Measuring magnetism in ferroelectrics using neutron scattering

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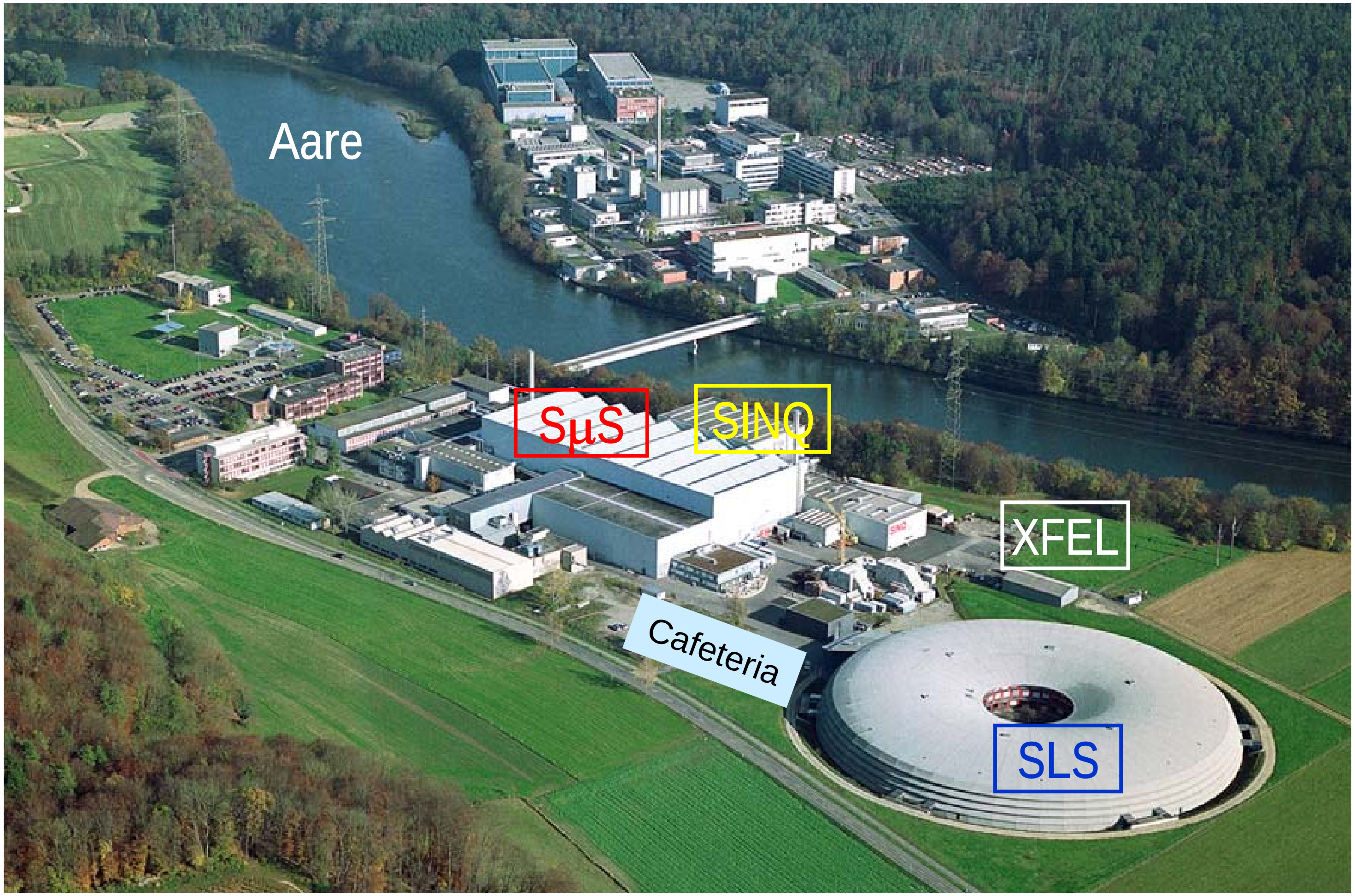
Outline

- Introduction in neutron scattering
- Magnetic neutron scattering in magnetic ferroelectrics
- Determination of magnetic structures
- Symmetry properties of magnetically-induced ferroelectricity

Paul Scherrer Institute



User facilities with neutron, muon and synchrotron sources, and (hopefully) soon a free-electron laser

Neutron scattering

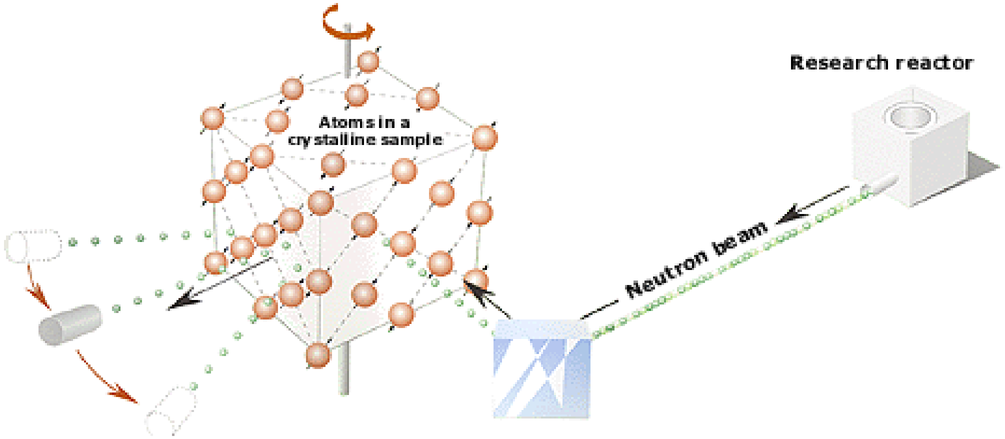
Structure, vibrations, magnetic order, magnetic correlations

where the atoms and what do they do?
how do the magnetic moments fluctuate or order?

Advantages:

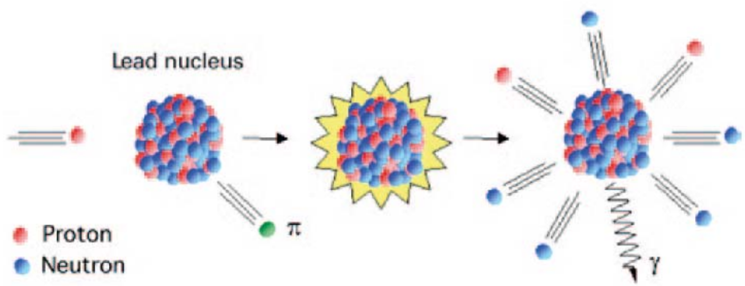
1) Wavelength comparable with interatomic spacings
2) Kinetic energy comparable with that of moving atoms in a solid
3) Penetrating => bulk properties are measured & sample can be contained
4) Weak interaction with matter aids interpretation of scattering data
5) Wave-vector and energy control

