Complex Ordering Phenomena in Multifunctional Oxides

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JARA-FIT, Forschungszentrum Jülich GmbH

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Complex ordering phenomena in multi-functional oxides

Young-Investigators-Group funded by Helmholtz association,
part of the institute of scattering methods JCNS-2 & PGI-4 (director Th. Brückel)

Joost de Groot
(former member,
PhD RWTH 2012)

Giorgi Khazaradze   Pankaj Thakuria   Thomas Müller

Shilpa Adiga   Hailey Williamson   Manuel Angst

IVANE JAVAKHISHVILI TBILISI STATE UNIVERSITY

(PhD advisor Alexander Shengelaya)

RWTH AACHEN UNIVERSITY

Technical Approach

- Exploratory **synthesis** and crystal growth.

Feedback

- **In-house characterization**
  (Diffraction, Macroscopic Properties).

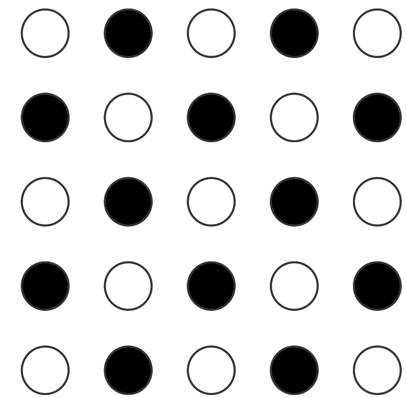
- Discern detailed electronic ordering
  and excitations at remote
  neutron/synchrotron facilities

Transition metal oxides

Substantial ionicity and correlation-effects provide a tendency towards localization of the electrons, which acquire „atomic-like“ properties.

Electrons can hop between sites, providing interaction and facilitating

<u>ordering processes</u> of **charge** degrees of freedom:



Valence e.g. **2+/3+**

Electrons delocalized

Transition metal oxides

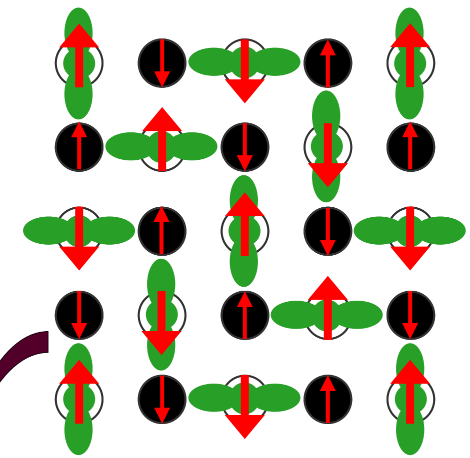
Substantial ionicity and correlation-effects provide a tendency towards localization of the electrons, which acquire „atomic-like“ properties.

Electrons can hop between sites, providing interaction and facilitating

<u>ordering processes</u> of

charge
orbital
spin
lattice

subtle interplay



Valence e.g. **2+/3+**

Shape of electron cloud

Magnetic moment

Scattering methods

Transition metal oxides

Substantial ionicity and correlation-effects provide a tendency towards localization of the electrons, which acquire „atomic-like“ properties.

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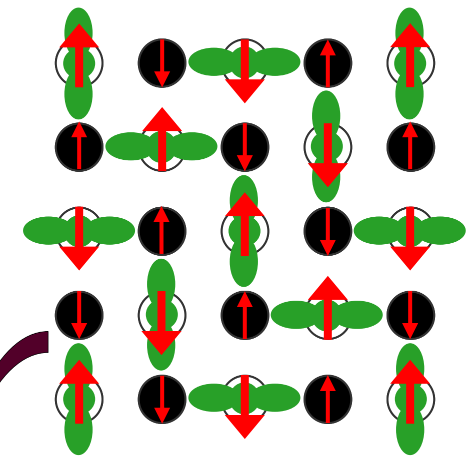


Valence e.g. **2+/3+**

Shape of electron cloud

Magnetic moment

Scattering methods

Functionalities :

Magnetism, ferroelectricity, superconductivity, resistive switching, magnetoresistance…

Applications :

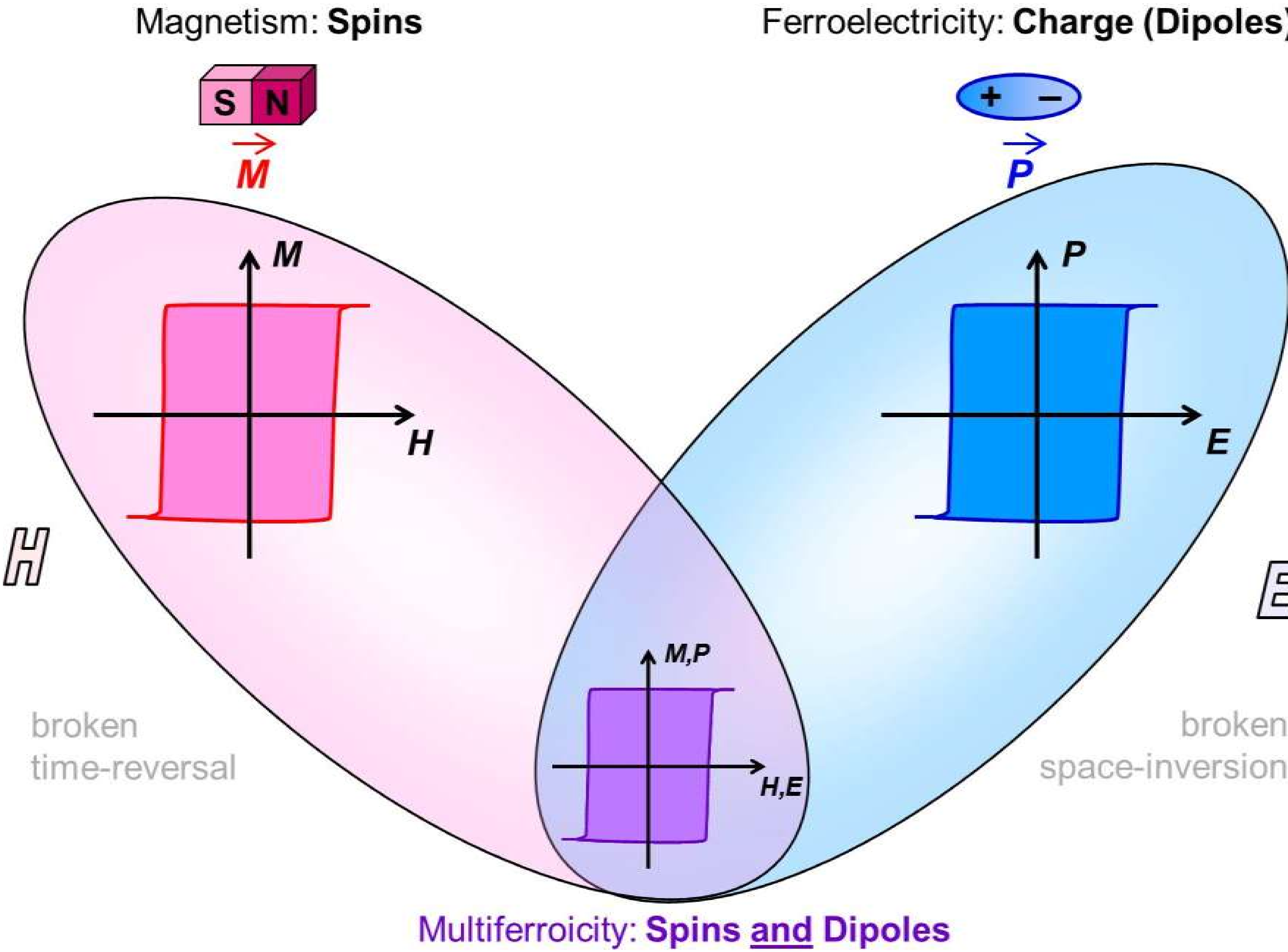
Memory devices, signal switching, spintronics, …

Transition metal oxides

Functionalities :

