Conventional Multiferroics and its modification: a case of $BiMnO_3$

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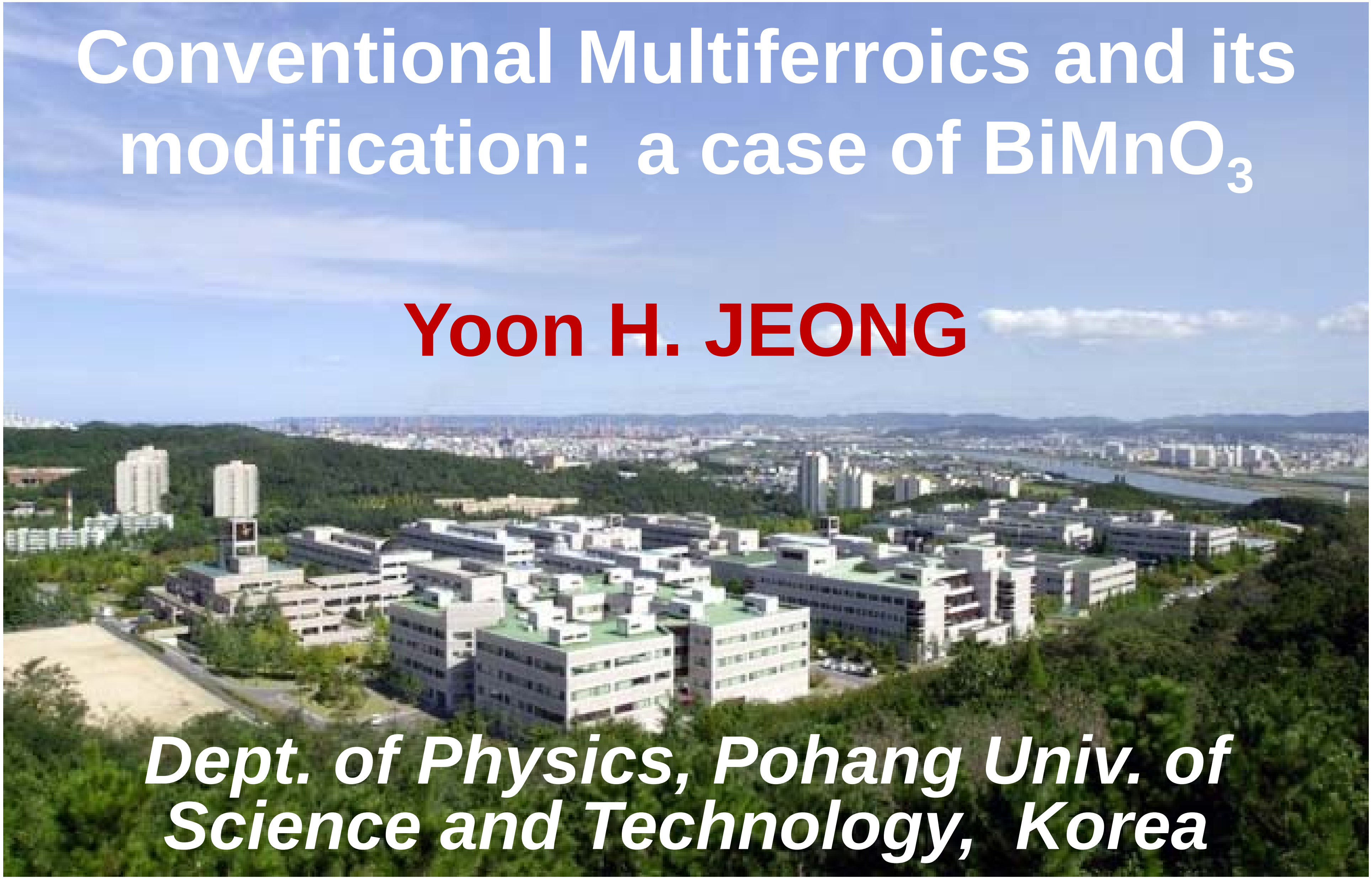

Sep 4, 2008; Grenoble

PAL 포항가속기연구소 Pohang Accelerator Laboratory

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This work was part of C.-H. Yang's thesis project.

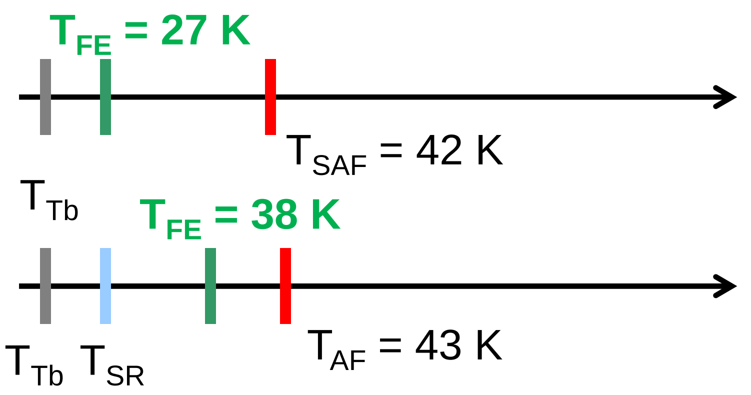
- "Orbital ordering and enhanced magnetic frustration of $BiMnO_3$ thin films", C.-H. Yang et al., Europhys. Lett. (2006).
- "Resonant x-ray scattering study on multiferroic $BiMnO_3$", C.-H. Yang et al., Phys. Rev. B (2006)
- "Dynamically enhanced magnetodielectric effect and magnetic field controlled electric relaxations in modified $BiMnO_3$", C.-H. Yang et al., Phys. Rev. Lett. Submitted (2007)
- "Exchange bias effects for inducing magnetoelectric coupling in a nanoscale composite of $MnFe_2O_4$ and Mn-doped $BiFeO_3$", C.-H. Yang et al., Appl. Phys. Lett. In press (2007)

