Induced Multiferroic behaviour in single crystals of Manganites

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Multiferroics

$RMnO_3$ – Most extensively studied Multiferroic class

Large high quality crystals are available –have been investigated earlier in GMR/CMR context

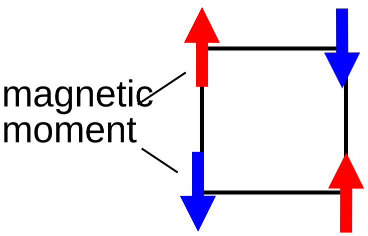
RMn_2O_5- Also well studied, although large crystals are not as easily available- flux grown crystals

Frustrated Magnets- Key indicators of multiferroic behaviour

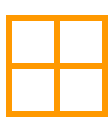
Frustrated Magnets-Multiferroics

magnetic insulators with modulated magnetic structures (e.g. spiral) as candidates of new multi-ferroics.

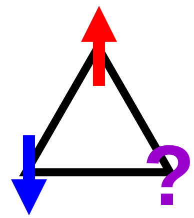
Normal antiferromagnet



e.g.
Square lattice



Geometrical spin frustration

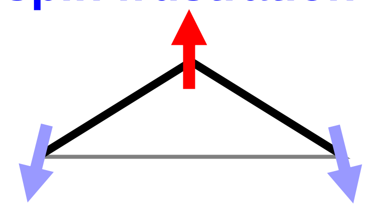


No spin order down to low-*T*

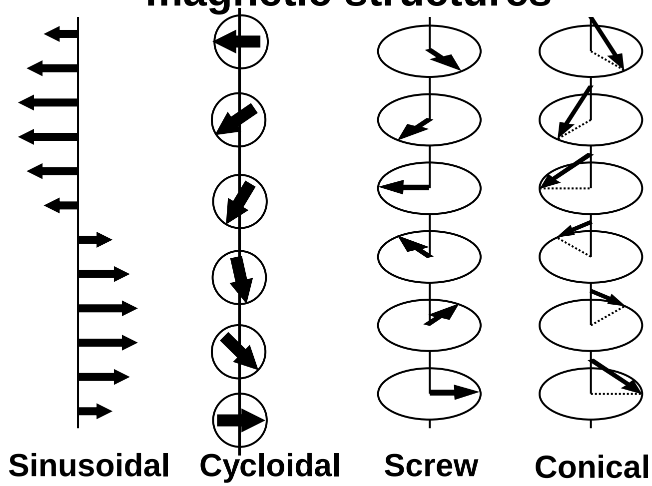
e.g.
Triangular lattice

Kagome lattice

Quasi- spin frustration



Complex modulated magnetic structures



Frustrated Magnets - Multiferroics

Delafossite $CuFeO_2$

Kagome Staircase Compounds $Ni_3V_2O_8$, $Co_3V_2O_8$

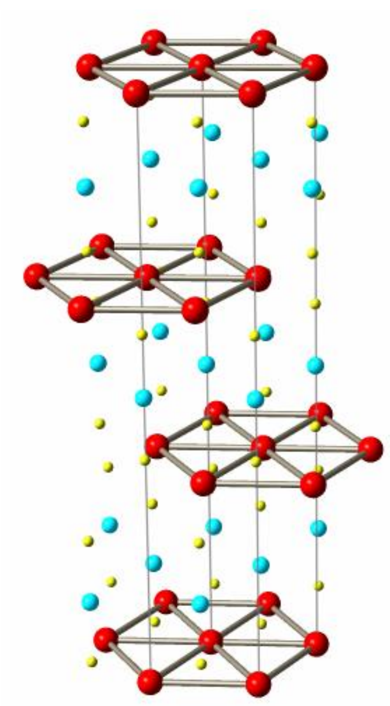
Extensive investigations of the magnetic properties by Warwick Group

Magnetic Frustration - $CuFeO_2$

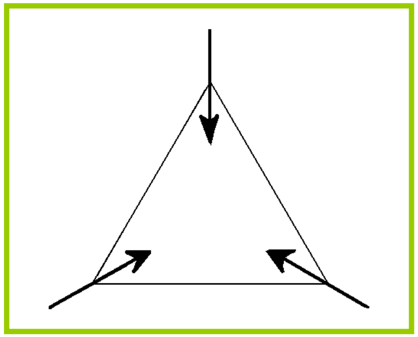
Cu^+ → nonmagnetic
Fe^{3+} (^6S state) → S = 5/2
Space group *R3m*

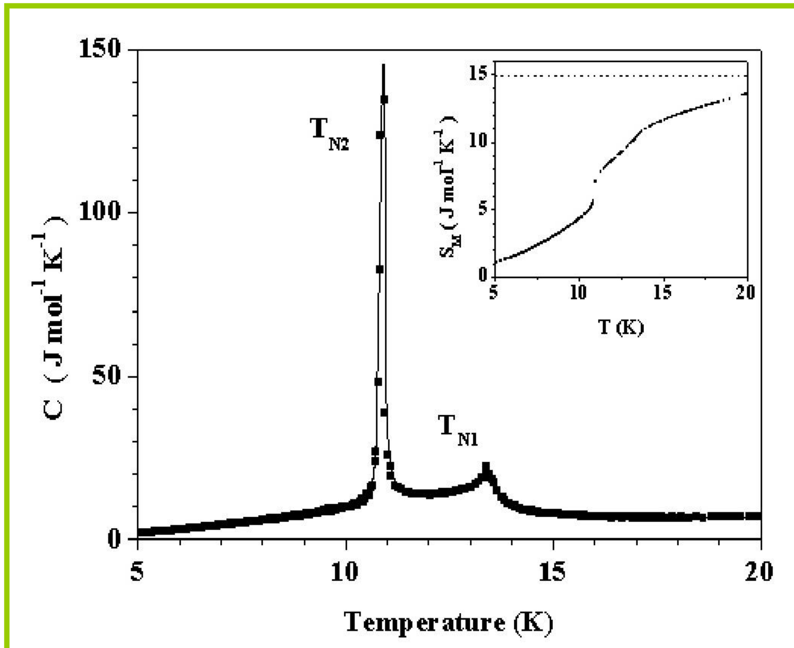
- **quasi 2D**
- **double frustration**

Low-temperature heat capacity of $CuFeO_2$ single crystal. The inset shows the temperature dependence of the magnetic entropy.



Crystal structure of $CuFeO_2$



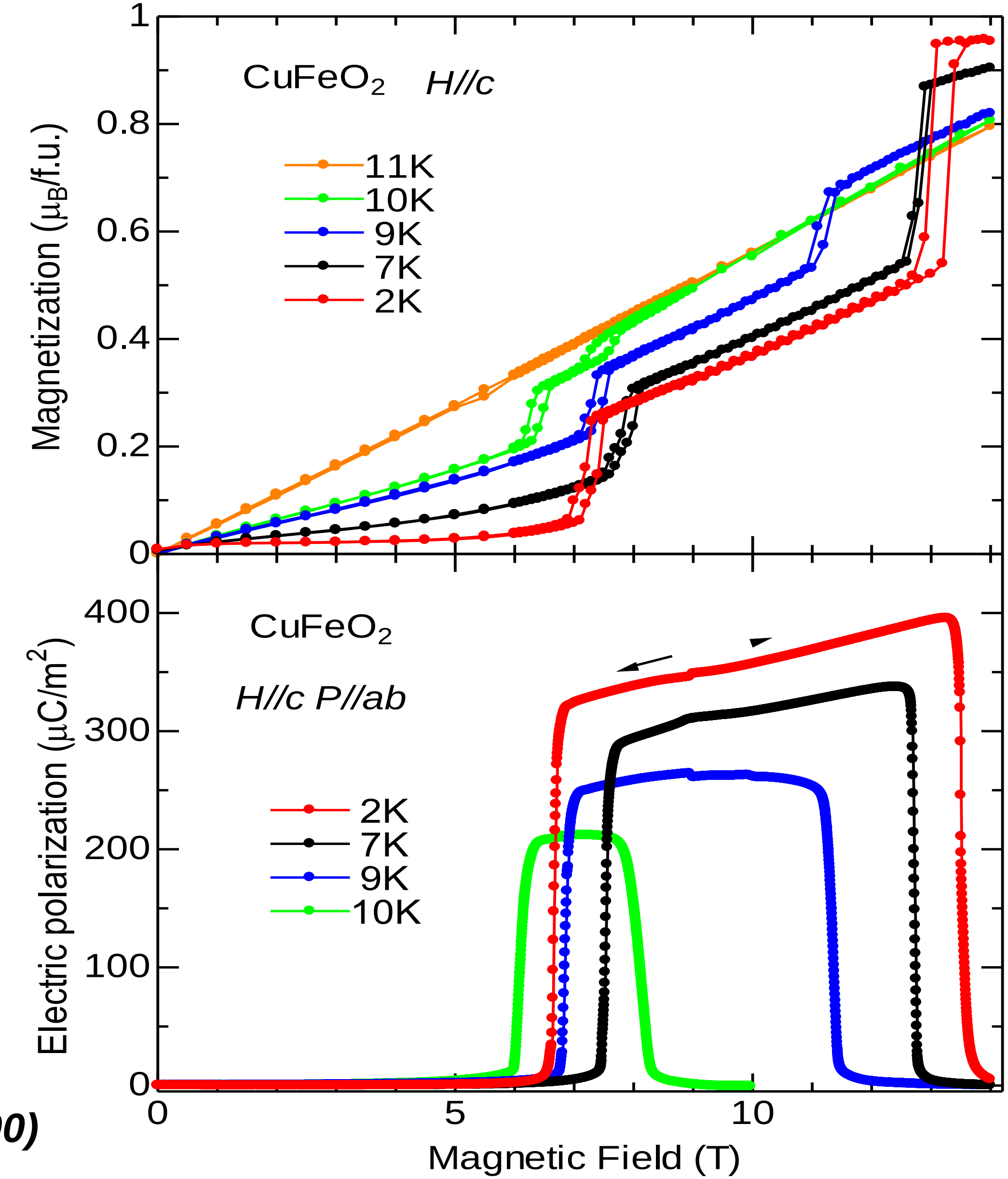


O.A. Petrenko, G.Balakrishnan et al PRB 62 8983-8988 (2000)

$CuFeO_2$- Multiferroic properties

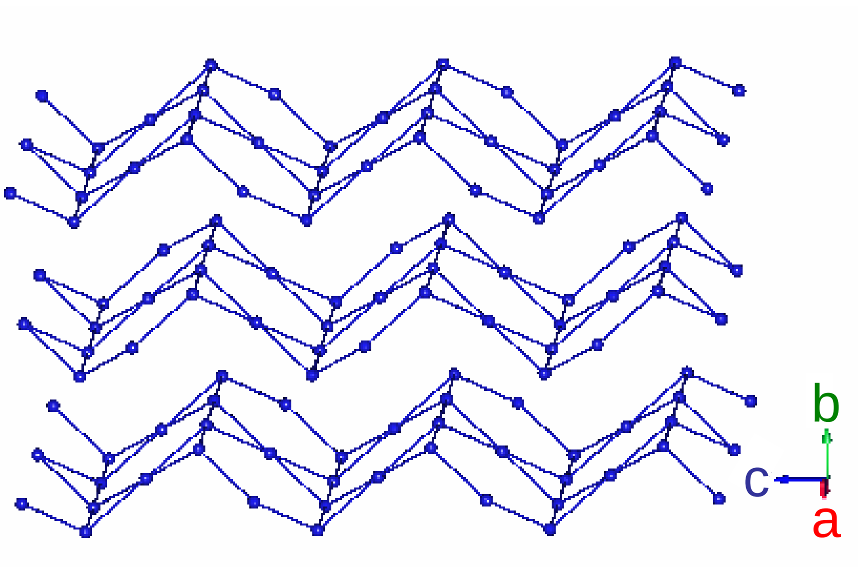
Finite polarisation appears only in the non collinear incommensurate magnetic phase

T.Kimura et al PRB 73 220401 (2006)



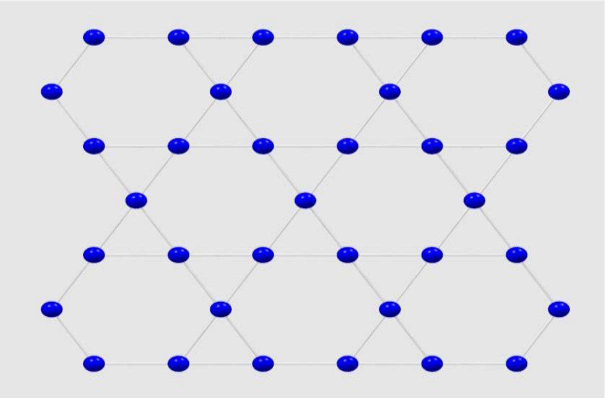
S. Mitsuda et al., JPSJ 69, 3513 (2000)