Nobel Prize 1994:
Shull and Brockhouse

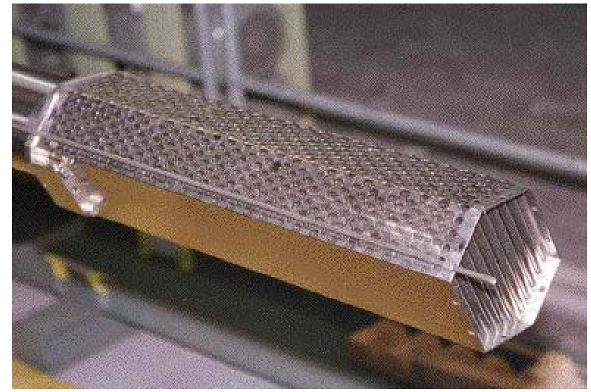


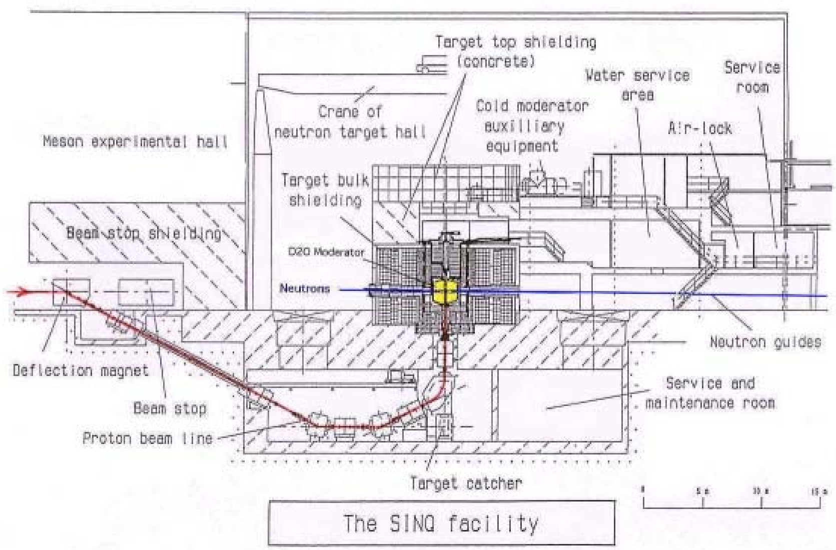
http://www.nobelprize.org

SINQ spallation neutron source

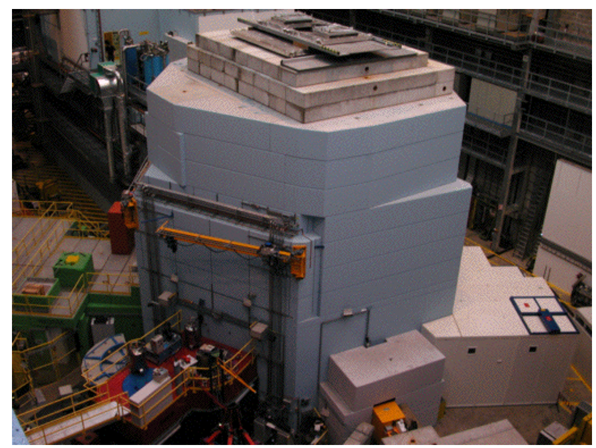


Spallation process


Heavy-metal target



Side view of proton current hitting target

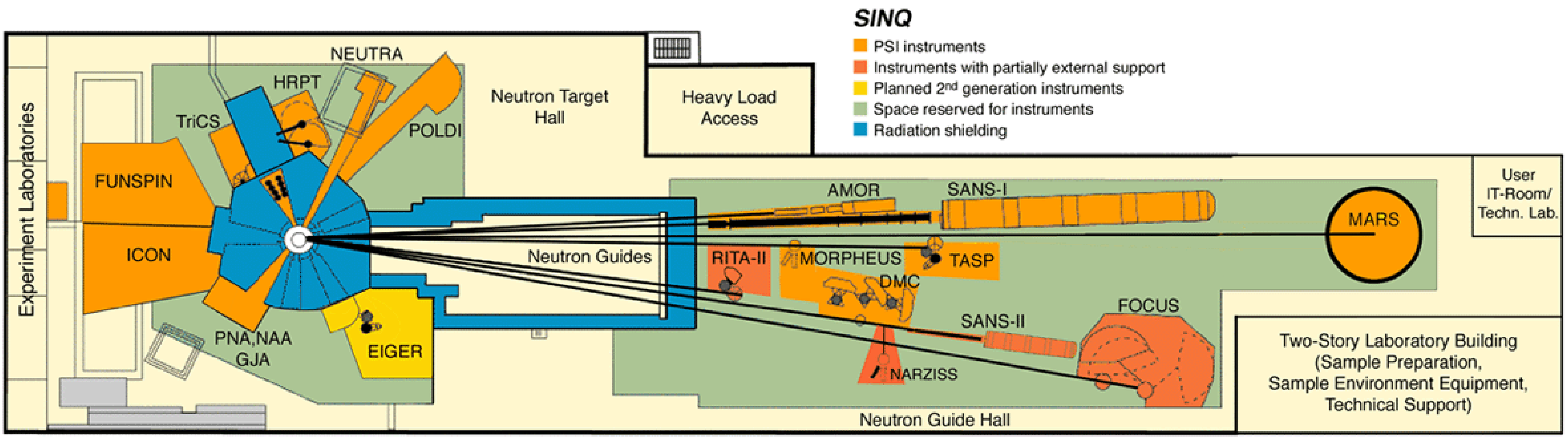

Radiation shielding for target

Next European neutron source

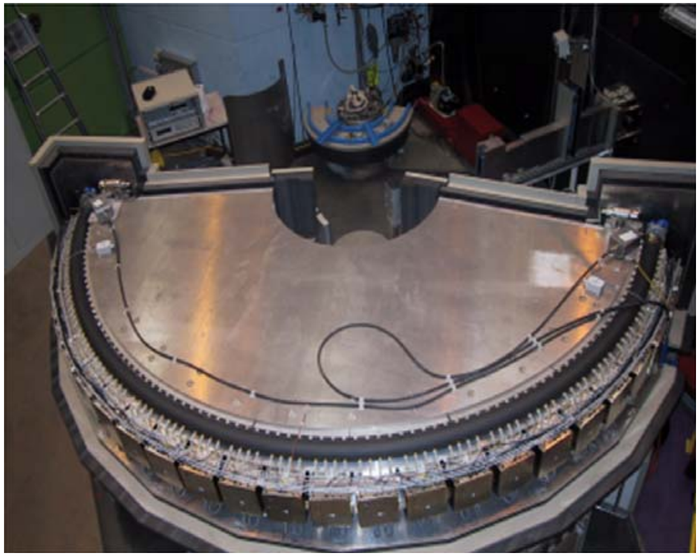
1) Pulsed neutron source with 5 MW proton current
2) First neutrons planned for 2019
3) Supported by 17 European nations
4) ESS will be most powerful neutron source worldwide

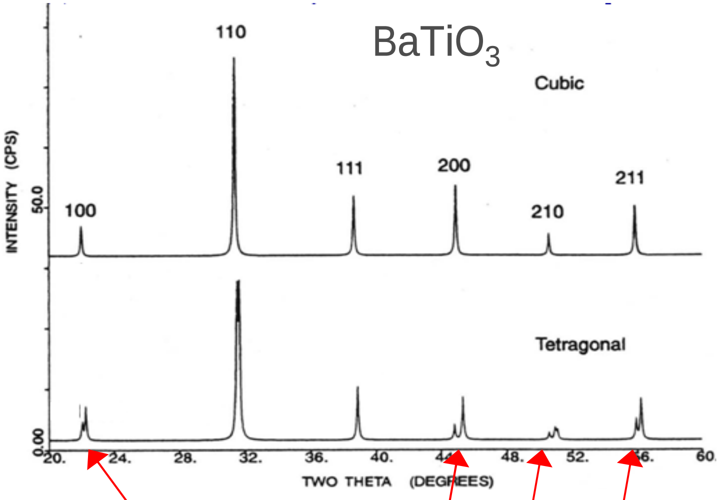
Lund, Sweden

Large variety of neutron scattering instruments



Neutron powder diffractometer



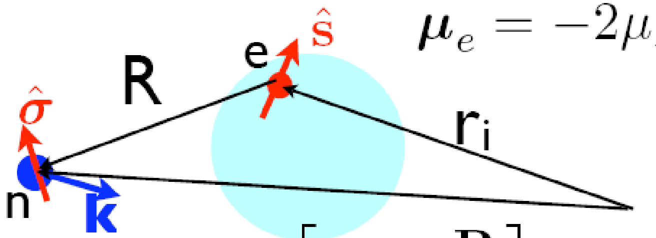


Splitting of nuclear Bragg peaks

Cross-section of magnetic neutron scattering

$$\boldsymbol{\mu}_n = 2\gamma\mu_n \frac{\hat{\boldsymbol{\sigma}}}{2}$$

$$\boldsymbol{\mu}_e = -2\mu_B \hat{\mathbf{s}}$$



Magnetic field from electron:

$$\mathbf{H}(\mathbf{R}) = -\mathrm{rot}\left[\frac{\boldsymbol{\mu}_e \times \mathbf{R}}{|\mathbf{R}|^3}\right] + \mathrm{transl.part}$$

Neutron-electron interaction:

$$V(\mathbf{R}) = -\gamma\mu_n \hat{\boldsymbol{\sigma}} \mathbf{H}(\mathbf{R})$$

Average over neutron coordinates:

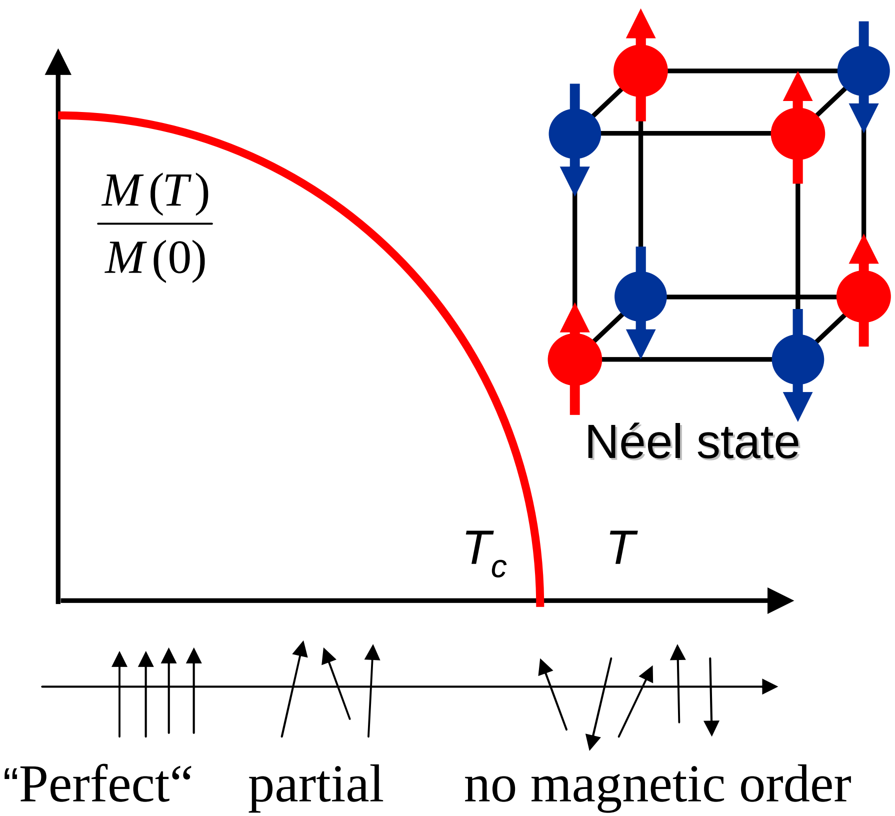
$$\langle \mathbf{k}' | V(\mathbf{R}) | \mathbf{k} \rangle = \gamma r_e \hat{\boldsymbol{\sigma}} \frac{1}{q^2} \underbrace{[\mathbf{q} \times [\underbrace{\hat{\mathbf{s}}_i e^{i\mathbf{q}\mathbf{r}_i}}_{\hat{\mathbf{Q}}} \times \mathbf{q}]]}_{\hat{\mathbf{Q}}_\perp}$$

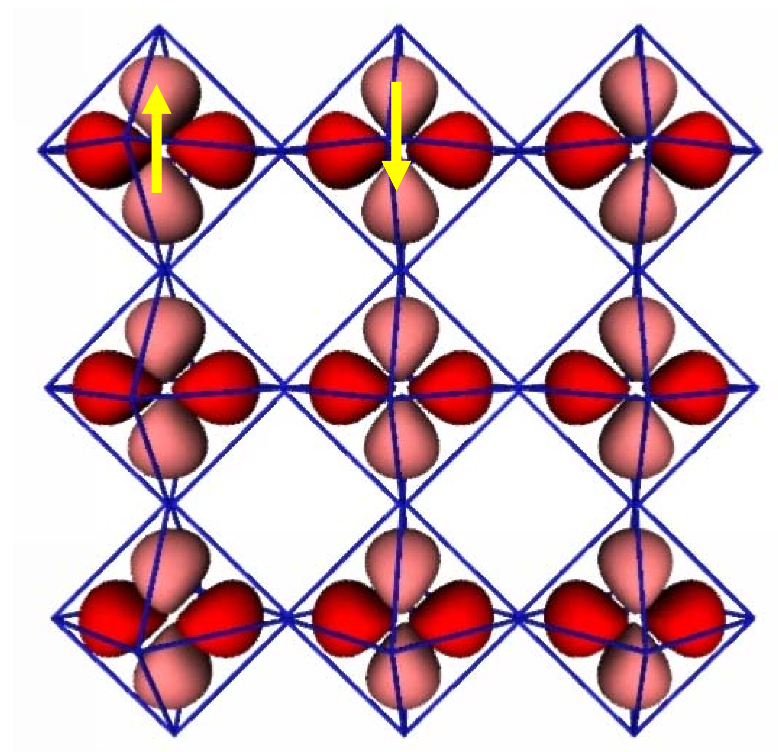
$$\mathbf{q} = \mathbf{k}' - \mathbf{k}$$

magnetic interaction operator $\hat{\mathbf{Q}}_\perp$

Onset of “classical long-range order”

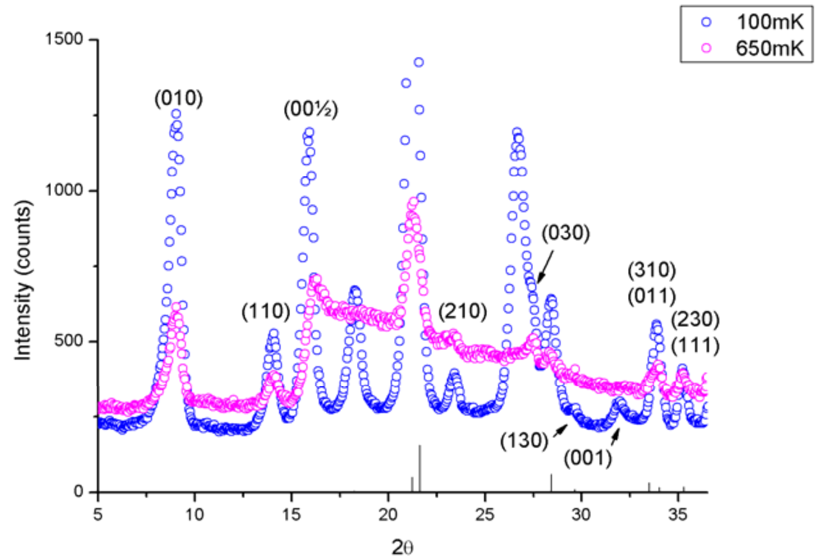
- T >>J: strong fluctuations
- cooperative phase transition for T < J