Magnetism, ferroelectricity,

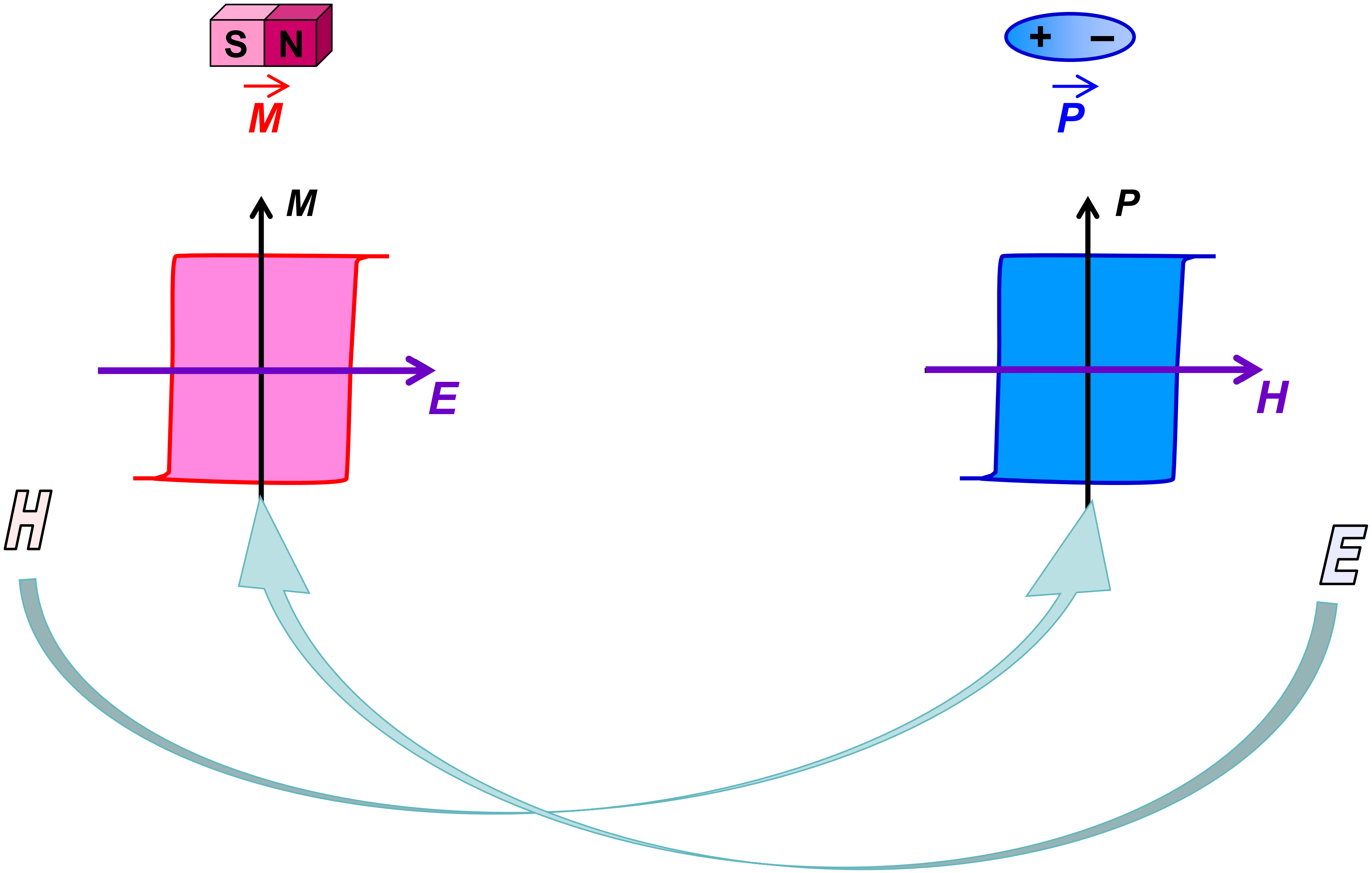
Multiferroics



Multiferroics : Cross-coupling

Magnetism: **Spins**

Ferroelectricity: **Charge (Dipoles)**



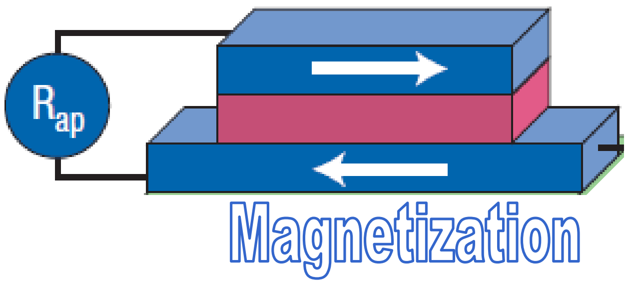
Multiferroicity: **Spins and Dipoles**

MF for non-volatile memories

MRAM

Write : requires remagnetization – high currents
(slow, high power consumption)

Read
with GMR



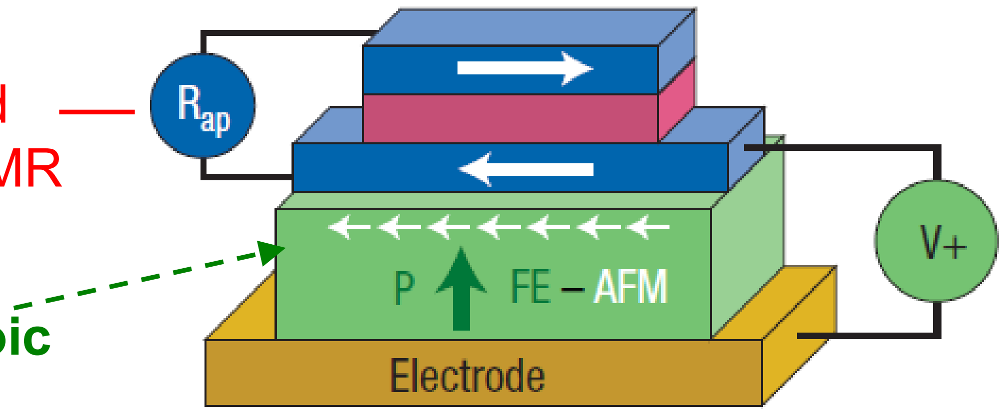
MF for non-volatile memories

MRAM

Write : requires remagnetization – high currents
(slow, high power consumption)

Read
with GMR

Multiferroic



MF-RAM :

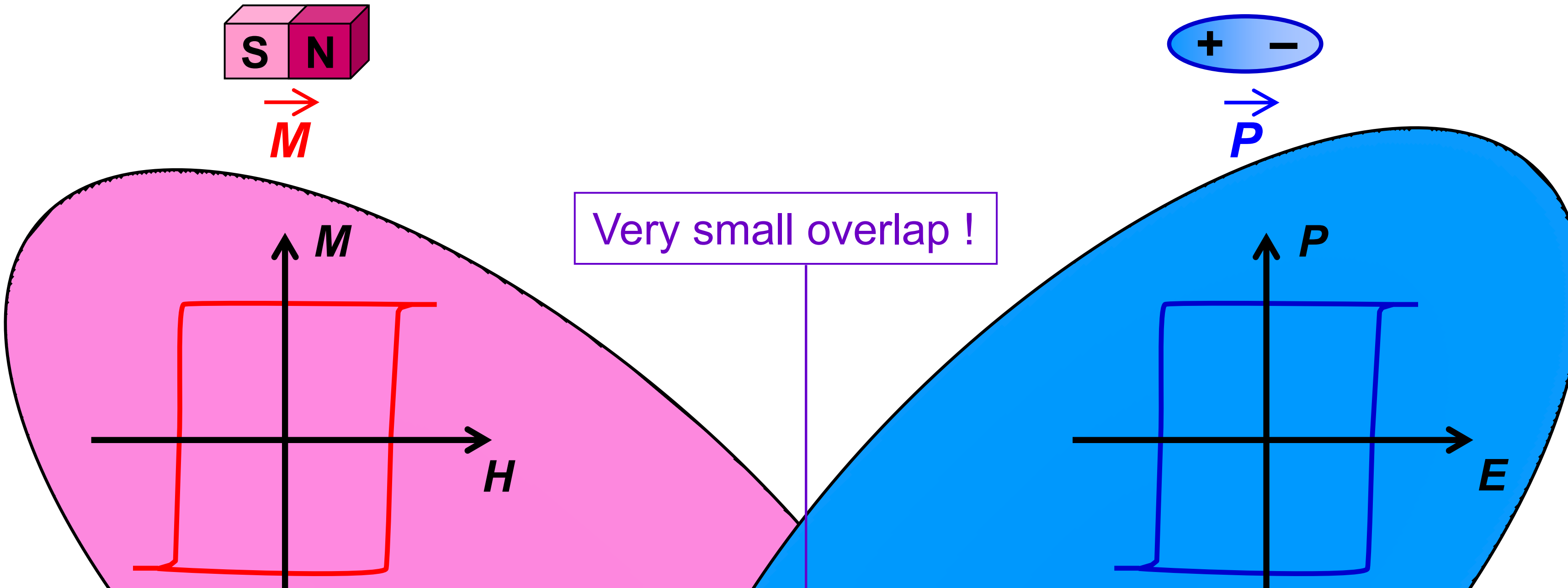
Write with a
Voltage

[M. Bibes and A. Barthélémy, Nat. Mater. **7**, 425 (2008)]

MF : only few materials

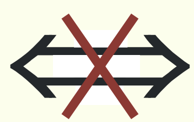
Magnetism: **Spins**

Ferroelectricity: **Charge (Dipoles)**

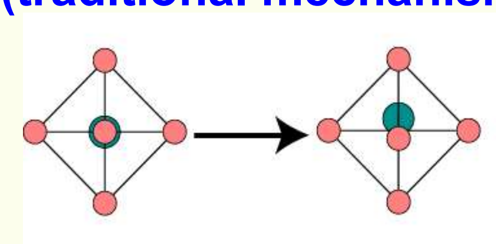


Magnetism

Ferroelectricity (traditional mechanism)



Contra-indicated



requires partially filled *d*-shell

requires empty *d*-shell

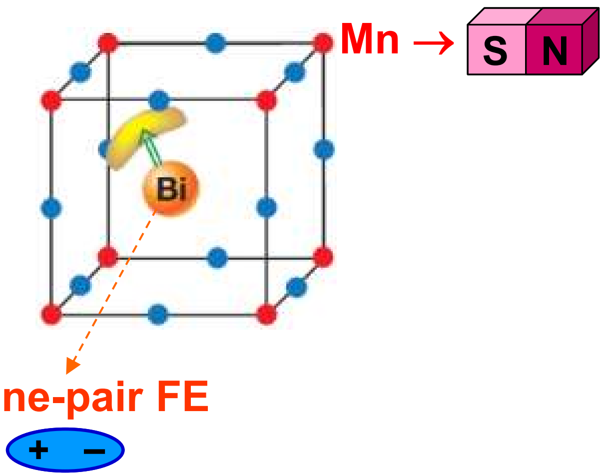
[N.A. Hill (now Spaldin), *Why are there so few magnetic ferroelectrics?* J. Phys. Chem. B **104**, 6694 (2000)]