KAGOME staircase compounds



$Co_3V_2O_8$

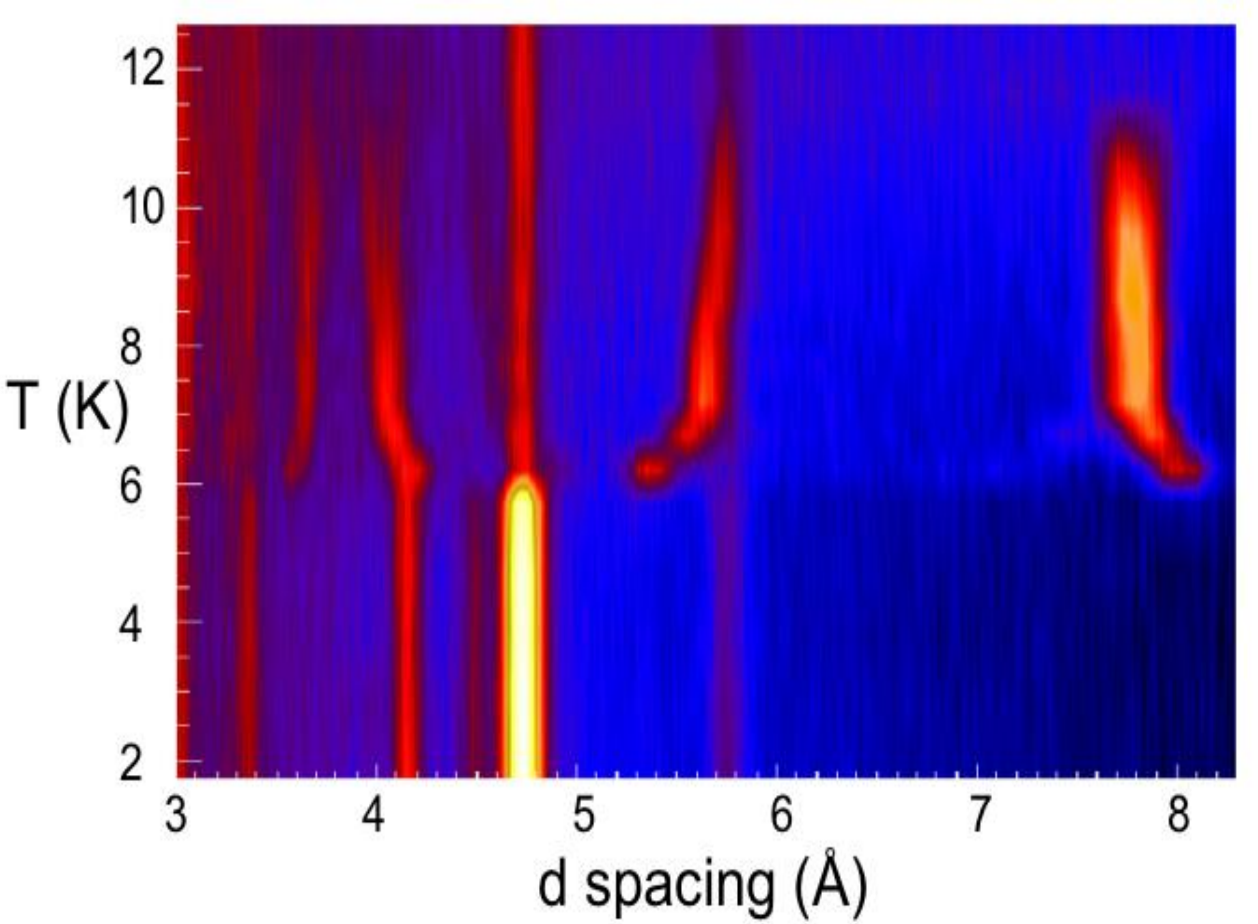
$M_3V_2O_8$



$Ni_3V_2O_8$

G. Balakrishnan et al, J. Phys. Condensed Matter 16 L347-L350 (2004)

$Co_3V_2O_8$



Powder neutron diffraction pattern of $Co_3V_2O_8$ as a function of temperature. The data were recorded on the GEM diffractometer (time-of-flight, medium resolution) at the ISIS pulsed neutron source.

N.R. Wilson, O.A. Petrenko and L.C. Chapon, Physical Review B 75 094432 (2007)
N.R. Wilson, O.A. Petrenko and G. Balakrishnan, Journal Of Physics-Condensed Matter 19 145257 (2007).

$Ni_3V_2O_8$ Kagome – Magnetically driven Ferroelectric order

G.Lawes et al PRL 95 087205 (2005)

Development of ferroelectric order is coincident with an incommensurate magnetic phase.

Since ferroelectricity occurs only in the phase for which magnetic ordering breaks inversion symmetry, one can reversibly switch the polarization on and off using an external magnetic field.

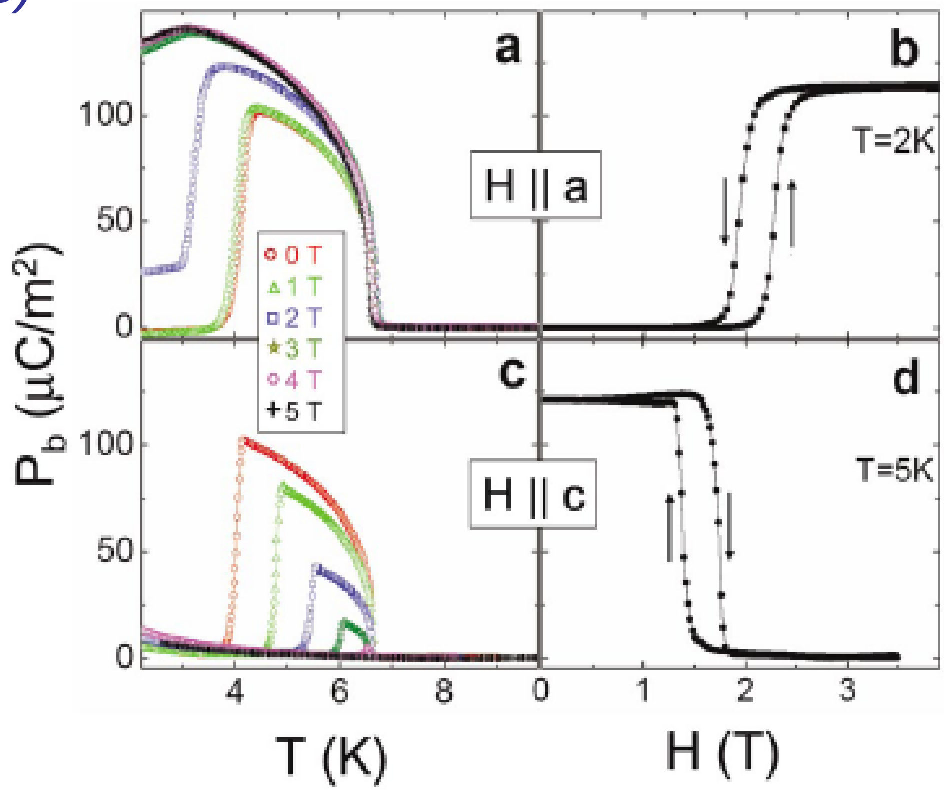


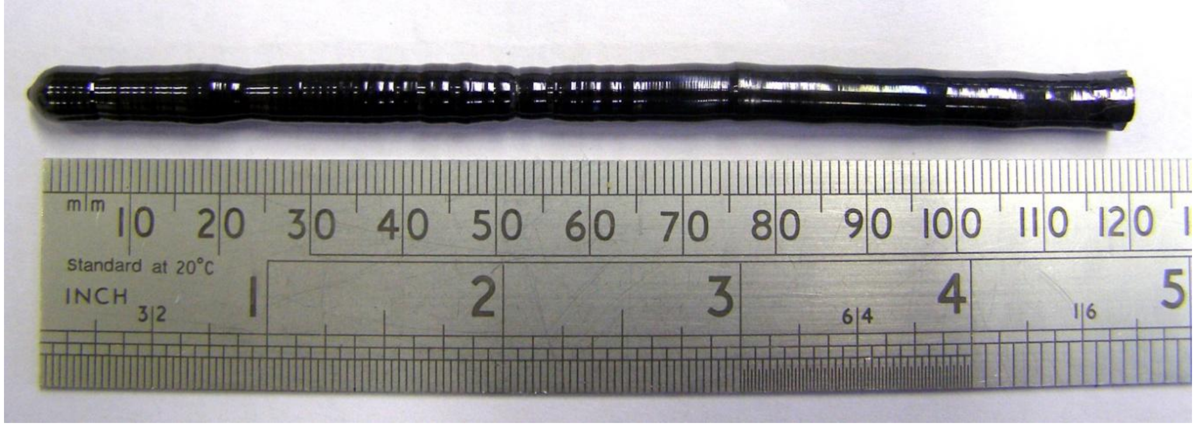
FIG. 3 (color). Promotion and suppression of electric polarization by applying magnetic fields in NVO. Temperature and magnetic-field dependence of electric polarization along the *b* axis for **H** along the *a* [frames (a) and (b)] and *c* [frames (c) and (d)] axes.

Manganites - $RMnO_3$

Large single crystals can be obtained- Floating Zone technique*

La, Nd based Manganites investigated in the past
$La_{1-x}Sr/Ca_xMnO_3$, $Nd_{1-x}Pb/Sr_xMnO_3$

*Using Optical Mirror furnaces



$La_{0.6}Sr_{0.4}MnO_3$

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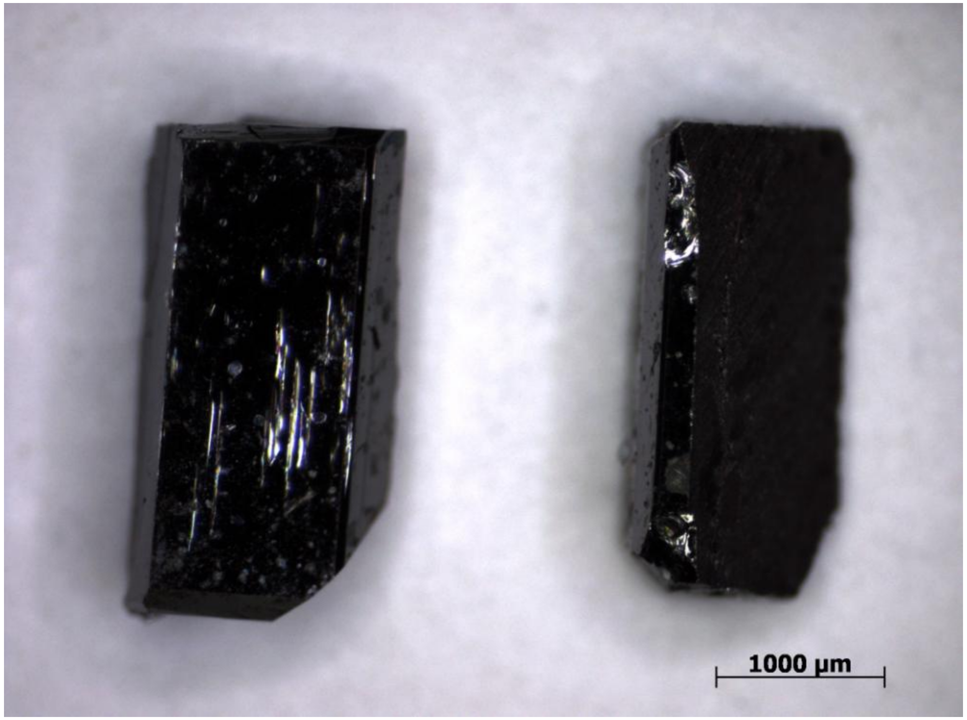
RMn_2O_5

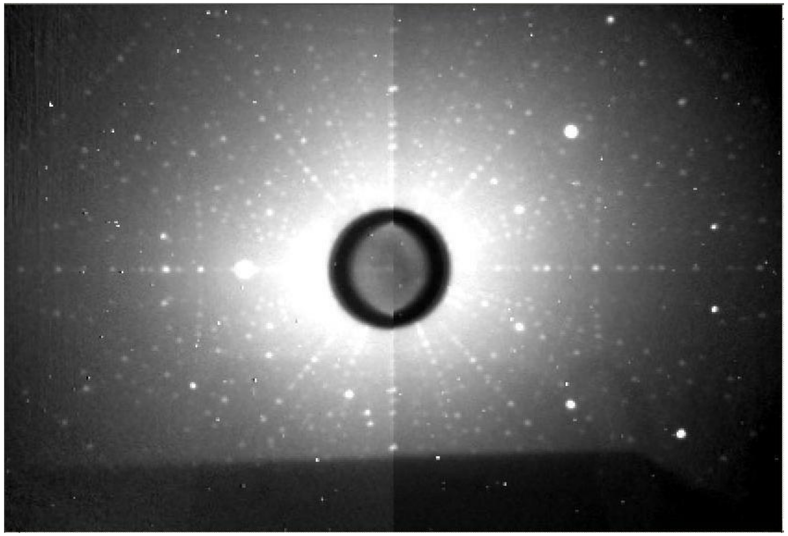
Difficulty obtaining large crystals

Crystals mostly obtained by the Flux Method

$TbMn_2O_5$ crystals grown by the flux method
(B_2O_3-PbO-PbF_2-PbO_2 flux)