Multiferroics

Magnetically induced Ferroelectrics

$TbMnO_3$ — $P < 100\ nC/cm^2$

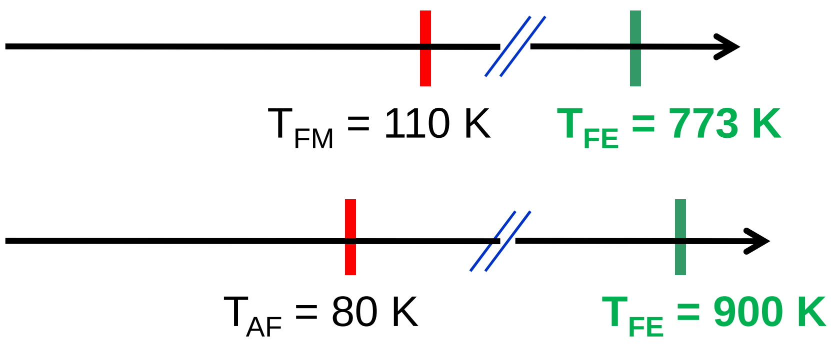
$TbMn_2O_5$ — $P < 100\ nC/cm^2$



Conventional magnetic Ferroelectrics

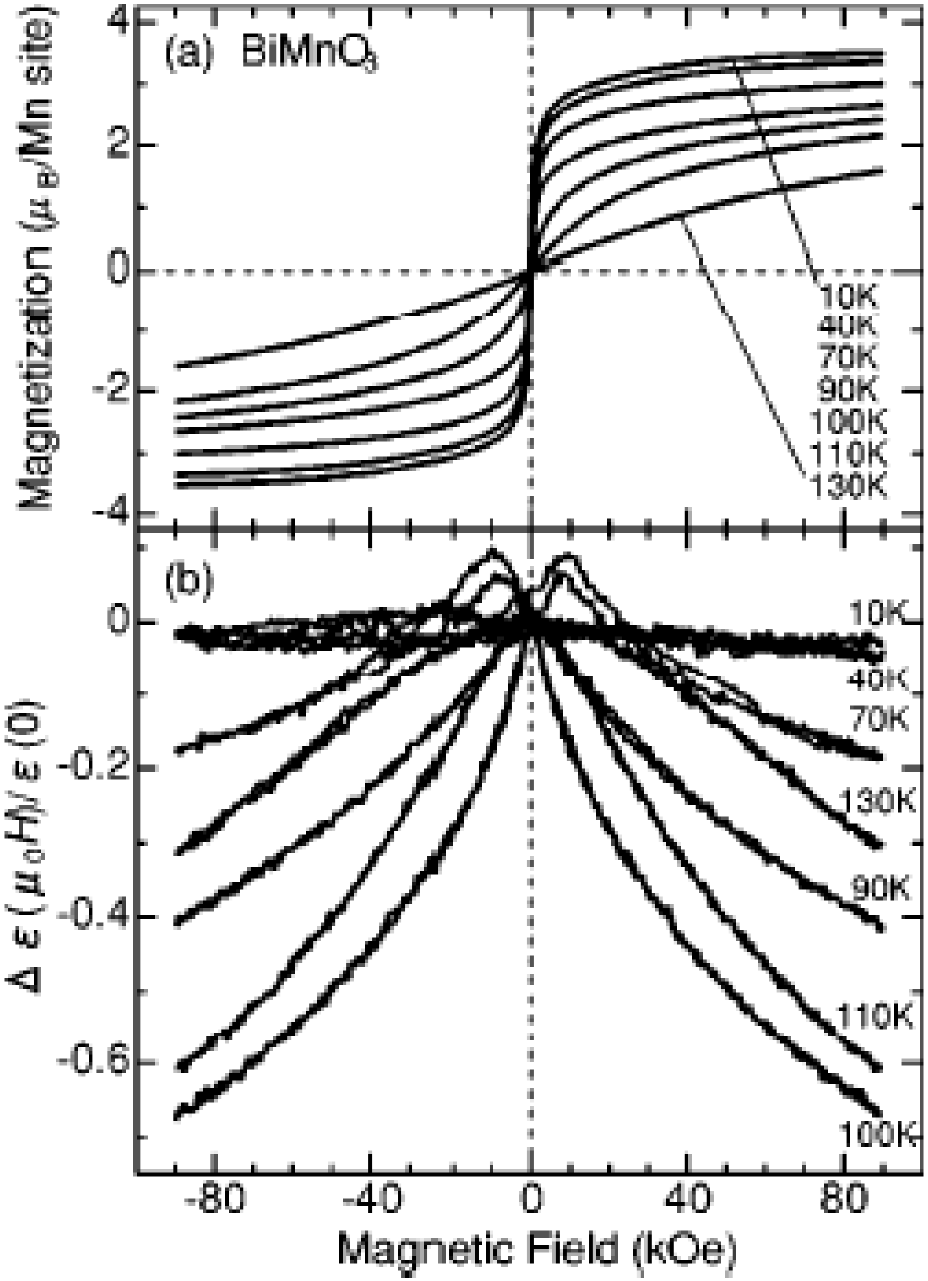
$BiMnO_3$ — $P \sim 1\ \mu C/cm^2$

$YMnO_3$ — $P < 5.0\ \mu C/cm^2$



Characteristics of conventional multiferroics

- **strong disparity in ferroelectric Tc and magnetic Tc**
- **weak coupling between the electric and magnetic degrees of freedom**



Kimura (2003)

Less than −0.6 % at 10 T

General features of 2nd order Phase transitions

(1) Susceptibility becomes large in the vicinity of the transition point.