Jülich Aachen Research Alliance

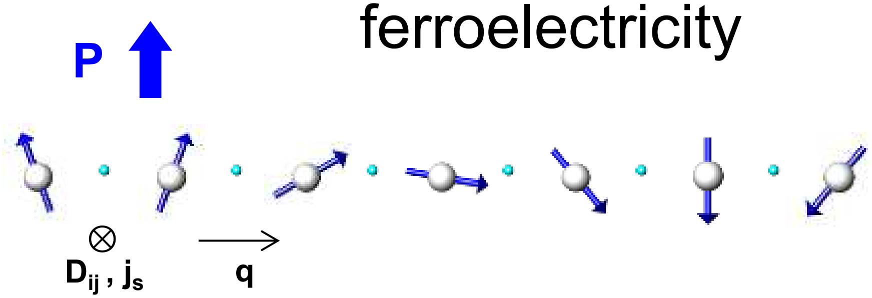
Different routes to MF

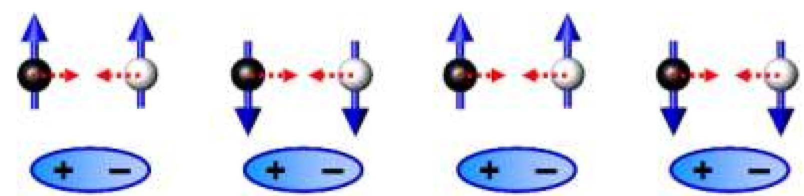
independent subsystems

gen. weak electromagnetic coupling

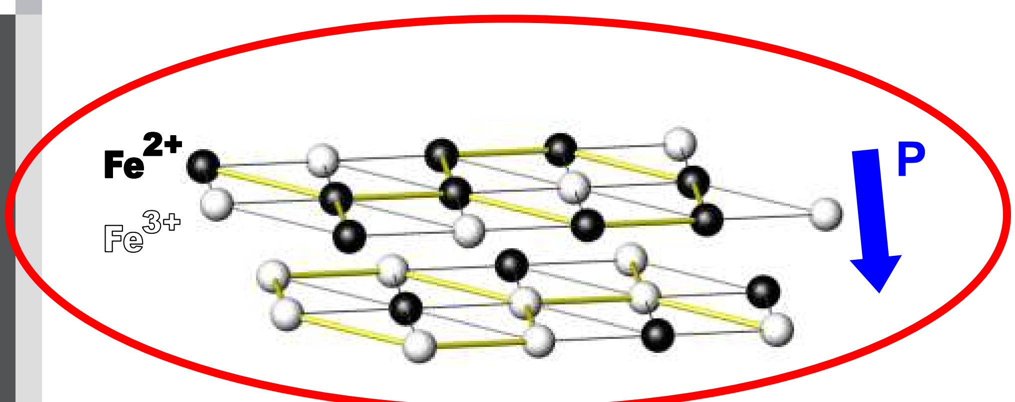


spin-spiral ferroelectricity





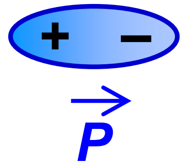
(symmetric) exchange striction



Charge-order-based

Multiferroicity from charge order

Ferroelectricity: **Charge (Dipoles)**

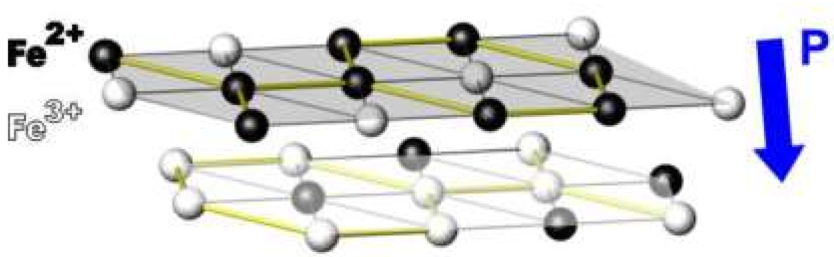


Any charge order breaking inversion-symmetry is polar.

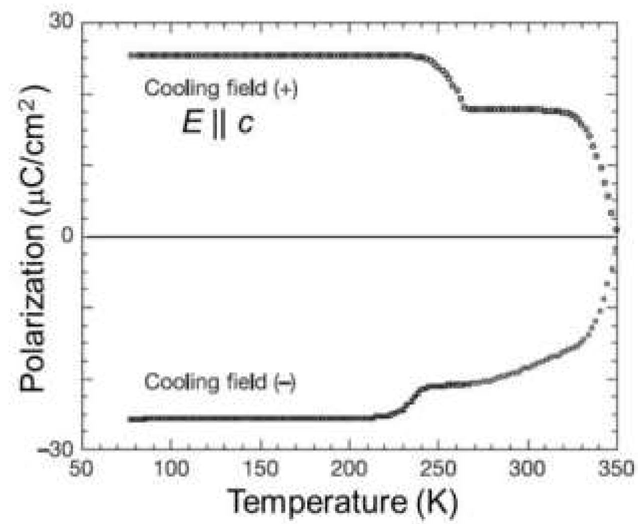
- Can in principle lead to very **large polarizations**
- Spins are for free **!**
- same sites involved in charge and spin order

$\rightarrow$ **sizeable magnetoelectric coupling** possible

Examples ???



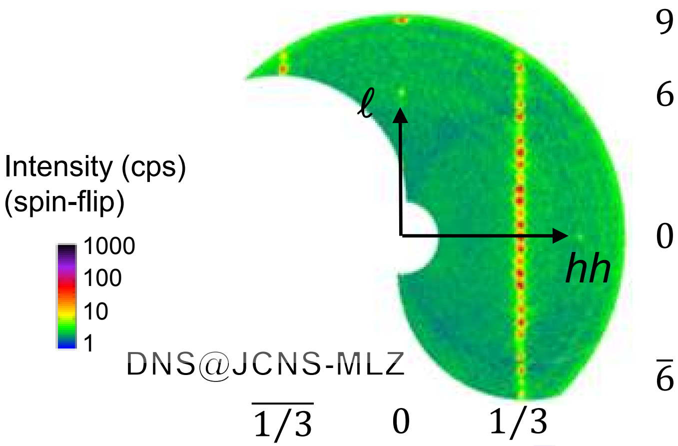
$LuFe_2O_4$



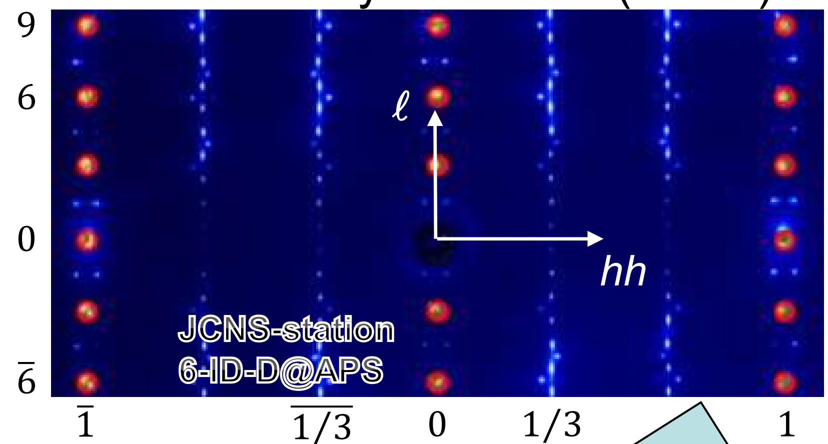
Ikeda *et al.*, Nature **436**, 1136 (2005)

CO Bilayers: charged rather than polar

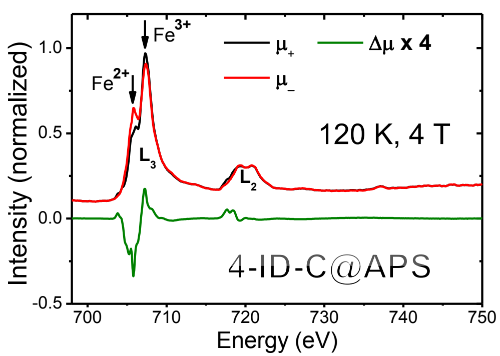
Polarized Neutron Diffraction (220 K)

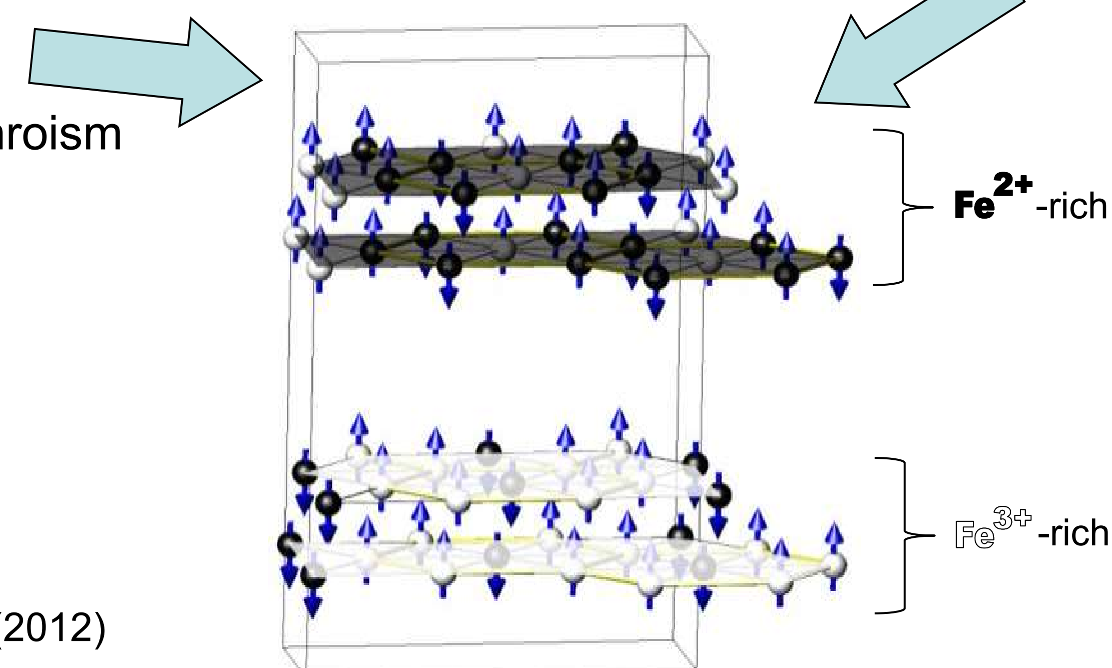


100 keV X-ray diffraction (300 K)



