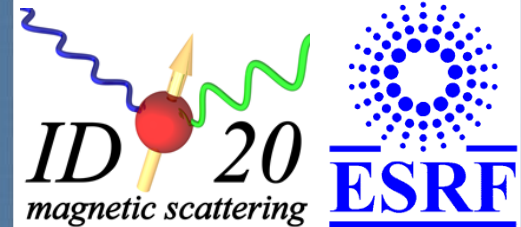




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Resonant Elastic X-ray Scattering and Neutron Scattering investigation of Magneto-Electric materials

C. Mazzoli,
Synchrotron group, Physics Dep., Politecnico di Milano



- Multiferroics and MagnetoElectrics
- REXS technique point of view on electronic degrees of freedom
- REXS and neutron investigations of MEs: some relevant cases in external fields
- Conclusions



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- T. A. W. Beale
- P. D. Hatton (Univ. of Durham, Durham, UK)

- **S. Partzsch**
- **J. E. Hamann-Borrero**
- J. Geck (IFW, Dresden, D)

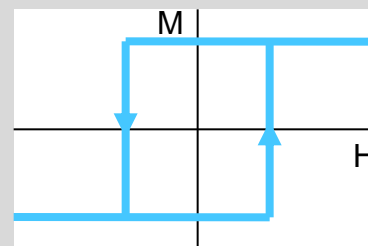
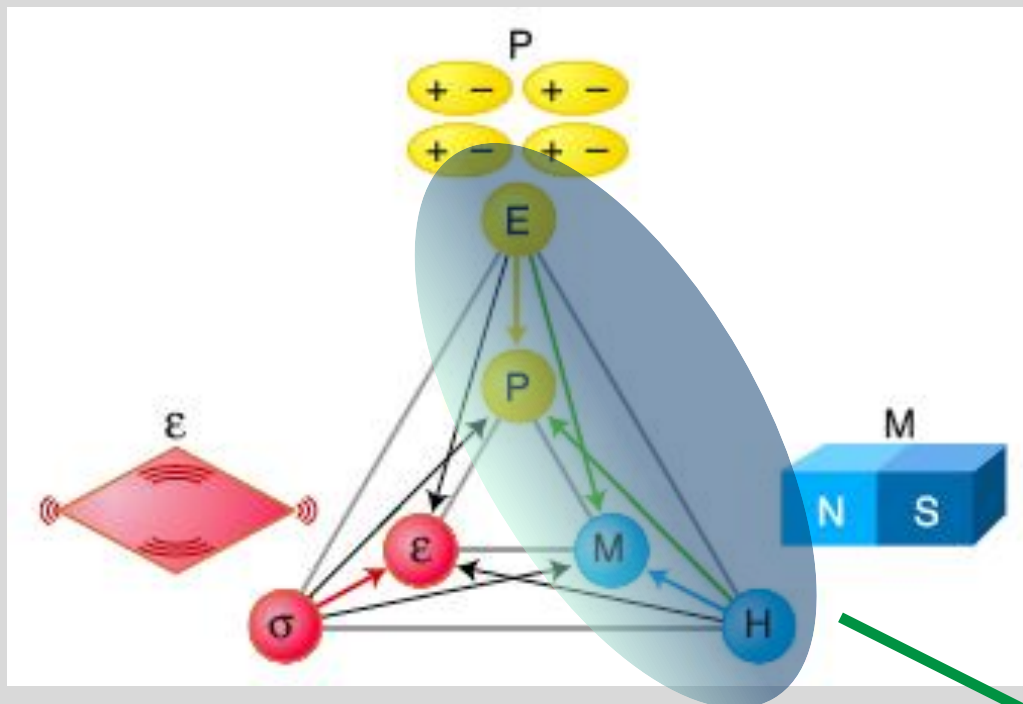
- **M. Allieta**
- M. Scavini (Univ. di Milano, Milan, I)

- V. Scagnoli (SLS, PSI, Villigen, CH)

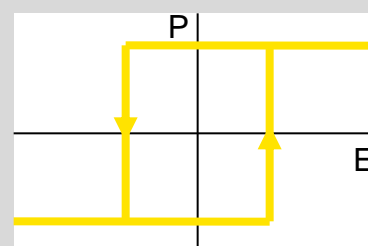
- H. C. Walker (P09, Petra, DESY, Hamburg, D)



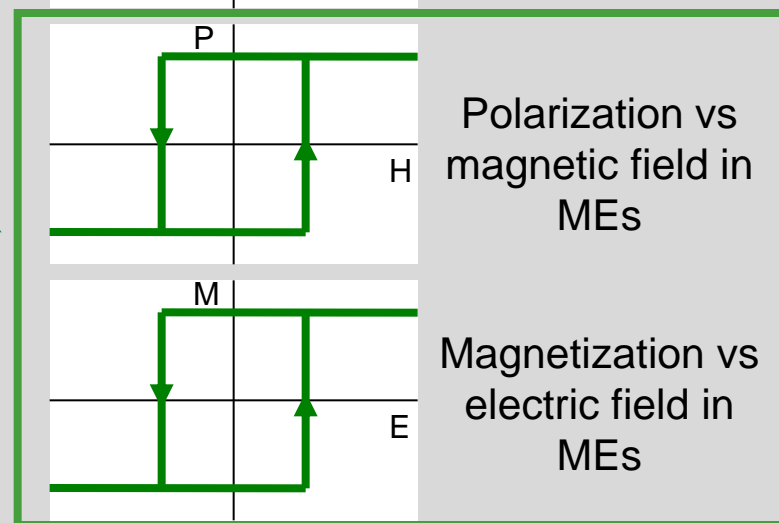
EO in multiferroics and magnetoelectrics



Magnetization vs magnetic field in FMs



Polarization vs electric field in FEs



Polarization vs magnetic field in MEs

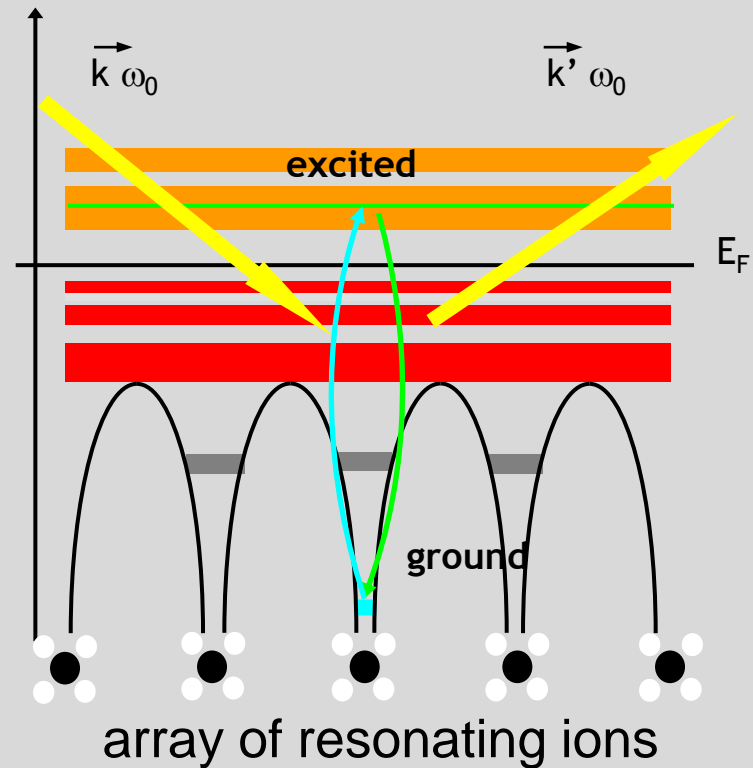
Magnetization vs electric field in MEs

- **Ferroic:** P, M or ϵ have divergent components at $Q=0$, so giving rise to ferroelectricity, ferromagnetism or ferroelasticity
- **Multiferroic:** coexistence of at least two kinds of long-range ordering

