X-ray scattering techniques to explore in-situ properties of multiferroic materials

Prof. Peter D. Hatton

Department of Physics, Durham University

Acknowledgements

- Co-authors (who did most of the work)
- Roger Johnson (PhD student) Durham
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- Dr. Thomas Beale (Research associate) Durham
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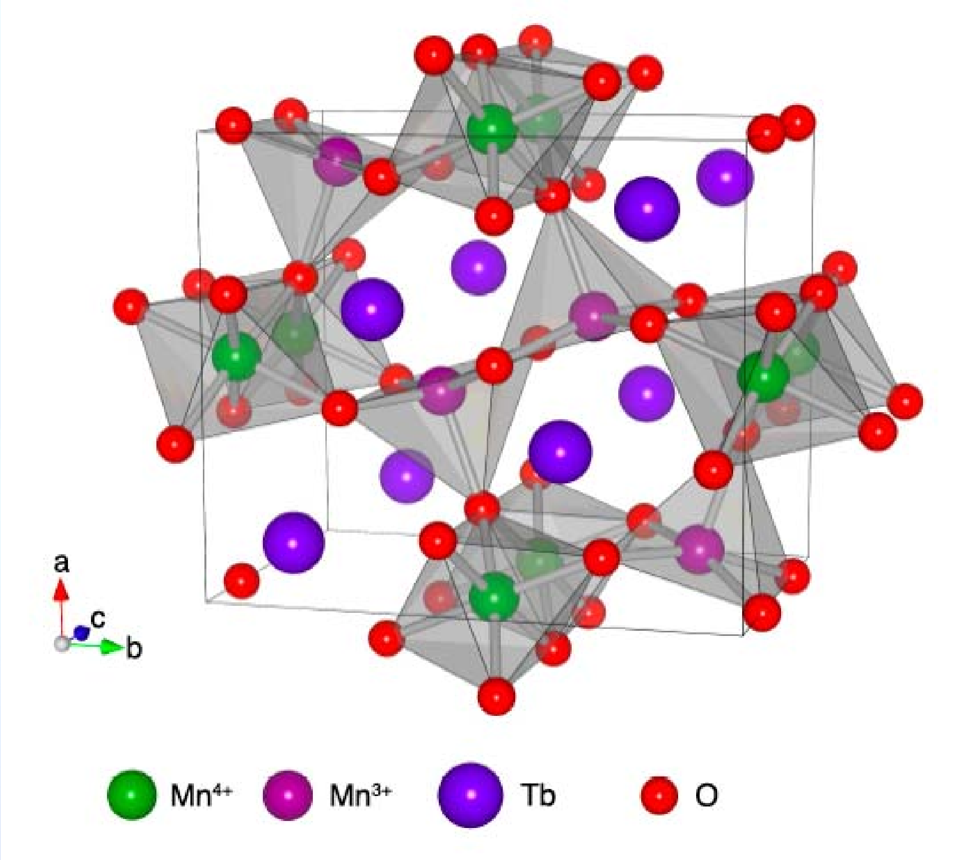
$TbMn_2O_5$ crystal structure

- Adopts a low symmetry orthorhombic unit cell with both octahedral $Mn^{4+}O_6$ and square pyramidal $Mn^{3+}O_5$ units linked via oxygen atoms.



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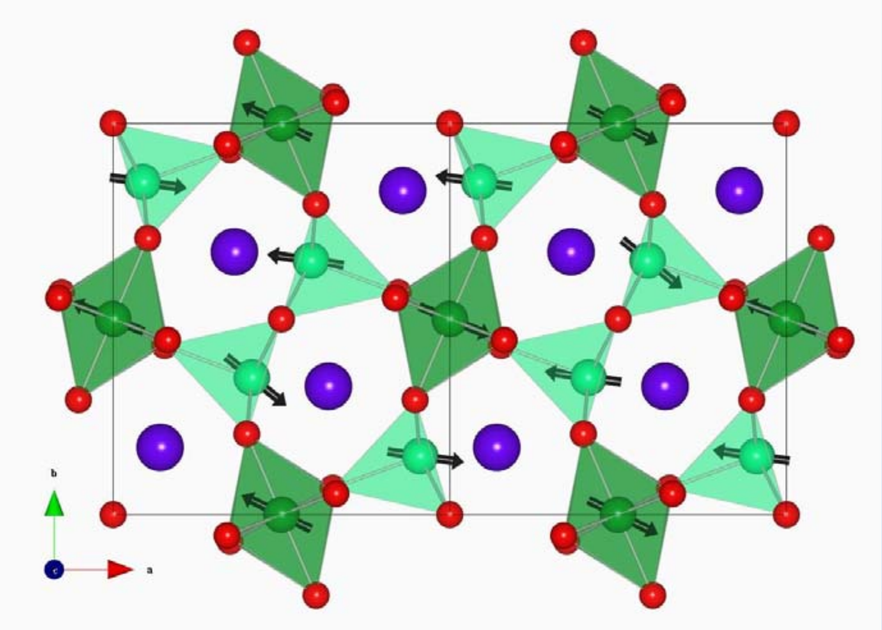
$TbMn_2O_5$ magnetic structure

$TbMn_2O_5$ is a famous magnetoelectric multiferroic. It displays complete reversal of electric polarization at 2 Tesla.

Below T_N (43 K) it forms an incommensurate antiferromagnetic structure (ICM2).

Ferroelectric order observed at 38 K where system becomes commensurate (CM).

Below 24 K become incommensurate again (ICM1). The Mn magnetic structure polarizes the Tb ions.



Commensurate low temperature Mn magnetic structure containing both Mn^{3+} (light green) and Mn^{4+} (dark green) ions.

G.R. Blake *et al.*, Phys. Rev. B **71** 214402 (2005)

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Why use X-rays to study multiferroics?

- Multiferroics often display low symmetry complex crystal structures with multiple order parameters.
- Low temperature phase transitions often involve subtle crystallographic effects, magnetic structures, incommensurate structures etc.
- X-rays are normally not very sensitive to magnetic structure, but can be made to be, by using resonances at atomic edges.
- Resonant x-ray scattering is an atomic selective, band specific technique well suited to complex structures.

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The need for synchrotron radiation

- But scattering is really WEAK from magnetic ordering!
- Typically 10^{-8} weaker than typical charge scattering.
- Use a tuneable high intensity, polarized synchrotron source.
- Resonantly enhance scattering from the electrons to see spin ordering by tuning to an atomic resonance.