X-ray Magnetic Circular Dichroism

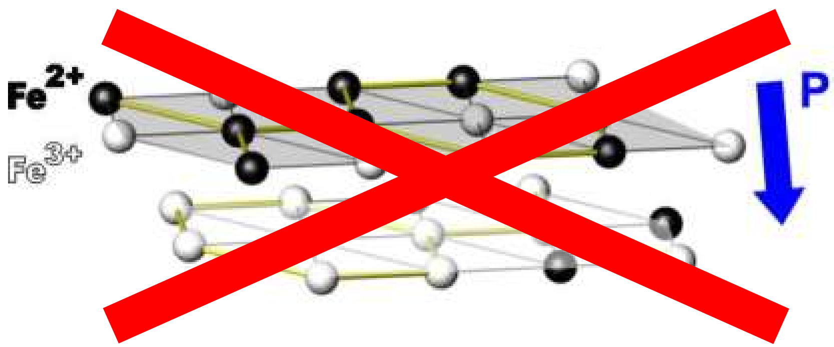




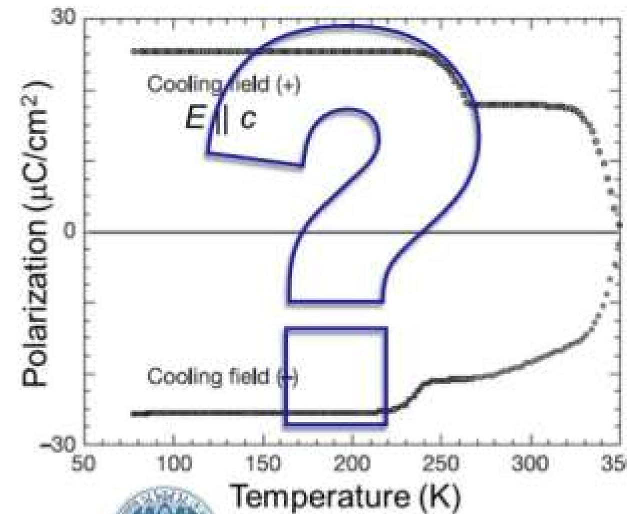
de Groot *et al.*, PRL **108**, 037206 (2012)

de Groot *et al.*, PRL **108**, 187601 (2012)

MF from charge order: $LuFe_2O_4$ is a non-example



$LuFe_2O_4$



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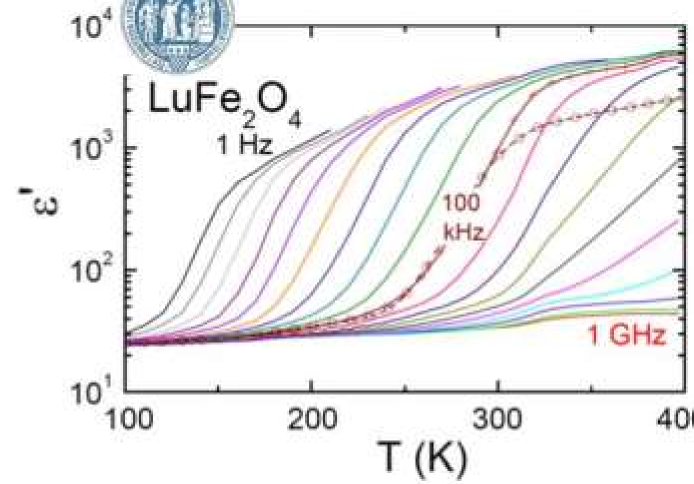
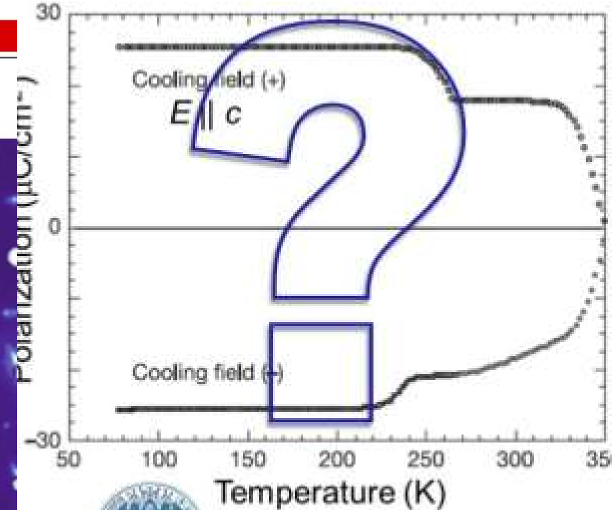


Niermann *et al.*, PRL **109**, 016405 (2012)

e order:
-example



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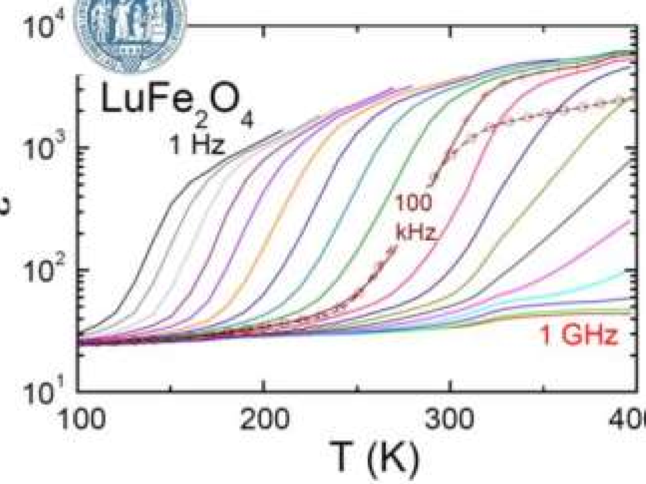
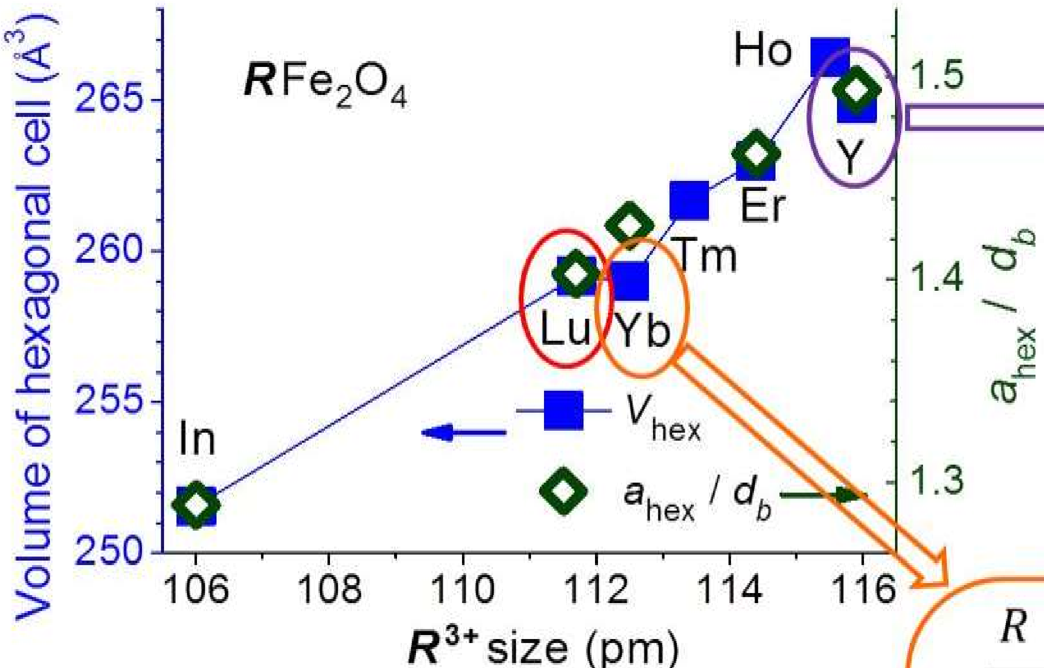