- **Magnetoelectrics:** cross control P (M) via H (E)



- Electromagnetic field (photons) as a probe for e^- states of the matter ($\mathbf{A}_{\text{radiation}} \leftrightarrow \mathbf{E}, \mathbf{B}_{\text{atomic charges}}$)
- Chemical selectivity
(absorption related \rightarrow site and band selective)
- 3D e^- distributions
(due to atomic scattering factor, in diffraction condition, site contrast due to structure factor)
- to fulfill Bragg's law:
 $\lambda \sim \text{atomic spacing} \leftrightarrow \text{keV}$ (hard regime: K 3d, L 4f, M 5f; soft regime: $L_{2,3}$ 3d)



REXS \rightarrow RXD

CM et al., EPJ-ST 208 (2012) 89



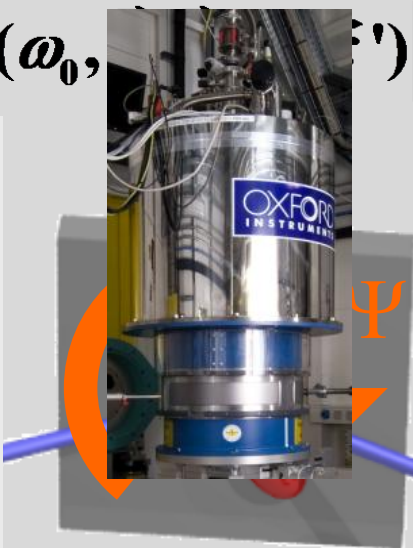
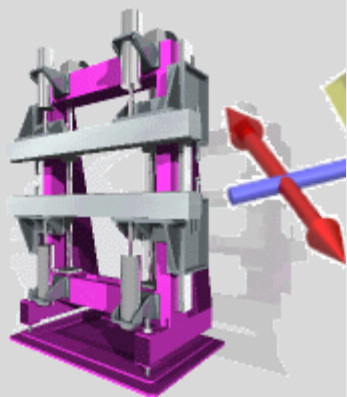
REXS experiments: measurement strategies



$$I_{RXS} \propto |f(\omega_0, \psi)|^2$$

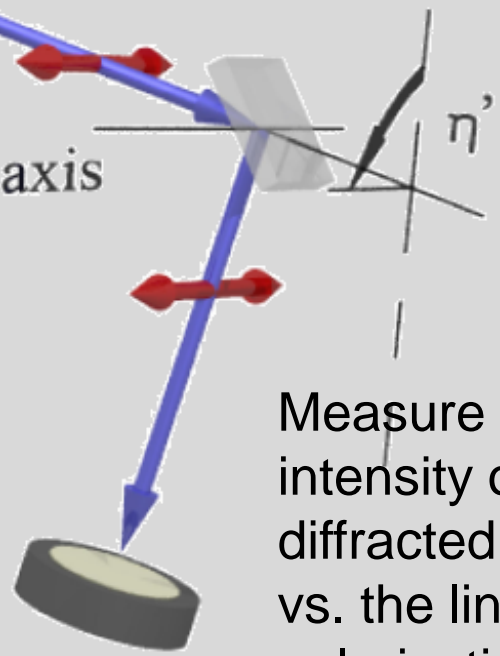
CM et al.
PRB 76 (2007) 195118
V. Scagnoli, CM et al.
JSR 16 (2009) 778

1' Change the polarisation of the incident beam



1 Azimuth variation θ_{PA} axis

Polarization analyser crystal



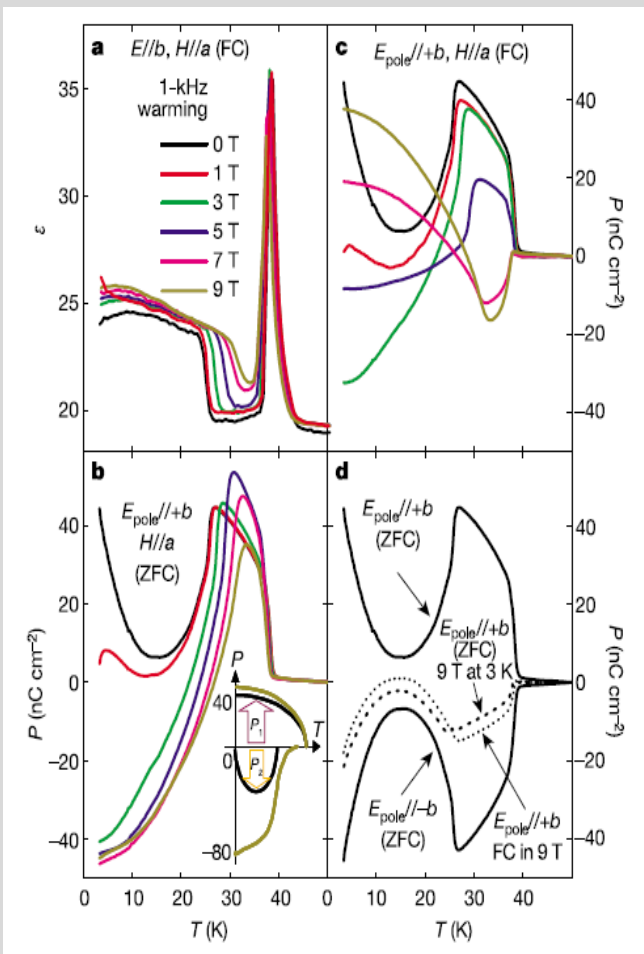
2 Measure the intensity of the diffracted beam vs. the linear polarization dir.