An overlap of the two transitions would result in amplification of the mutual coupling, albeit intrinsically small, and thus if one can force an overlap in a material with high Tc's, one may get strong effects at room temperature.

(2) Two transitions of different origins (weak or no coupling) cannot occur at the same temperature except by accident.

Critical regions associated with pure transitions are usually narrow.

Thus inducing two transitions of different origins to overlap in temperature may not be a simple matter.

***"Disorder"* can control transition temp and also broaden phase transitions.**

$BiMnO_3$

$BiMnO_3$ is a *conventioal* *multiferroic* material.

- highly distorted perovskite (monoclinic space group *C2*)

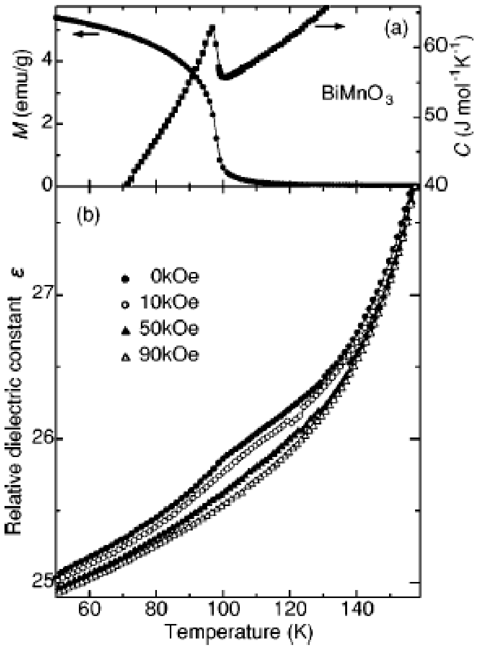
- a rare ferromagnetic due to Mn^{3+} ions: T_{FM} = 105 K , M = 3.6 μ_B

-ferroelectric due to stereoactive Bi^{3+}:

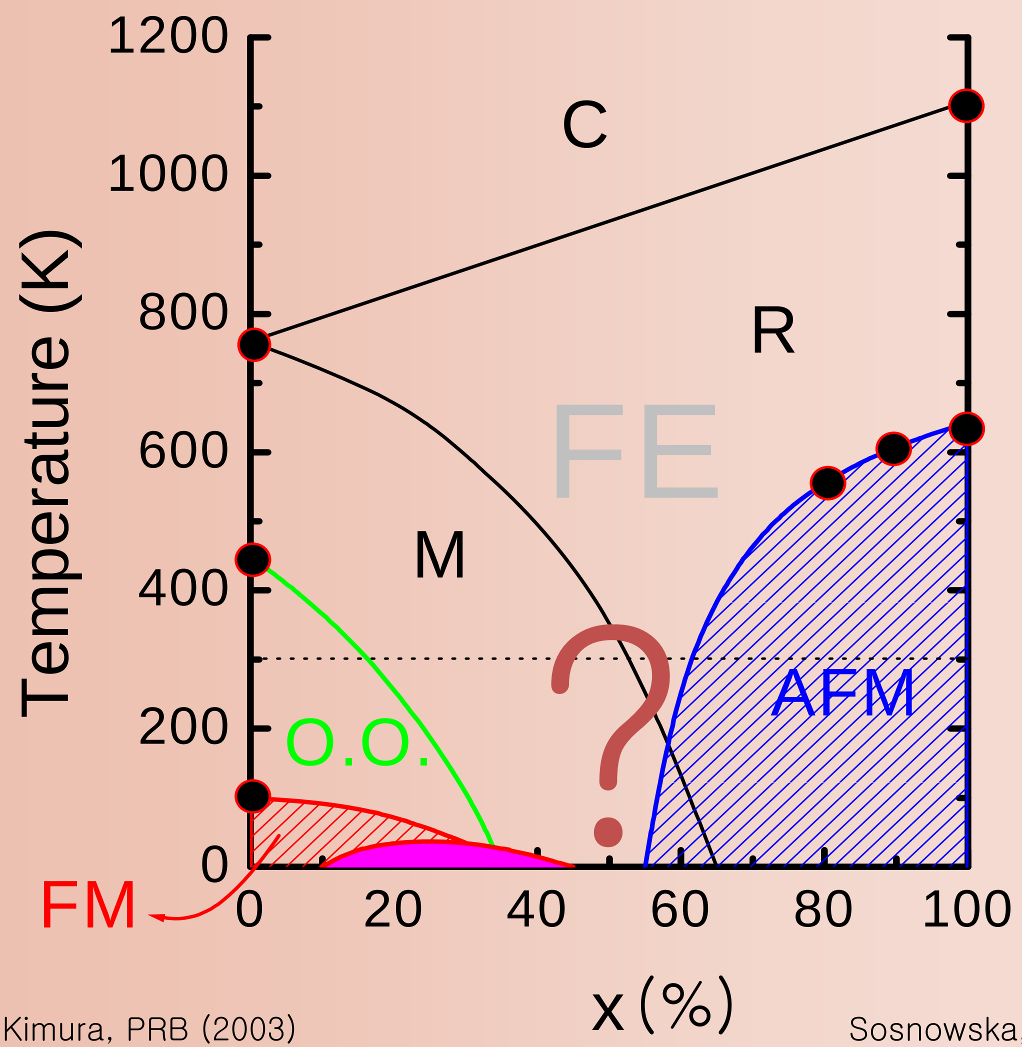
T_{FE} = 750~770 K , P = 0.1 $\mu C/cm^2$