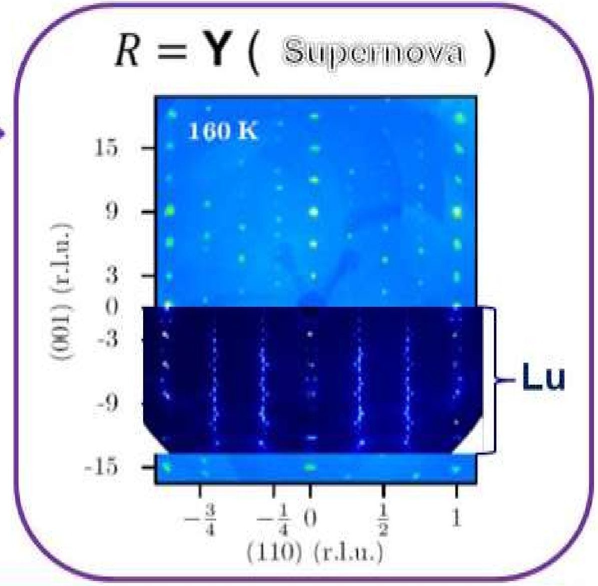
Niermann *et al.*, PRL **109**, 016405 (2012)

MA, PSS RRL **7**, 383 (2013)

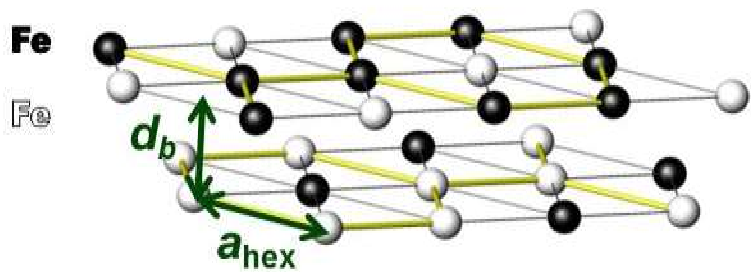
Tuning ferrites

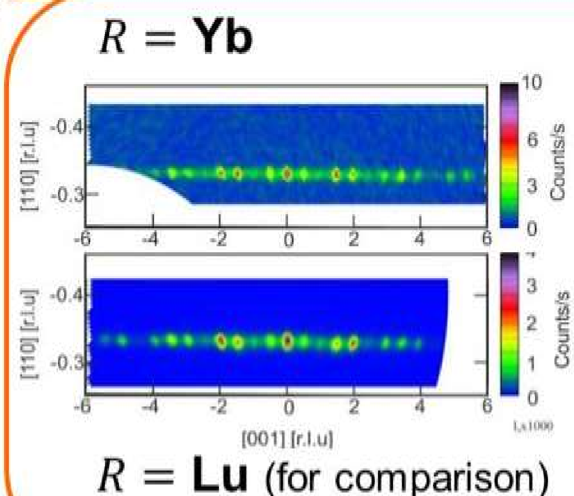
Can a ferroelectric CO be stabilized ?

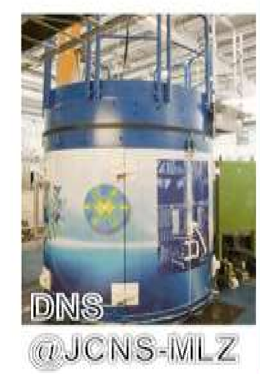




PSS RRL **7**, 383 (2013)





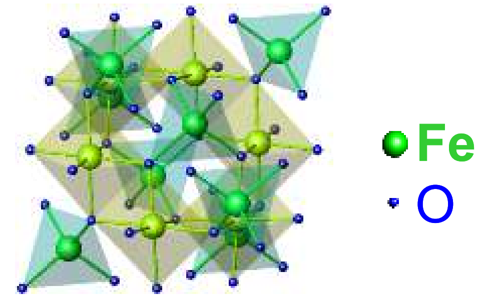


+ layer intercalation …

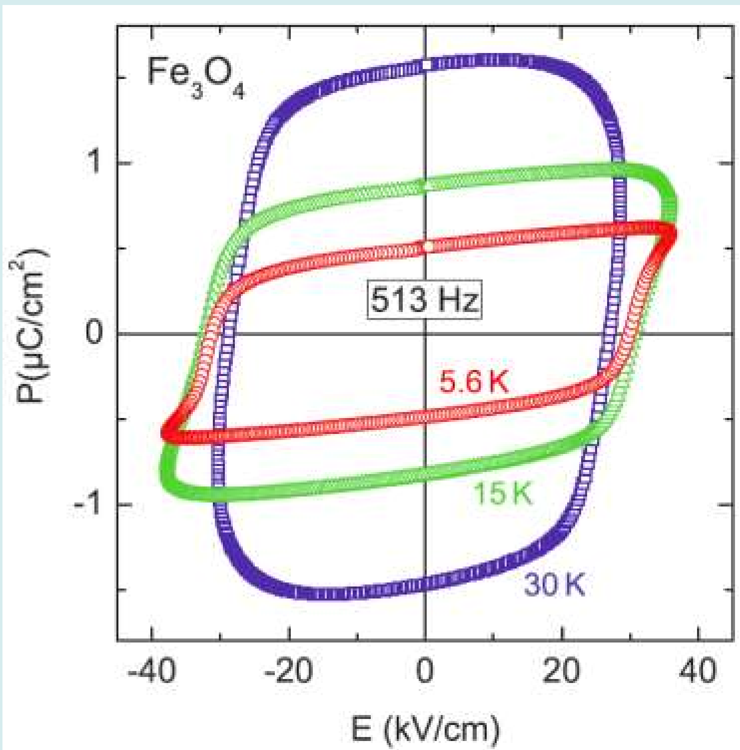
Magnetite

Ancient „*lodestone*“: oldest known magnetic material

Compass (circa 4th Century BC)



Classical example of charge order [Verwey, Nature 144, 327 (**1939**)]: **Vervey transition** in Magnetite Fe_3O_4



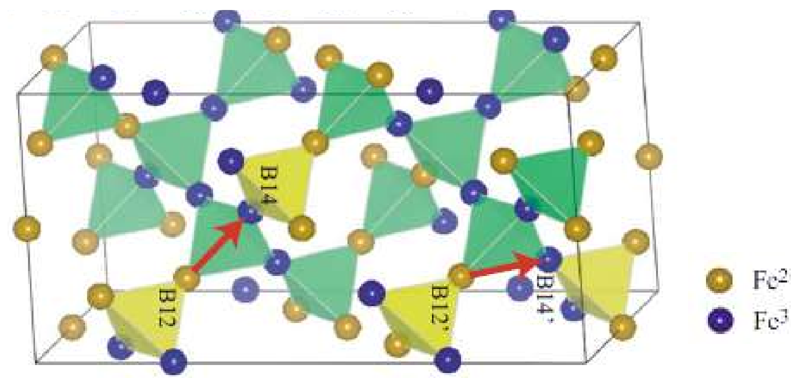
Macroscopic indications of switching

[Schrettle *et al*., PRB **83**, 195109 (2011)]

Complex charge order only recently solved

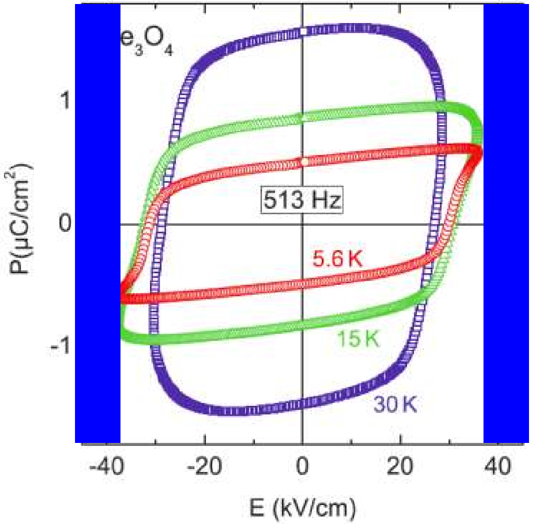
[Senn *et al*., Nature **418**, 173 (**2012**)]:

It is **polar**

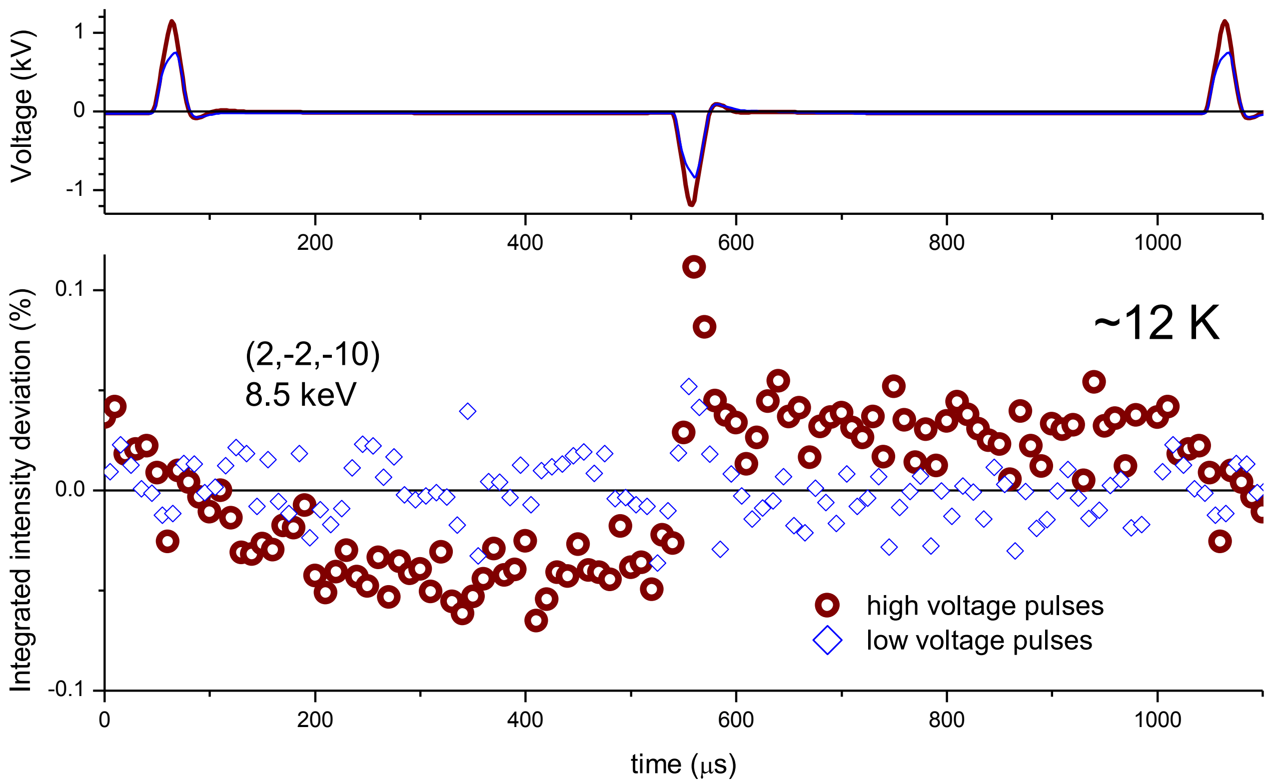


[Yamauchi *et al*., PRB **79**, 212404 (2009) – DFT calc.]