Azi-scan (ψ) or pol-scan (η):
"complementary" information

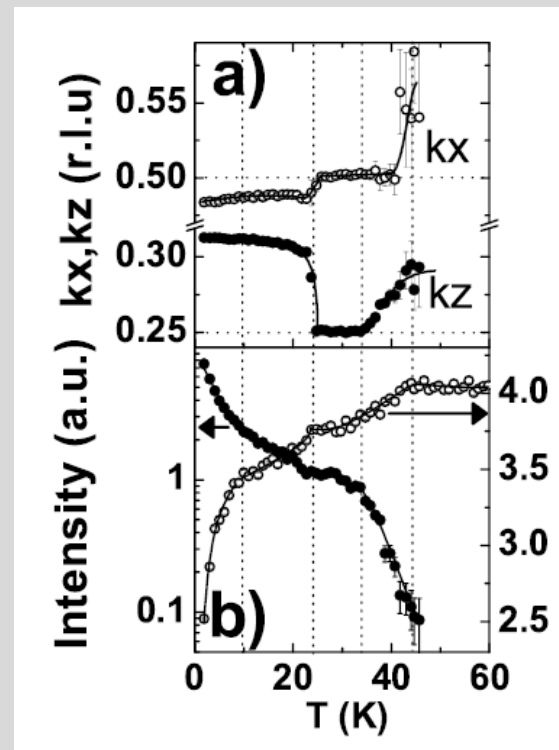
Detector

2

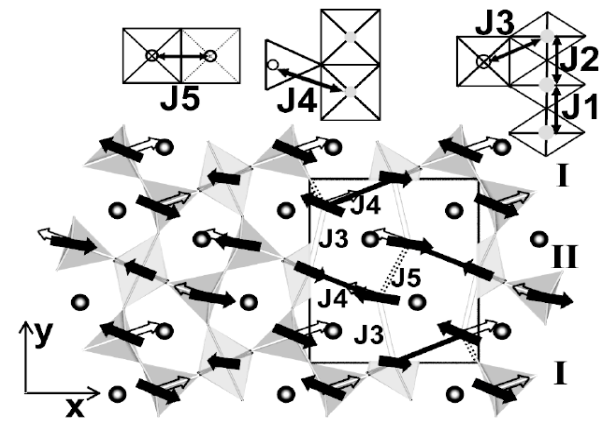
TbMn₂O₅: ME is spin mediated



N. Hur et al.
Nature 429 (2004) 392



L.C. Chapon et al.
PRL 93 (2004) 177402
G.R. Blake et al.
PRB 71 (2005) 214402



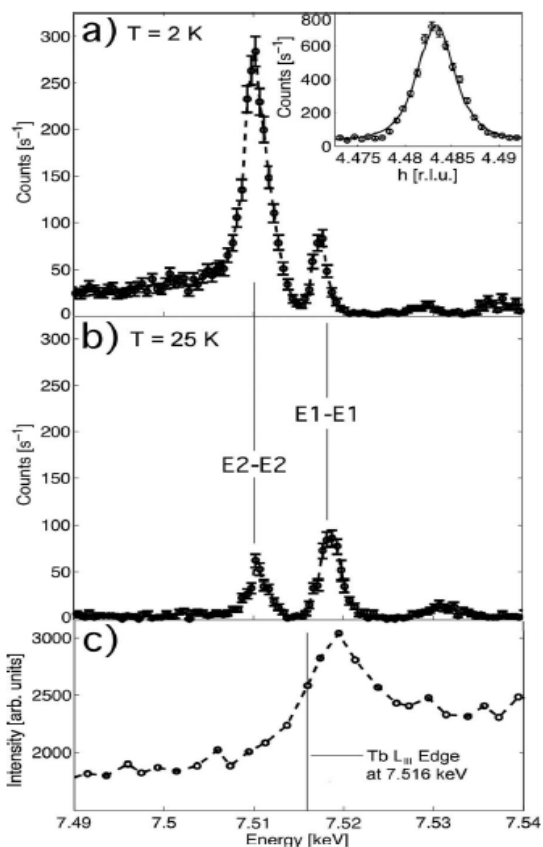
CM structure

In TbMn₂O₅
Mn **collinear magnetic structure**
breaks the inversion symmetry!

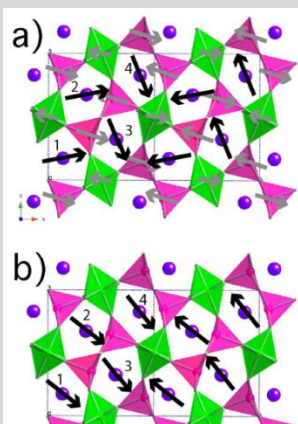
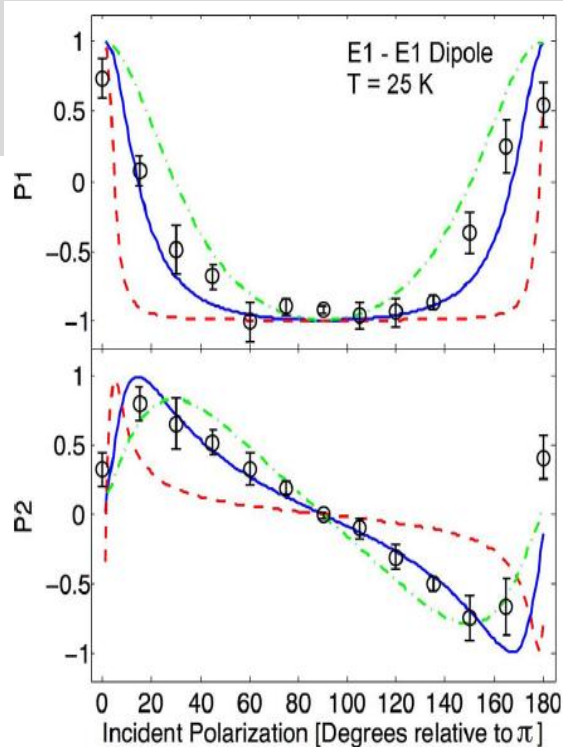