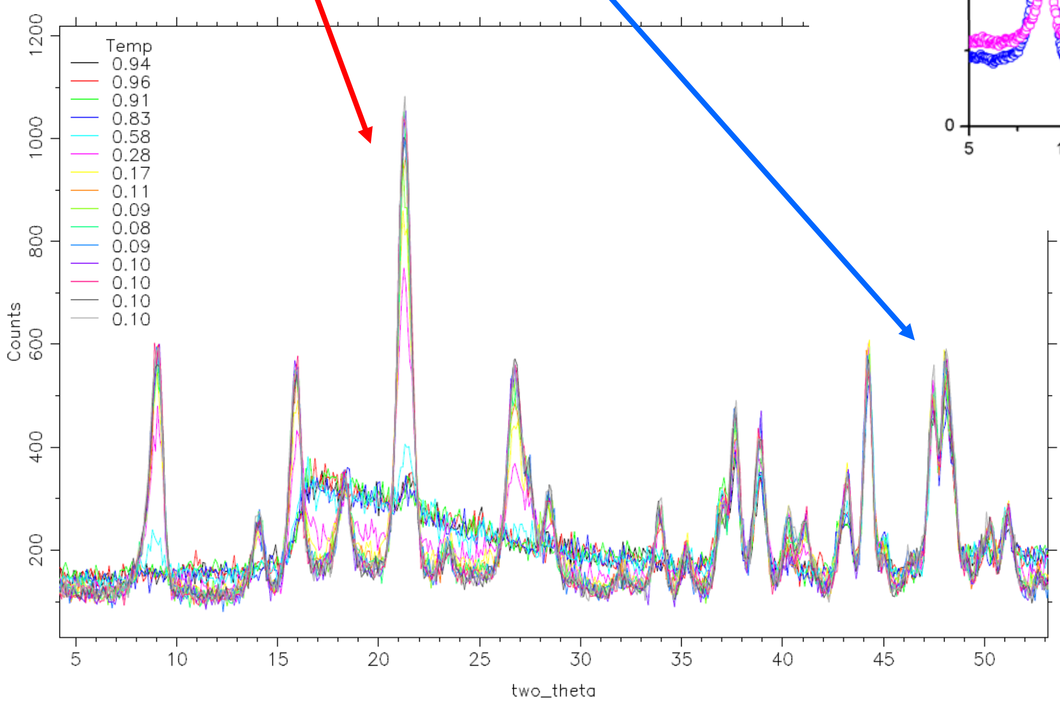




Example of a powder neutron pattern

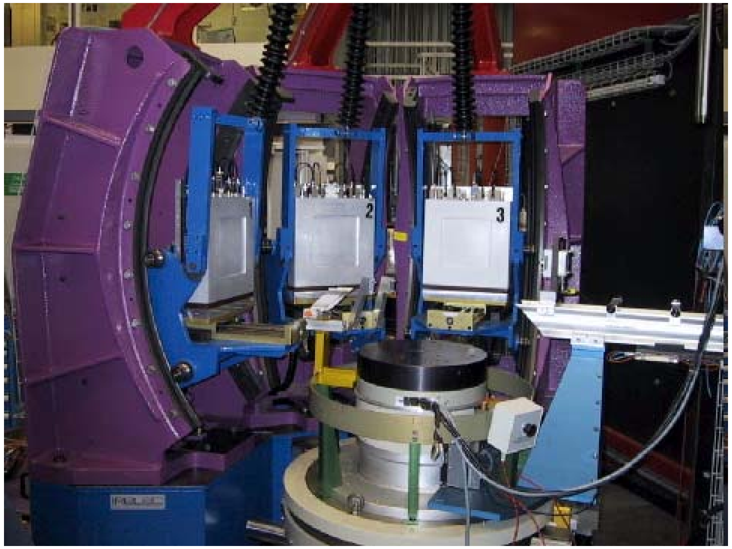
- Magnetic neutron diffraction an be larger than nuclear scattering
- Cross-section are exactly known



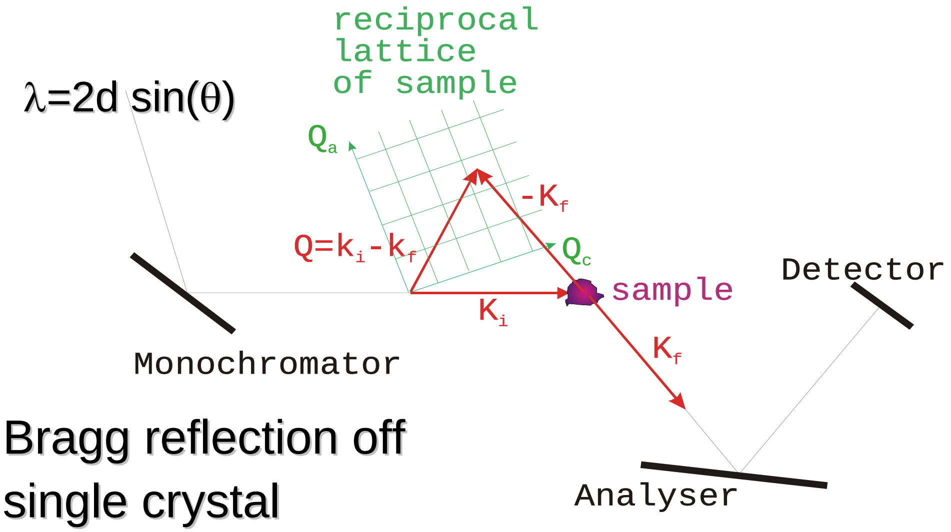


Information about-range and long-range magnetic correlations

Single-crystal neutron scattering

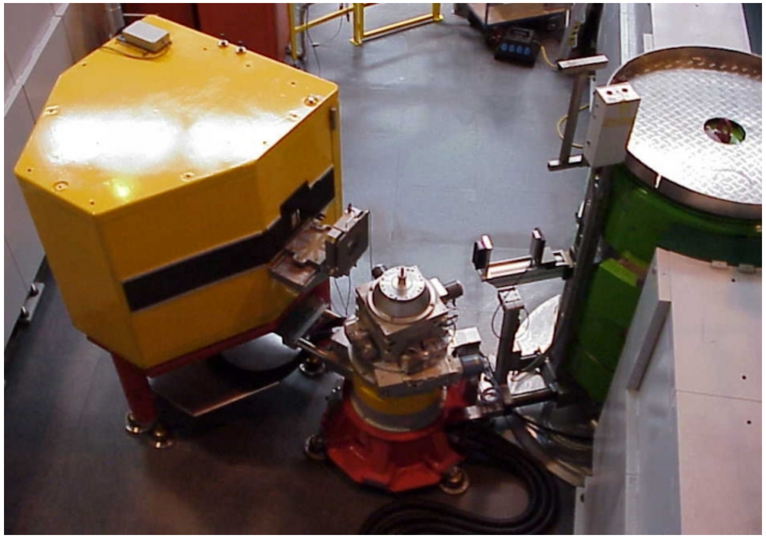


TriCS diffractometer at PSI



Bragg reflection off single crystal

- Structural and magnetic order
- Phonons
- Magnetic excitations



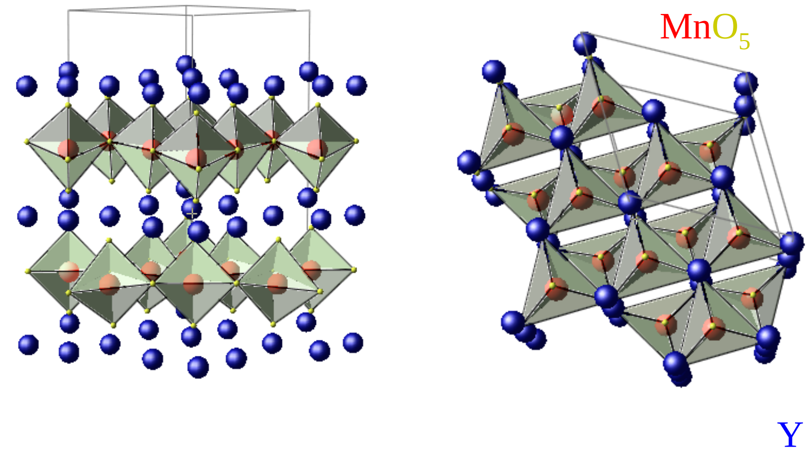
RITA spectrometer at PSI

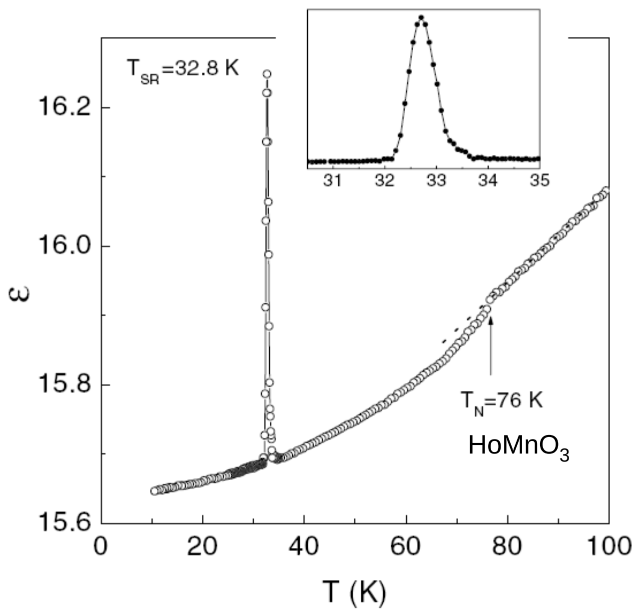
Ferroelectrics that order magnetically: h-$RMnO_3$

1) ferroelectric at high T ~900K
   (gemoetric ferroelectricity)

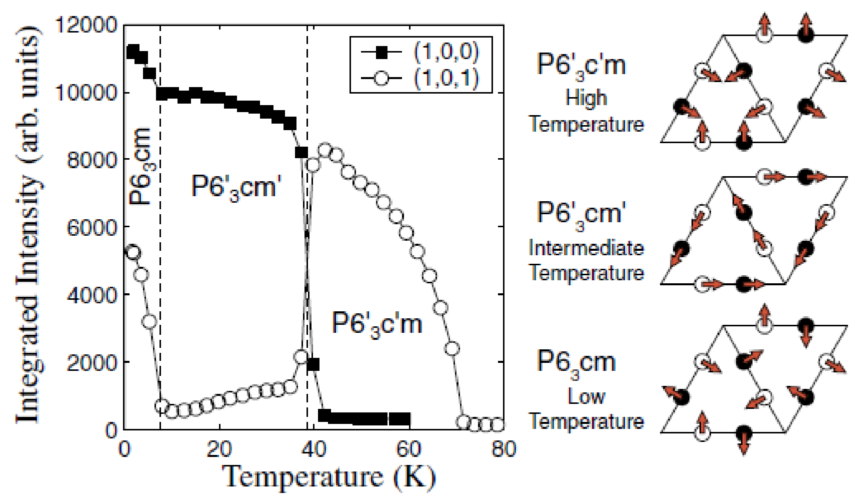
2) Magnetism at much lower T~70K

3) Strong dielectric signal at spin
   reorientation transition



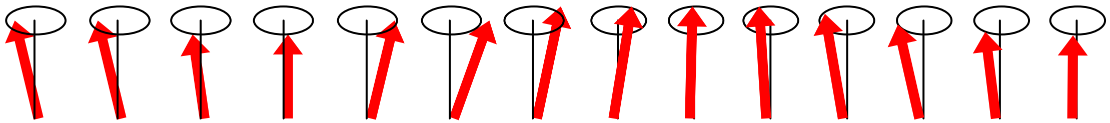


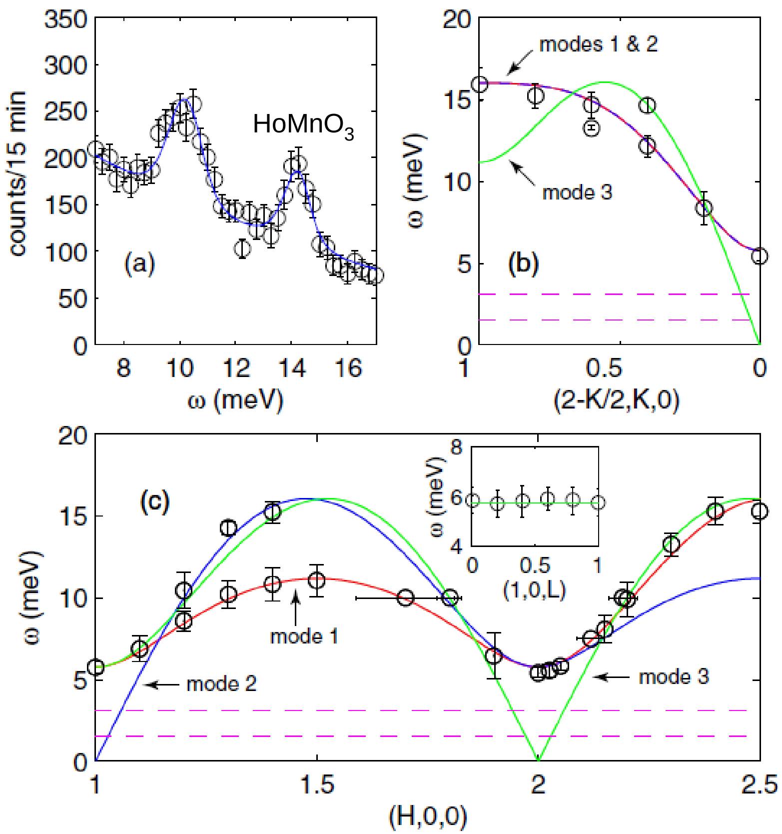
B. Lorenz et al, Phys. Rev. Lett. **92**, 087204 (2004)