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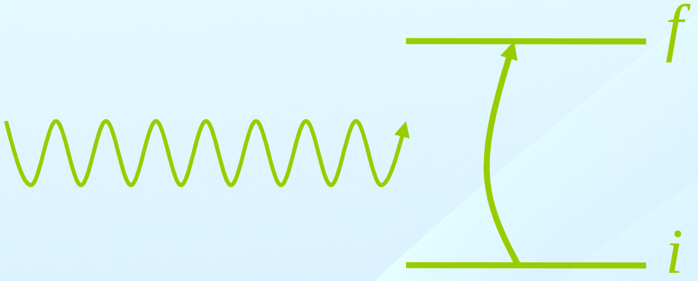
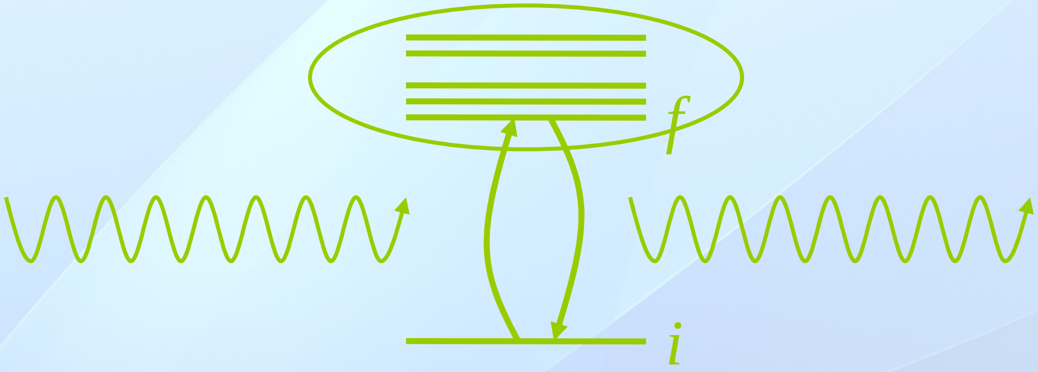
Resonant polarized x-ray magnetic scattering

- Absorption



- Scattering



- Cross-section

$$I_{\mathrm{DIPOLE}} = \left| F_0\left(\varepsilon' \cdot \varepsilon\right) + F_1\left(\varepsilon' \times \varepsilon\right) \cdot \mathbf{z} + F_2\left(\varepsilon' \cdot T \cdot \varepsilon\right) \right|^2$$

Polarization

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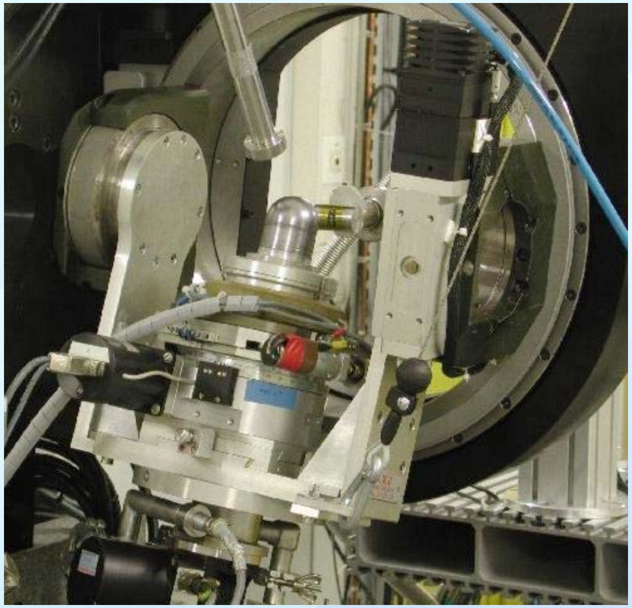
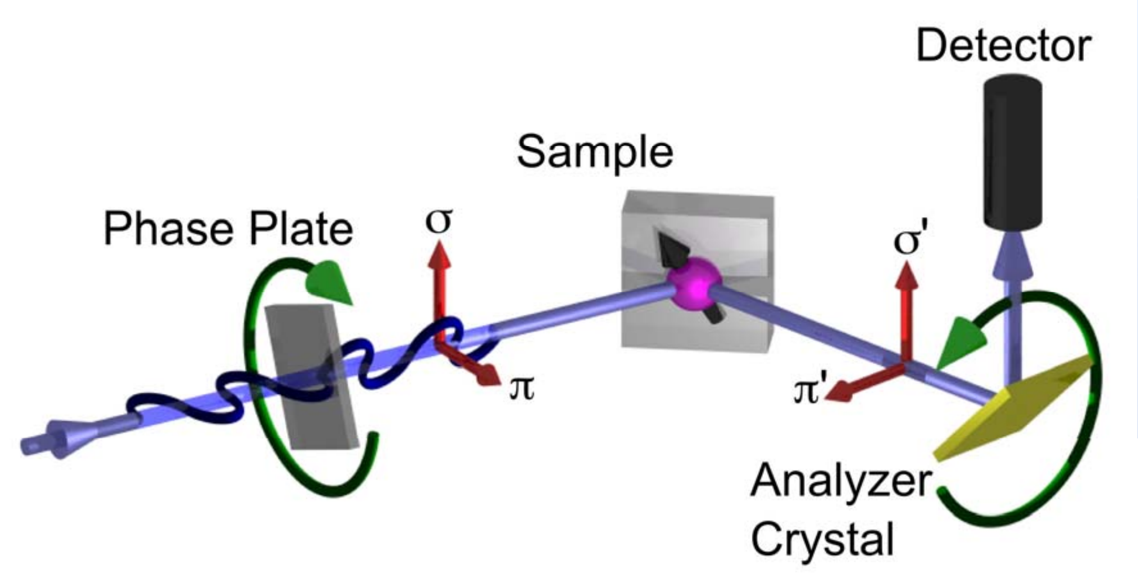
Experimental

Use a polarized undulator x-ray source (ESRF) tuned to the Tb L3 edge and a multi-axis diffractometer.

Employ a diamond phase plate to control incoming polarization and a polarization analyzer to detect scattered radiation.