$TbMn_2O_5$- Crystals





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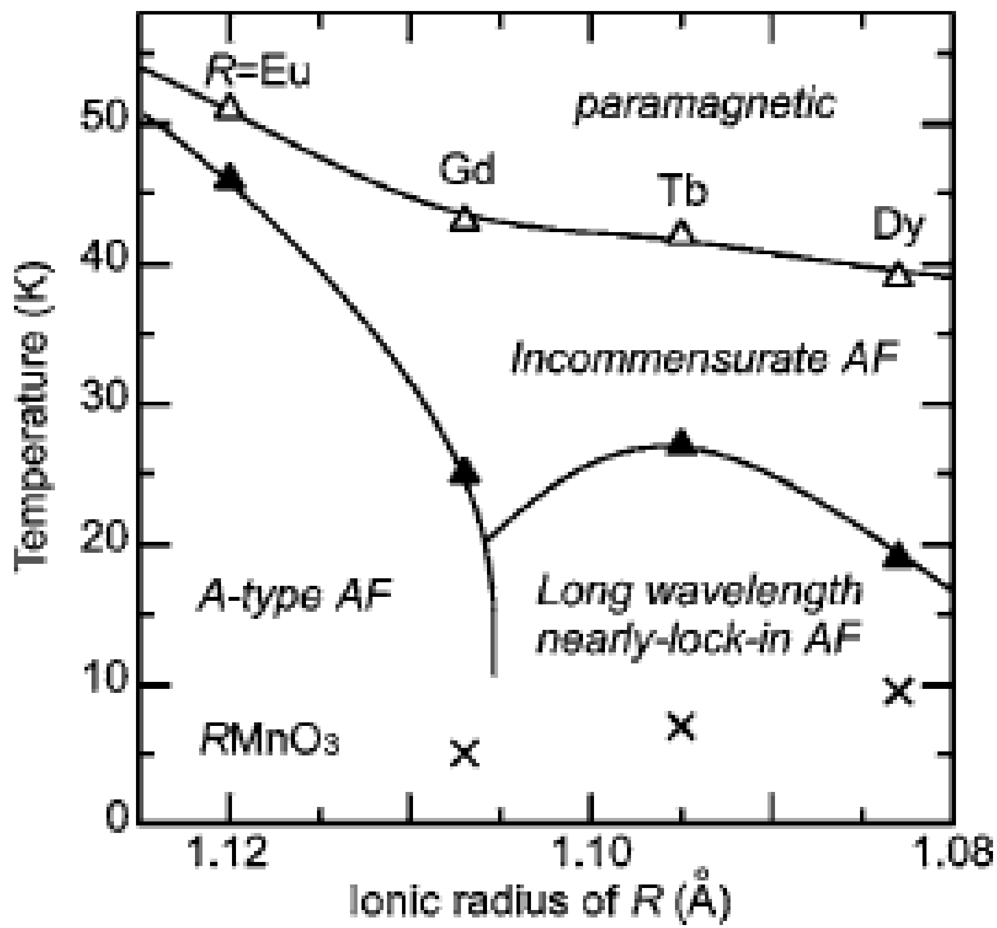
Phase Diagram of $RMnO_3$- R Ionic radii

•Multiferroic properties seen in $RMnO_3$ compounds with intermediate $\mathbf{r_R}$

•Decreasing $\mathbf{r_R}$ enhances the competition in the FM interactions between NN Mn sites and AFM between NNN sites.

•In Gd,Tb and Dy, this competition results in long wavelength AFM order- magnetoelastically induced lattice modulations



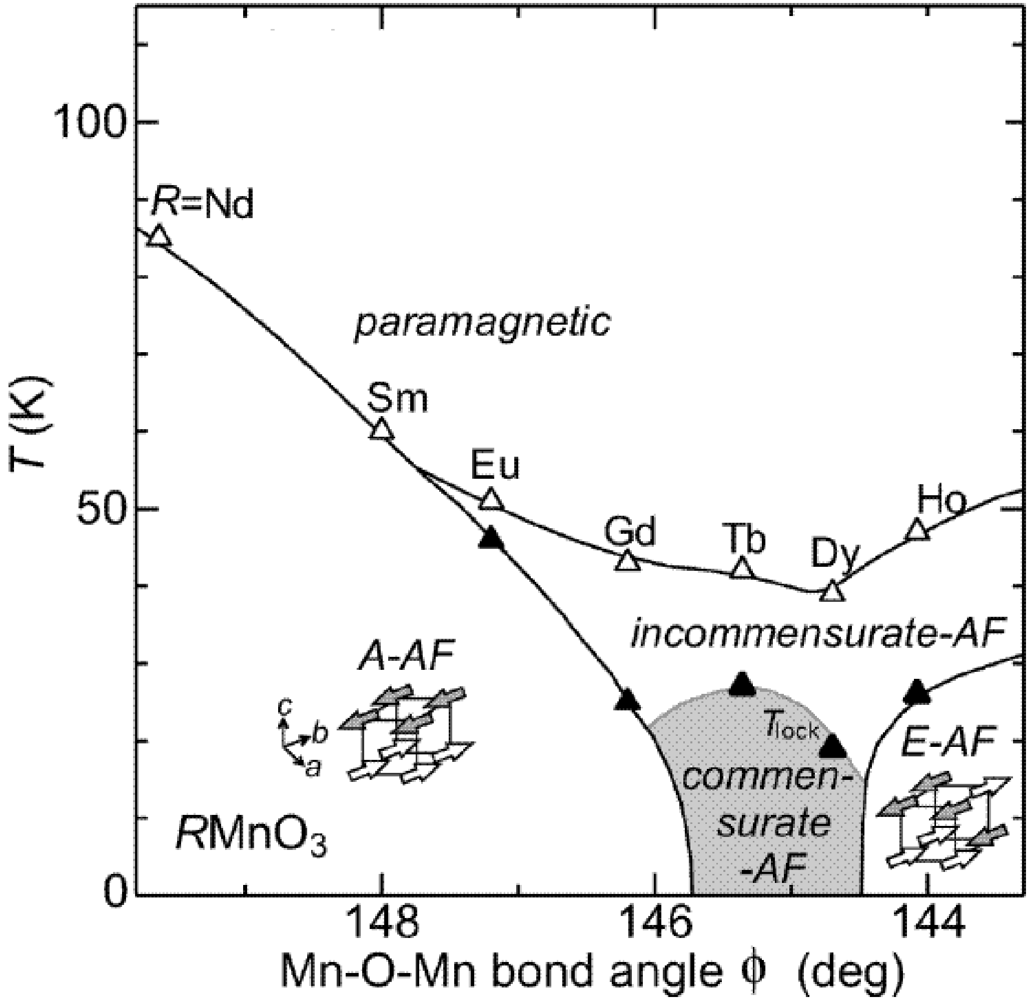
Kimura et al PRB 71 224425 (2005)

Phase Diagram of $RMnO_3$
Mn-O-Mn bond angle Φ

Decrease of **Φ** suppresses layer type (A-type) AF order of the Mn spins.

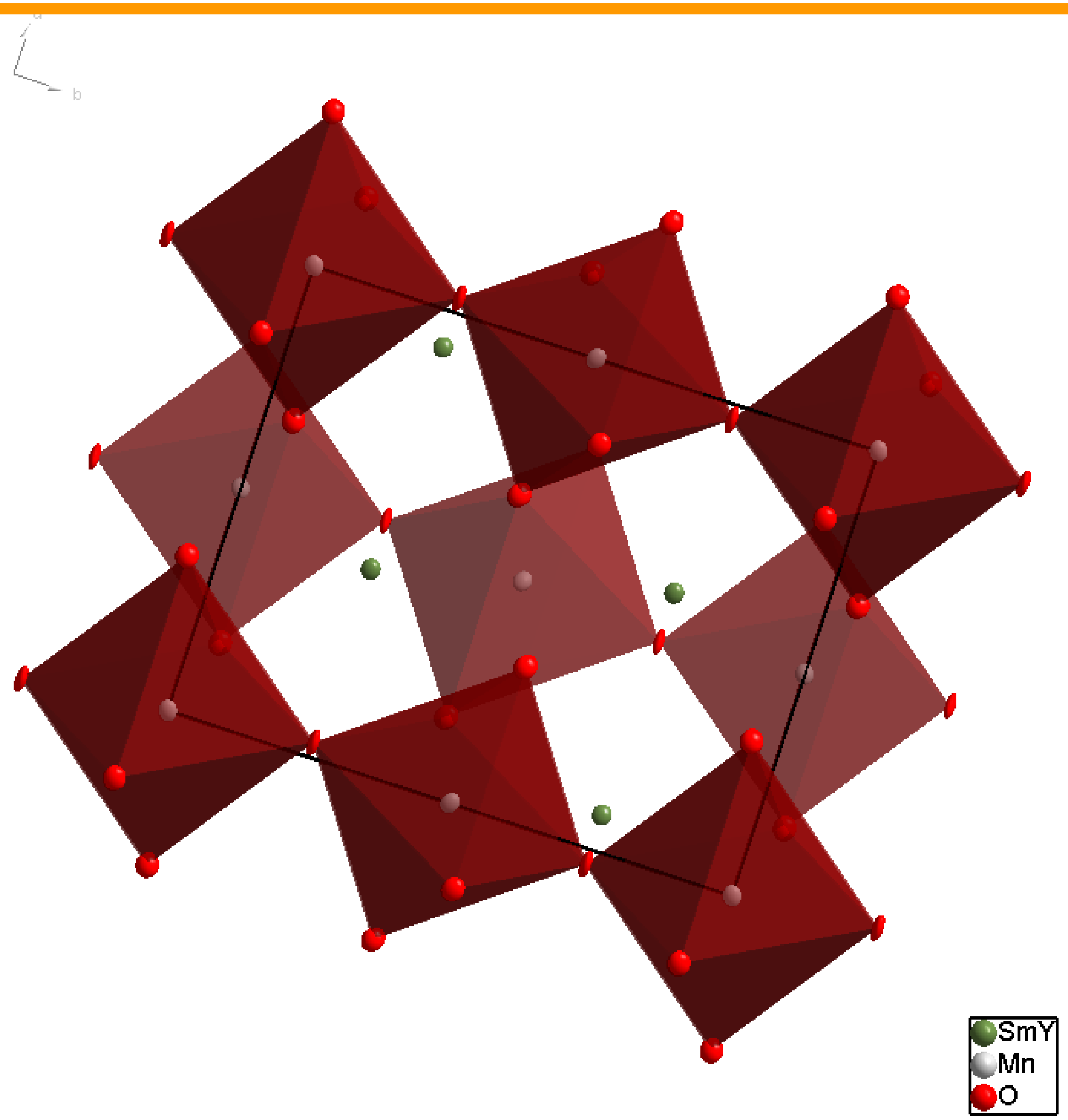
Sinusoidal/cycloidal AF order appears at intermediate Φ (as in Tb, Dy)

Smaller Φ results in a ziz-zag type (E-type) AF order as in Ho



Goto et al PRL 92 257201 (2004)