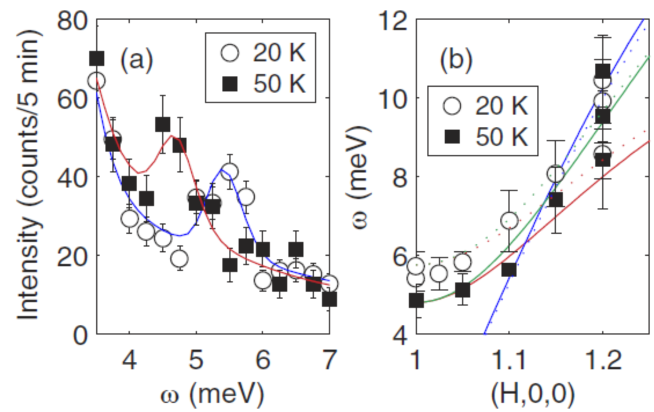
O. Vajk et al, Phys. Rev. Lett. **94**, 087601 (2005).

Measurement of spin-waves $HoMnO_3$





O. Vajk et al, Phys. Rev. Lett. **94**, 087601 (2005).



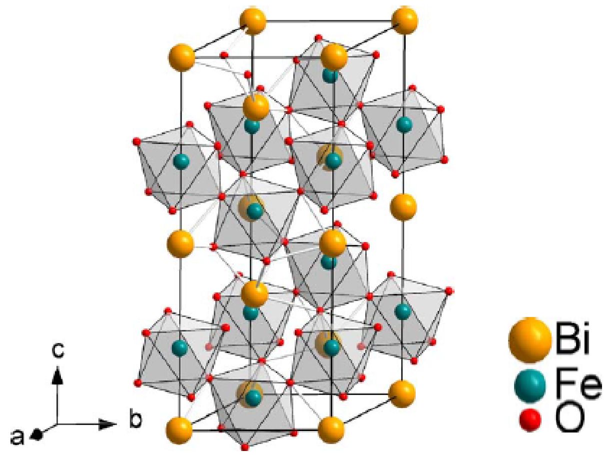
1) well-defined excitation as a function of wave-vector and energy

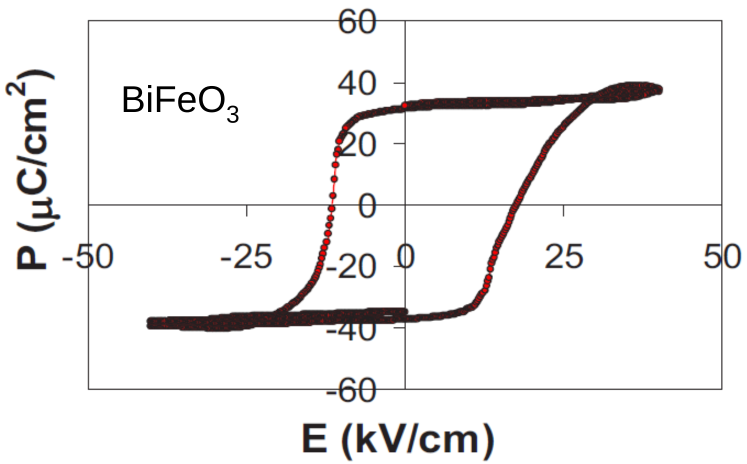
2) Determination of spin

$$H = J\sum_{\langle i,j\rangle} \mathbf{S}_i \cdot \mathbf{S}_j + D\sum_i S_i^z S_i^z$$

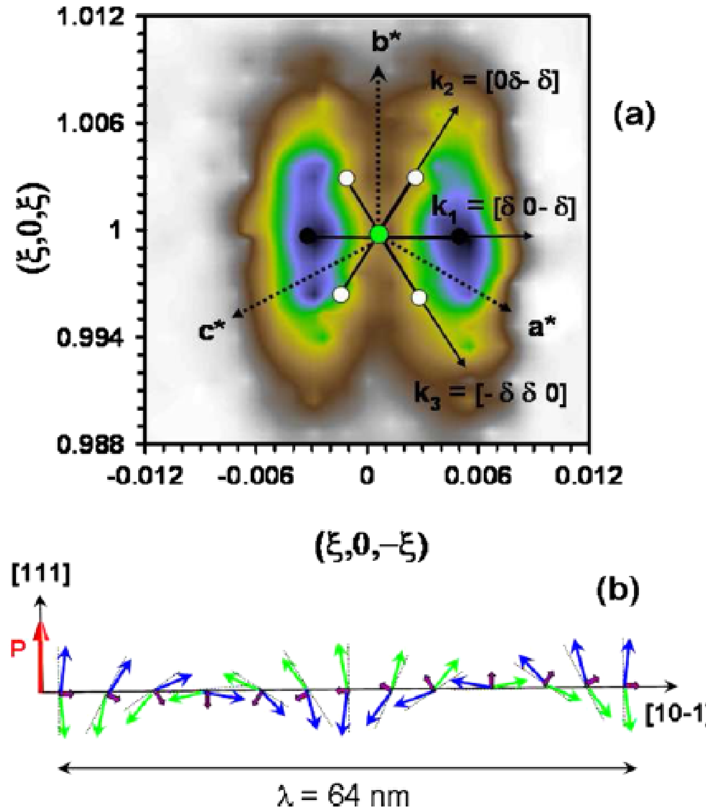
3) Direct o observation of spin-lattice coupling

Neutron scattering on $BiFeO_3$



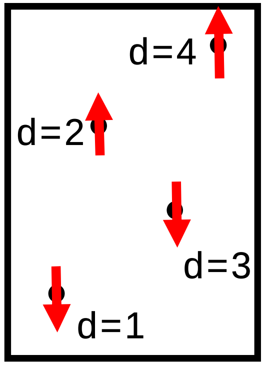


D. Lebeugle et al, Phys. Rev. B **76**, 024116 (2007).

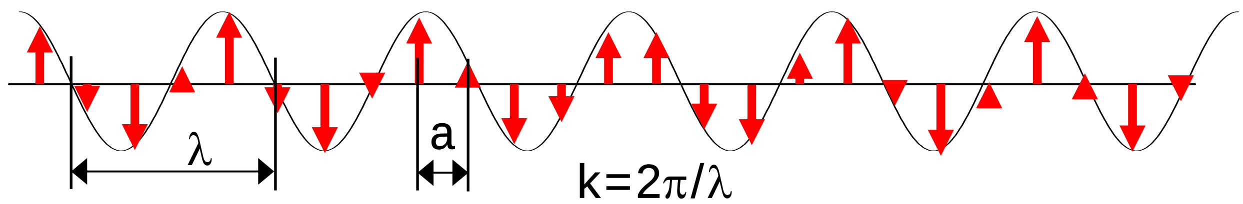


D. Lebeugle et al, Phys. Rev. Lett. **100**, 227602 (2008)

Determination of magnetic structures



Example: Transverse-modulated spin structure



order in unit cell

propagation of magnetic structure is given by **k**

$$m^{\alpha}_{\mathbf{d}+\mathbf{R}} = \psi^{\alpha}_{d} \exp(i2\pi\mathbf{k}\cdot(\mathbf{d}+\mathbf{R})) + (\psi^{\alpha}_{d})^{*} \exp(-i2\pi\mathbf{k}\cdot(\mathbf{d}+\mathbf{R}))$$

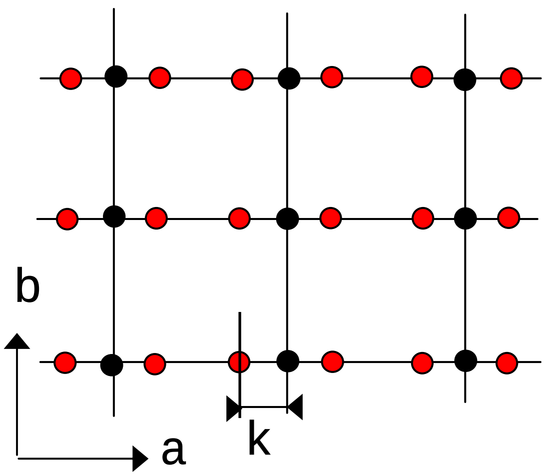
Determination of magnetic structure from diffraction experiment

$$\frac{d^2\sigma}{dEd\Omega} \propto \sum_{\alpha\beta}(\delta_{\alpha\beta} - \hat{Q}_{\alpha}\hat{Q}_{\beta})S^{\alpha\beta}(Q,\omega)$$

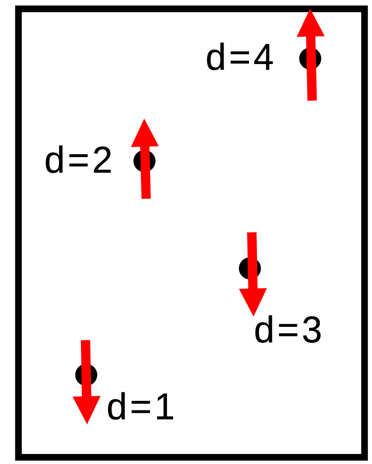
measurements in reciprocal space

Determination of magnetic structures

$$S(\mathbf{Q}) = N\left[|F_\perp(\boldsymbol{\tau})|^2\delta((\boldsymbol{\tau}-\mathbf{k})-\mathbf{Q}) + |F_\perp(-\boldsymbol{\tau})|^2\delta((\boldsymbol{\tau}+\mathbf{k})-\mathbf{Q})\right]$$



Magnetic Bragg peaks occur at satellite positions around Bragg peaks of the reciprocal lattice of the nuclear lattice



Spin ordering in unit cell from relative intensities of magn. Bragg peaks

$$F^\alpha(\mathbf{Q}) = \sum_d \psi_d^\alpha \exp(i\mathbf{Q}\cdot\mathbf{d})$$

F(Q) are different for Ψ_d vectors possible by symmetry

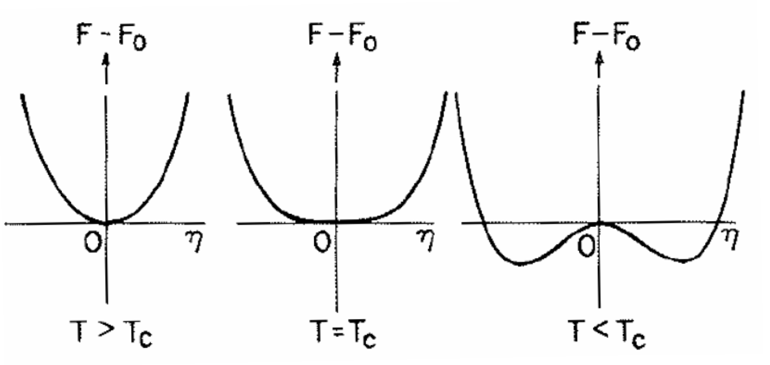
Symmetry restricts what type of magnetic structures are possible