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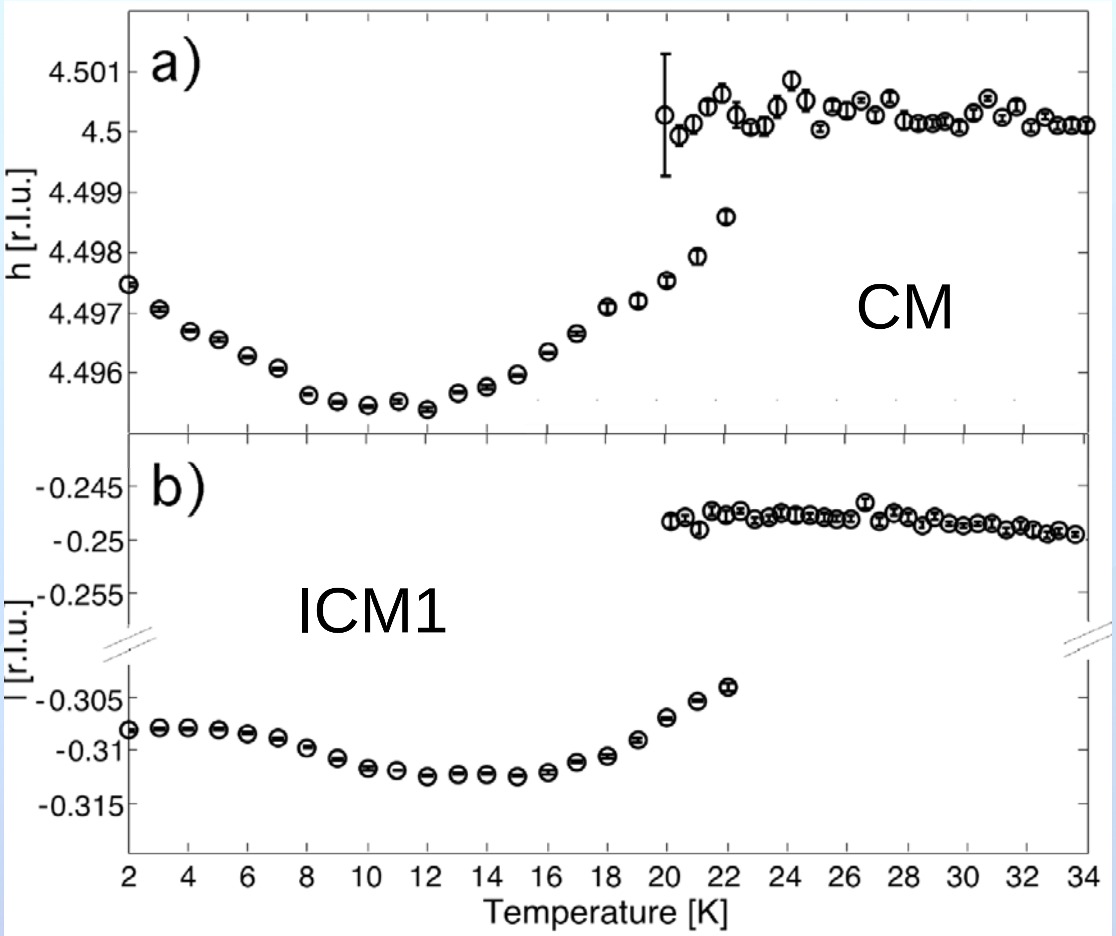
Commensurate - incommensurate transition

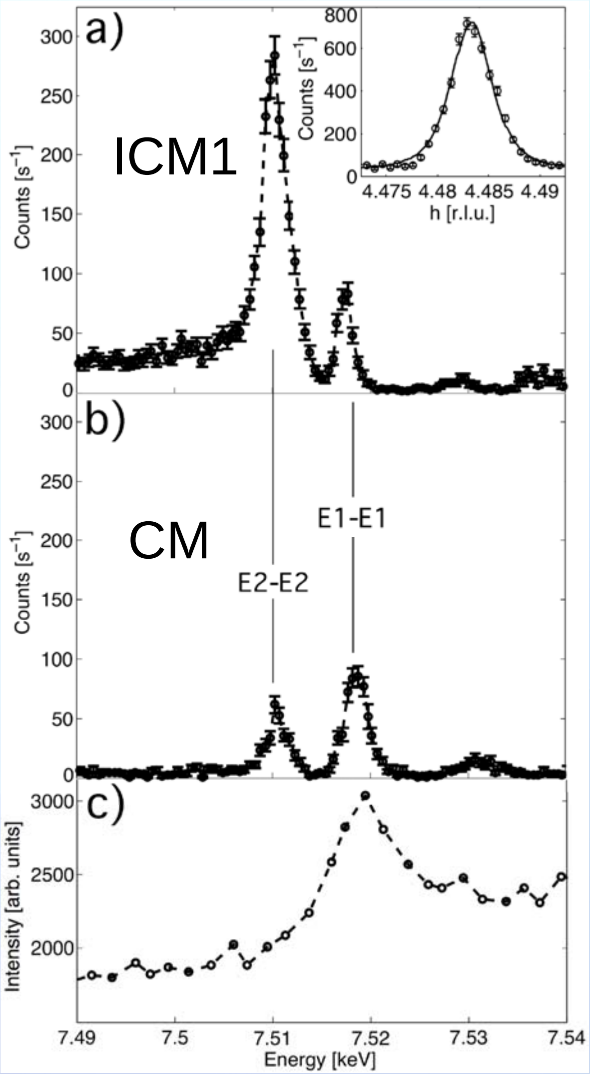
Measuring the magnetic satellite peak position clearly displays the 1st order phase transition from the commensurate (CM) phase to the low temperature incommensurate (ICM1) phase.

The (4+δ, 4, 0-τ) satellite moves from δ = 0.5 and τ = 0.25 to irrational values below the transition.