Magnetite



Intensity modulation can be attributed to structural switching between inversion-twins:
Microscopic proof of ferroelectricity!



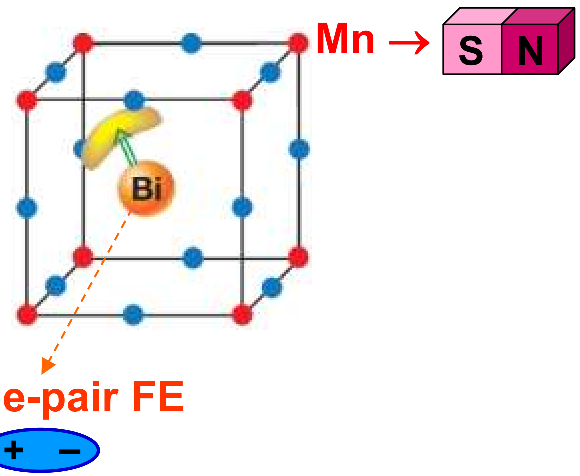
time-resolved X-ray diffraction

P09@PETRAIII, DESY

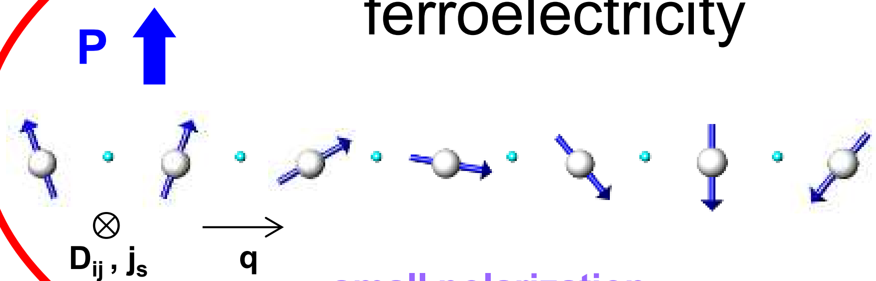
Different routes to MF

independent subsystems

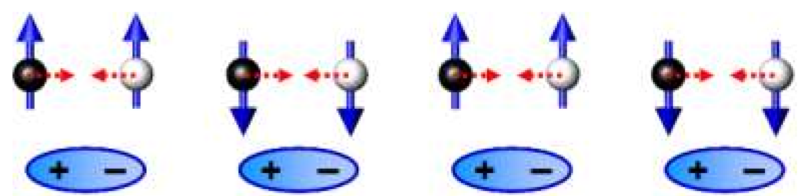
gen. weak electromagnetic coupling



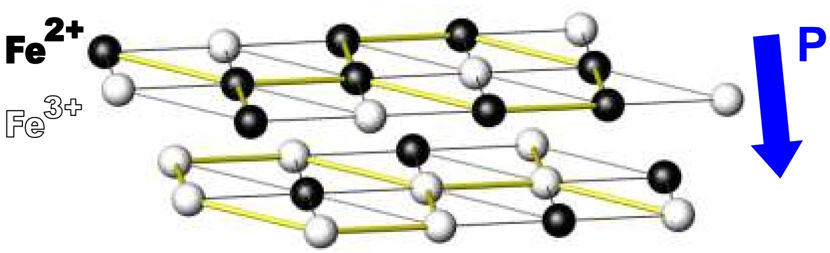
spin-spiral ferroelectricity



small polarization
usually low *T* only



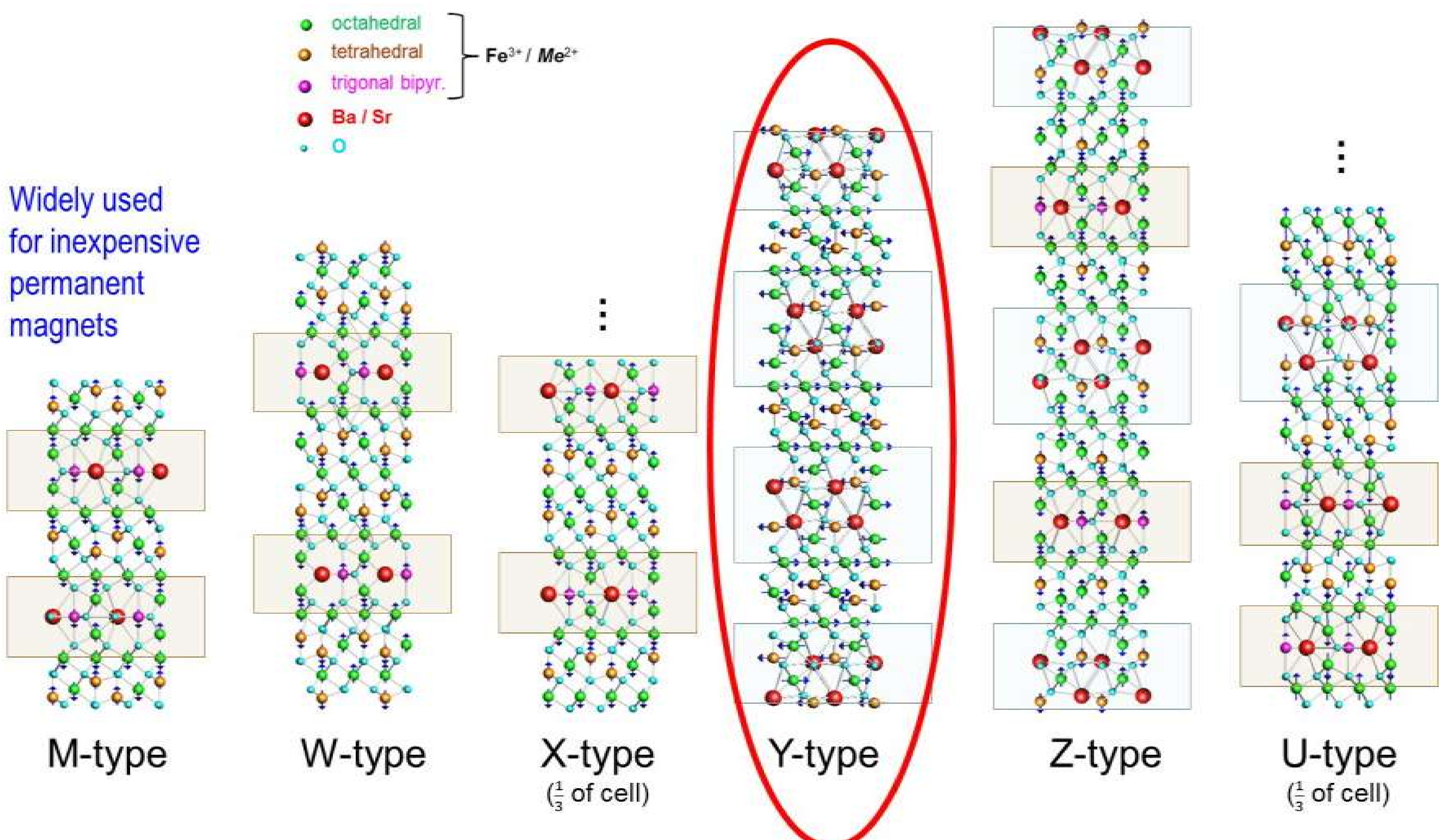