Structure - $RMnO_3$

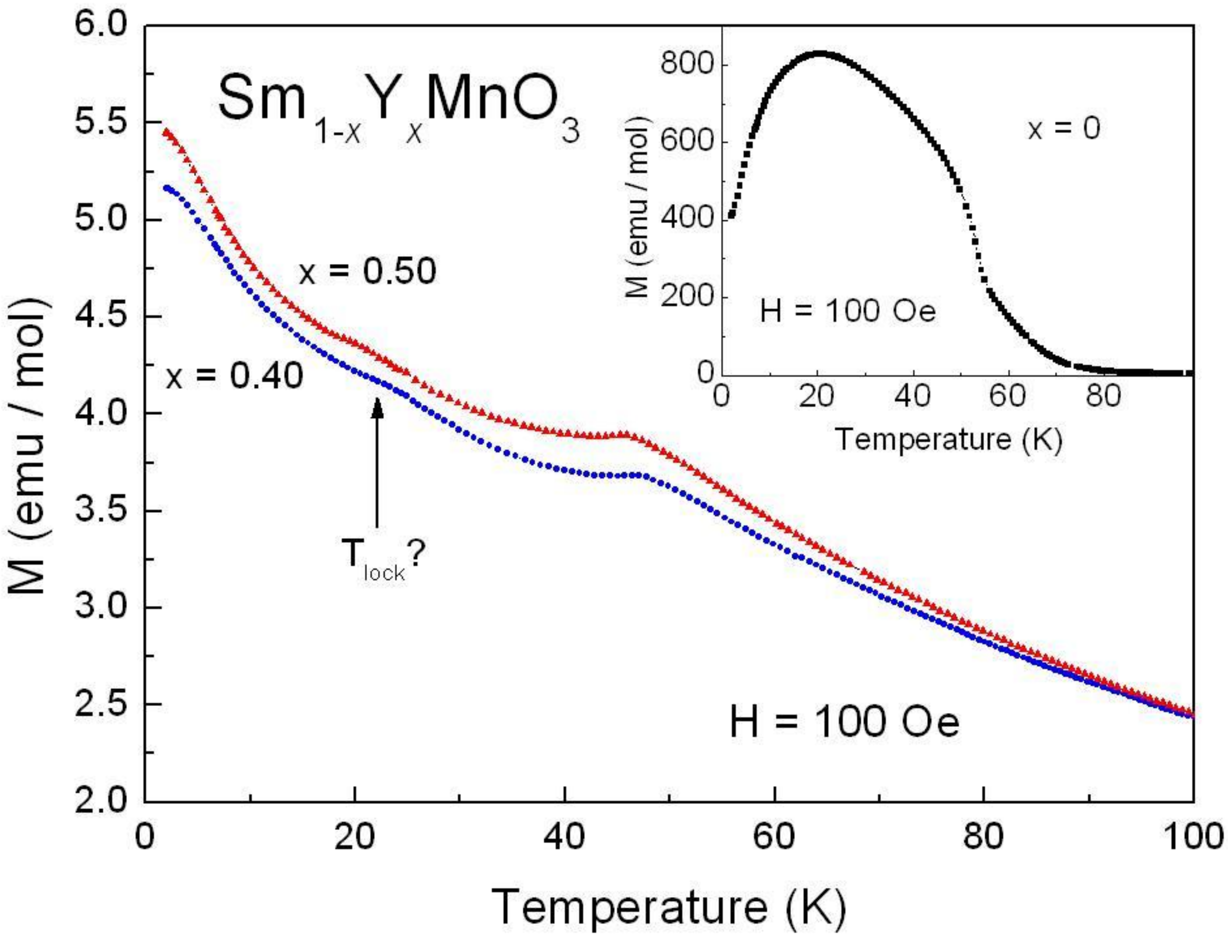


$SmMnO_3$

Substitution of Y at the Sm site to vary **Φ** to bring it into the region in the phase diagram where cycloidal magnetic order is observed in $TbMnO_3$ and $DyMnO_3$

- $Sm_{1-x}Y_xMnO_3$, for x = 0 to 0.6
- Preliminary investigations on polycrystalline samples
- Single crystals produced
- Phase pure for x =0 to 0.5
- Bond angle Φ for the doped samples determined through single crystal X-ray diffraction measurements.

$Sm_{1-x}Y_xMnO_3$- M vs T



Two anomalies seen in the magnetisation data of polycrystalline powder samples.

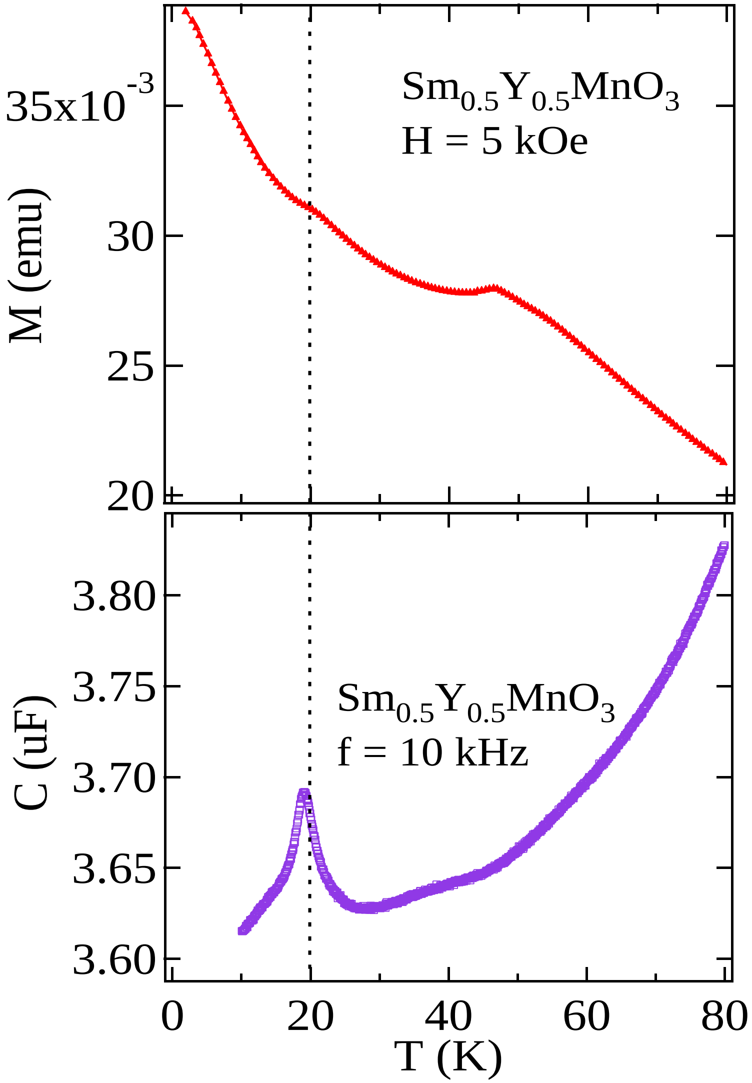
The anomaly at ~20K is seen for x between 0.4 and 0.5, similar to that seen in $TbMnO_3$

$Sm_{1-x}Y_xMnO_3$ Dielectric properties

The magnetisation data shows two anomalies:

(a) at ~60K due to the Mn spins, similar to that seen in $SmMnO_3$
(b) An additional one at ~20K

The anomaly in the dielectric property is seen at the same temperature at which the second anomaly in the magnetisation is seen.



$Sm_{1-x}Y_xMnO_3$ Dielectric properties

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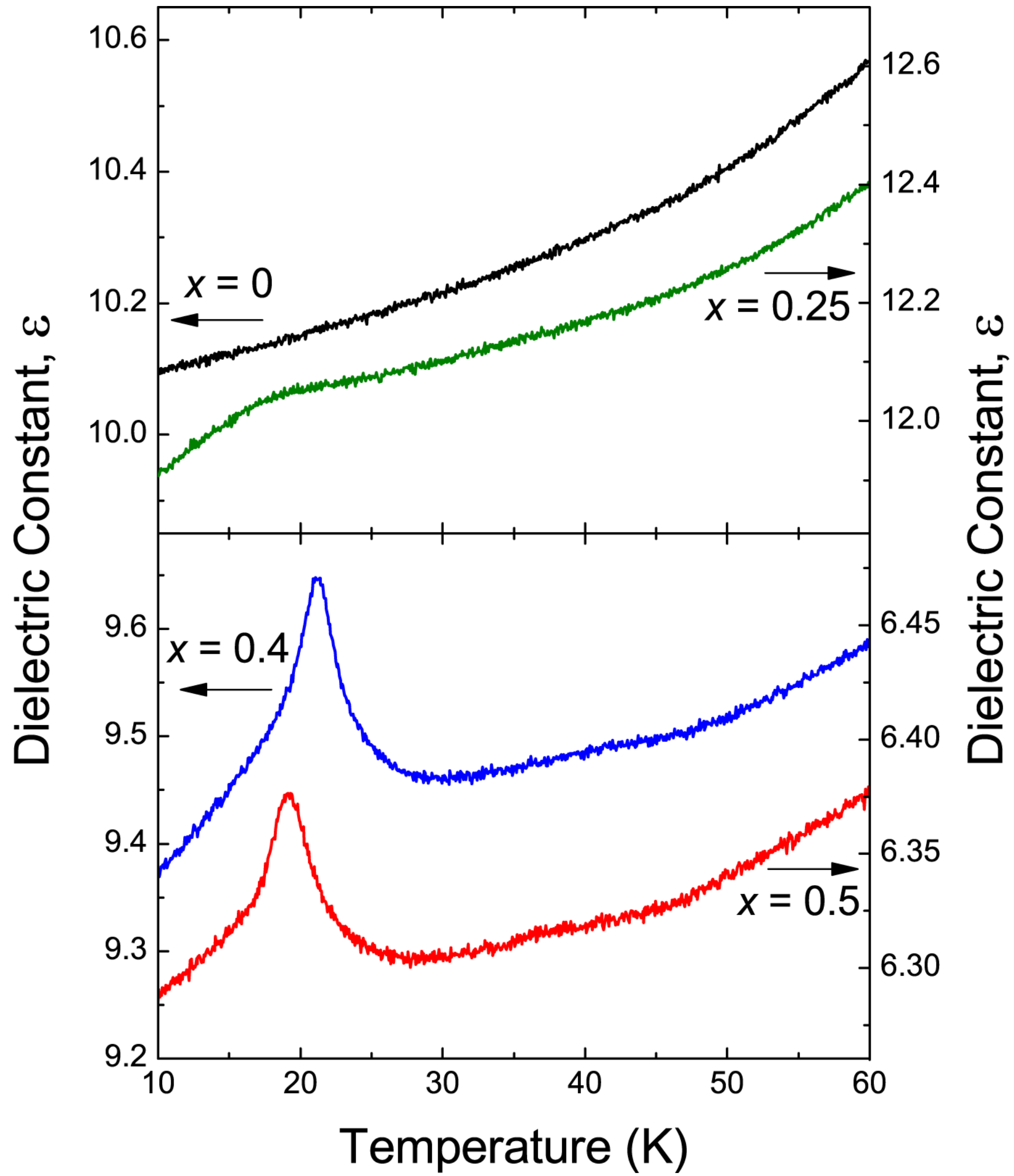

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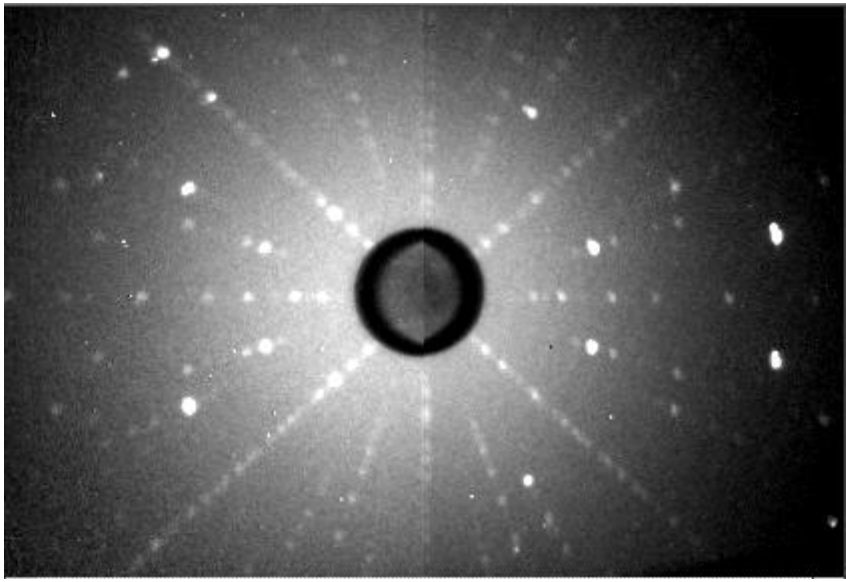
$Sm_{1-x}Y_xMnO_3$ Crystals

- Large single crystals were grown by the floating zone technique
- Two Mirror as well as Four Mirror furnaces were used
- Structural information was obtained using an X-ray Single Crystal Diffractometer
- Oriented crystal pieces used for Magnetisation, Specific Heat, Dielectric and Polarisation measurements
- Multiferroic behaviour starts to appear for a substitution level of $x > 0.3$ and is optimum for $x \sim 0.4$ to 0.5
- Not phase pure for $x > 0.5$