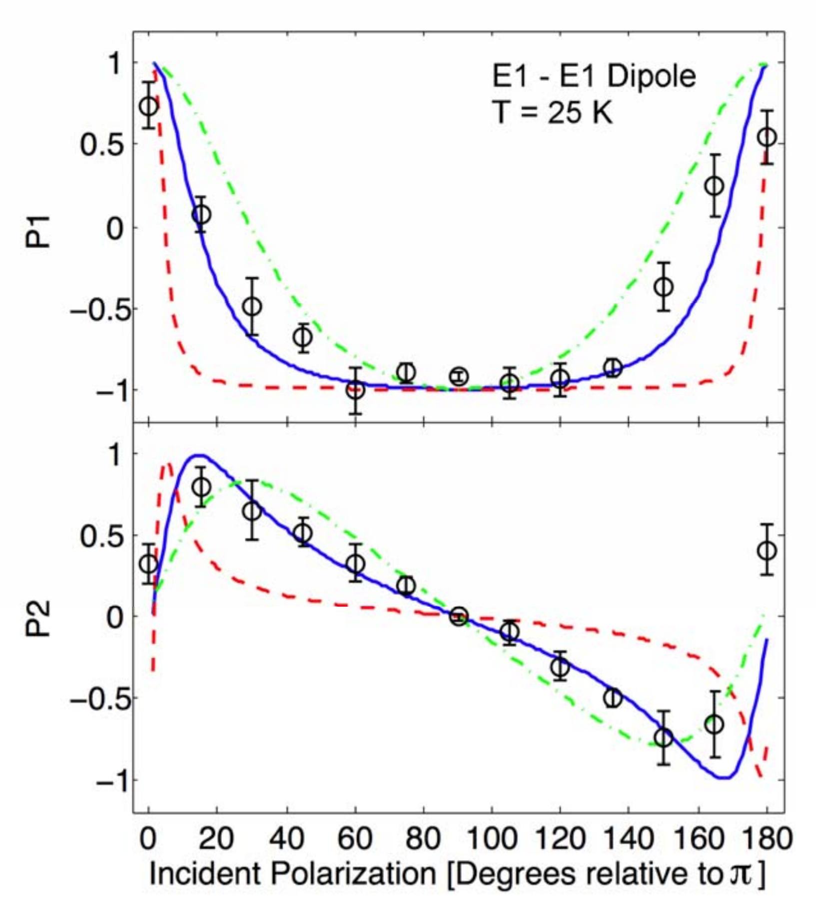
Resonances in the energy scans

- At the Tb L3 edge the empty 5d band, polarised by the Mn magnetism, is probed by a 2p→5d dipole transition. The 4f band (unpaired electrons) is probed by the 2p→4f quadrupole transition.
- At 2 K (ICM1) 1st satellite around (440) Bragg found at (4.48, 4, 0.32) in rotated π-channel, expected for a magnetic signal.
- Scan of energy at constant wavevector displays 2 excitations, a quadrupole transition just below the edge and a dipole transition at the edge.
- Similar resonances found at 25 K in the commensurate CM phase (4.5, 4, 0.25).



Fitting the commensurate reflection I Dipole transition

- Full polarization measurements were taken of the dipole transition. We assume that the Tb ions are polarized by the Mn4+ spin density. The Tb 5d band has a large overlap with the Mn 3d band. Using the proposed Mn magnetic lattice we can calculate the expected Poincaré-Stokes parameters.
- $P1 = (I_{\sigma\sigma'}-I_{\sigma\pi'})/(I_{\sigma\sigma'}+I_{\sigma\pi'})$
- $P2 = (I_{+45^{o}{}'} - I_{-45^{o}{}'})/(I+_{45^{o}{}'}+I_{-45^{o}{}'})$
- Fit indeed is much better with Mn4+ ions than with Mn3+ ions.



Mn4+ full blue line

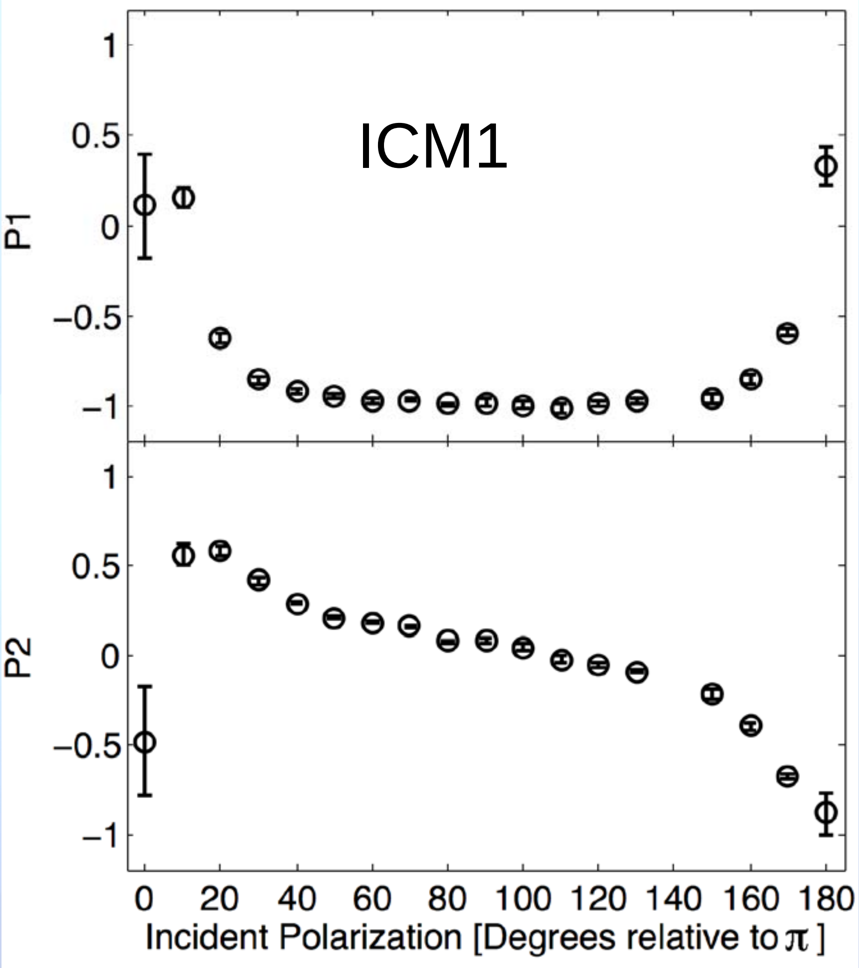
Mn3+ dashed red line

Incommensurate phase
I Dipole resonance

There has been no proposed magnetic model for the low temperature incommensurate phase (ICM1) as yet.

Plot of Poincaré - Stokes parameters display a large change from the CM phase.

Too many parameters for us to fit data. Hoping for neutron data by Chapon et al.



