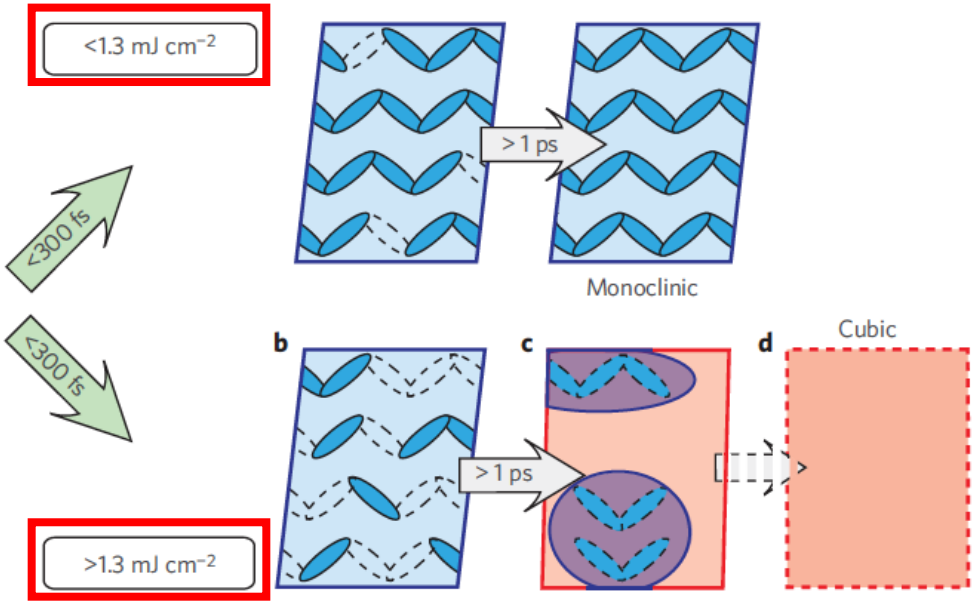
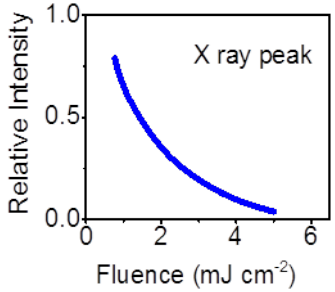
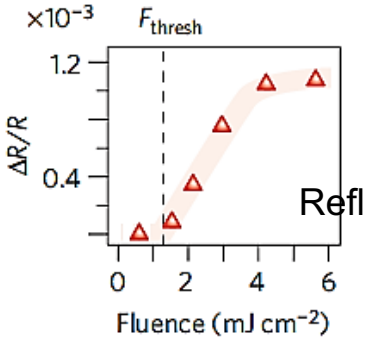
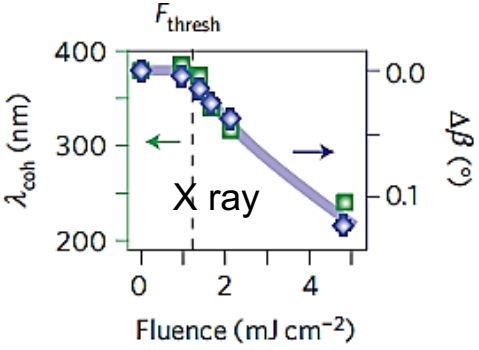










Large fluence: Many trimeron holes formation + lattice metallic-like phase formation + metallic reflectivity