$SmMnO_3$ Crystal

Crystal grown by the Floating Zone method

X-ray Laue along *'a'*

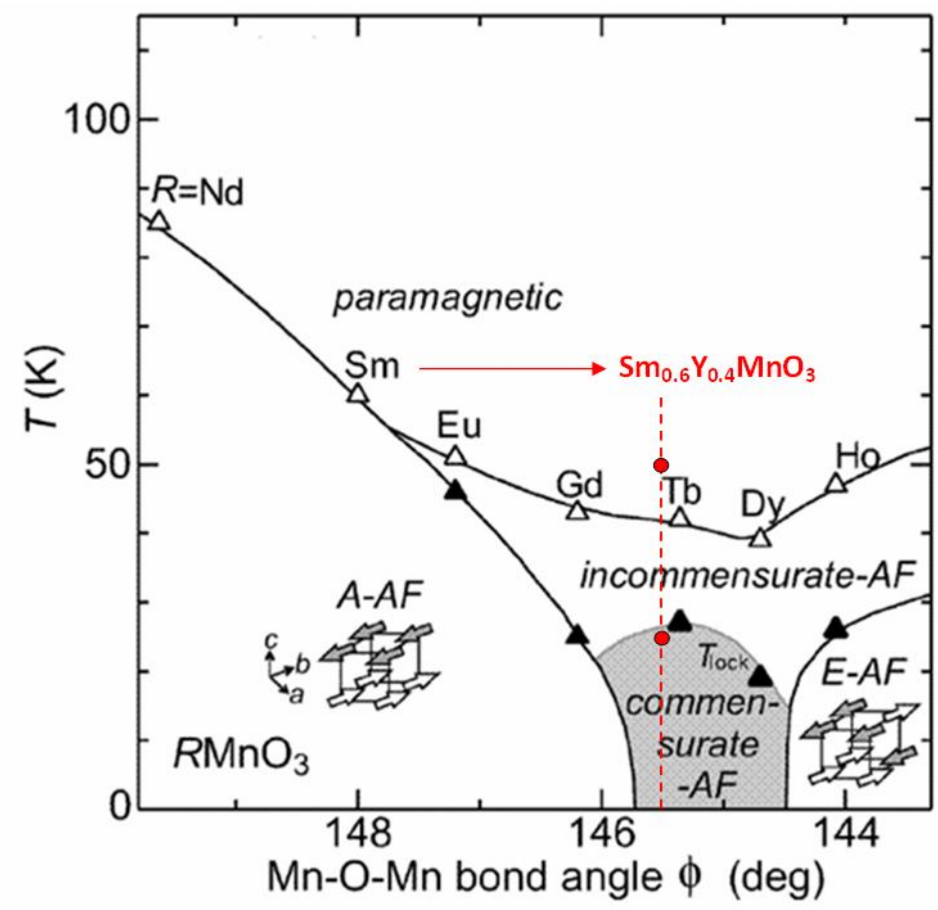


$SmMnO_3$
Mn-O-Mn Bond angle Φ

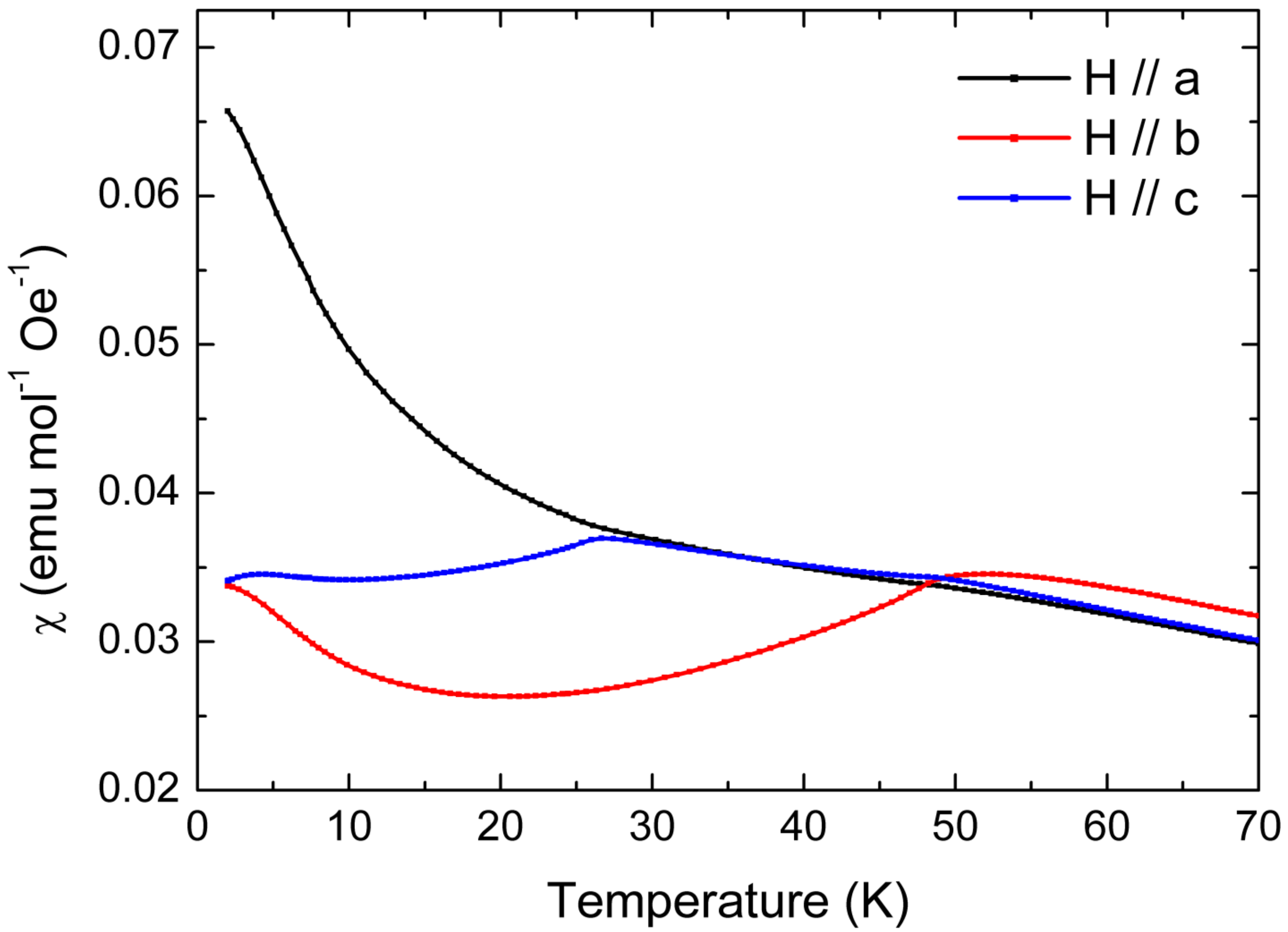
Bond Angles **Φ** (deg) measured at 296 K (RT)

Single crystal X-ray Diffraction

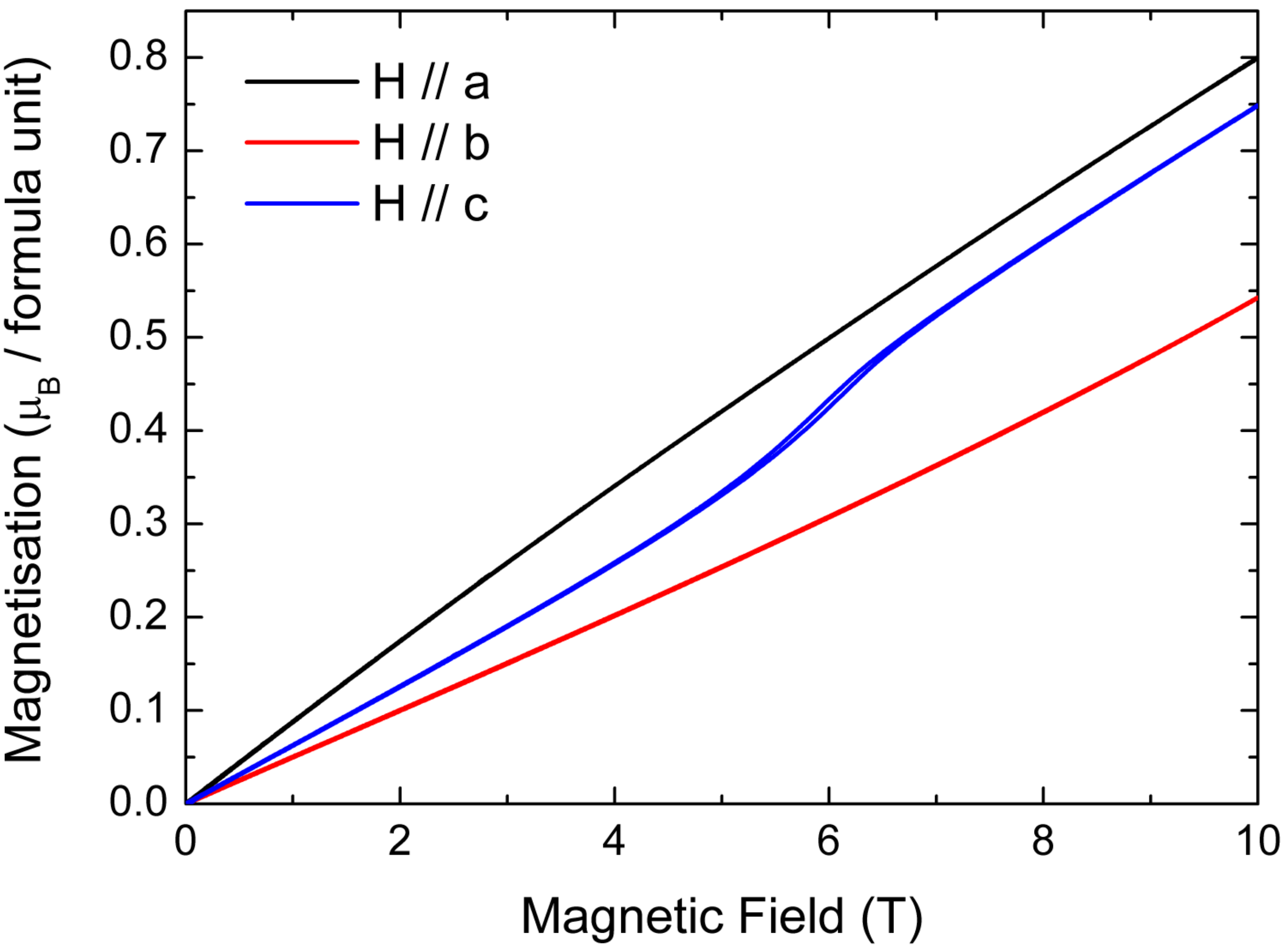
$SmMnO_3$	148.504(4)
$Sm_{0.6}Y_{0.4}MnO_3$	145.116(1)
$Sm_{0.5}Y_{0.5}MnO_3$	145.55(6)
$TbMnO_3$ *(present study)*	145.2(2)



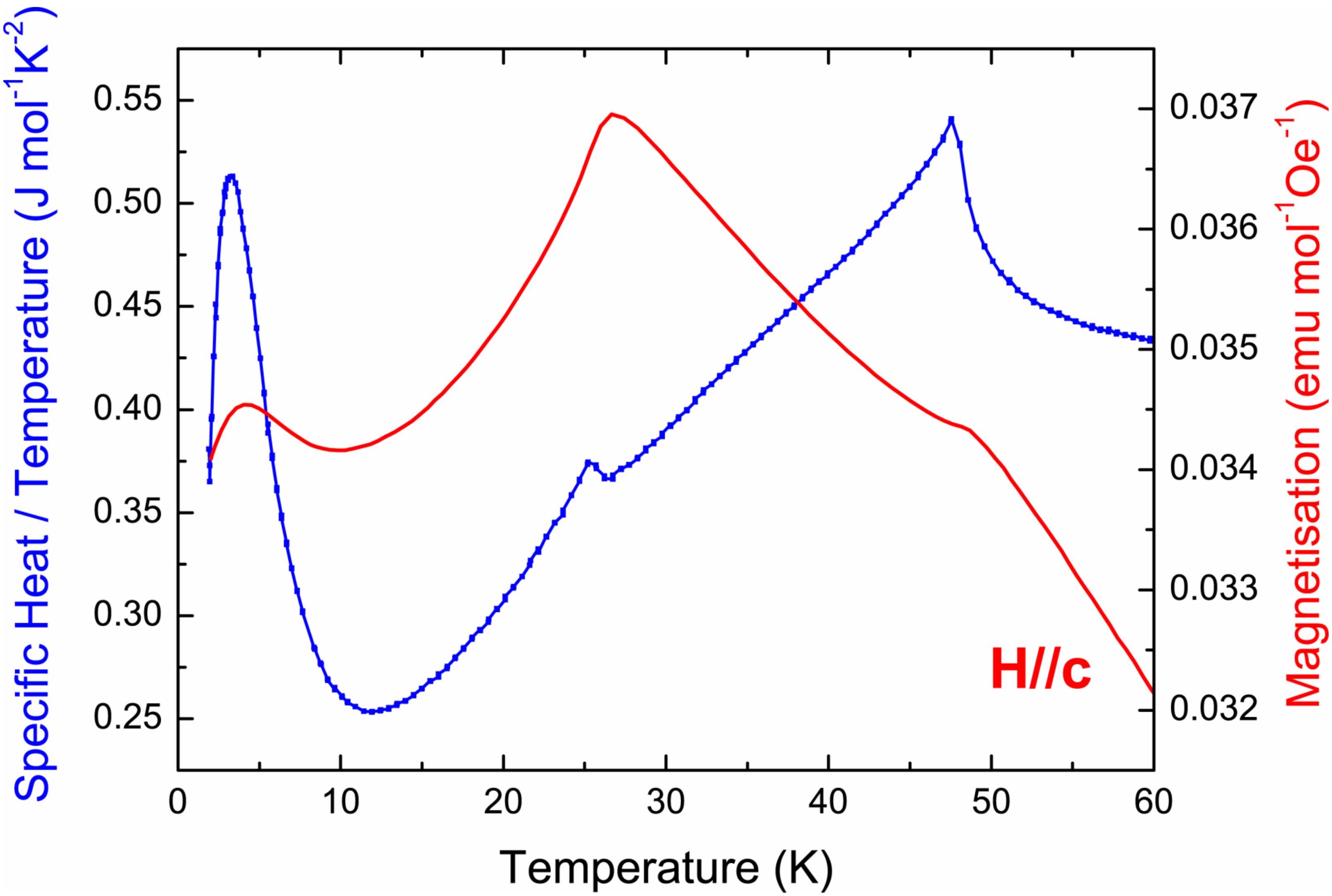
$Sm_{0.6}Y_{0.4}MnO_3$ Crystal- Magnetic Susceptibility