- Many parameters → few parameters
- Symmetry identifies the physical degrees of freedom
- Determined through the symmetry of the space group and the order wave-vector (modulation of the magnetic order)

Continuous phase transition

- Landau theory of free energy

$$F(T,M) = F_0(T) + \alpha_2(T)M^2 + \alpha_4(T)M^4 + \cdots$$



- time reversal symmetry → only even powers of M
- α_2 changes sign at transition
- Free energy is unstable for M non zero for T < T_c (M minimizes the free energy F(T):

$$M^2 \propto (T_c - T)$$

Continuous phase transition

$$F = \alpha_2(T)M^2 + \alpha_4(T)M^4 - MH + \ldots$$

For small H the magnetization M is

$$M\ 2\alpha_2(T) = H \Rightarrow \alpha_2 = \tfrac{1}{2}\chi^{-1}$$

The coefficient, α_2, of M^2 is proportional to the inverse susceptibility:

$$F = \tfrac{1}{2}\chi^{-1}M^2 + \ldots$$

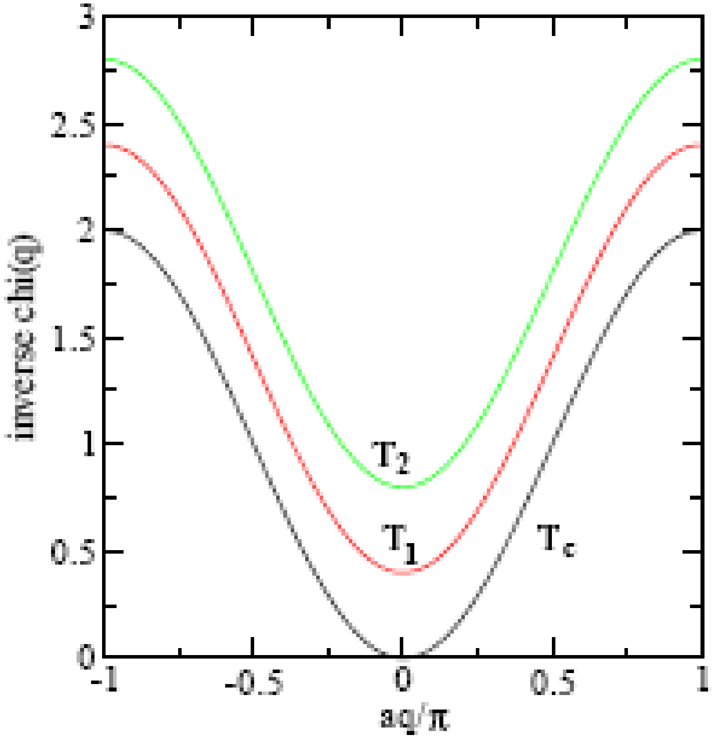
α_2 changes sign at transition → the susceptibility diverges at a continuous transition.

More generally: for all Fourier components:

$$F = \frac{1}{2}\sum_q \chi^{-1}(q)|M(q)|^2$$

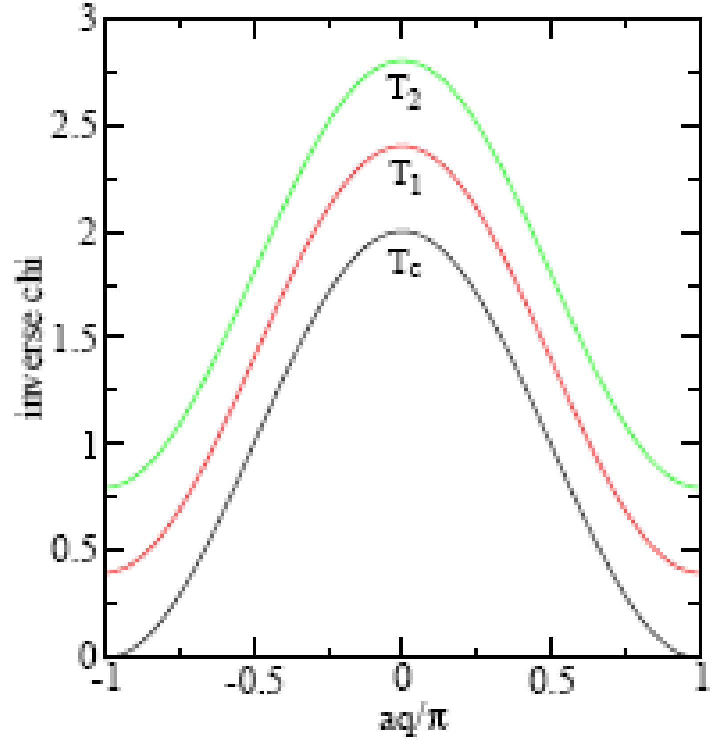
Inverse susceptibility

Ferromagnet



the instability occurs at q=0

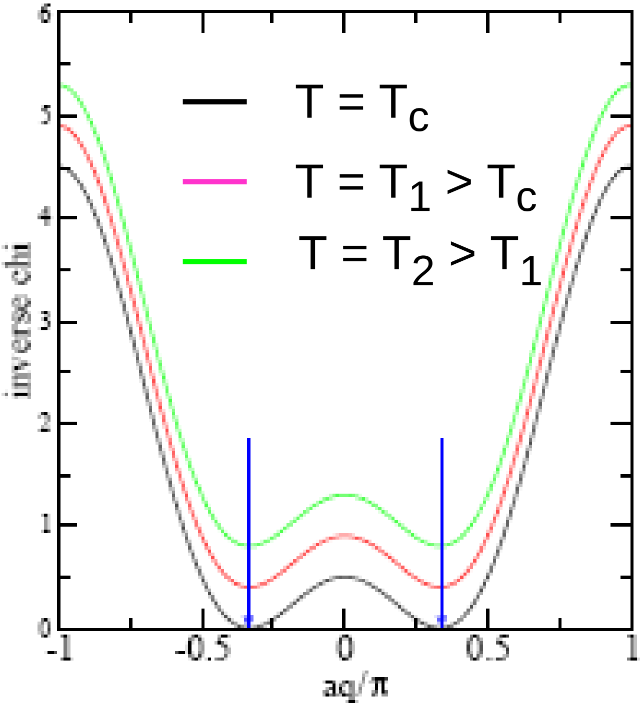
Antiferromagnet



The instability occurs at wave-vector q=π/a

Wave-vector selection: incommensurate order

Incommensurate Magnet



For competing interactions, the minimum in inverse $\chi(Q)$ can be anywhere in the zone.

The minimum in inverse $\chi(Q)$ locates the wavevector of the ordered state ("wavevector selection")

In simple cases, inverse $\chi(Q)$ is given by the Fourier transform of the interactions

Easy-axis antiferromagnets

So far M was a scaler, what happens when the M is a vector?

Suppose we have vector spins with an easy axis along z.

$$F = \frac{1}{2}[T - T_c]|\overrightarrow{M}|^2 + K[M_x^2 + M_y^2] + O(M^4),$$

where K>0 is the anisotropy energy.

Here as T approaches T_c from above, only M_z becomes unstable relative to long-range order.

Several magnetic ions in the unit cell

$$S_\alpha(\vec{R},\vec{\tau}) = \sum_q s_\alpha(\vec{q},\vec{\tau})\exp[-iq\bullet(\vec{R}+\vec{\tau})],$$

Define spin vector describing all spins in the unit cell:

$$s_\alpha(\vec{q}) = [s(\vec{q},\vec{\tau}_1), s(\vec{q},\vec{\tau}_2), s(\vec{q},\vec{\tau}_3),\ldots]$$

Then free energy can be written as:

$$F = \sum_{\alpha\beta\tau\rho} F_{\alpha\tau;\beta\rho}(\vec{q})\, s_\alpha(\vec{q})^*\, s_\beta(\vec{q}).$$

One of the eigenvalue of *F* that becomes first zero. The susceptibility of the associated eigenvector diverges and the system orders.

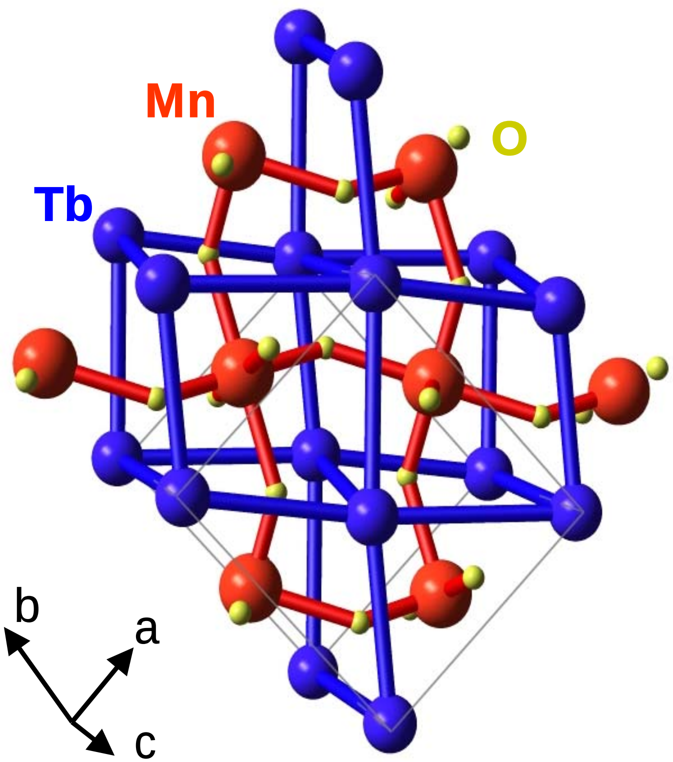
Magnetic order at a second order phase transition
Is described by one irreducible representation.

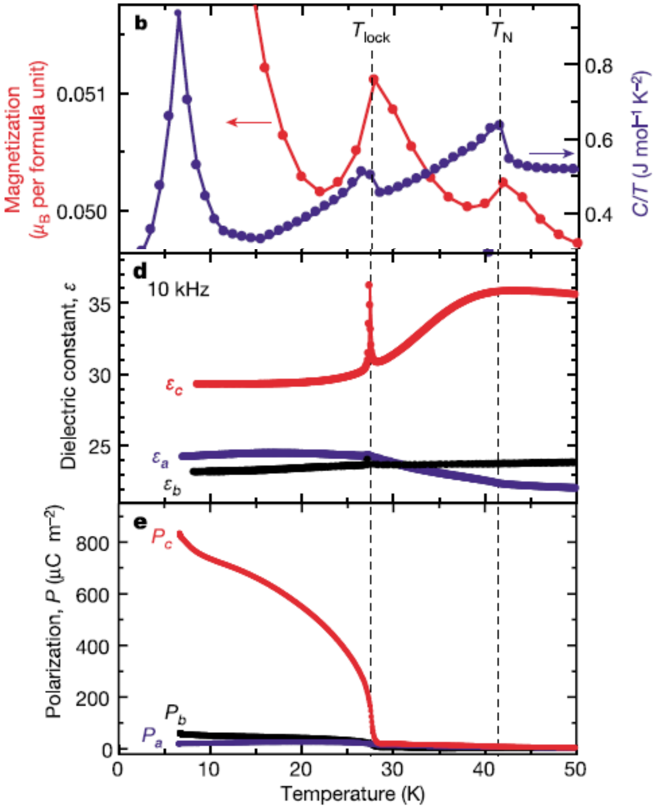
Recipe to determine the irreducible representations

- Determination of the ordering wave-vector (via diffractive methods)
- Determination of the symmetry elements that leave the ordering wave-vector invariant: **little group**
- **Character table** of little group: → determine the number and symmetry properties of the **irreducible representations**
- **Projector method** to find possible magnetic order parameters