Tb spins in TbMn_2O_5

At Tb L3-edge

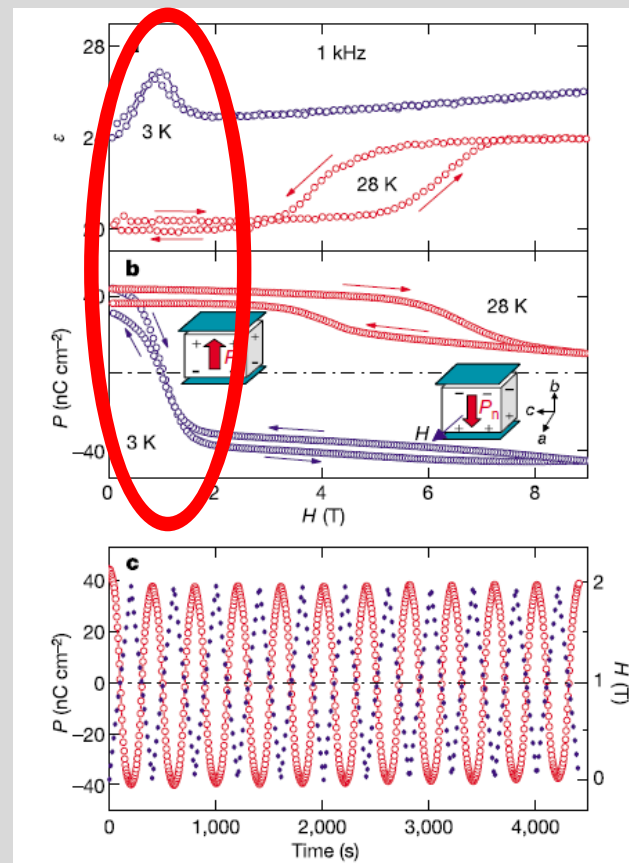


R.D. Johnson, CM et al.
PRB 78 (2008) 104407



CM

ICM

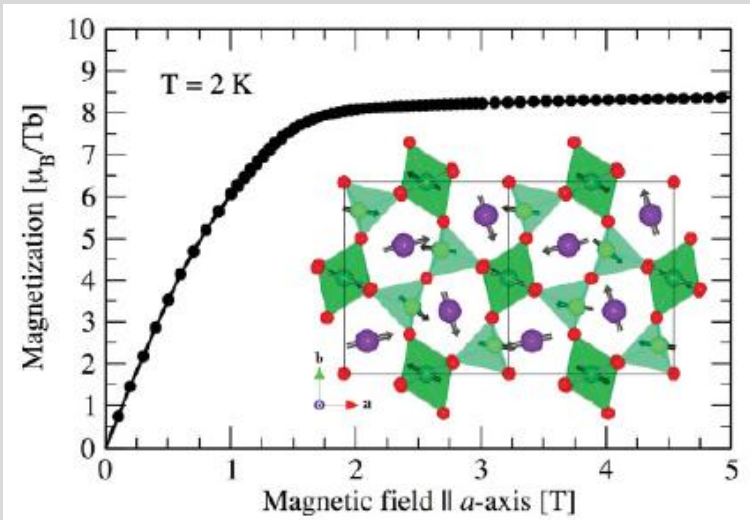


P reversed by H in ICM

Tb spins are **not**
collinear to Mn ones

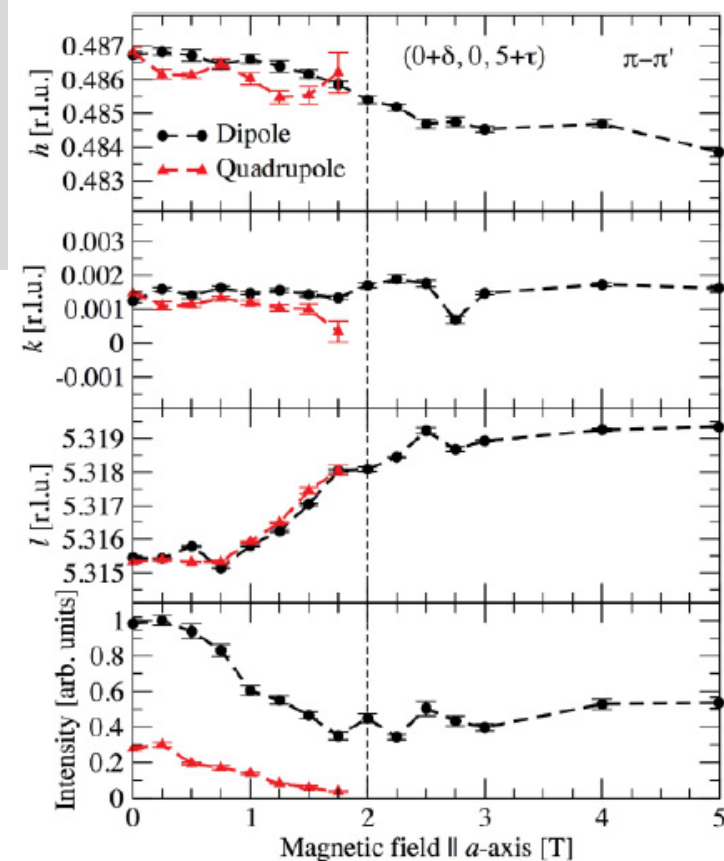
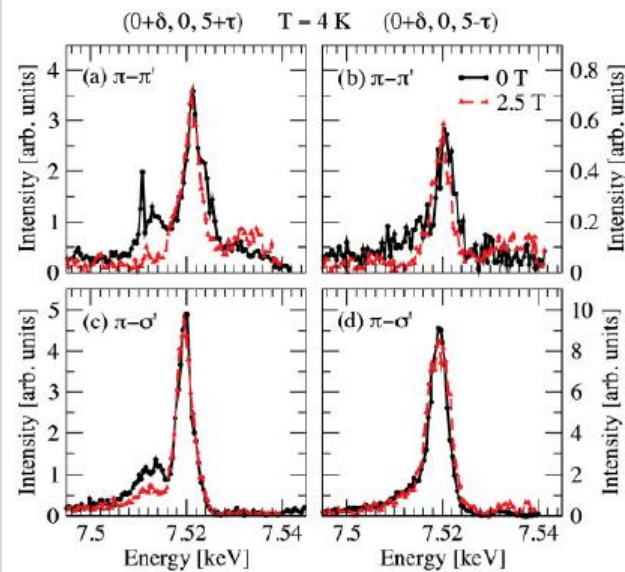


Tb spins role in TbMn_2O_5



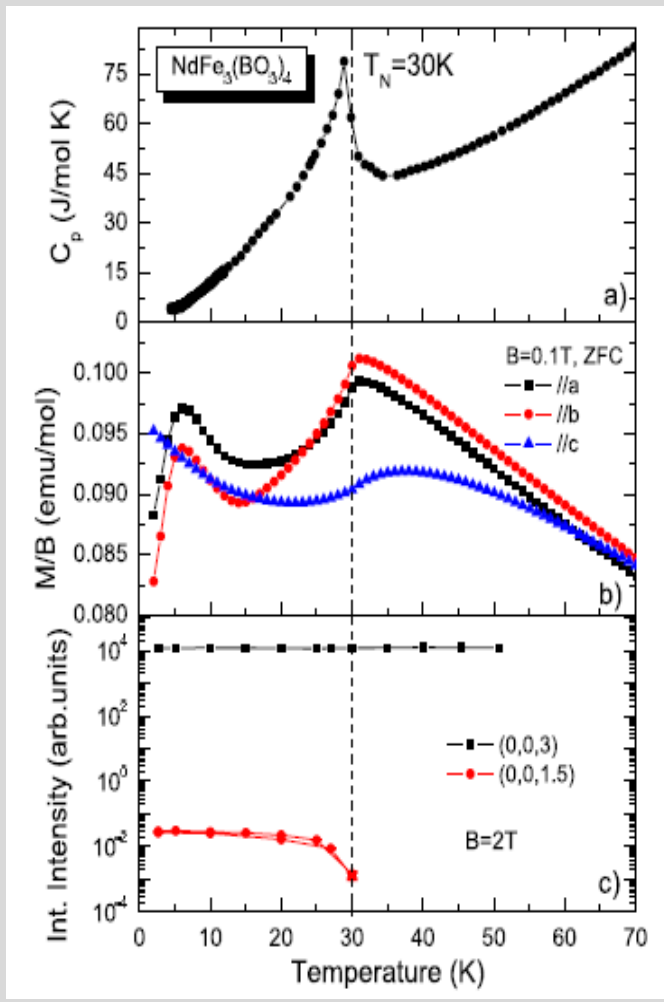
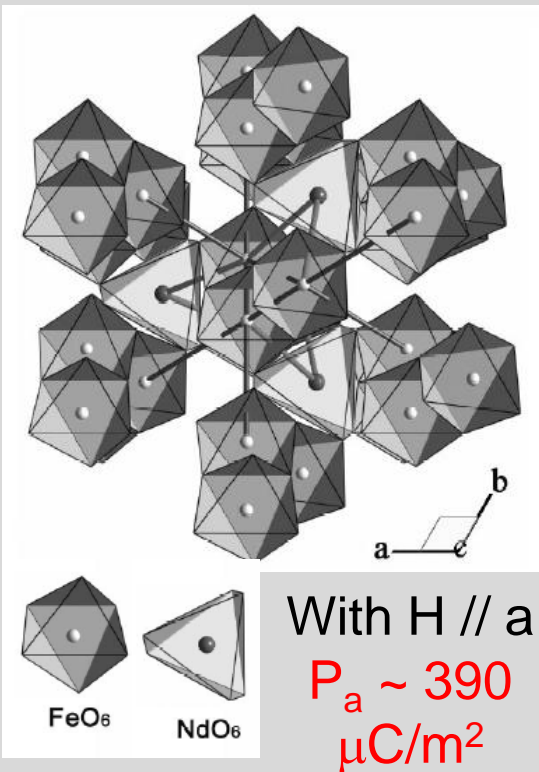
Tb spins
are actors
of the P
reversal,
not just
spectators

R.D. Johnson, CM et al.
PRB 83 (2011) 054438



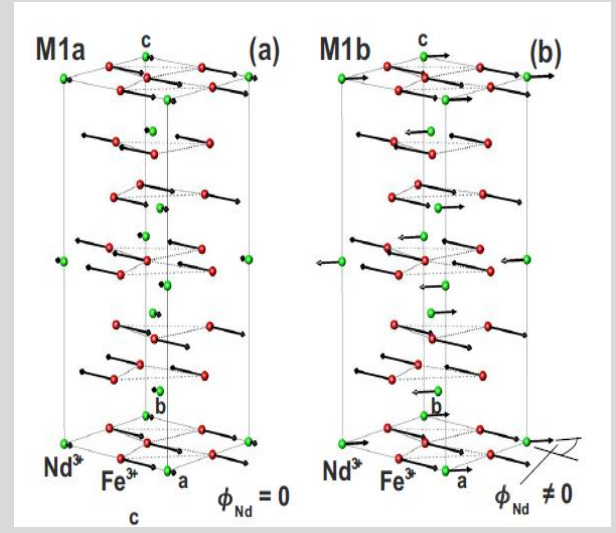
NdFe₃(BO₃)₄: which mechanism?

At RT: R32, although
 no inversion symmetry
 SG is non-polar so
 no net **P** allowed
 by the structure!