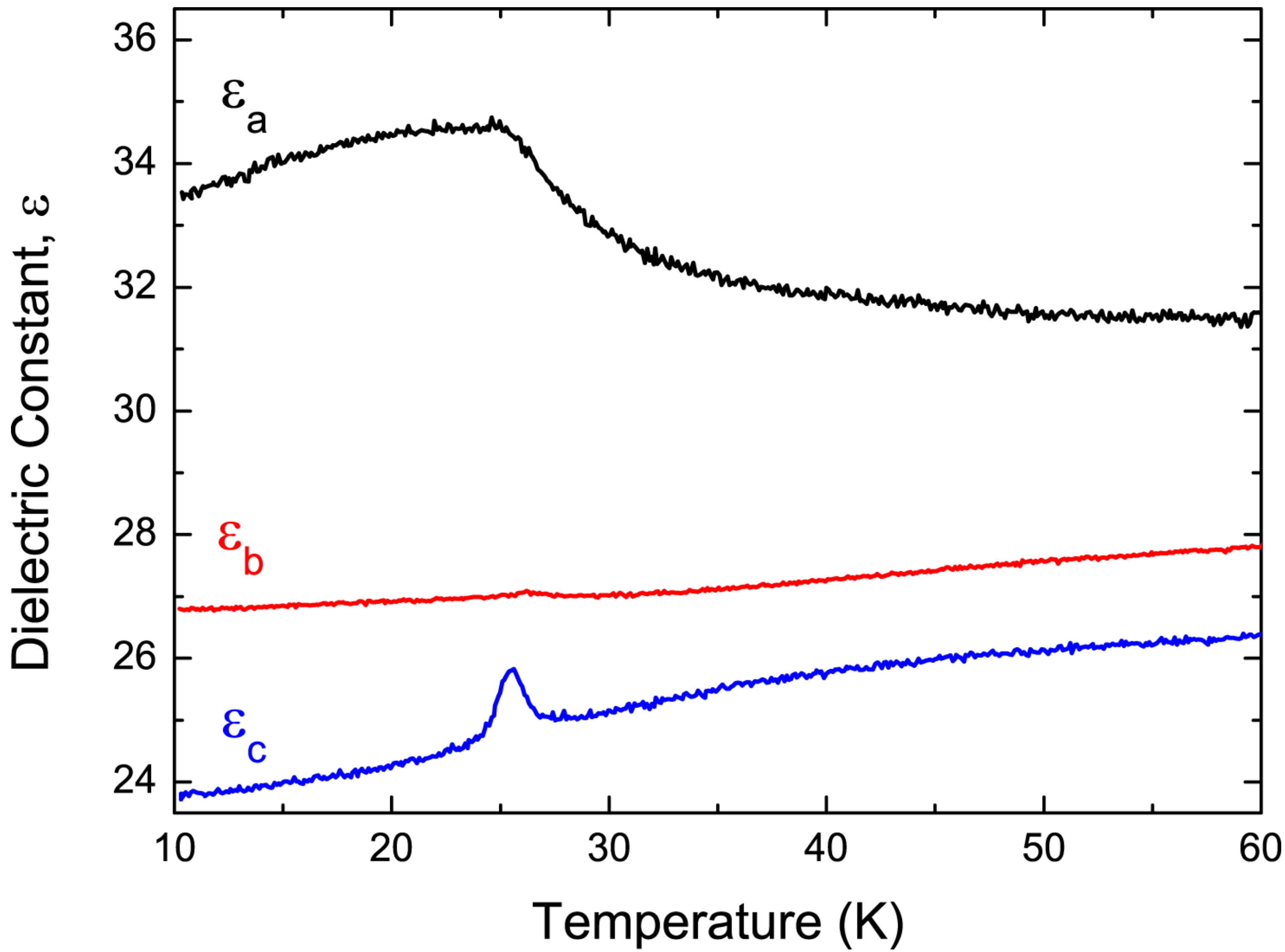
$Sm_{0.6}Y_{0.4}MnO_3$ Crystals-Magnetisation



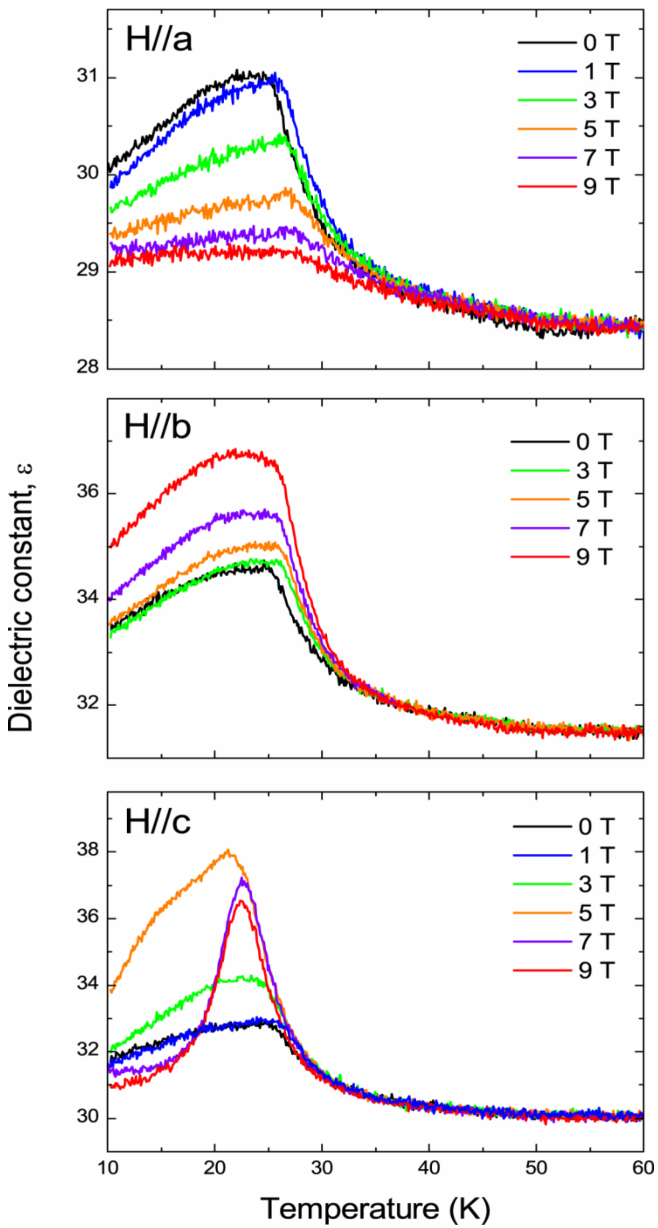
Specific Heat - $Sm_{0.6}Y_{0.4}MnO_3$- Crystal



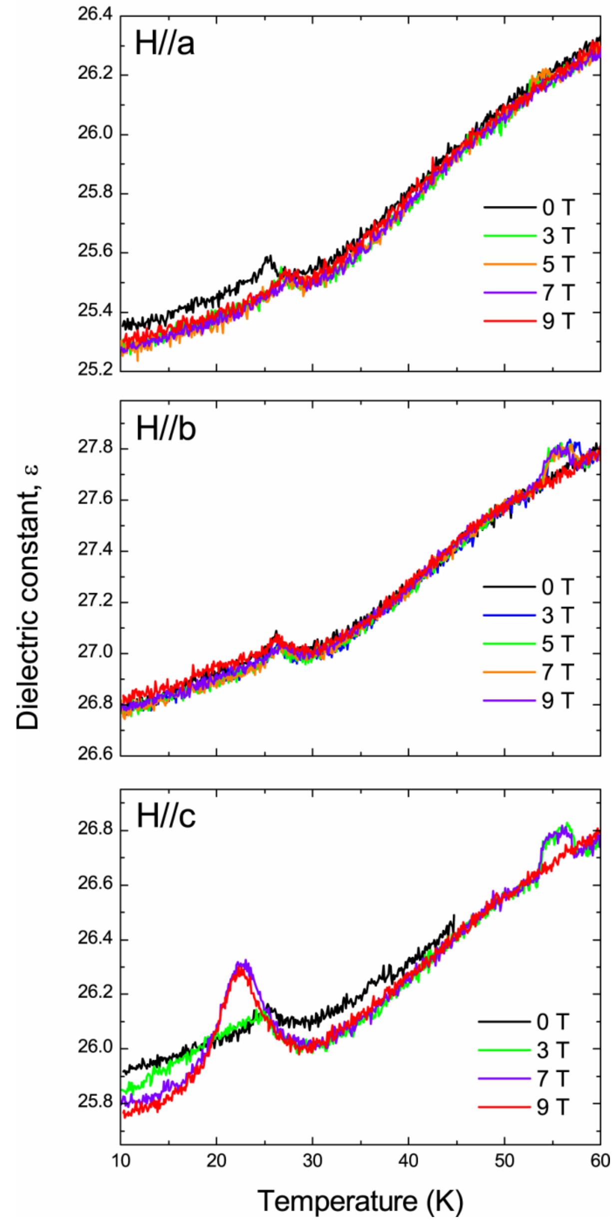
$Sm_{0.6}Y_{0.4}MnO_3$ Crystals-Dielectric Properties