Fitting the Quadrupole transition

- At the Tb L3 edge the empty 5d band, polarised by the Mn magnetism, is probed by a 2p➔5d dipole transition. The 4f band (unpaired electrons) is probed by the 2p➔4f quadrupole transition.
- At 2 K (ICM2) 1st magnetic satellite around (440) Bragg found at (4.48, 4, 0.32) in rotated π-channel.
- Scan of energy at constant wavevector displays 2 excitations, a quadrupole transition just below the edge and a dipole transition at the edge.
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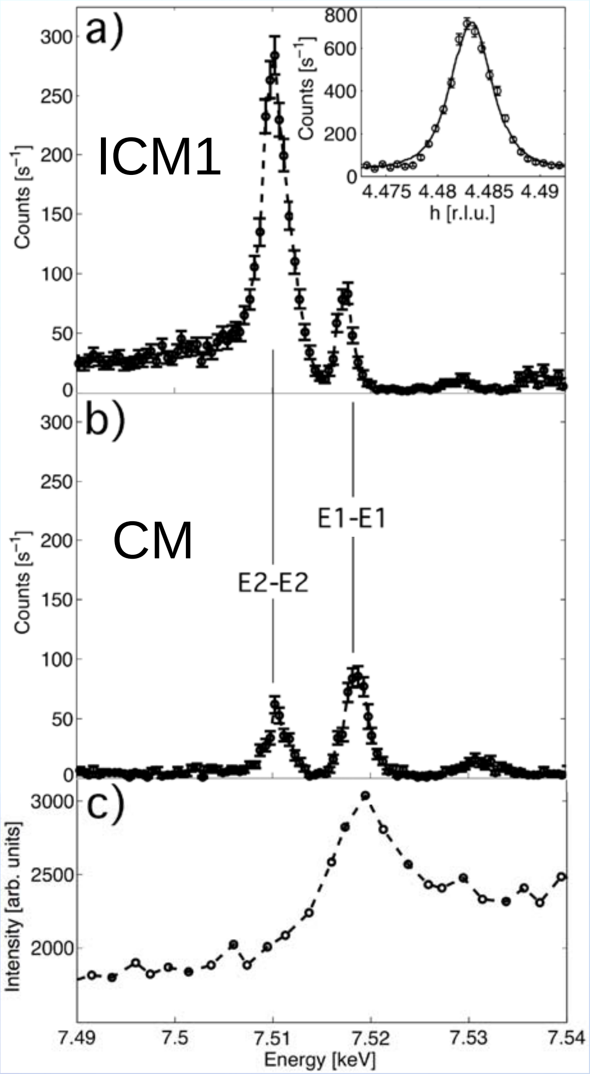
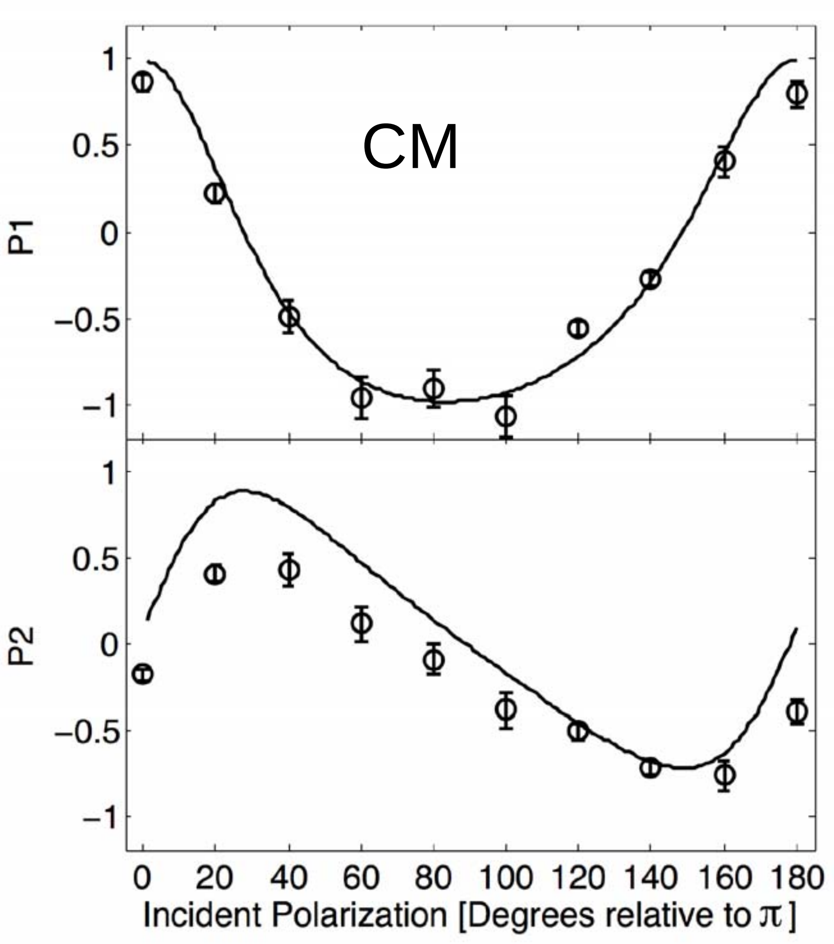


Fitting the quadrupole resonance I commensurate phase

Fitting the Poincaré-Stokes parameters of the quadrupole (E2-E2) transition in the CM proved impossible with the old published magnetic model.

Instead used recent $HoMn_2O_5$ model and refined moment directions to obtain best fit in $TbMn_2O_5$.

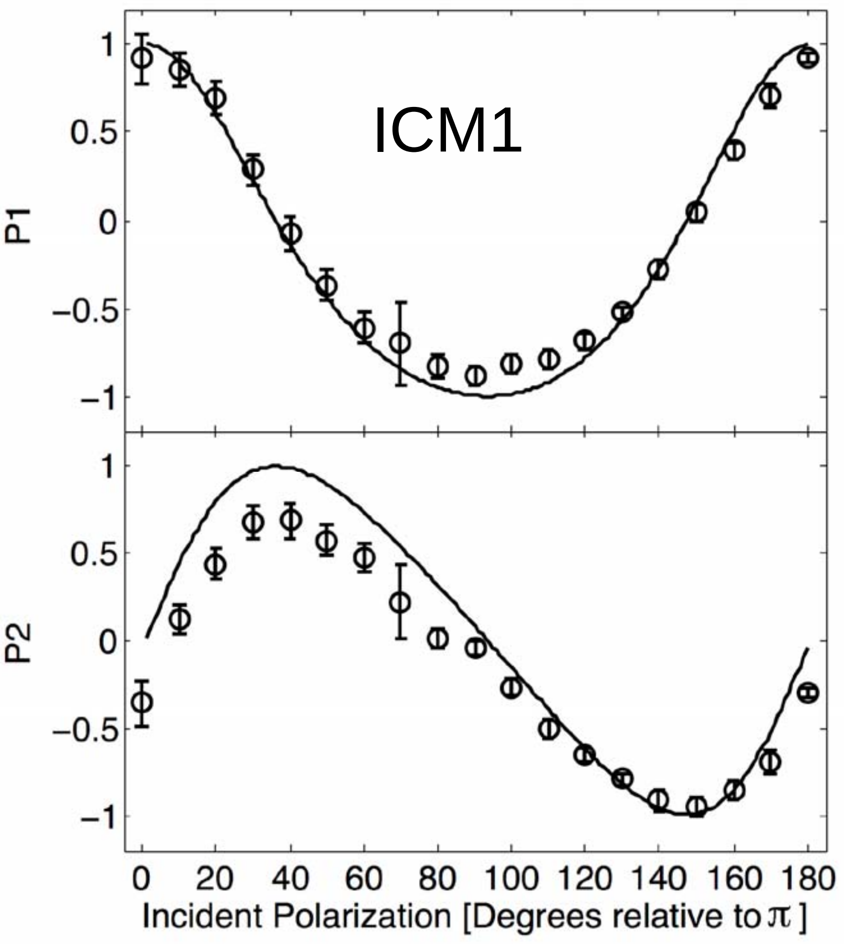
Result: A new refined magnetic structure for $TbMn_2O_5$ in the CM phase.



C. Vecchini *et al.*, Phys. Rev. B **77** 134434 (2008)

Fitting the quadrupole resonance II incommensurate phase

Similarly we can use the $HoMn_2O_5$ magnetic structure and refine the moment directions in the low temperature incommensurate ICM1 phase.