J.E. Hamann-Borrero et al.
 PRB 82 (2007) 094411

M. Janoschek et al.,
 PRB 81 (2010) 094429



$$q = [0 \ 0 \ 3/2 + \delta]$$

$$e_{ij} \parallel c^*$$

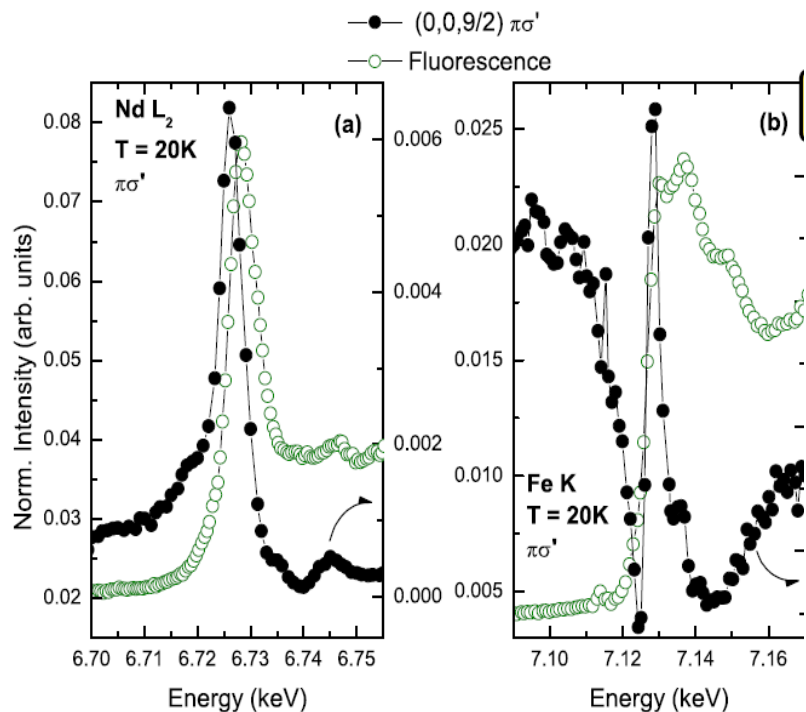
$$\mathbf{P} = \mathbf{e} \times \mathbf{q} = 0!$$