MODY program does it for you, others available

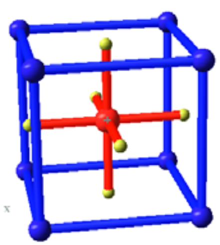
Ferroelectricity in $TbMnO_3$





T. Kimura et al, Nature **426**, 55 (2003)

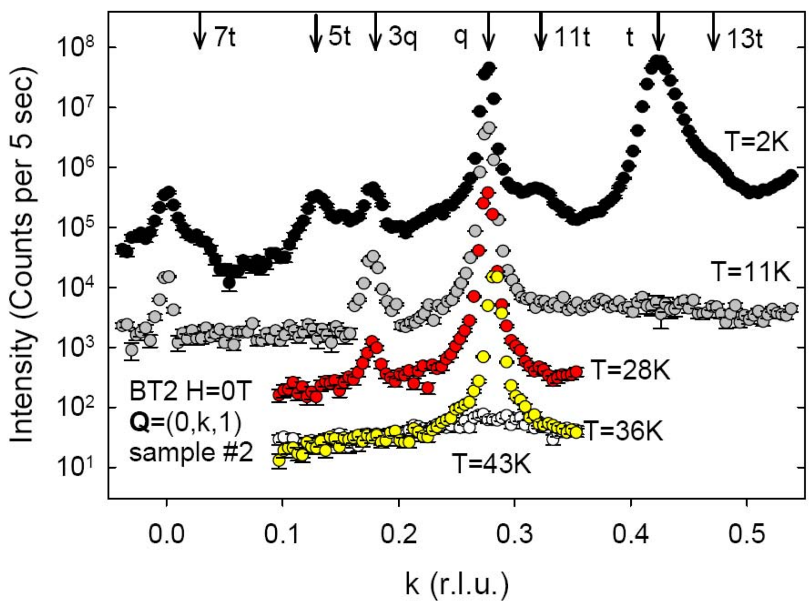
distorted perovskite structure
space group Pbnm
Mn^{3+} carries S=2

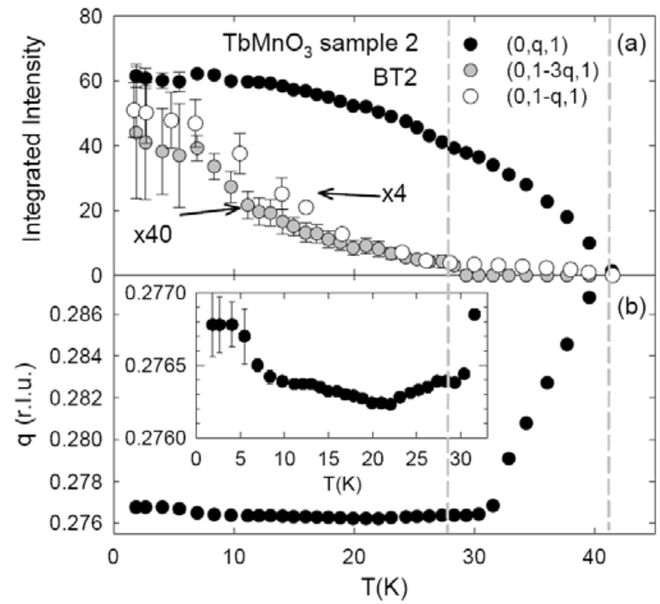


$BaTiO_3$

ferroelectric below 27K
direct coupling to magnetic field observed

T-dependence of magnetic order parameter

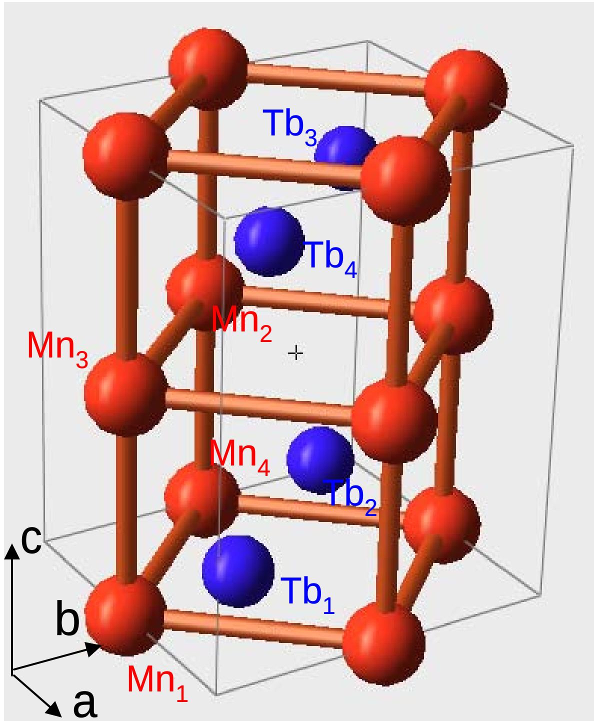




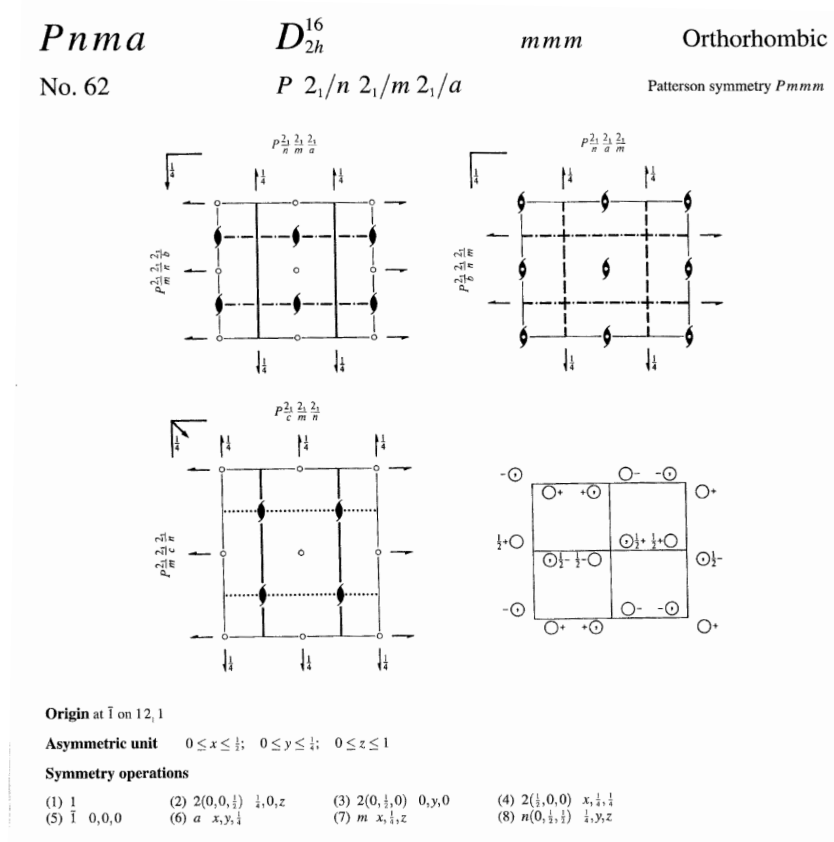
M. Kenzelmann et al, Phys. Rev. Lett. **95**, 087206 (2005)

- No lock-in transition at T=28K
- Development of higher-order peak below T=28K
- Onset of ferroelectricity coincides with strengthening of (0,1-q,1) Bragg peak
- Development of Tb order below 8K

Space group of $TbMnO_3$



$$
\begin{aligned}
\mathrm{Mn_1}: \ \mathbf{r} &= (0.50,\ 0.00,\ 0.00)\\
\mathrm{Mn_2}: \ \mathbf{r} &= (0.00,\ 0.50,\ 0.50)\\
\mathrm{Mn_3}: \ \mathbf{r} &= (0.50,\ 0.00,\ 0.50)\\
\mathrm{Mn_4}: \ \mathbf{r} &= (0.00,\ 0.50,\ 0.00)\\
\mathrm{Tb_1}: \ \mathbf{r} &= (0.985,\ 0.08,\ 0.25)\\
\mathrm{Tb_2}: \ \mathbf{r} &= (0.515,\ 0.58,\ 0.25)\\
\mathrm{Tb_3}: \ \mathbf{r} &= (0.015,\ 0.92,\ 0.75)\\
\mathrm{Tb_4}: \ \mathbf{r} &= (0.485,\ 0.42,\ 0.75)
\end{aligned}
$$


$Pnma$ D_{2h}^{16} mmm Orthorhombic

No. 62 $P\ 2_1/n\ 2_1/m\ 2_1/a$ Patterson symmetry $Pmmm$

Origin at $\bar{1}$ on 12_11

Asymmetric unit $0 \le x \le \frac{1}{2}$; $0 \le y \le \frac{1}{4}$; $0 \le z \le 1$

Symmetry operations

(1) 1 (2) $2(0,0,\frac{1}{2})$ $\frac{1}{4},0,z$ (3) $2(0,\frac{1}{2},0)$ $0,y,0$ (4) $2(\frac{1}{2},0,0)$ $x,\frac{1}{4},\frac{1}{4}$

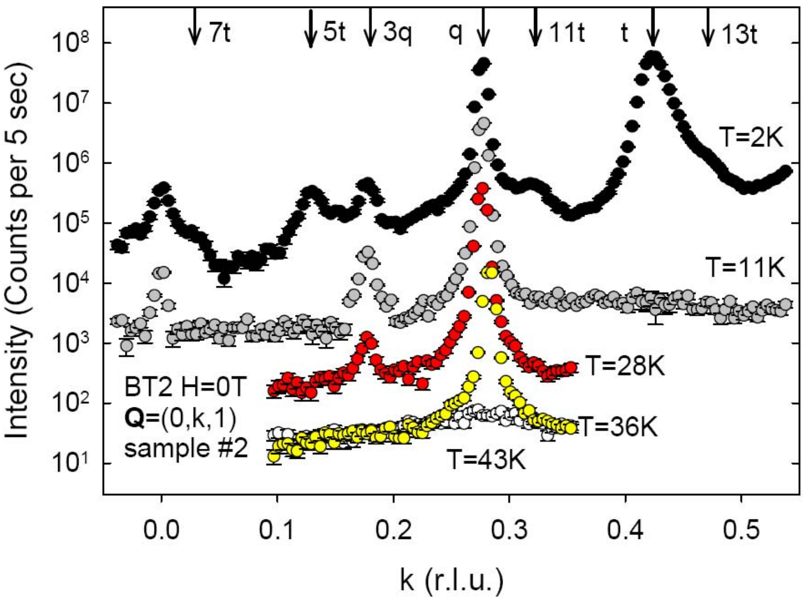
(5) $\bar{1}$ $0,0,0$ (6) a $x,y,\frac{1}{4}$ (7) m $x,\frac{1}{4},z$ (8) $n(0,\frac{1}{2},\frac{1}{2})$ $\frac{1}{4},y,z$

Pbnm (different setting: abc→ bca)

$$\{1,\ \bar{1},\ 2_x,\ 2_y,\ 2_z,\ m_{xy},\ m_{xz},\ m_{yz}\}$$

2 (1/2,0,0) (x,1/4,0) | 2 (0,1/2,0) (¼,y, ¼) | 2 (0,0,1/2) (0,0,z) | m (x,y, ¼) | n (x, ¼,z) | b (¼,y,z)

Little group for magnetic order in $TbMnO_3$



$$\mathrm{Mn}_1: \mathbf{r} = (0.50, 0.00, 0.00)$$
$$\mathrm{Mn}_2: \mathbf{r} = (0.00, 0.50, 0.50)$$
$$\mathrm{Mn}_3: \mathbf{r} = (0.50, 0.00, 0.50)$$
$$\mathrm{Mn}_4: \mathbf{r} = (0.00, 0.50, 0.00)$$
$$\mathrm{Tb}_1: \mathbf{r} = (0.985, 0.08, 0.25)$$
$$\mathrm{Tb}_2: \mathbf{r} = (0.515, 0.58, 0.25)$$
$$\mathrm{Tb}_3: \mathbf{r} = (0.015, 0.92, 0.75)$$
$$\mathrm{Tb}_4: \mathbf{r} = (0.485, 0.42, 0.75)$$