- weak coupling between E & M components

Bi^{3+} : [Xe] $4f^{14}5d^{10}$ $6s^2$ stereo−active 1.24 A
cf. La^{3+} : [Xe] 1.216 A
Mn^{3+} : $3d^4$ ($t_{2g}{}^3$ $e_g{}^1$) JT−ion



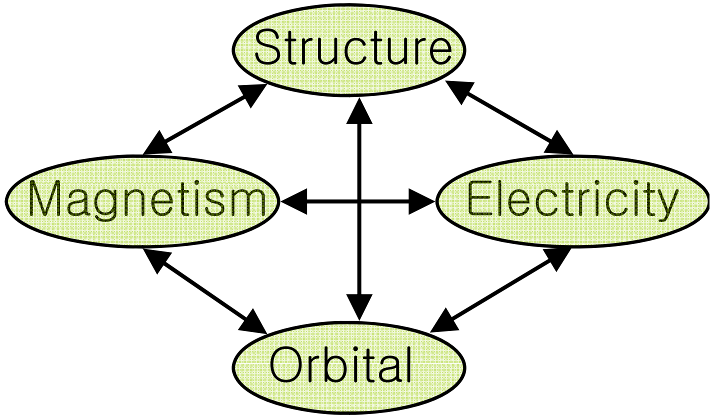
$BiMn_{1-x}Fe_xO_3$ Phase diagram (추정)



Kimura, PRB (2003)

Sosnowska, Physica B(2002)

- Ferroelectricity
- Ferromagnetism
- Antiferromagnetism
- Competing ground states
- Structural transition
- Orbital Ordering
- Dilute Jahn-Teller effect

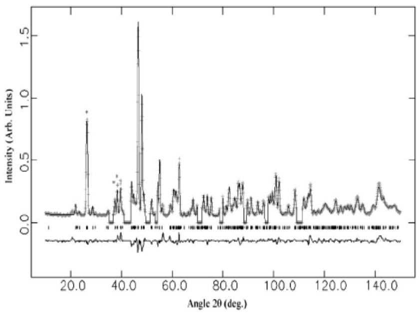


eSSC

Multiferroic $BiMnO_3$

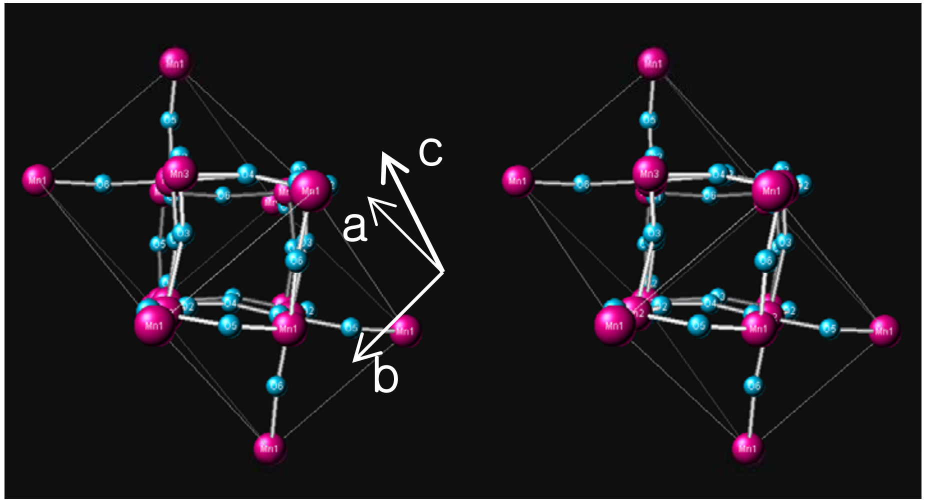
distorted perovskite

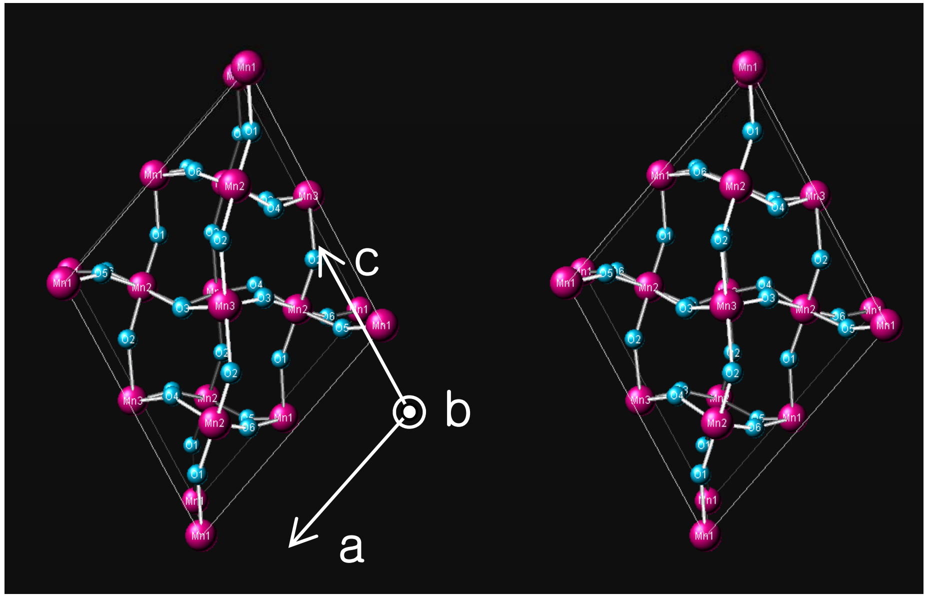
Neutron powder diffraction
Structure Refinement