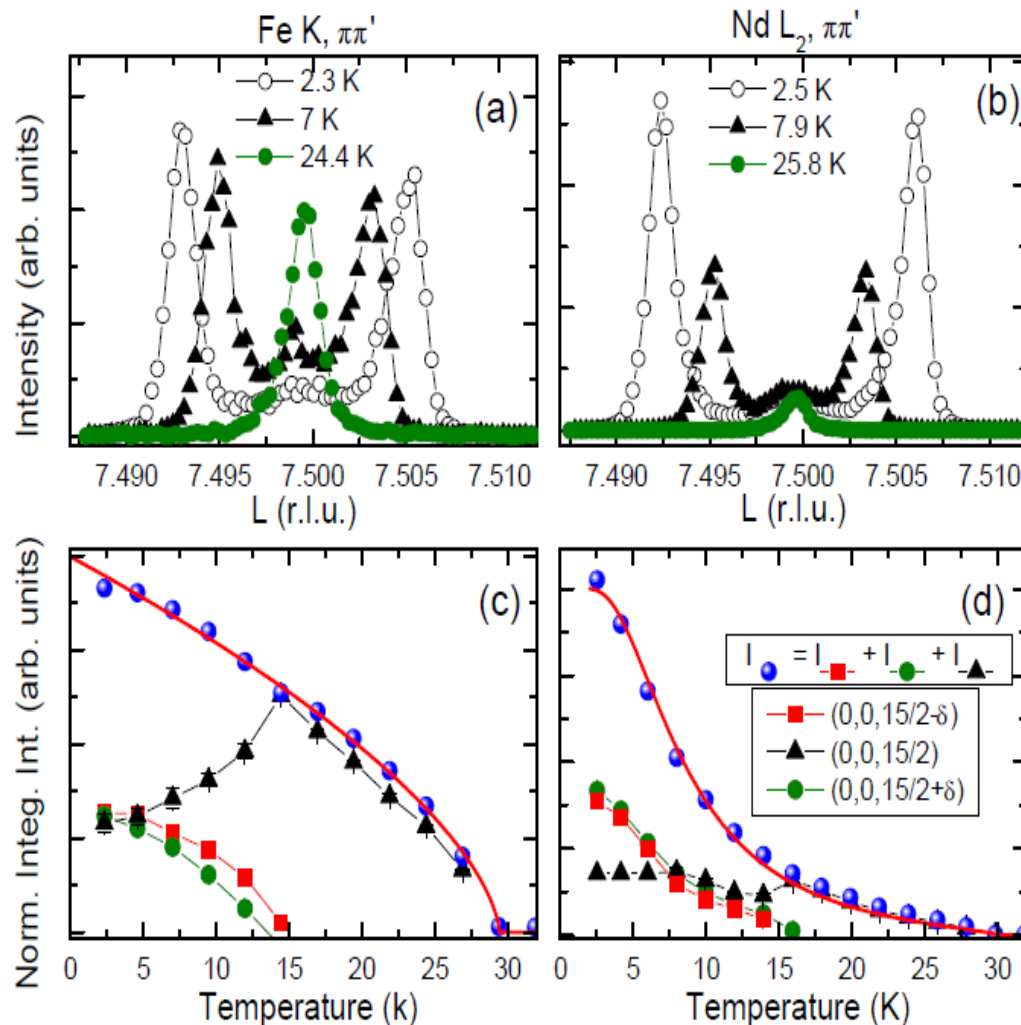
NdFe₃(BO₃)₄: incommensurate magnetism



At Nd L₂-edge
and Fe K-edge

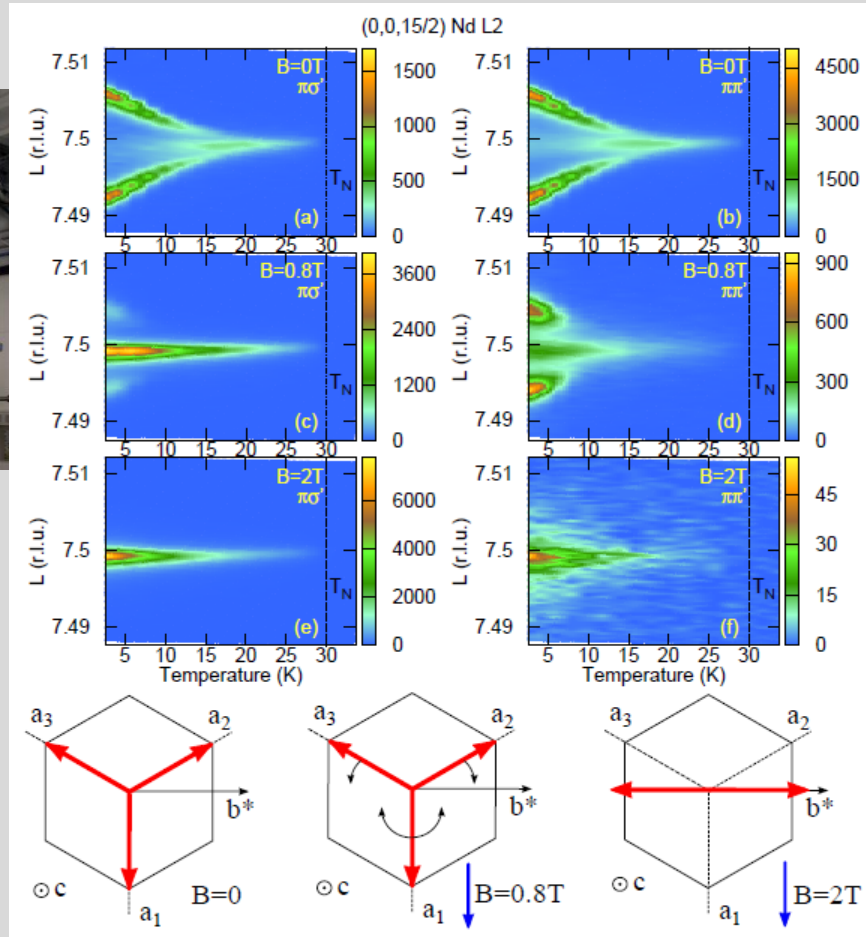
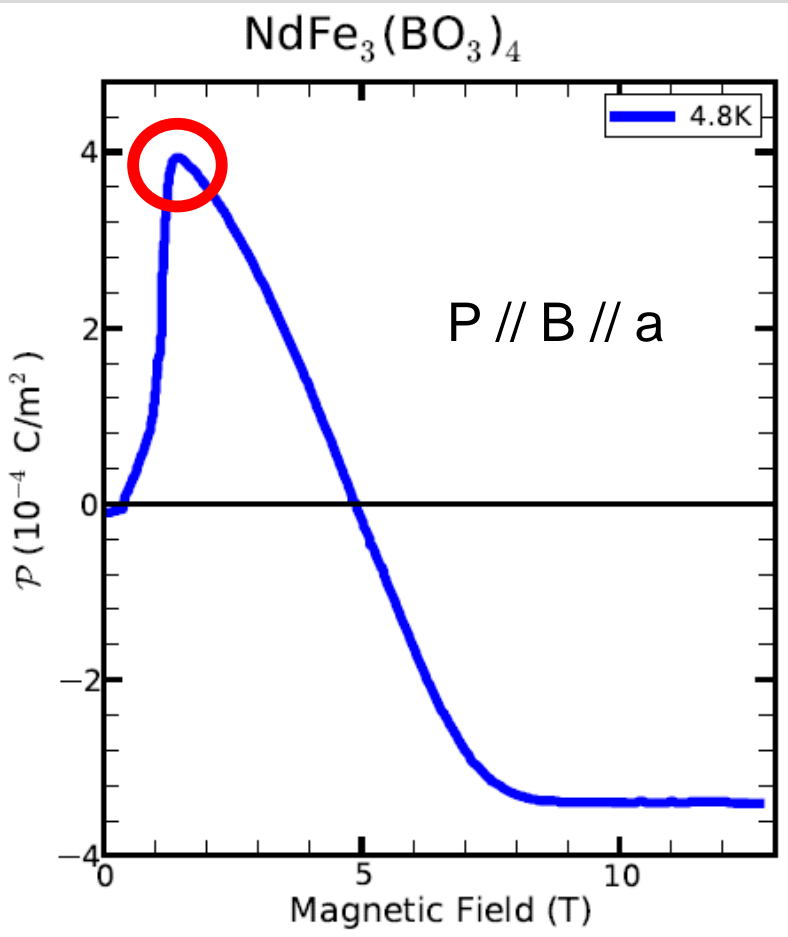


Nd magnetism
induced by Fe





NdFe₃(BO₃)₄: REXS in magnetic field



J.E. Hamann-Borrero, SP, CM et al. submitted to PRL

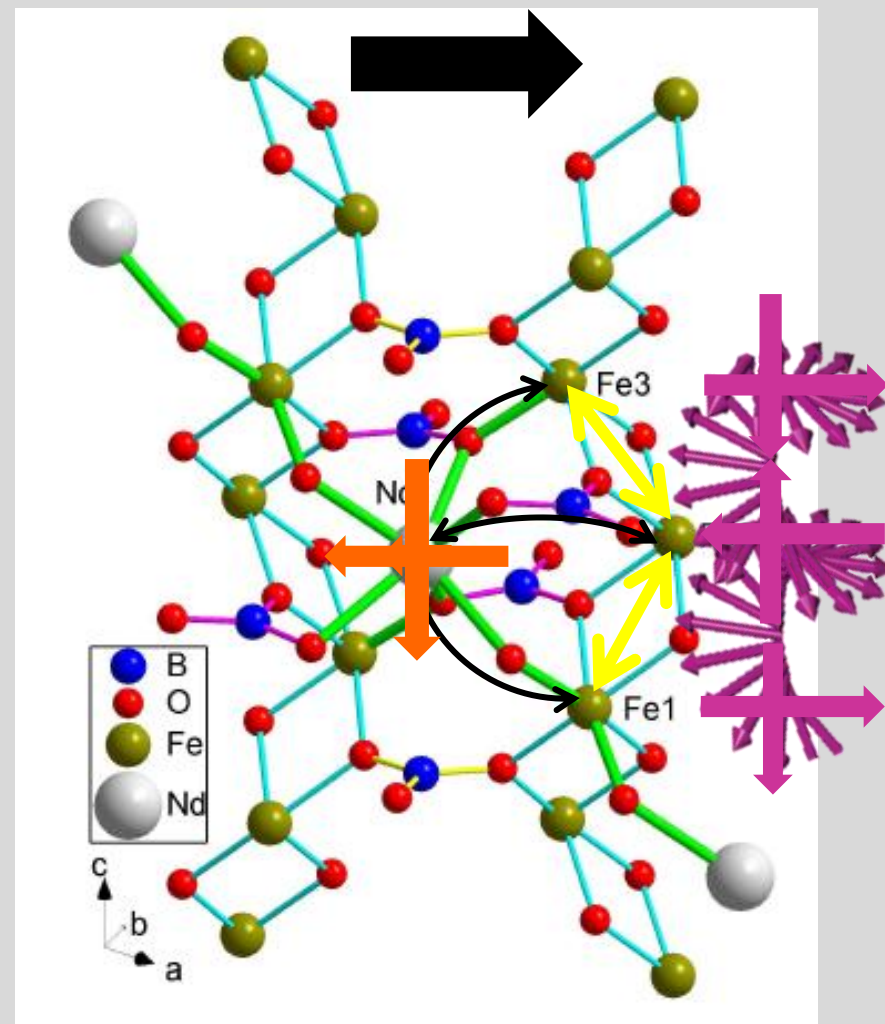
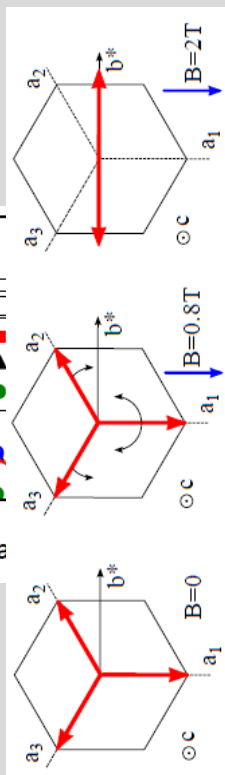
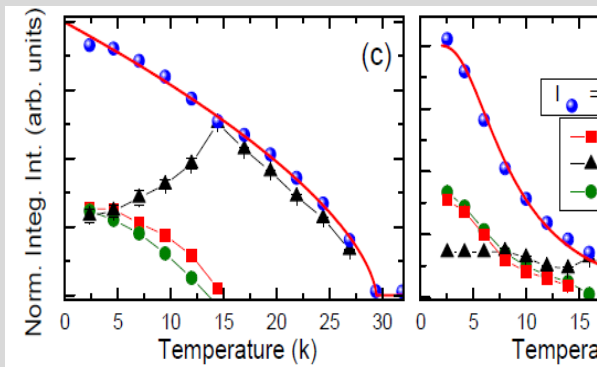
The **polarization** exists in the **CM** structure!