(symmetric) exchange striction



Charge-order-based

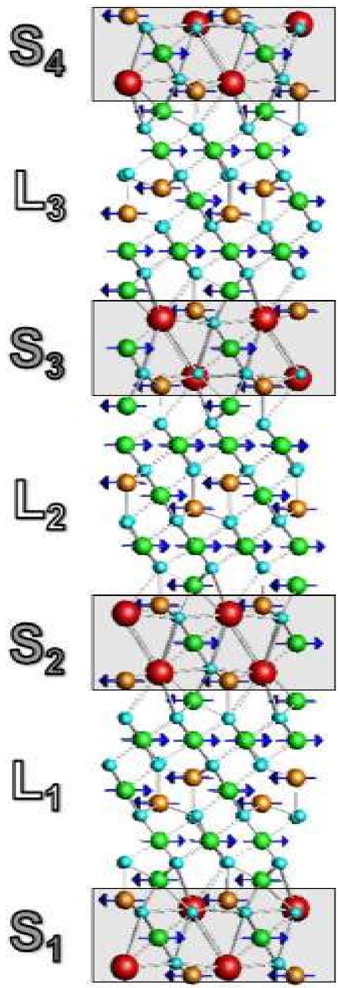
Hexaferrites: high-*T* MF

Widely used for inexpensive permanent magnets

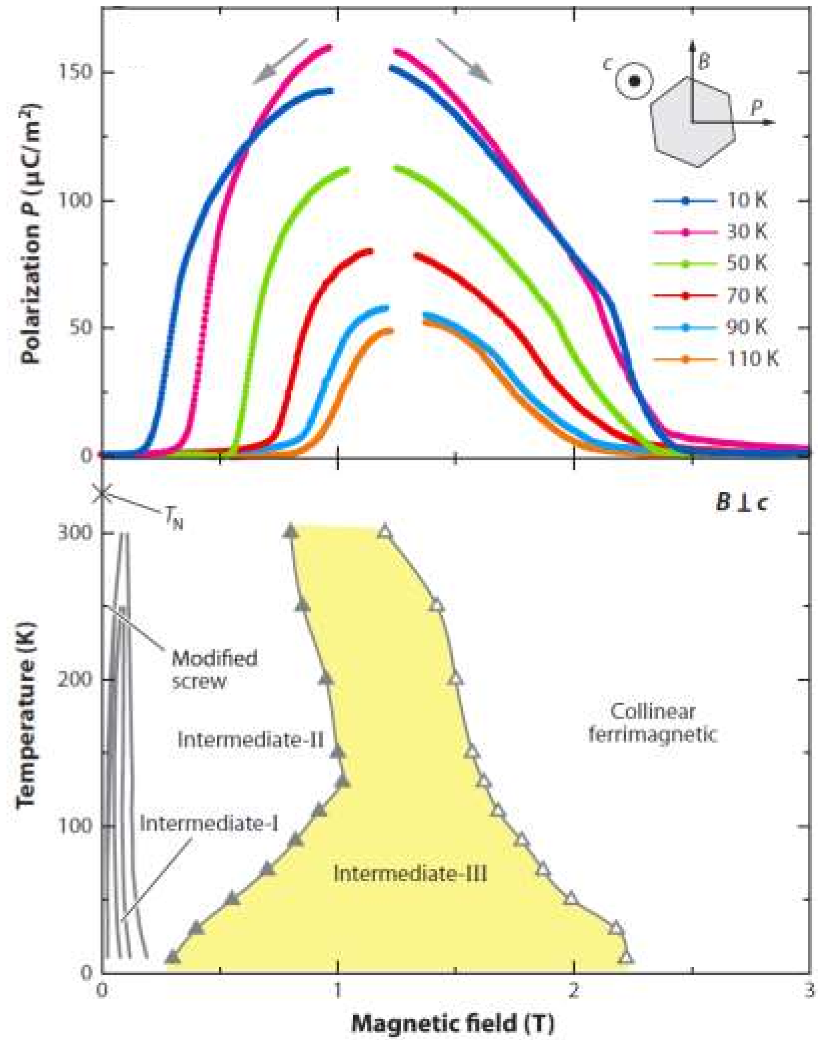


Hexagonal ferrites: based on spinel-structure, but rich variation of structures by interspersing of „R-blocks“ and „T-blocks“

Hexaferrites: high-T MF



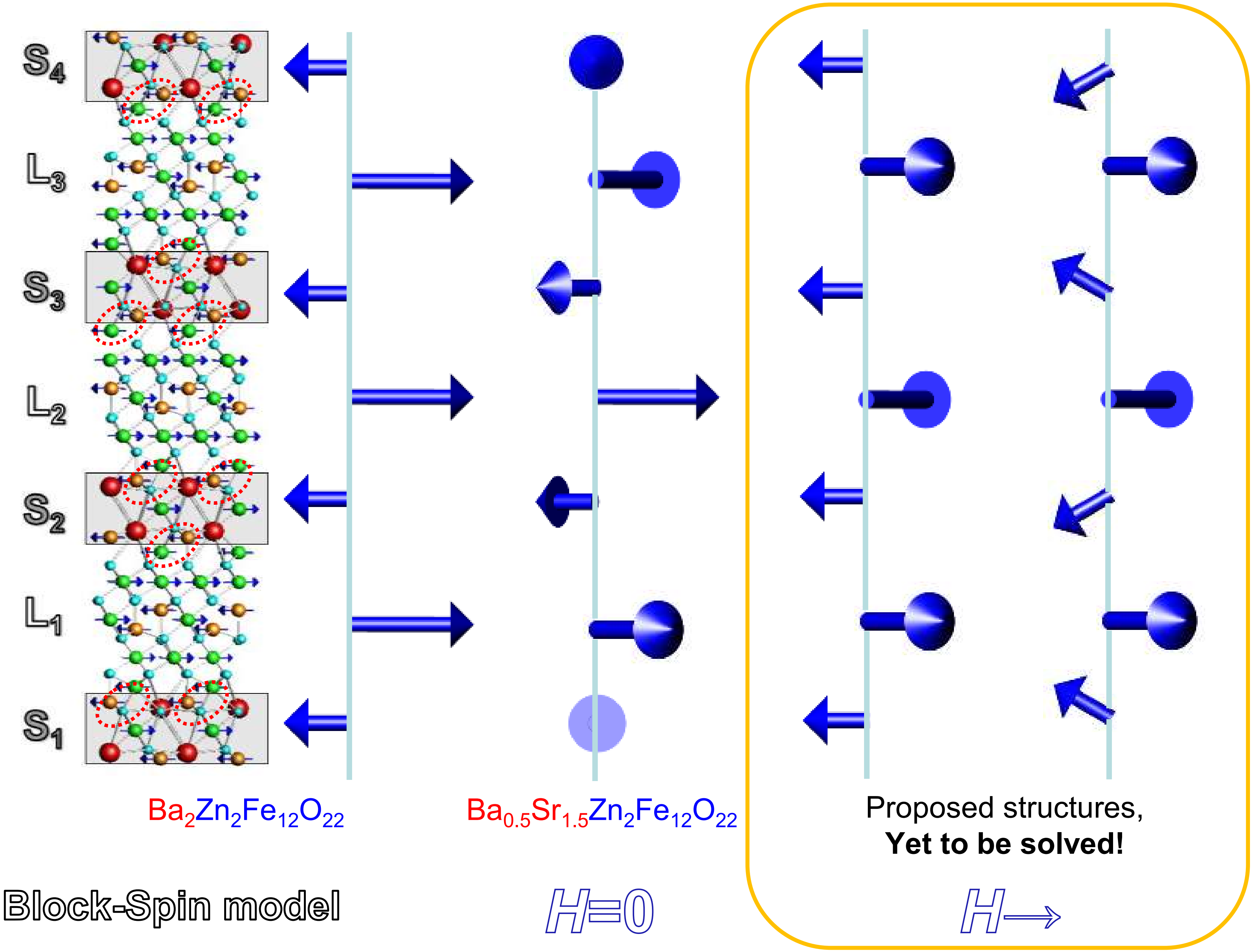
$Ba_2Zn_2Fe_{12}O_{22}$



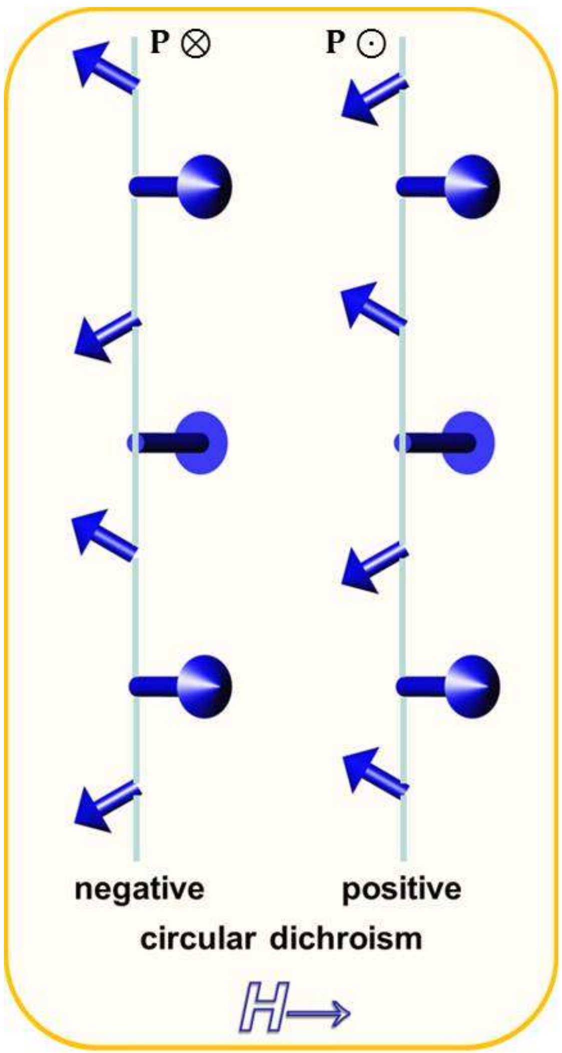
$Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$ [Kimura *et al.*, PRL **94**, 137201 (2005)]