A. M. Santos,C. N. R. Rao *et al*.

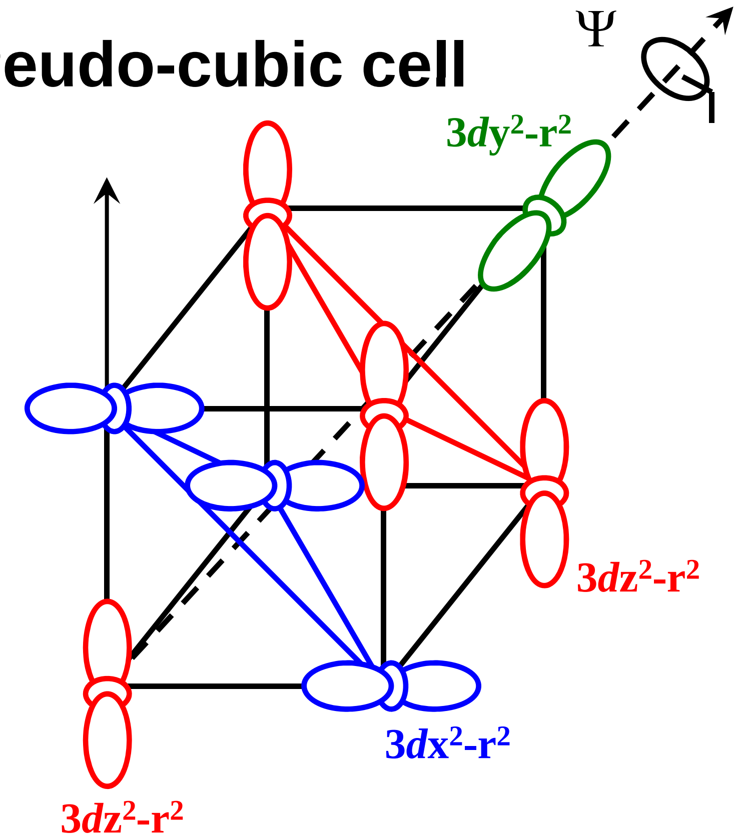
Space group :
C2 (monoclinic)

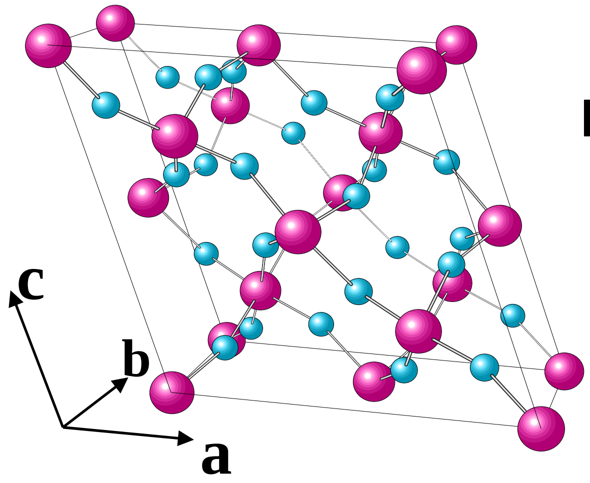




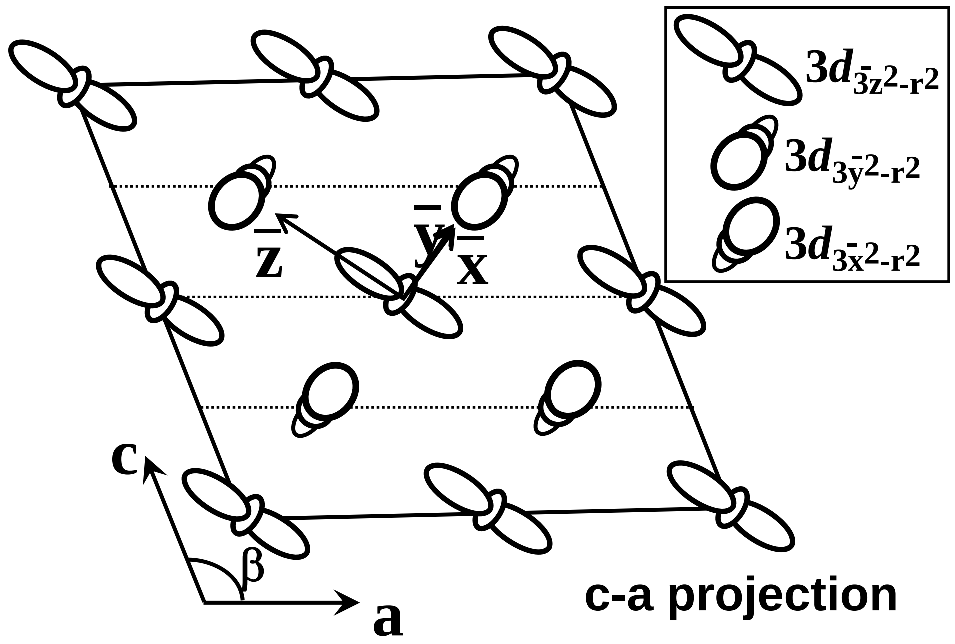
The unit cell of $BiMnO_3$ and Mn 3d e_g orbitals