C. Vecchini *et al.*, Phys. Rev. B **77** 134434 (2008)

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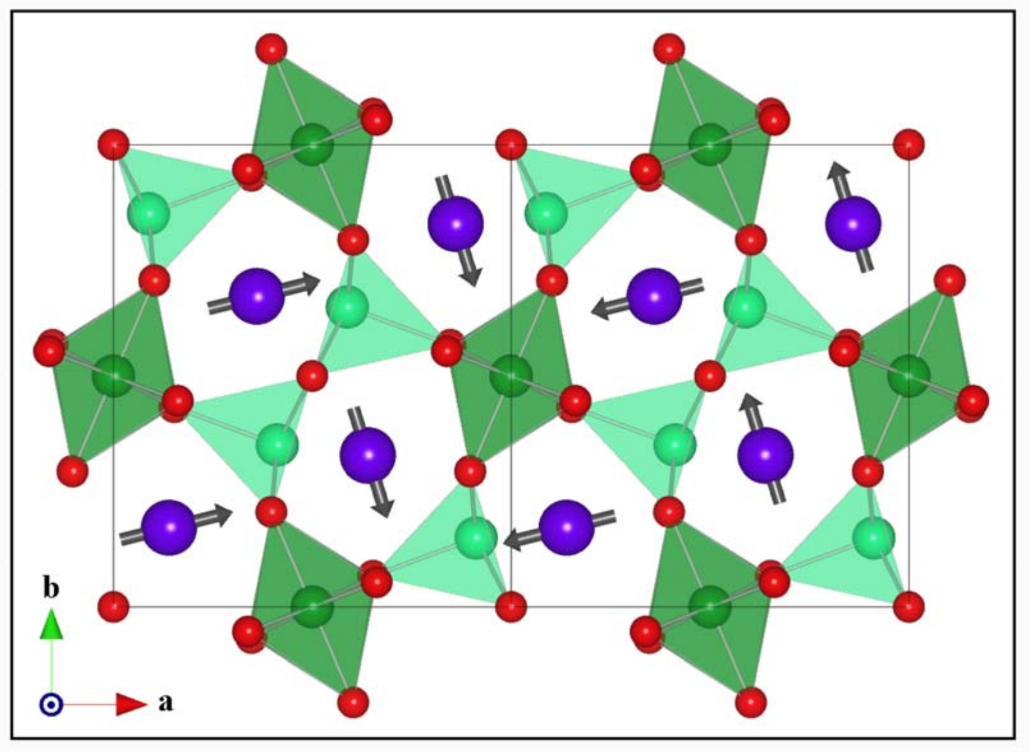
Our model for the terbium ions I Commensurate phase

Refined moment directions:

Tb(1&2) 26.5º±1.5 to the *a* axis in the *ab* plane and 0.8º±0.1 out of plane.

Tb(3&4) 284.4º ±1.9 to the *a* axis in the *ab* plane and 0.7º±0.1 out of plane.



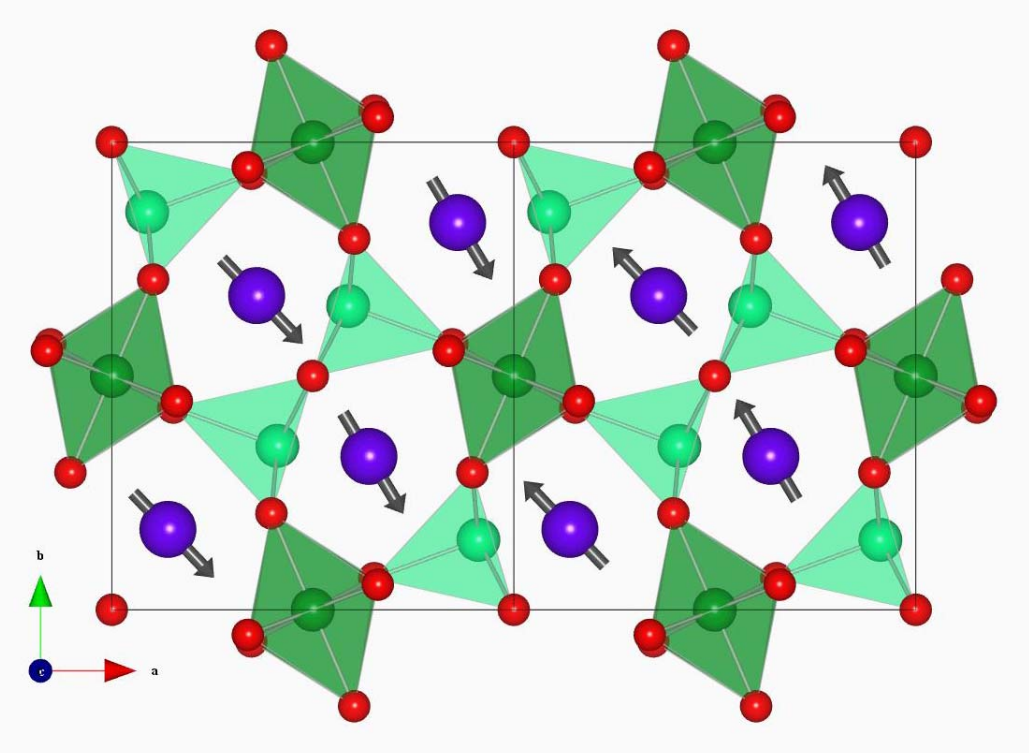
Our model for the terbium ions II Incommensurate phase

Refined moment directions:

Tb (1&2) 7.0º±2.0 to the *a* axis in the *ab* plane and 1.4º±0.1 out of plane.

Tb(3&4) 279.0º ±1.7 to the *a* axis in the *ab* plane and 1.2º±0.1 out of plane.

A rotation of the Tb(1&2) magnetic moments at low temperatures.