Block-Spin model

Hexaferrites: high-T MF



Hexaferrites: high-*T* MF



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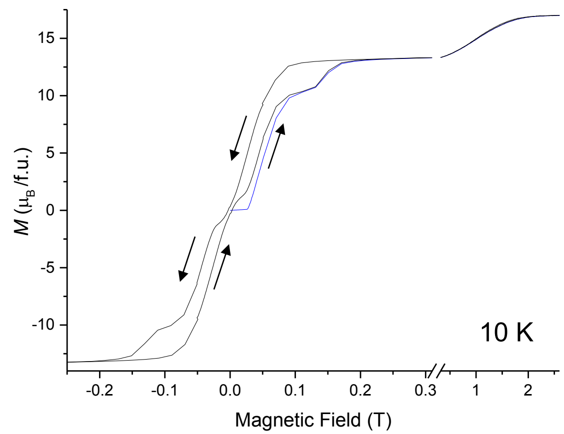
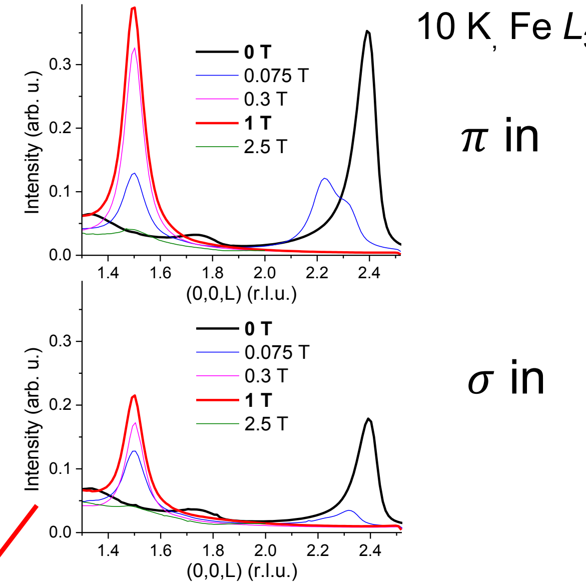
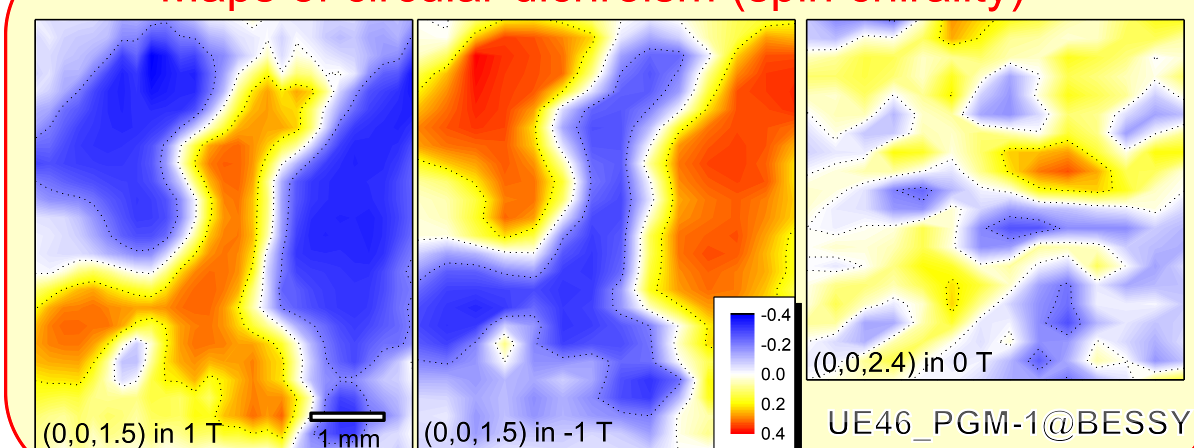


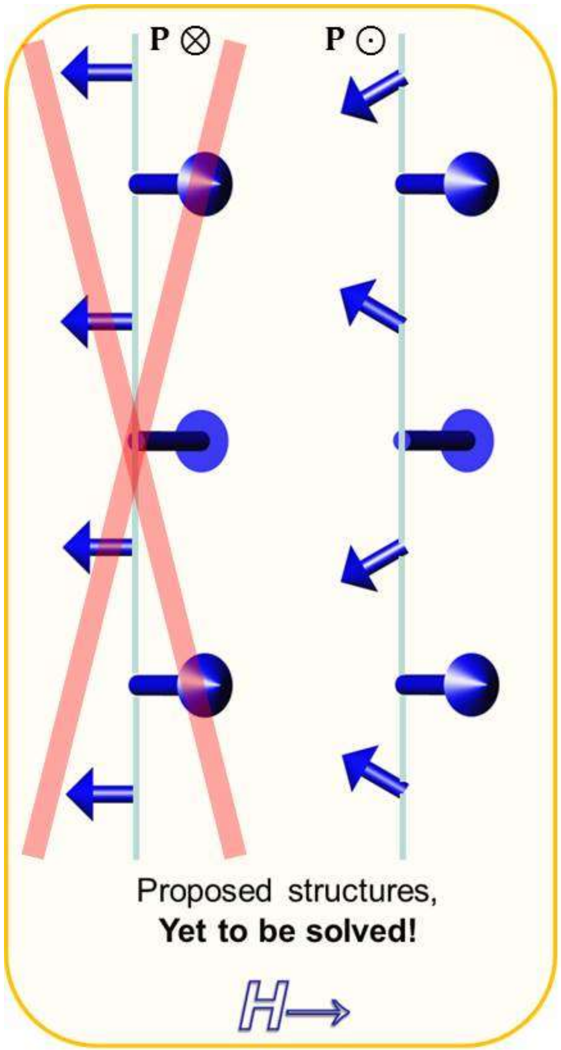


Maps of circular dichroism (spin chirality)



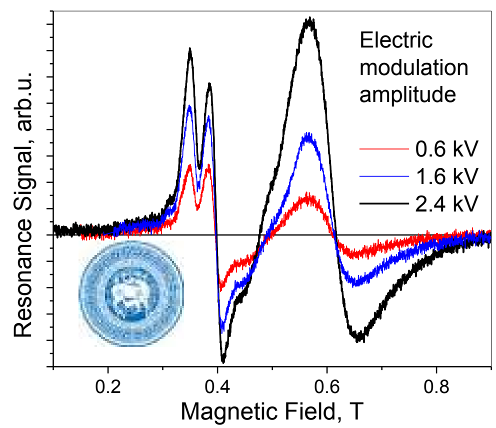
UE46_PGM-1@BESSY

Hexaferrites: high-T MF



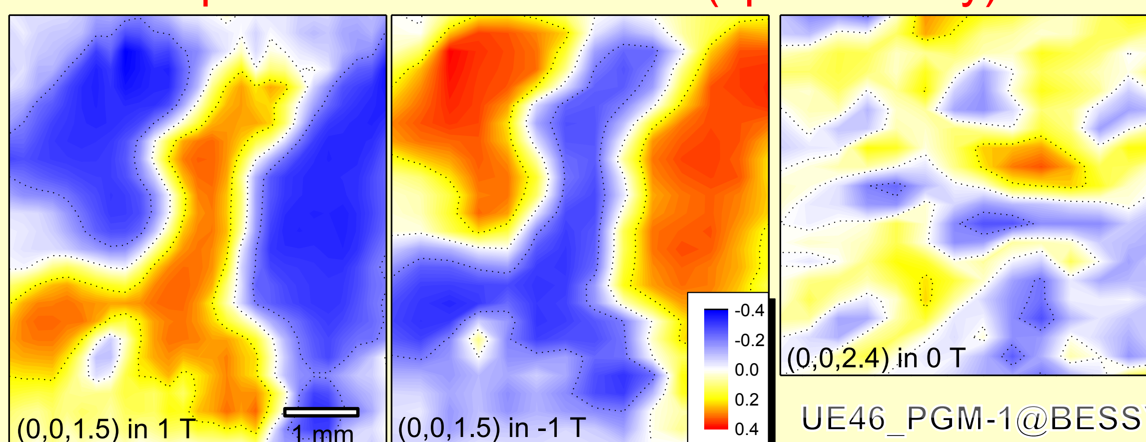
$Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$

In addition, direct determination of magnetoelectric coupling in this compound is pursued by ESR/EPR/FMR techniques with electric-field modulation, at TSU



→ See talk of
Giorgi Khazaradze,
FZJ & TSU
Parallel Session 9
(Thu afternoon, Aud. 401)

Maps of circular dichroism (spin chirality)



UE46_PGM-1@BESSY

Conclusions / Outlook

Rare earth ferrites

- Contrary to expectation, $LuFe_2O_4$, is a non-example for CO-driven multiferroicity
  likely same for $YbFe_2O_4$
- What drives spin- & charge order (which does not minimize electron-electron repulstion)?
  → INS: TOF to be complemented by TAS, in progress
- Further explore ion-size effects, intercalation.

Other potential charge-order-driven multiferroics

- Magnetite **is** an example, as demonstrated on a microscopic level
- Further examples ? (possibly including organics)

High-temperature multiferroic phases in hexaferrites

- „Classical“ Y-type hexaferrite has spin-structure compatible with „Dzyaloshinskii-Moriya“-driven ferroelectricity
- Fine-tune properties by substitutions and explore other hexaferrite structure types

Other projects in multiferroicity resarch

- E.g. other spin-based mecha-nisms such as ferrotoroidicity are being studied

Plenty of research opportunites ...

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Selected external collaborations on results presented

Groups of:

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Dr. J. Strempfer – DESY

Dr. U. Staub – PAUL SCHERRER INSTITUT PSI

Dr. S. Haskel – Argonne

Dr. E. Schierle – HZB Helmholtz Zentrum Berlin

Dr. S. Nagler – Oak Ridge

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Shilpa Adiga Hailey Williamson Manuel Angst

Joost de Groot (former member, PhD 2012)

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SHOTA RUSTAVELI NATIONAL SCIENCE FOUNDATION, JÜLICH FORSCHUNGSZENTRUM – „Joint Research and Education programme“, call for proposals 2012