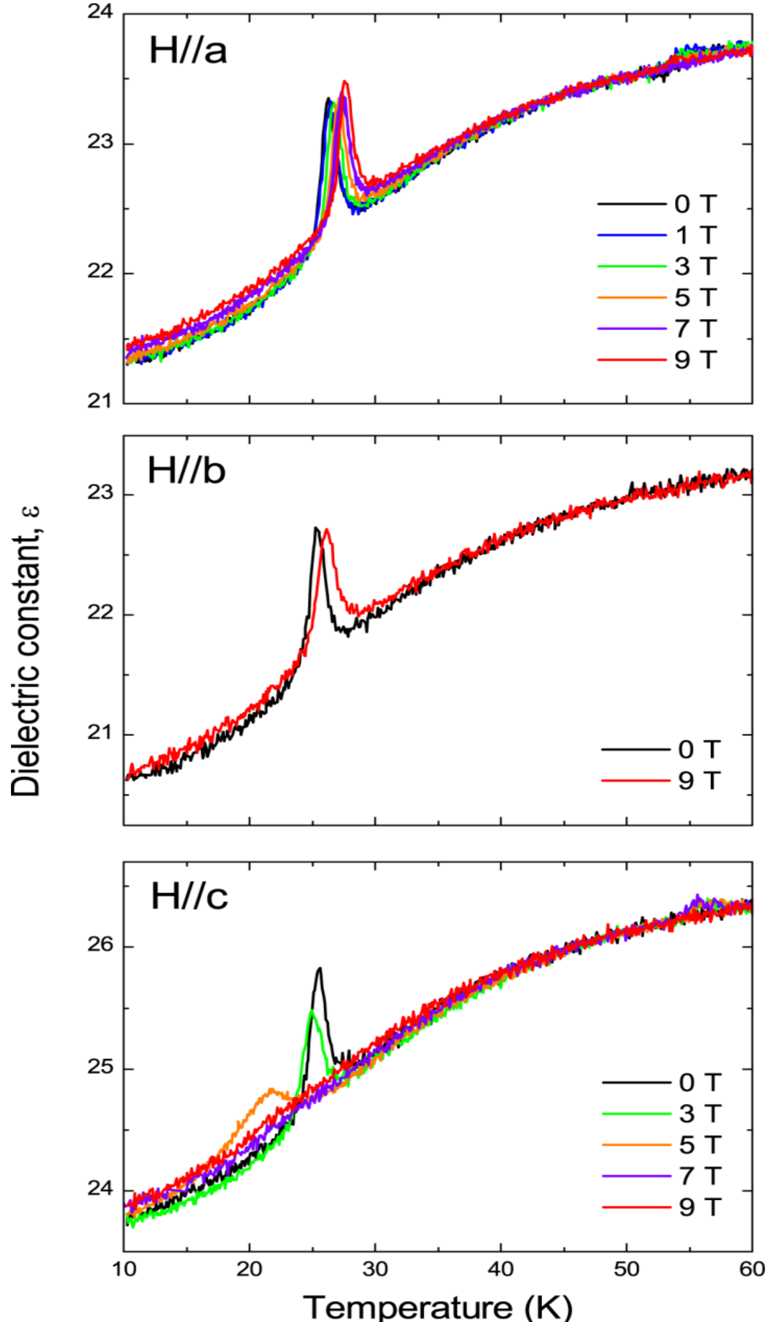
$Sm_{0.6}Y_{0.4}MnO_3$ - E//a



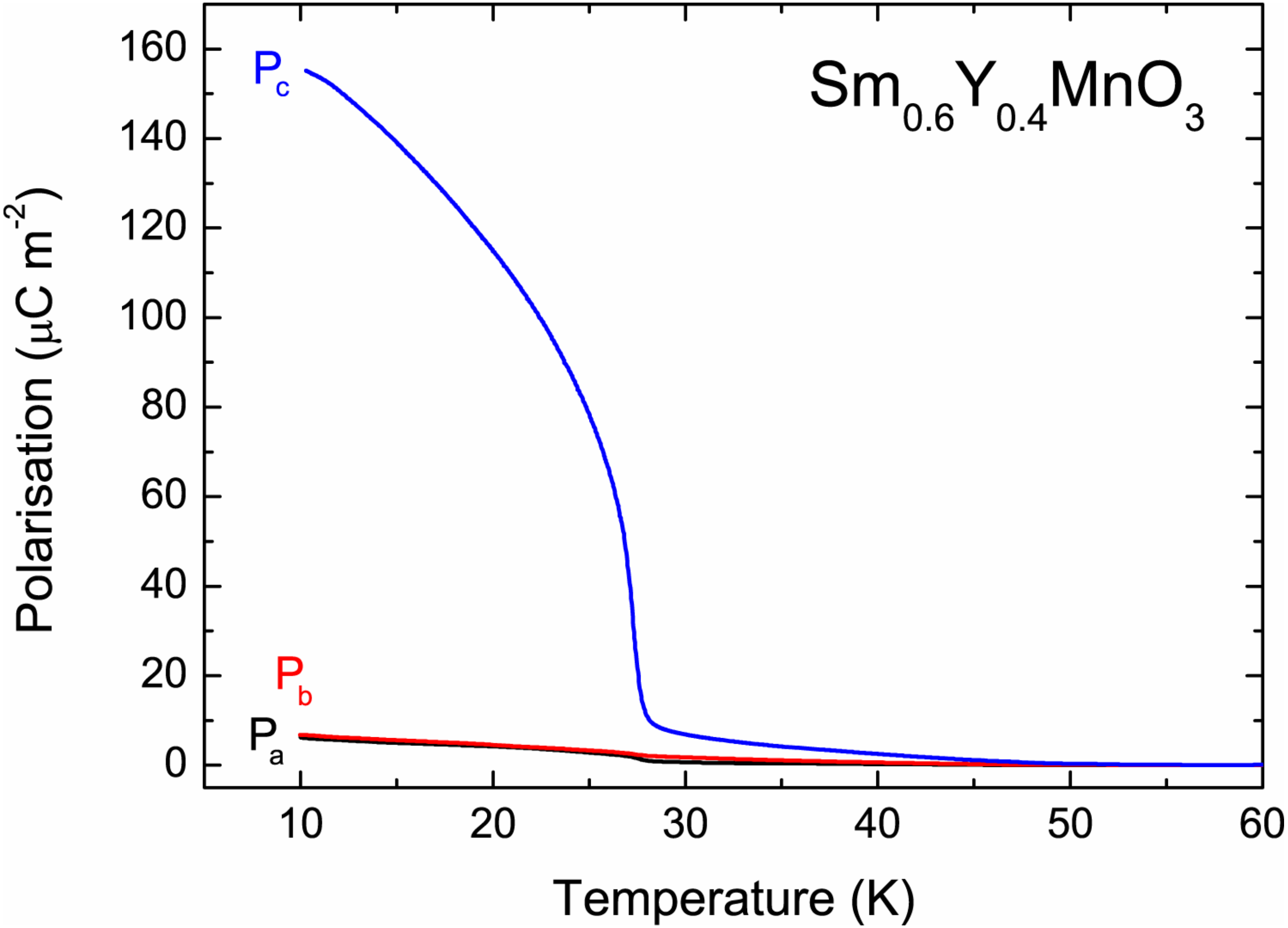
$Sm_{0.6}Y_{0.4}MnO_3$ - E//b



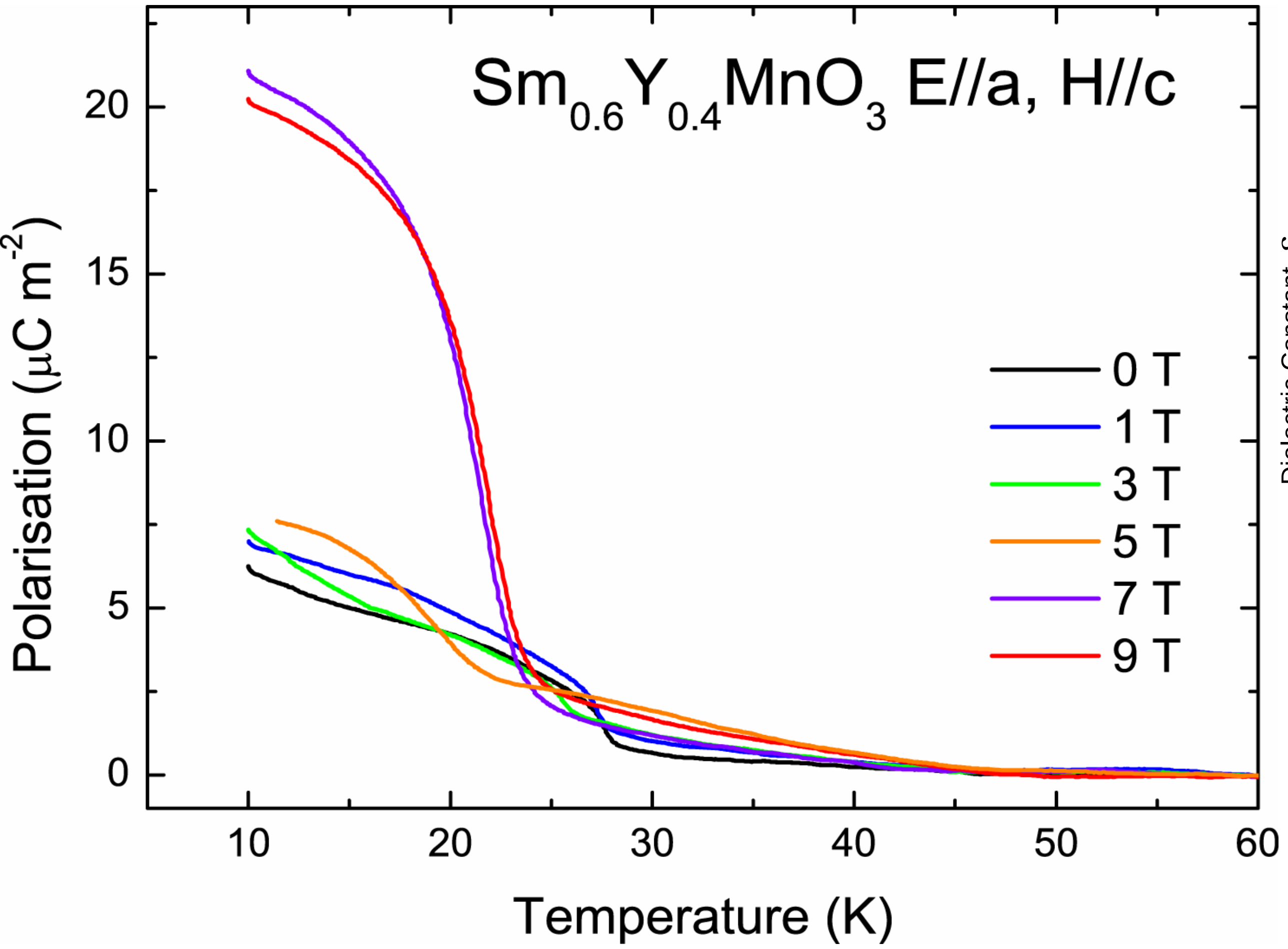
$Sm_{0.6}Y_{0.4}MnO_3$ - E//c

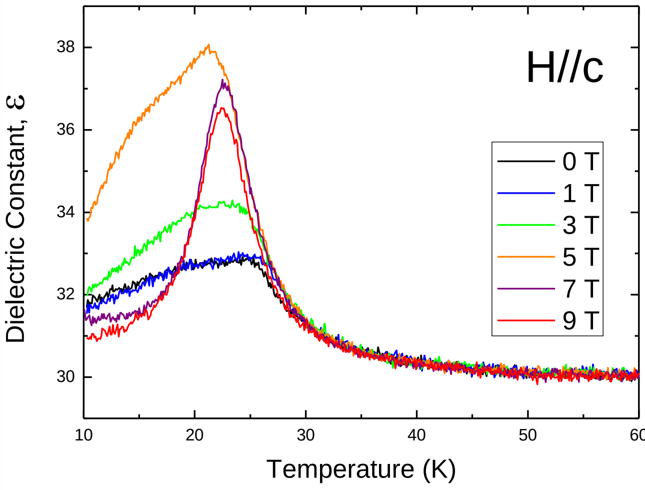


Polarisation

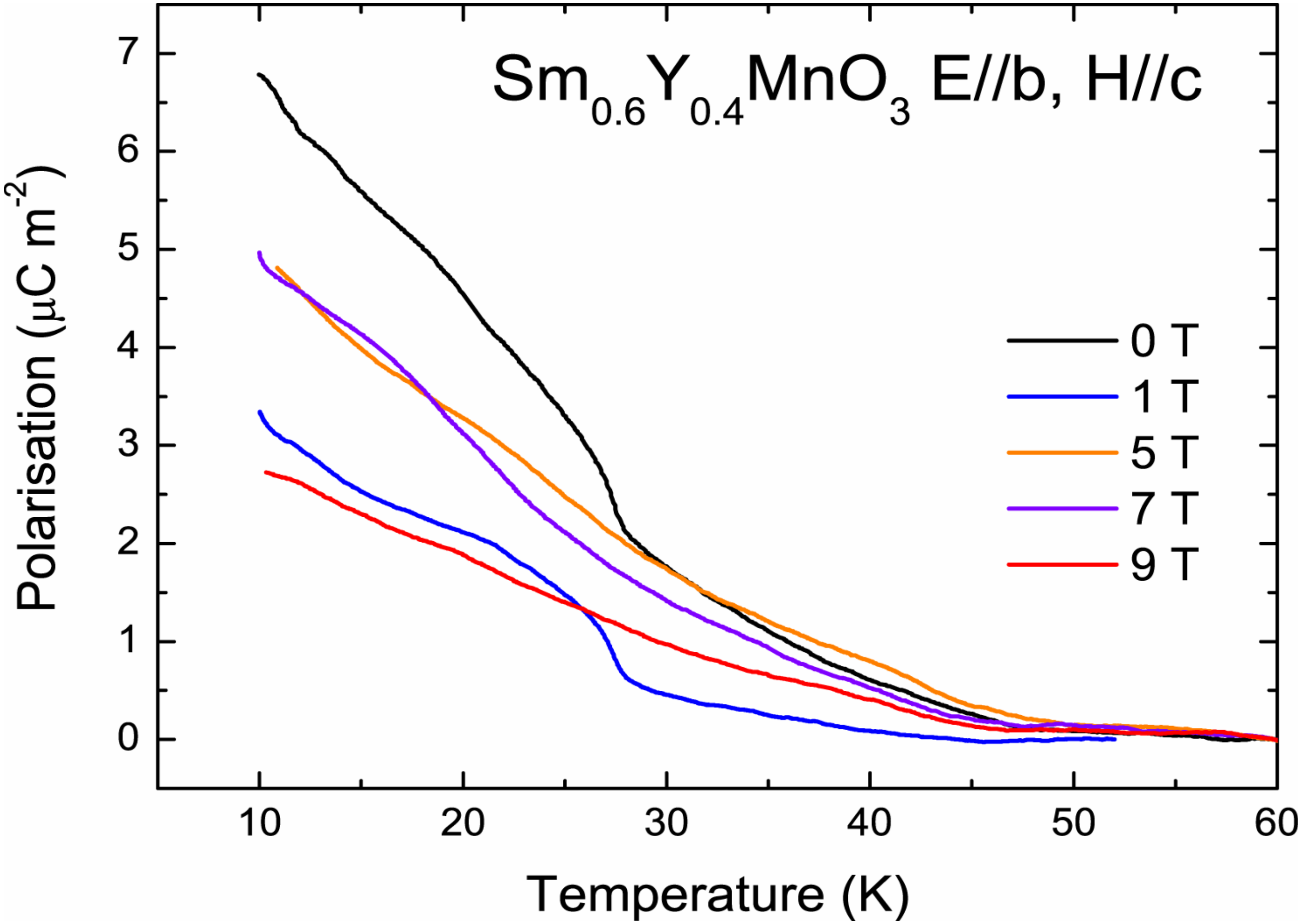


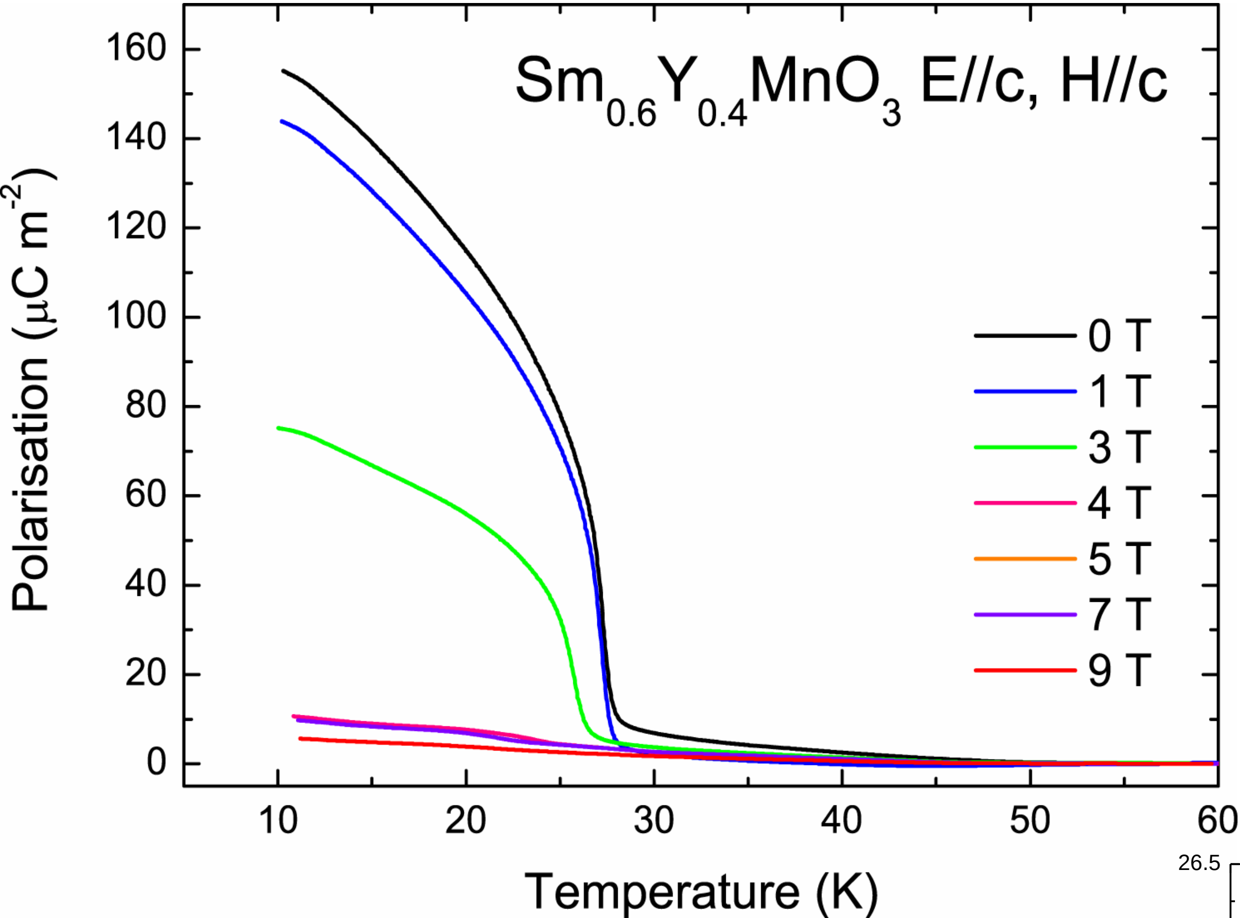
Field Dependence of the Polarisation



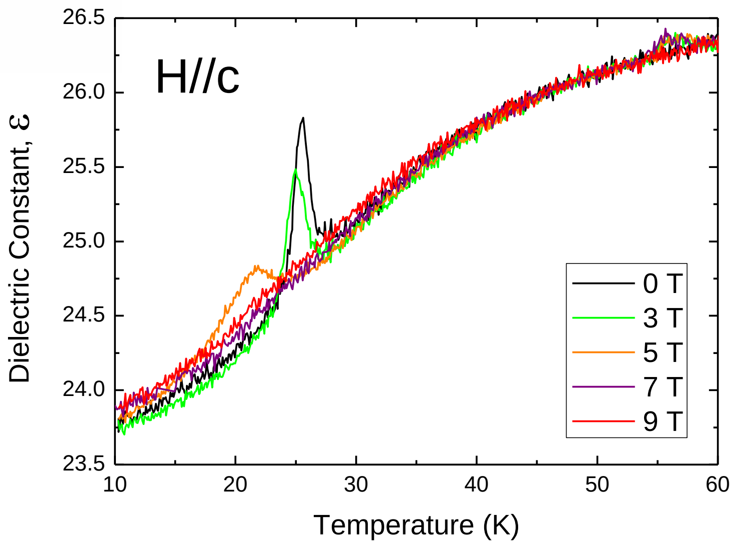


Field Dependence of the Polarisation



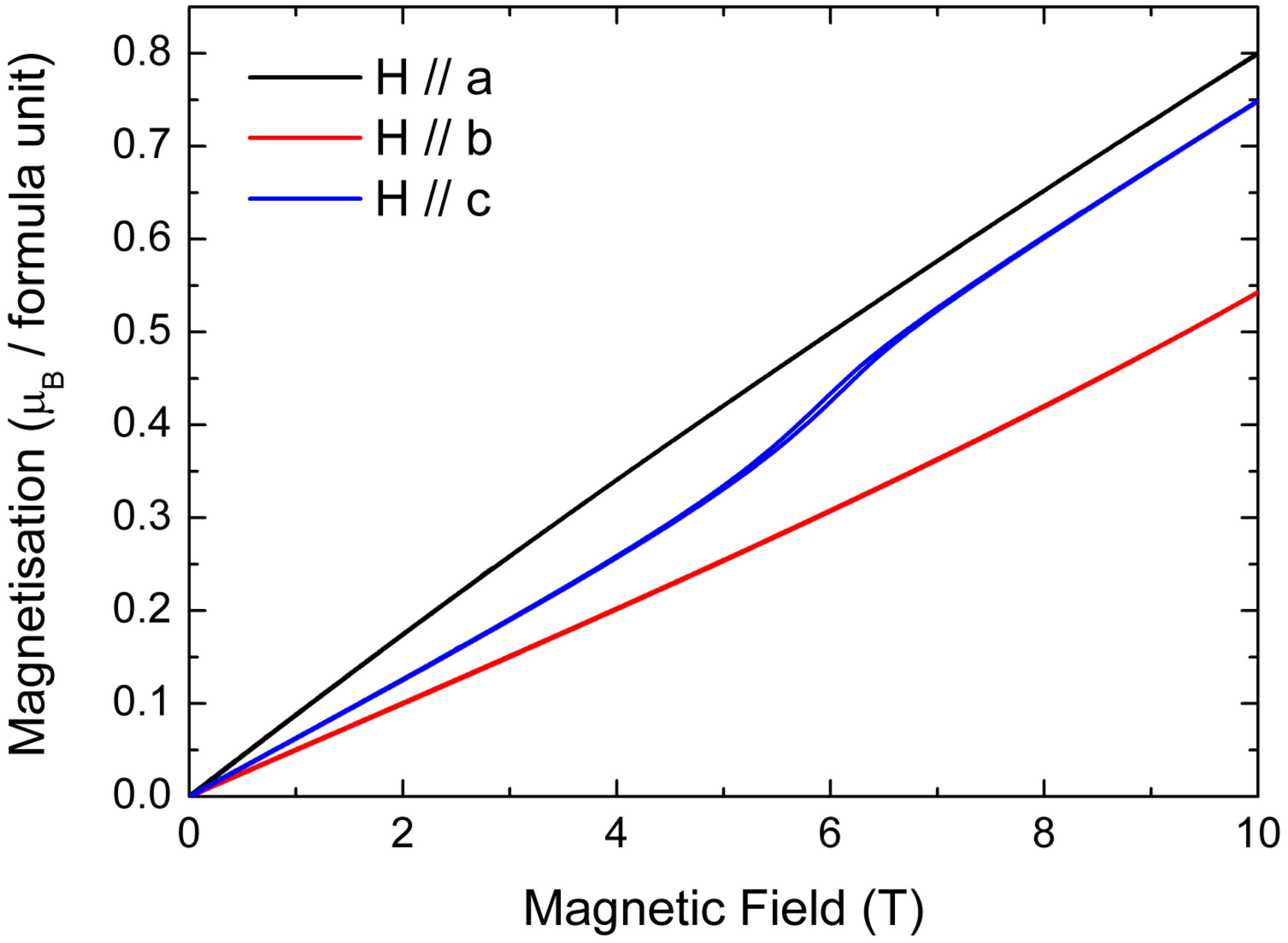


Sm$_{0.6}$Y$_{0.4}$MnO$_3$ E//c, H//c
Polarisation (μC m^{-2})
Temperature (K)
0 T
1 T
3 T
4 T
5 T
7 T
9 T
160
140
120
100
80
60
40
20
0
10
20
30
40
50
60



H//c
Dielectric Constant, ε
Temperature (K)
0 T
3 T
5 T
7 T
9 T
26.5
26.0
25.5
25.0
24.5
24.0
23.5
10
20
30
40