NdFe₃(BO₃)₄: magnetic frustration role



Magnetic frustration
alternative to
Ferroelectric phase



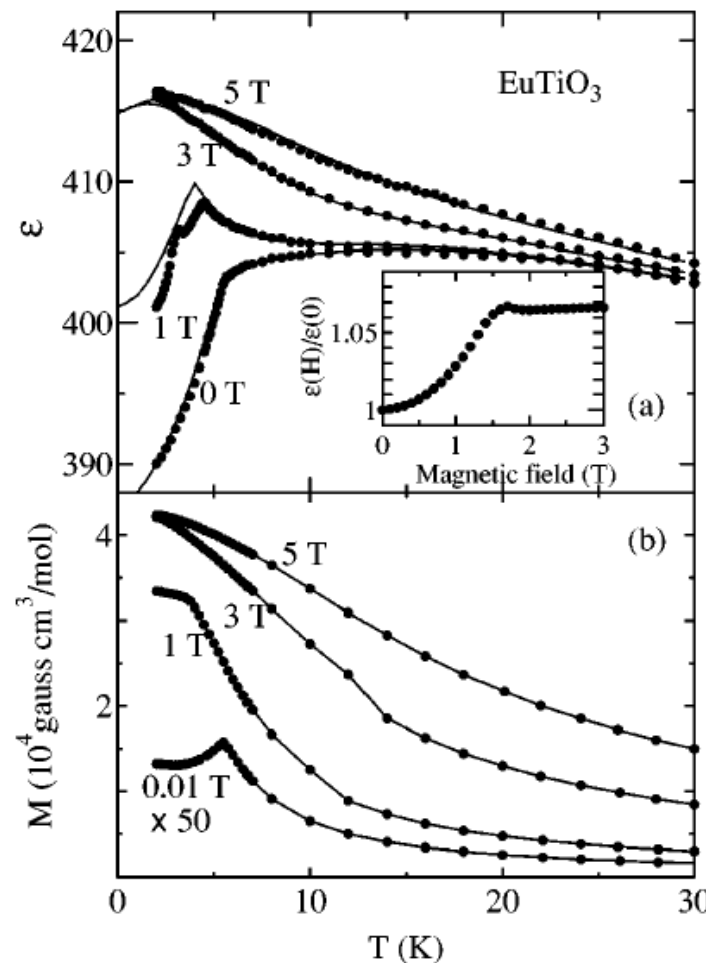
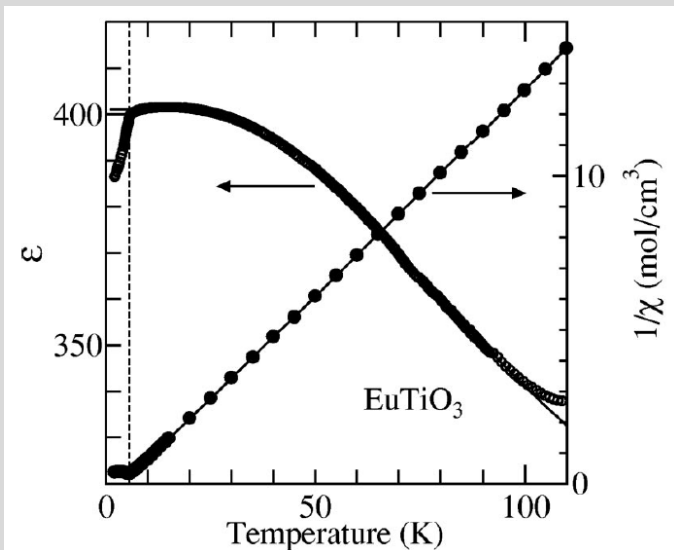


EuTiO₃: a peculiar ME

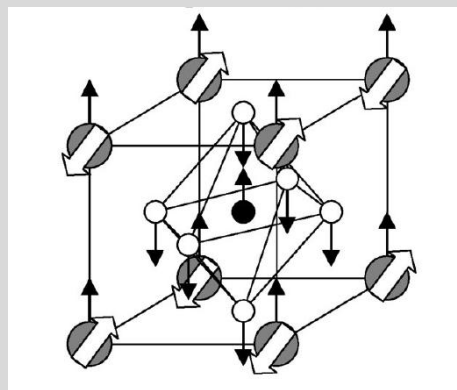


T. Katsufuji and H. Takagi
PRB 64 (2001) 054415

Quantum-
paraelectric
with
ME coupling



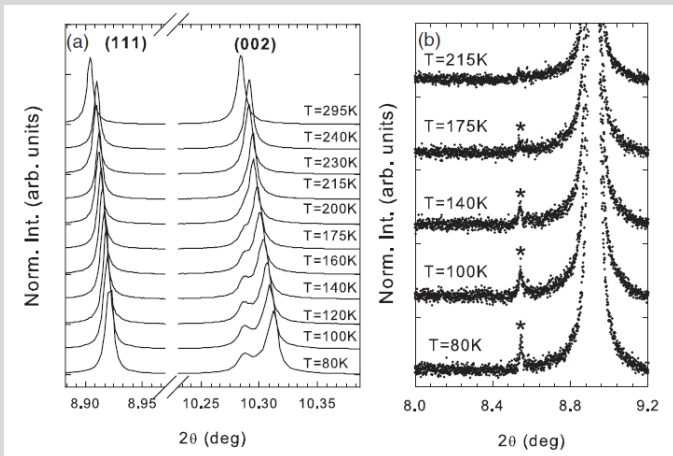
G-type
AFM
structure



T. R. McGuire et al.
JAP 37 (1966) 981

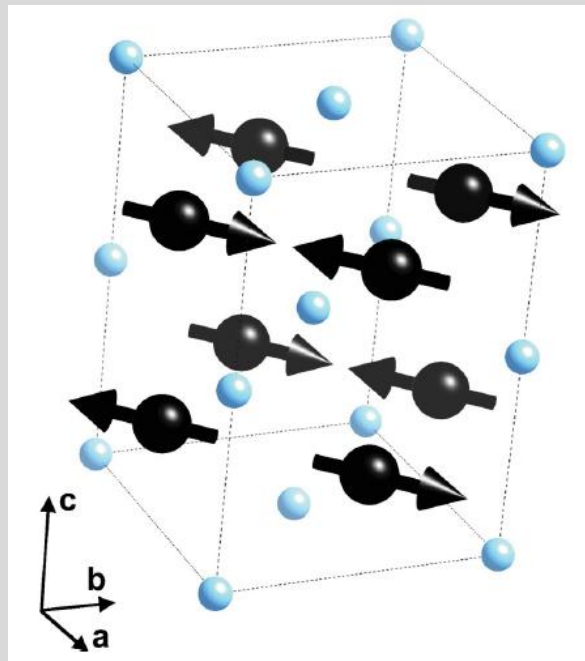
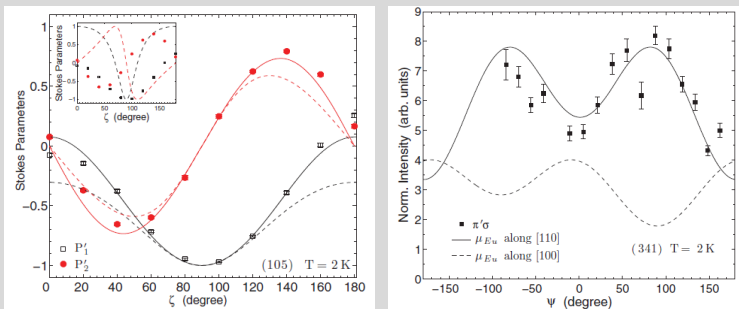
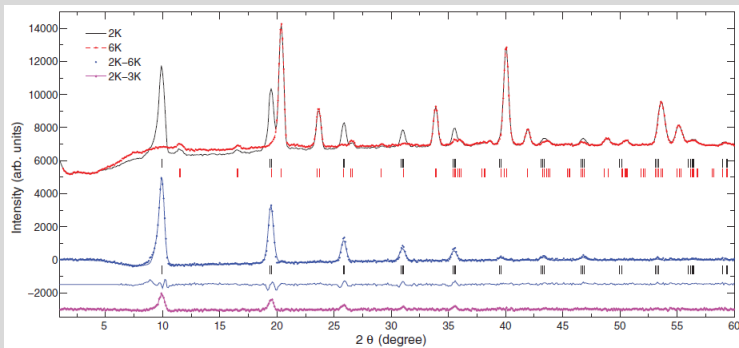
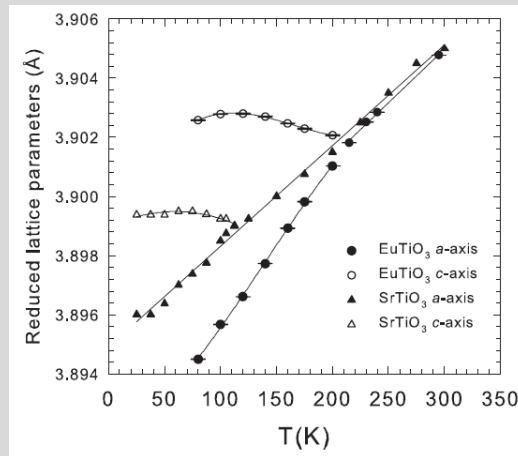