2_y $Mn_1 \rightarrow Mn_2$

m_{xy} $Mn_1 \rightarrow Mn_3$

m_{yz} $Mn_1 \rightarrow Mn_4$

2_y $Tb_1 \rightarrow Tb_2$

m_{xy} $Tb_1 \rightarrow Tb_1$

m_{yz} $Tb_1 \rightarrow Tb_2$

→ two orbits of Tb ions

Ordering wave-vector: **Q**=(0,q,0)

Little group $G_{\mathbf{k}}$: $1,\ 2_y,\ m_{xy},\ m_{yz}$

- 2_y: 2 (0,1/2,0) (¼,y, ¼)
- m_{xy}: m (x,y, ¼)
- m_{yz}: b (¼,y,z)

Basis vectors from the projector method

	1	2_y	m_{xy}	m_{yz}
Γ^1	1	α	1	α
Γ^2	1	α	-1	-α
Γ^3	1	-α	1	-α
Γ^4	1	-α	-1	α

$$\phi^\lambda = \sum_g \chi^\lambda(g) g(\phi)$$

1 $Mn_1 \rightarrow Mn_1$ 1 $(m_x,m_y,m_z) \rightarrow (m_x, m_y, m_z)$

2_y $Mn_1 \rightarrow Mn_2$ 2_y $(m_x,m_y,m_z) \rightarrow (-m_x, m_y,-m_z)$

m_{xy} $Mn_1 \rightarrow Mn_3$ m_{xy} $(m_x,m_y,m_z) \rightarrow (-m_x,-m_y, m_z)$

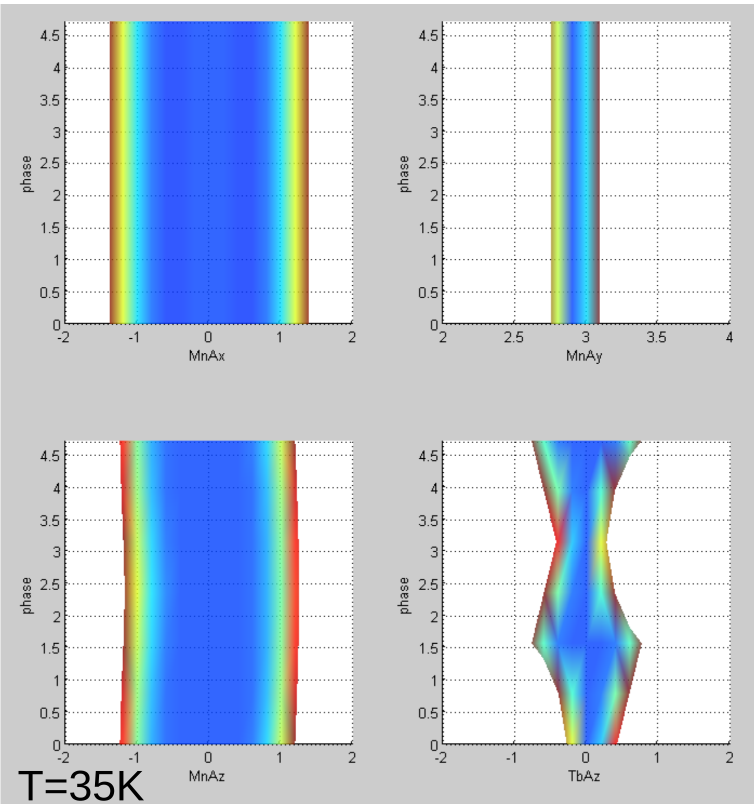
m_{yz} $Mn_1 \rightarrow Mn_4$ m_{yz} $(m_x,m_y,m_z) \rightarrow (m_x,-m_y,-m_z)$

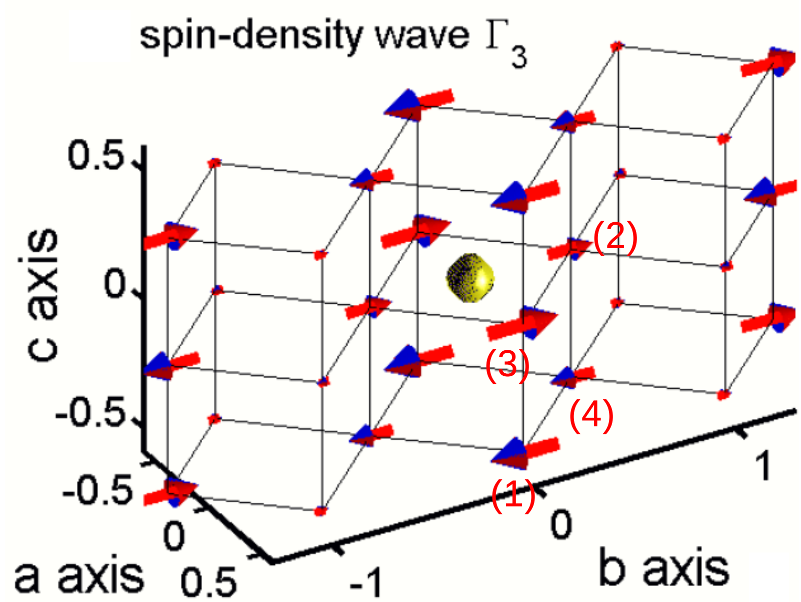
	Mn_1	Mn_2	Mn_3	Mn_4
ψ_1	m_x^1	$-\alpha m_x^1$	$-m_x^1$	αm_x^1
	m_y^1	αm_y^1	$-m_y^1$	$-\alpha m_y^1$
	m_z^1	$-\alpha m_z^1$	m_z^1	$-\alpha m_z^1$
ψ_2	m_x^2	$-\alpha m_x^2$	m_x^2	$-\alpha m_x^2$
	m_y^2	αm_y^2	m_y^2	αm_y^2
	m_z^2	$-\alpha m_z^2$	$-m_z^2$	αm_z^2
ψ_3	m_x^3	αm_x^3	$-m_x^3$	$-\alpha m_x^3$
	m_y^3	$-\alpha m_y^3$	$-m_y^3$	αm_y^3
	m_z^3	αm_z^3	m_z^3	αm_z^3
ψ_4	m_x^4	αm_x^4	m_x^4	αm_x^4
	m_y^4	$-\alpha m_y^4$	m_y^4	$-\alpha m_y^4$
	m_z^4	αm_z^4	$-m_z^4$	$-\alpha m_z^4$

	Tb_1	Tb_2	Tb_3	Tb_4
ψ_1	0	0	0	0
	0	0	0	0
	M_z^1	αM_z^1	N_z^1	αN_z^1
ψ_2	M_x^2	αM_x^2	N_x^2	αN_x^2
	M_y^2	$-\alpha M_y^2$	N_y^2	$-\alpha N_y^2$
	0	0	0	0
ψ_3	0	0	0	0
	0	0	0	0
	M_z^3	$-\alpha M_z^3$	N_z^3	$-\alpha N_z^3$
ψ_4	M_x^4	$-\alpha M_x^4$	N_x^4	$-\alpha N_x^4$
	M_y^4	αM_y^4	N_y^4	αN_y^4
	0	0	0	0

Fitting of the data: χ^2maps

$$\chi^2 = \Sigma_i^n w_i(|F_o^i| - |F_c^i|)^2/(n-m)$$





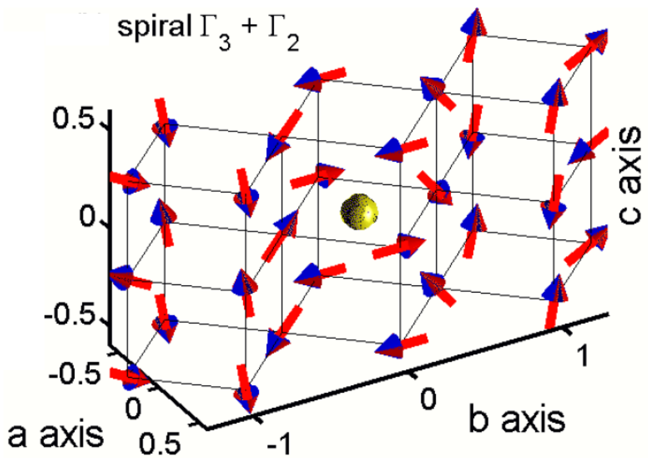
	Mn1	Mn2	Mn3	Mn4
ψ_1	m_x^1	$-\alpha m_x^1$	$-m_x^1$	αm_x^1
	m_y^1	αm_y^1	$-m_y^1$	$-\alpha m_y^1$
	m_z^1	$-\alpha m_z^1$	m_z^1	$-\alpha m_z^1$
ψ_2	m_x^2	$-\alpha m_x^2$	m_x^2	$-\alpha m_x^2$
	m_y^2	αm_y^2	m_y^2	αm_y^2
	m_z^2	$-\alpha m_z^2$	$-m_z^2$	αm_z^2
ψ_3	m_x^3	αm_x^3	$-m_x^3$	$-\alpha m_x^3$
	m_y^3	$-\alpha m_y^3$	$-m_y^3$	αm_y^3
	m_z^3	αm_z^3	m_z^3	αm_z^3
ψ_4	m_x^4	αm_x^4	m_x^4	αm_x^4
	m_y^4	$-\alpha m_y^4$	m_y^4	$-\alpha m_y^4$
	m_z^4	αm_z^4	$-m_z^4$	$-\alpha m_z^4$

$$\mathbf{m}_3^{\mathrm{Mn}} = [0.0(8), 2.90(5), 0.0(5)]\mu_B$$

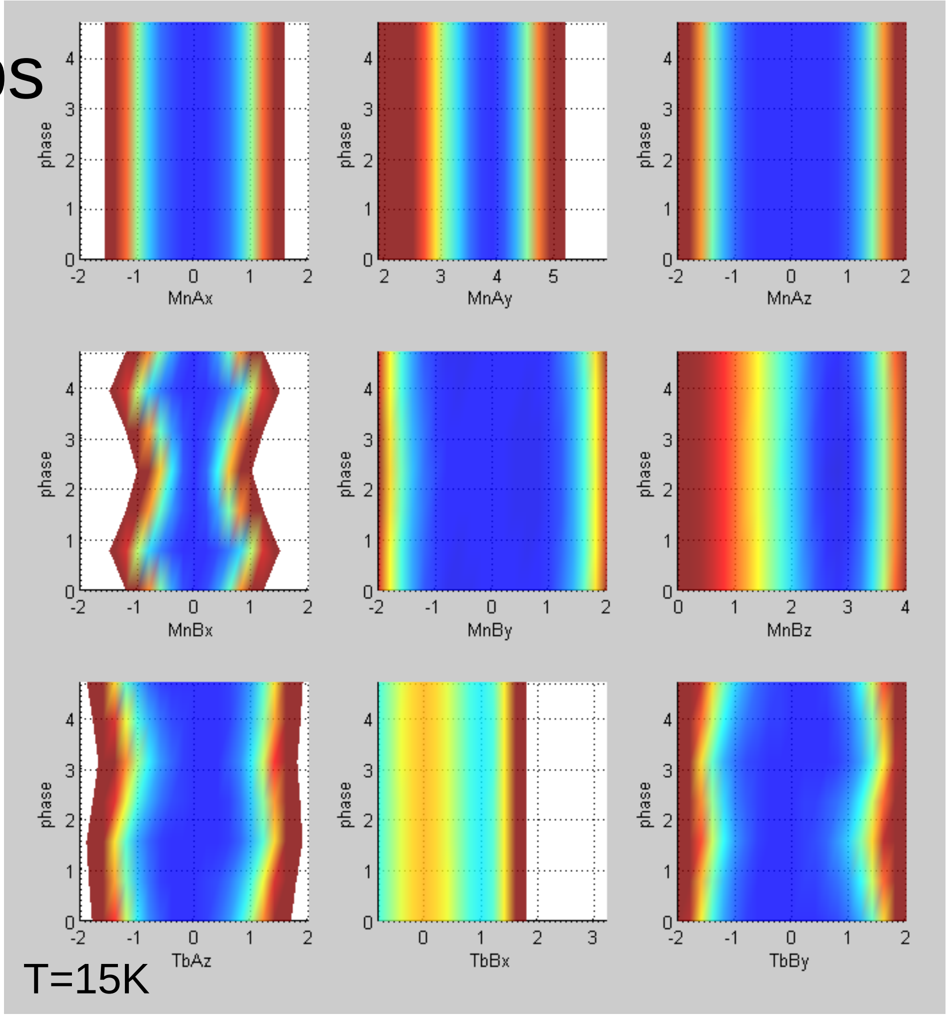
$$\mathbf{m}_3^{\mathrm{Tb}} = [0, 0, 0.0(4)]\mu_B$$