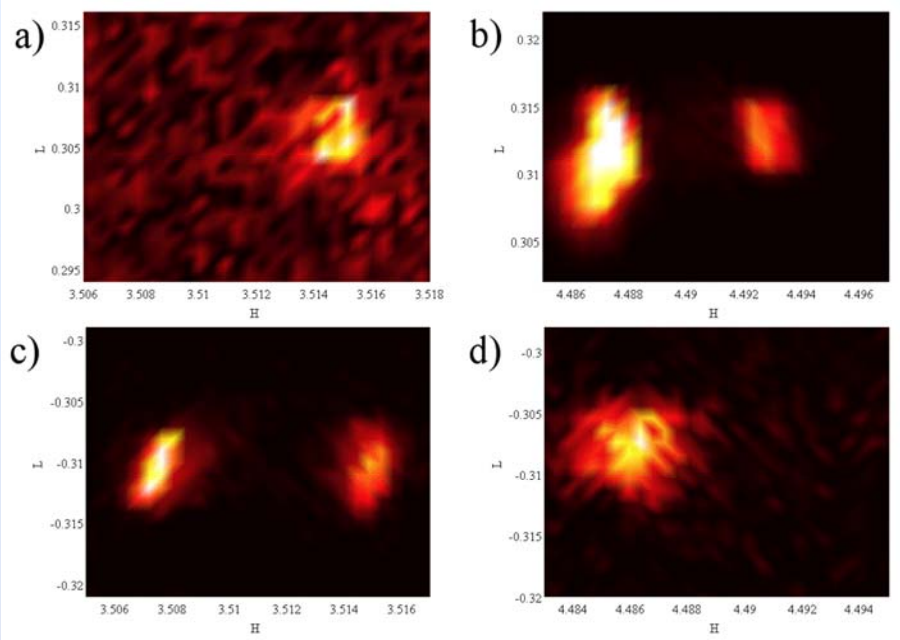


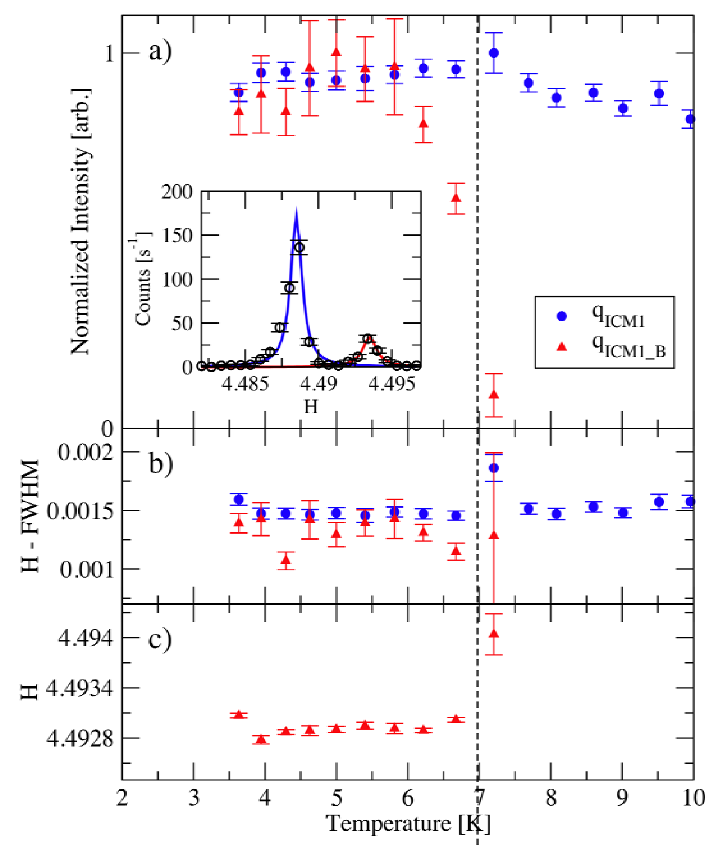
RXS in High Magnetic field

- At ID20, we can apply up to a 10 T magnetic field *in-situ,* perpendicular to the scattering plane
- In fields above 2.5 T, applied parallel to the *c* -axis, we have detected a new phase in $TbMn_2O_5$

New phase of TbMn$_2$O$_5$ observed above 2.5 T

- Additional magnetic diffraction peak observed
- Strong dependence on applied magnetic field and temperature





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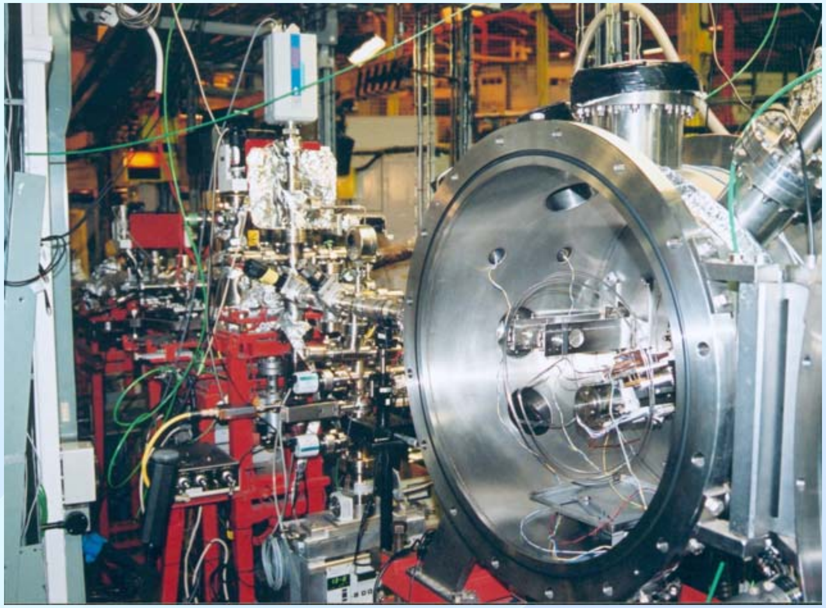
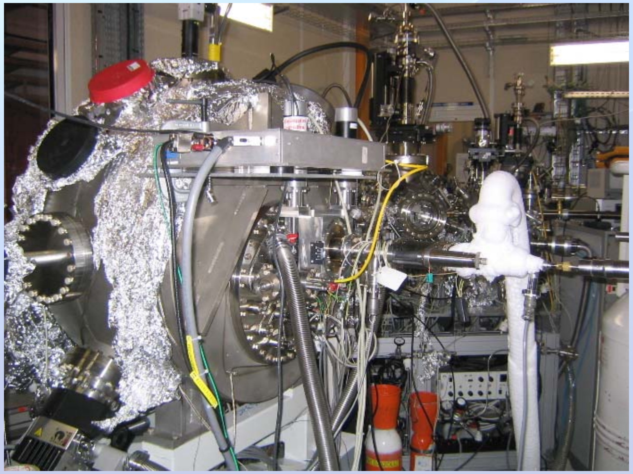
Electric field

- What happens if we can control the remaining environmental parameter – electric field?
- $TmMn_2O_5$ exhibits a rotation of electric polarization by 90^o due to a change in magnetic structure at 4.8 K. Can we control the magnetic structure by application of high electric fields?
- Experiment planned at XMaS beamline, ESRF, in collaboration with NPL to find out…

Going Soft

- Large enhancements occur when we tune to an absorption edge which probes the electron bands of interest.
- Have to use the L-edges for Mn hence Soft X-rays
- Experiments have to be performed in UHV.