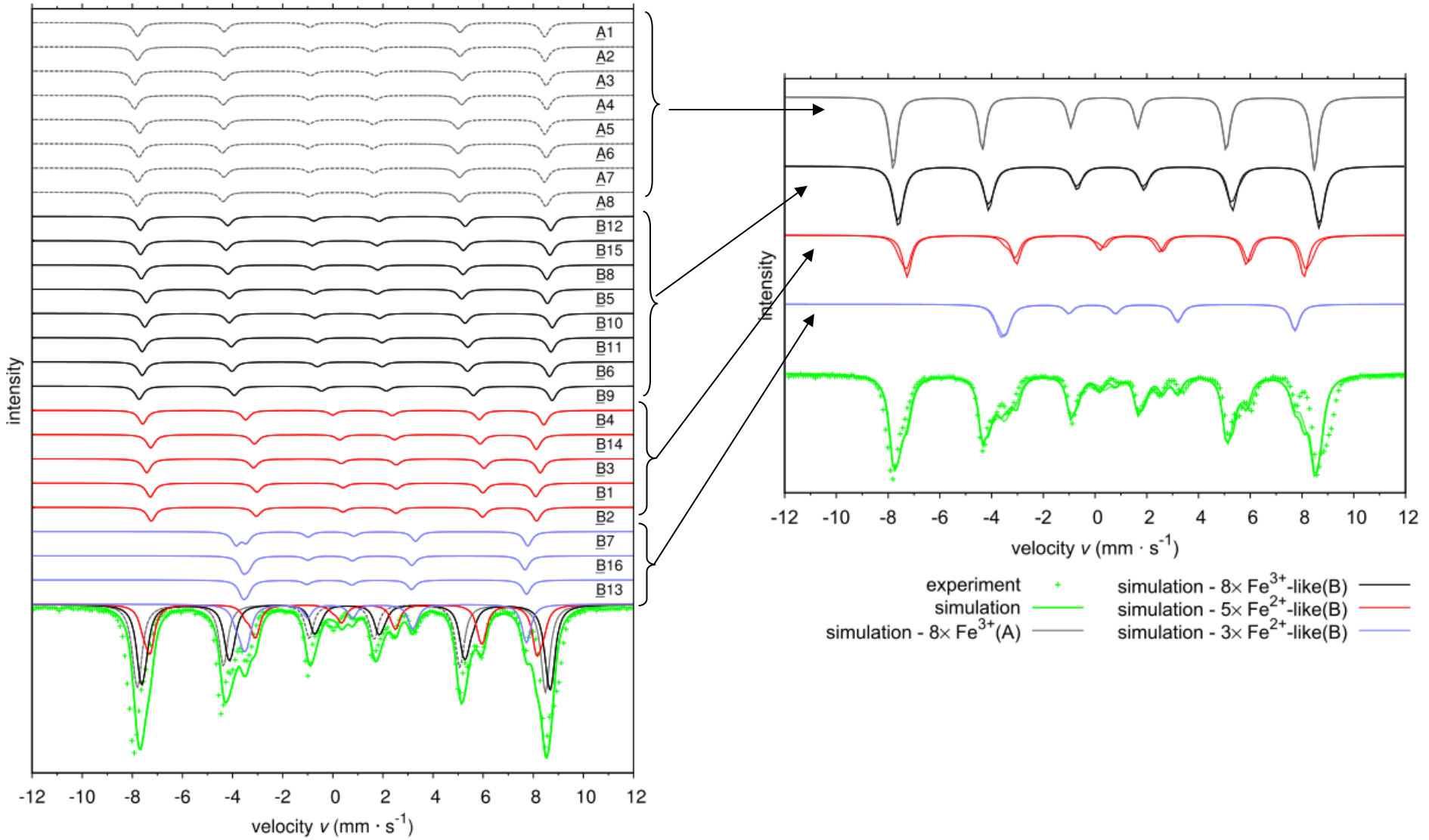
CONCLUSIONS

- Easy (magnetic and crystallographic) axis switching is closely linked to the electronic processes active also in the Verwey transition
- AS is visible in all phenomena that are affected by the Verwey transition (resistance, size, magnetization)
- Not only magnetic axis changes, but "ionic" arrangement is altered in AS; the NMR line pattern changes
- AS is the tunneling (activation process) between stable trimeron arrangements. Trimeron state can be "melted" into the high T state by the energy burst. These are complementary ways for electronic low T order rearrangement.

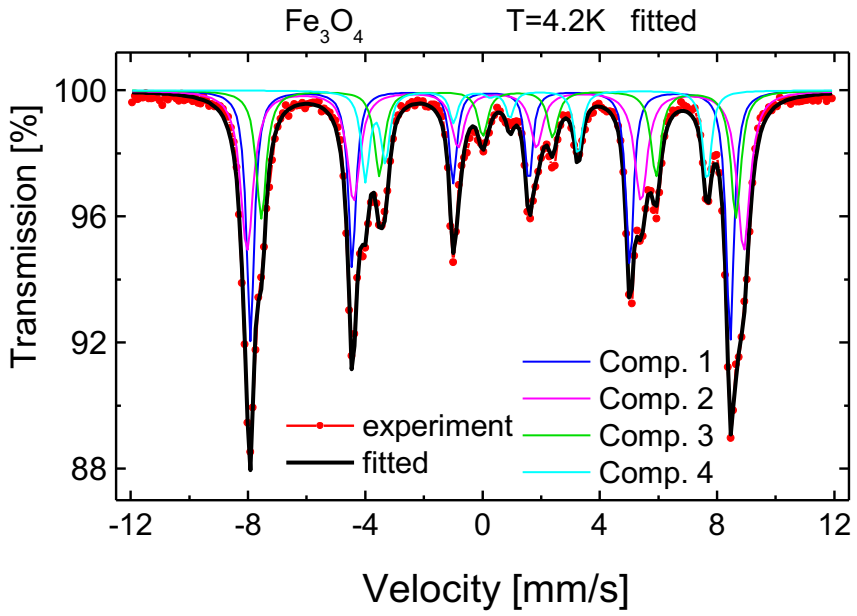
Recent results - Mössbauer spectra

R Reznicek et.al., Understanding Mossbauer spectrum of magnetite below the Verwey transition: ab initio calculations, simulation and experiment, 2017 in press

Mössbauer spectra calculated by DFT analysis



Recent results - Mössbauer spectra



Comp.	Site	IS [mm/s] relative to Fe in 300K		B [T]		Vzz [10^{21} Vm^{-2}]		
		suggested	measured	suggested	measured	suggested	measured	
1	8	0.35	0.387	50.6	50.68	1.8	-0.46	A Fe3+
2	8	0.56	0.581	50.5	52.47	2	-1.40	B Fe3+like
3	5	0.91	0.985	47.6.	49.65	12.8	9.42	B Fe2+like
4	3	0.96	1.014	35.4	35.74	13.7	12.12	B: Fe2+like

Recent results - Mössbauer spectra