EuTiO₃: structures



Structural
phase transition
Pm-3m → I4/mcm
XPD at ~235K

M. Allieta et al.
PRB 85 (2012) 184107



Magnetic
Structure

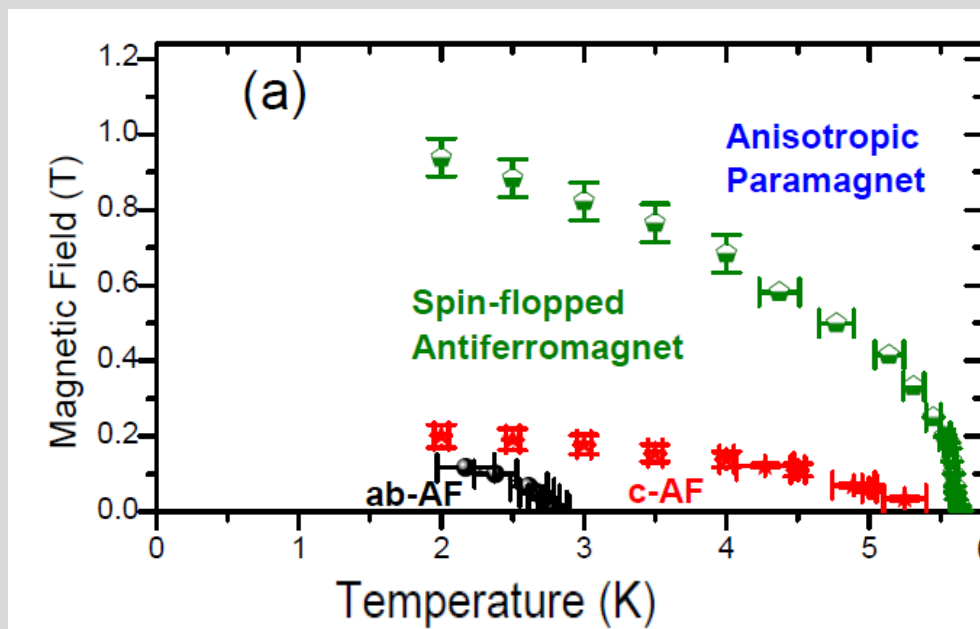
$$\Gamma_9$$

$$\mu // (110)$$

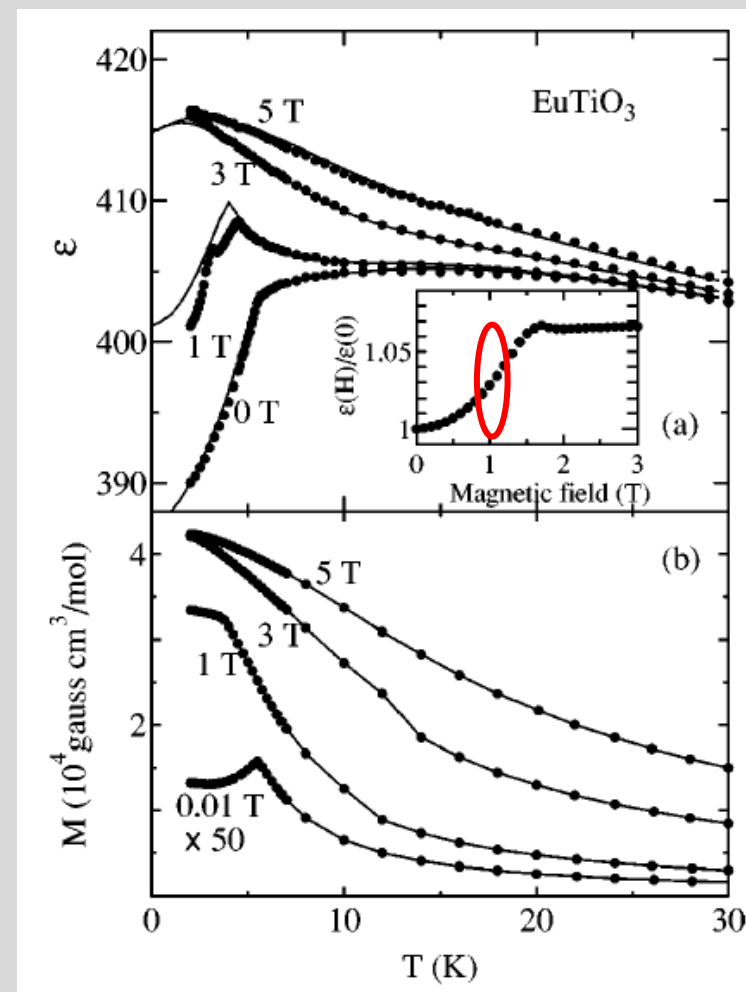
V. Scagnoli et al.
PRB 86 (2012)
094432



Complex magnetic phase diagram expected...
relation with the measured ME effect?

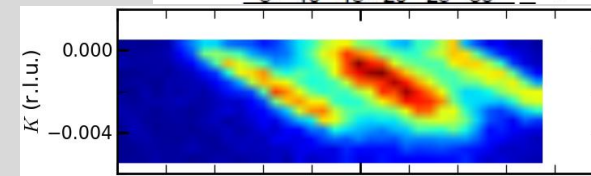
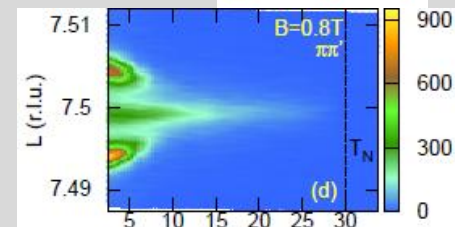
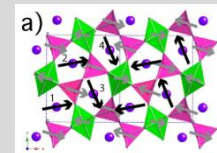


A. P. Petrovic et al.
arXiv:1204.0150





- By Resonant Elastic X-Ray Scattering (diffraction) access to important degrees of freedom is achievable (demanding data analysis)
- Key information on magnetic exchange paths, magnetoelectric and other electronic coupling mechanisms is possible (provided that a suitable ionic probe is present in the material, placed in a convenient position with respect to local symmetry elements...)
- Investigation in demanding sample environments to be performed via modern techniques (pol-scan)
- Attention should be put to the role of induced magnetism on Rare Earth ions for ME materials properties!





Acknowledgements



- ex-ID20 beamline team (F. de Bergevin, J. Herrero, B. Detlefs, F. Fabrizi, F. Yakhou, L. Paolasini)
ESRF, Grenoble, F
- S. Di Matteo
Univ. de Rennes1, Rennes, F
- Y. Joly
Inst. Néel, CNRS, Grenoble, F
- C. Detlefs
ID06, ESRF, Grenoble, F
- P. Thompson and L. Bouchenoire
XMAS, UK-CRG, ESRF, Grenoble, F
- R. Caciuffo
ITU, Karlsruhe, D
- S. Wilkins
BNL, Upton, NY, USA
- I16 beamline team (A. Bombardi, C. Vecchini, S. Collins)
Diamond, Chilton, UK