Peudo-cubic cell





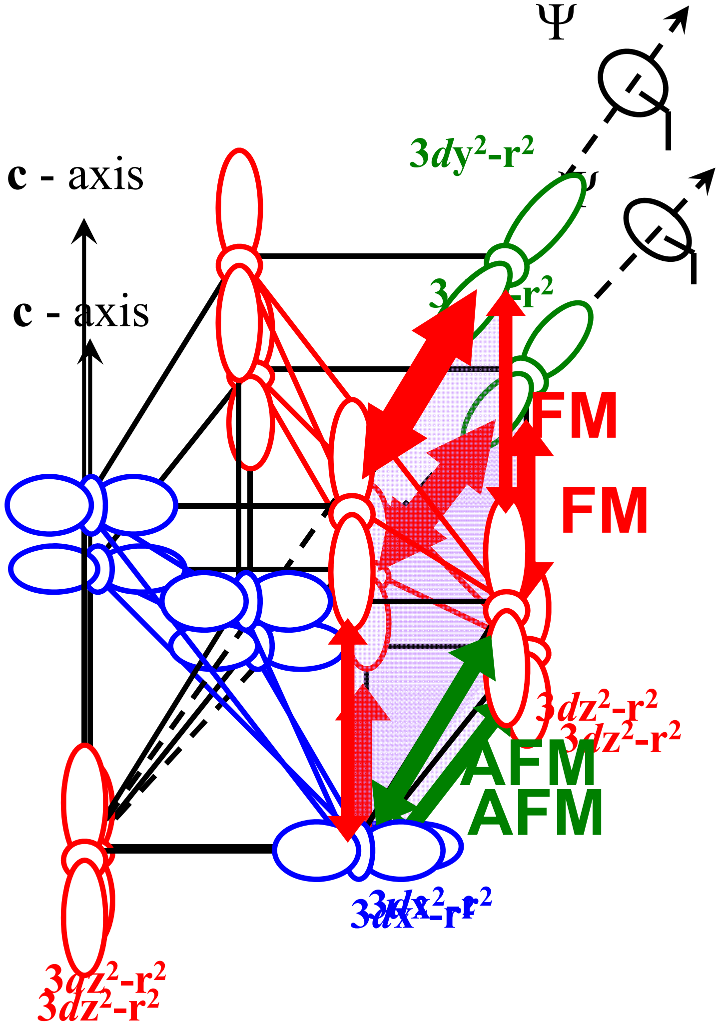
Monoclinic cell



c-a projection

(¼ ¼ ¼) superstructure modulation is expected due to orbital ordering

Orbital ordering and magnetic frustration: two issues addressed with thin films



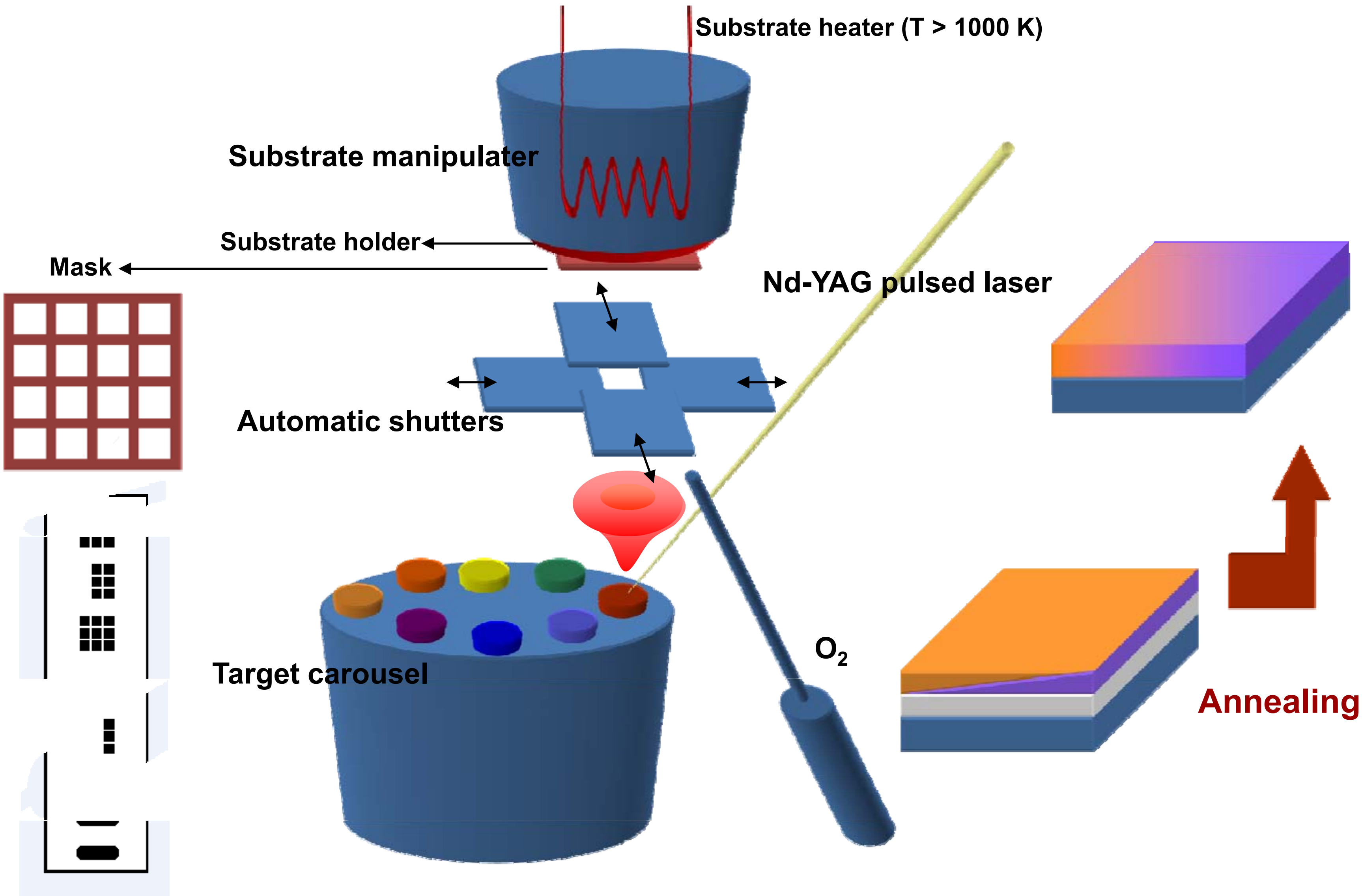
Q#1 (¼ ¼ ¼) superstructure ?