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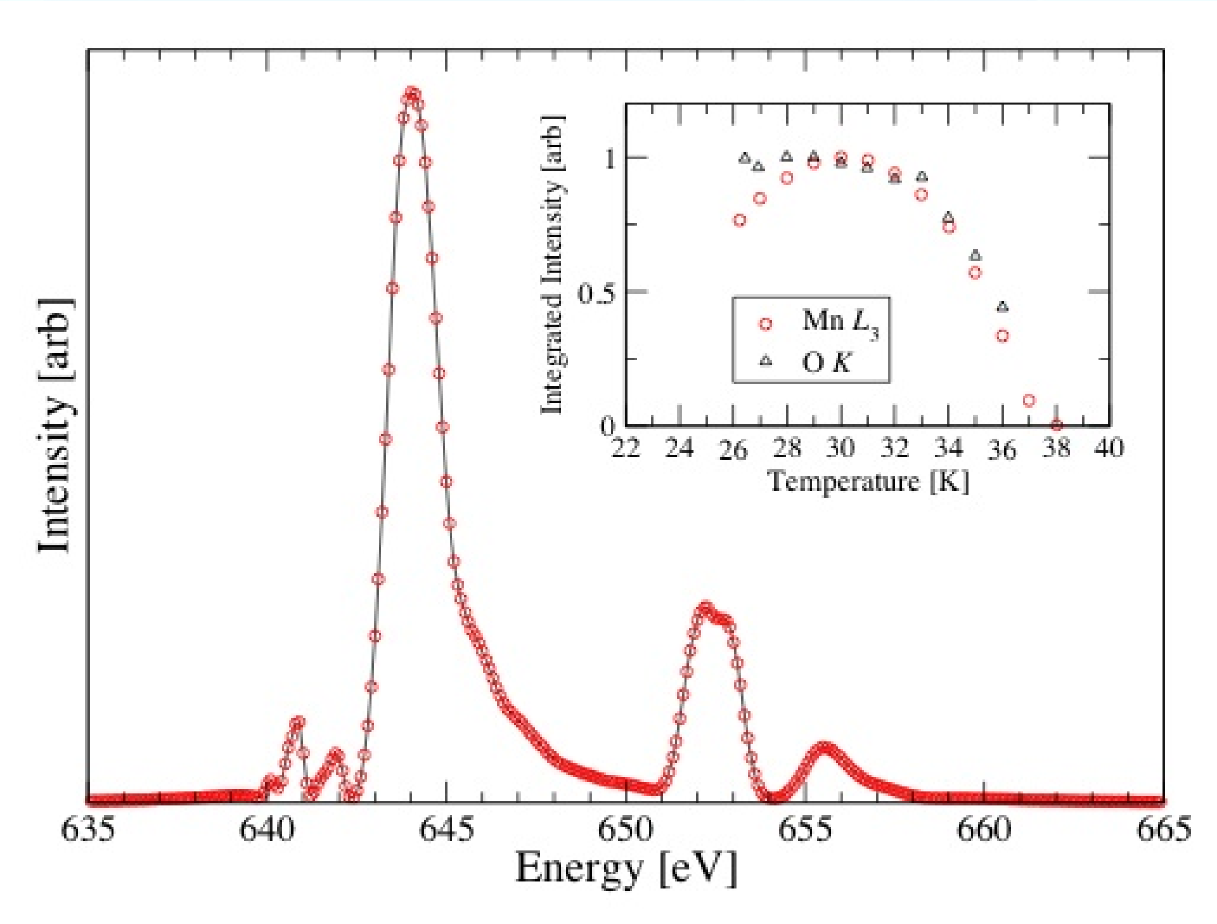
Soft X-ray Diffraction: Mn L edges

Similarly use of the L edges in Mn allow us to directly probe the magnetism in the 3d band using a dipole 2p→3d transition.

Multiplet transitions at L3 and L2 edges indicate distortions of Mn crystal field in square pyramid and octahedral oxygen polyhedra.



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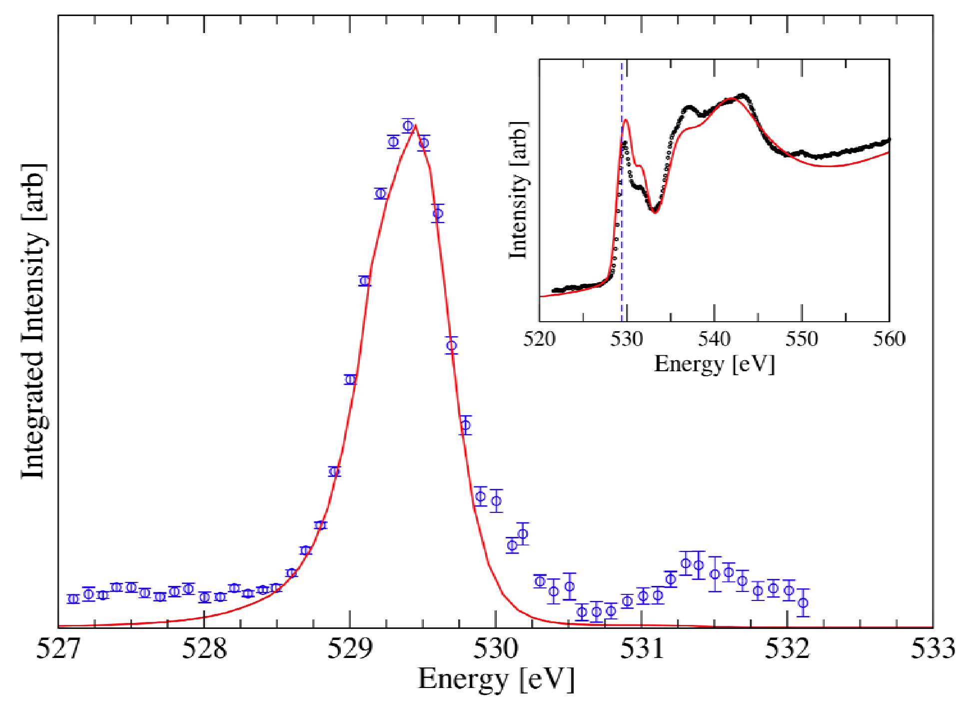
Soft X-ray Diffraction: Oxygen K edge

Resonant enhancement of the (0.5, 0, 0.25) reflection even found at the oxygen K edge (Is→2p).

Resonant enhancement suggests a strong hybridisation between the Mn and O ions.

FDMNES calculations show this primarily occurs on the displaced Mn^{3+} ions



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Conclusions

Resonant x-ray diffraction can be an atomically selective, band specific, probe of magnetism - useful in complex magnetic systems like multiferroics.

Polarized resonant x-ray magnetic diffraction can be used to refine magnetic structures.

Polarized resonant soft x-ray magnetic diffraction can directly probe induced magnetism on terbium, manganese and even oxygen ions in $TbMn_2O_5$.

A combination of spectroscopy with diffraction that directly probes not only the periodicity, but also the electronic state, magnetic moment and magnetic hybridization.

Gives a much deeper understanding of the electron correlations that are driving the physics of these materials.