Fitting of the data: χ^2 maps

$$\chi^2 = \Sigma_i^n w_i (|F_o^i| - |F_c^i|)^2 / (n-m)$$

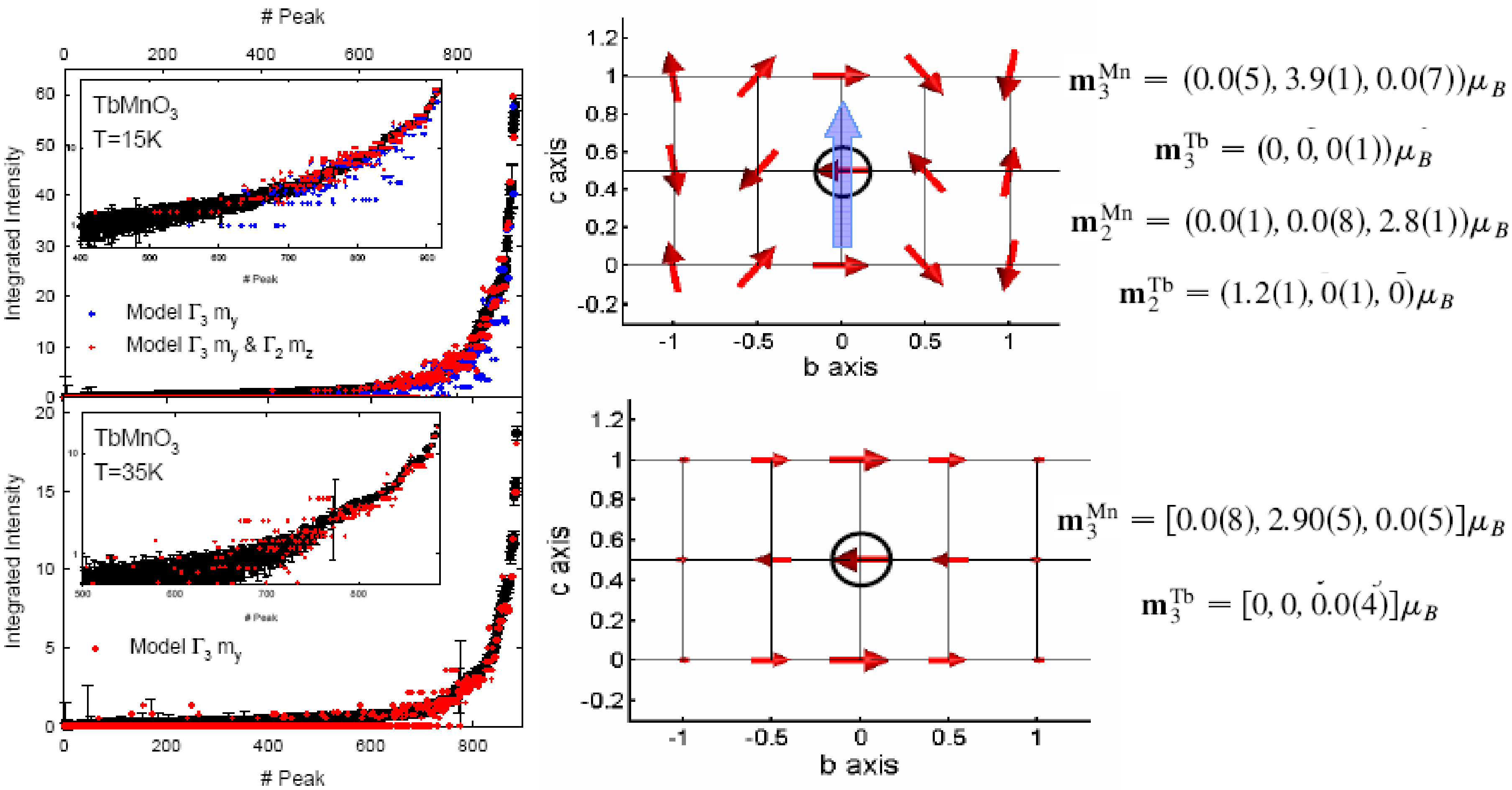


	Mn_1	Mn_2	Mn_3	Mn_4
ψ_1	m_x^1	$-\alpha m_x^1$	$-m_x^1$	αm_x^1
	m_y^1	αm_y^1	$-m_y^1$	$-\alpha m_y^1$
	m_z^1	$-\alpha m_z^1$	m_z^1	$-\alpha m_z^1$
ψ_2	m_x^2	$-\alpha m_x^2$	m_x^2	$-\alpha m_x^2$
	m_y^2	αm_y^2	m_y^2	αm_y^2
	m_z^2	$-\alpha m_z^2$	$-m_z^2$	αm_z^2
ψ_3	m_x^3	αm_x^3	$-m_x^3$	$-\alpha m_x^3$
	m_y^3	$-\alpha m_y^3$	$-m_y^3$	αm_y^3
	m_z^3	αm_z^3	m_z^3	αm_z^3
ψ_4	m_x^4	αm_x^4	m_x^4	αm_x^4
	m_y^4	$-\alpha m_y^4$	m_y^4	$-\alpha m_y^4$
	m_z^4	αm_z^4	$-m_z^4$	$-\alpha m_z^4$



$$\mathbf{m}_3^{\mathrm{Mn}} = (0.0(5), 3.9(1), 0.0(7))\mu_B$$
$$\mathbf{m}_3^{\mathrm{Tb}} = (0, 0, 0(1))\mu_B$$
$$\mathbf{m}_2^{\mathrm{Mn}} = (0.0(1), 0.0(8), 2.8(1))\mu_B$$
$$\mathbf{m}_2^{\mathrm{Tb}} = (1.2(1), 0(1), 0)\mu_B$$

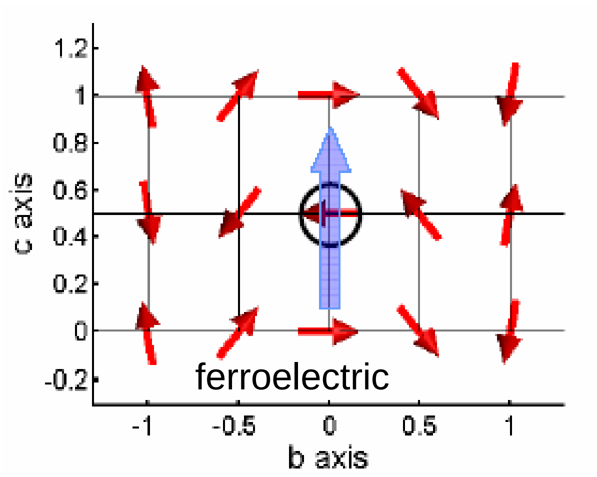
Magnetic structure of $TbMnO_3$

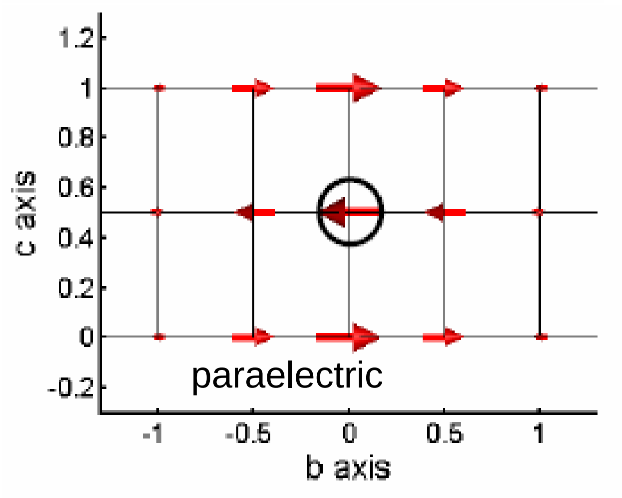


M. Kenzelmann et al, Phys. Rev. Lett. **95**, 087206 (2005)

Longitudinally-modulated spin phase at high temperature, low-temperature spiral phase break inversion symmetry and allows an electric polarization

Magnetic structure of $TbMnO_3$





$$\mathcal{H} = \sum_{\alpha\beta\gamma,\mathbf{q}} a_{\alpha\beta\gamma}(\mathbf{q}) M_\alpha(\mathbf{q}) M_\beta(-\mathbf{q}) P_\gamma(0) \; .$$

Trilinear Coupling of M and P is allowed

→ **P** has to transform as M_α (q) M_β(-q)

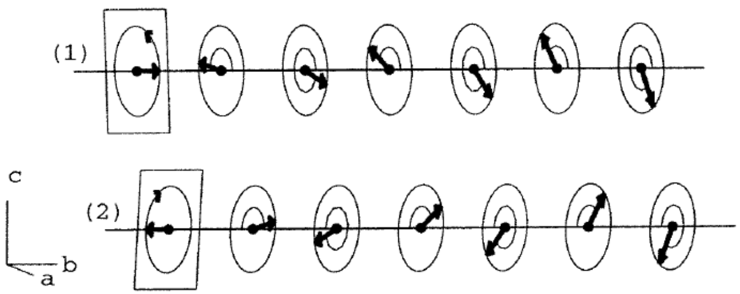
	1	2_y	m_{xy}	m_{yz}
Γ_1	1	1	1	1
Γ_2	1	1	-1	-1
Γ_3	1	-1	1	-1
Γ_4	1	-1	-1	1

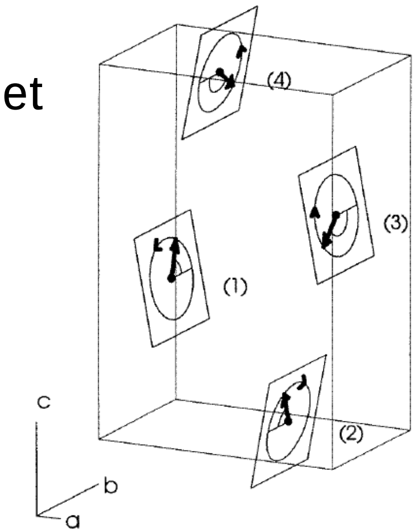
→ Electric polarization is only allowed along the c-direction as observed (P has to be even under 1 & m_{yz} and odd under 2_y & m_{xy})

M. Kenzelmann et al, Phys. Rev. Lett. **95**, 087206 (2005)

Not all spiral magnets are ferroelectric !

Example: Cs_2CuCl_4 - 2D triangular quantum magnet





R. Coldea et al, J. Phys.: Condensed Matter **8**, 7473 (1996)

- One phase transition as a function of temperature
- Magnetic structure is described by one irreducible representation
- Counter-rotating spirals
- Cannot lead to ferroelectricity

$$\mathcal{H} = \sum_{\alpha\beta\gamma,\mathbf{q}} a_{\alpha\beta\gamma}(\mathbf{q}) M_\alpha(\mathbf{q}) M_\beta(-\mathbf{q}) P_\gamma(0) \ .$$

Summary

- Introduction in neutron scattering
- Magnetic neutron scattering in magnetic ferroelectrics
- Determination of magnetic structures
- Symmetry properties of magnetically-induced ferroelectricity