~ superstructure modulation in RXS

Q#2 magnetic frustration

Could it be enhanced with strain in thin films ?

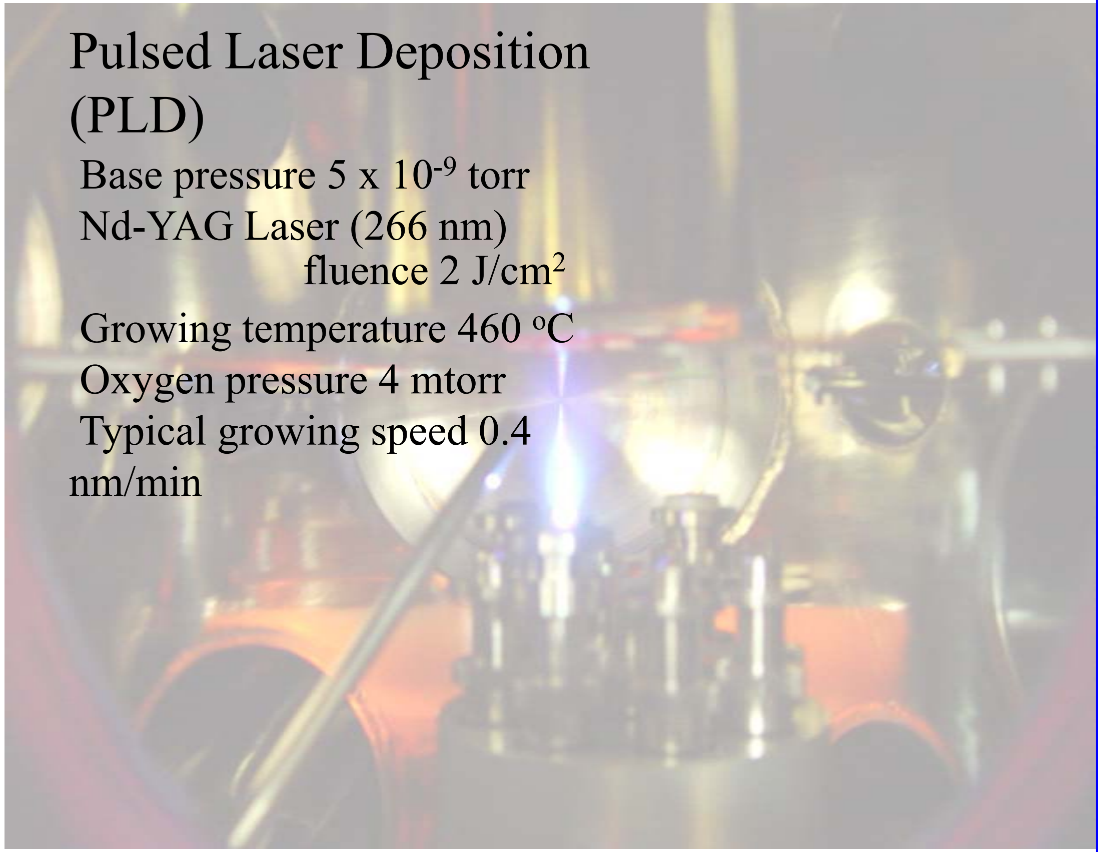
Making thin film samples



Fabrication – $BiMnO_3$ film

Different thickness of films are grown on $SrTiO_3$(001)&(111) substrates epitaxially.

Thin one 40 nm ;   Thick one 70 nm



Pulsed Laser Deposition (PLD)