50
60

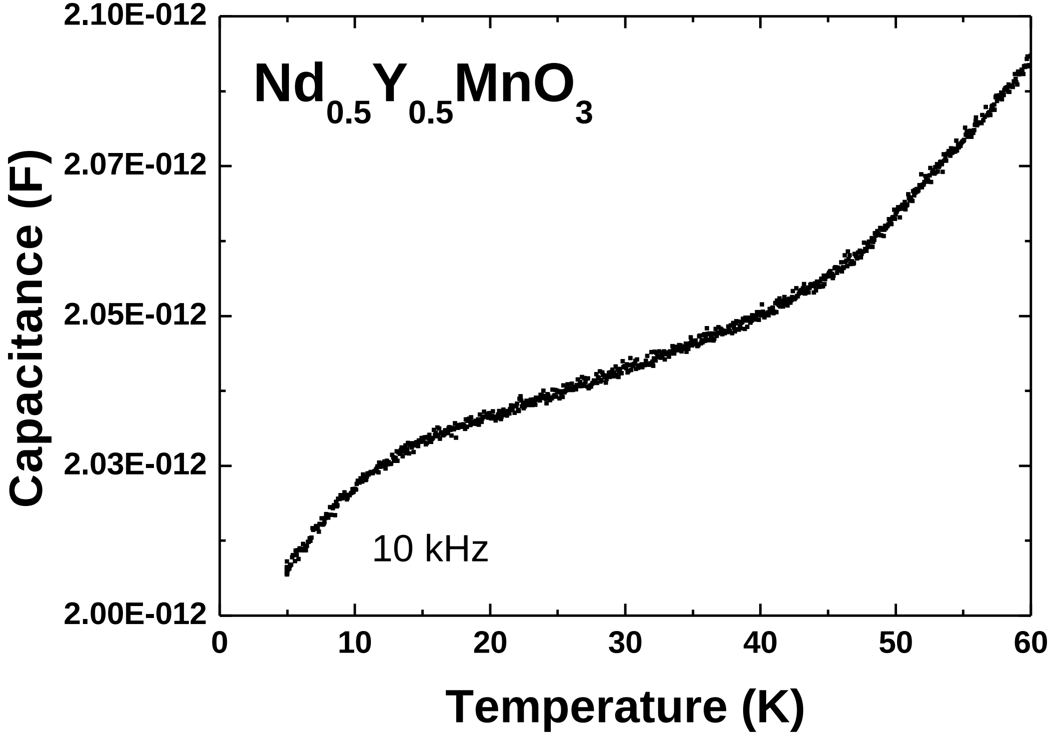
$Sm_{0.6}Y_{0.4}MnO_3$ Crystals-Magnetisation



$Nd_{1-x}Y_xMnO_3$

No anomalies seen in the dielectric properties for the Y substituted samples.

Polycrystalline samples for $Nd_{1-x}Y_xMnO_3$, x=0 to 0.5



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Future Work

•Detailed magnetic structure to be investigated using neutrons. ^{149}Sm highly absorbing for neutrons, isotopic (^{154}Sm) samples to be used

•Proposal submitted to study the magnetic ordering using neutron powder diffraction (GEM-ISIS) and X-rays (Xmas beamline at the ESRF)

•Structure-property correlations in manganites and other related materials- including frustrated magnets

http: //go.warwick.ac.uk/supermag
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