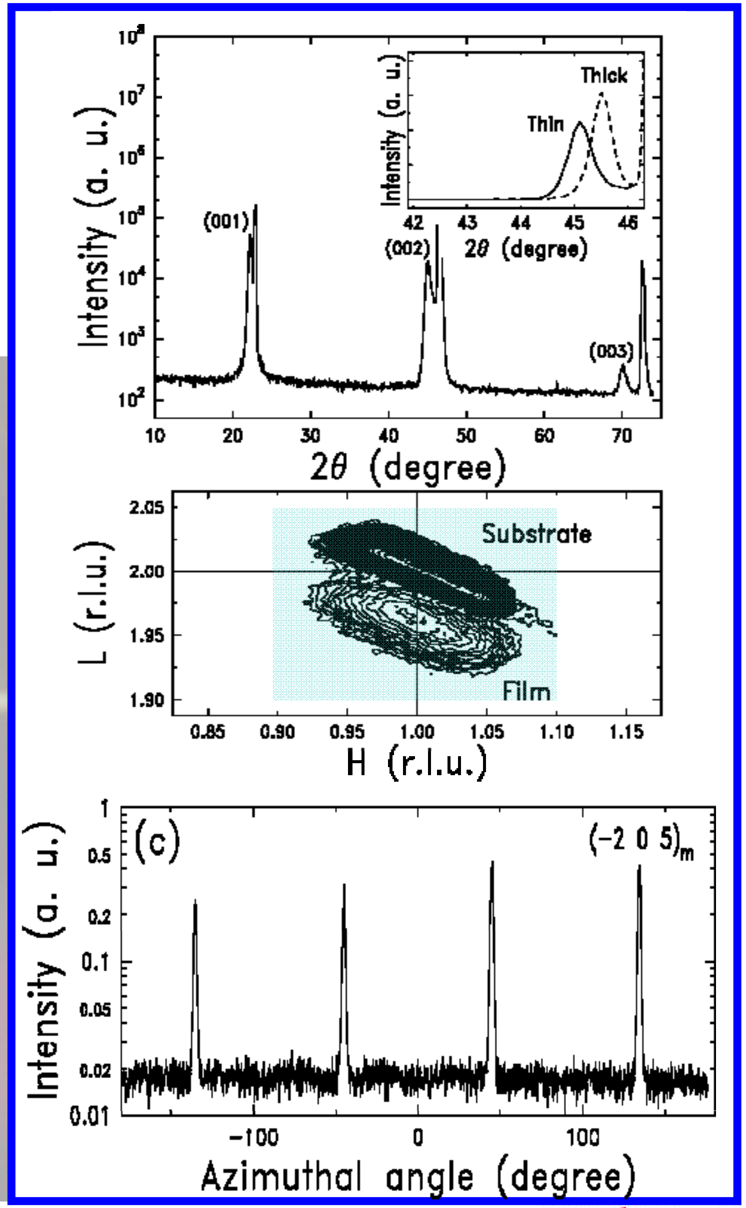
Base pressure 5 x 10^{-9} torr

Nd-YAG Laser (266 nm) fluence 2 J/cm^2

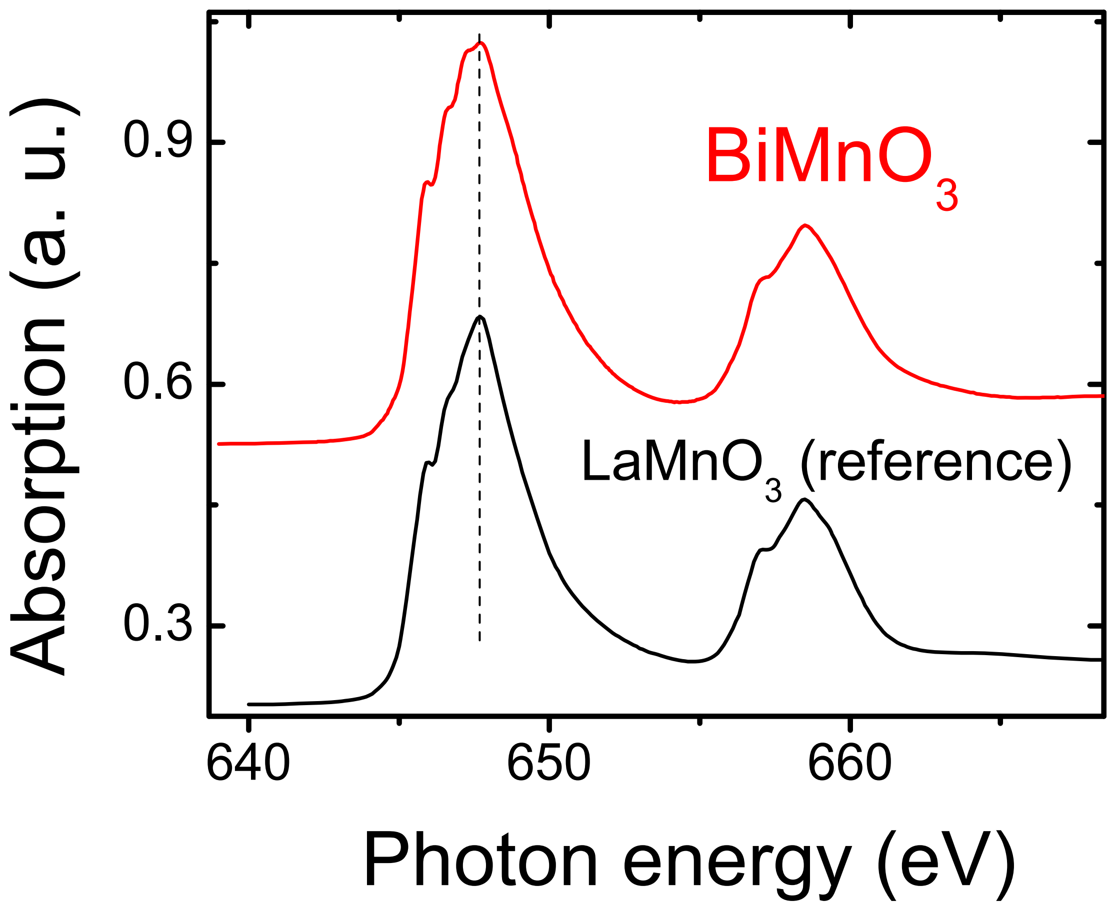
Growing temperature 460 ^oC

Oxygen pressure 4 mtorr

Typical growing speed 0.4 nm/min



Absorption at Mn-L edge



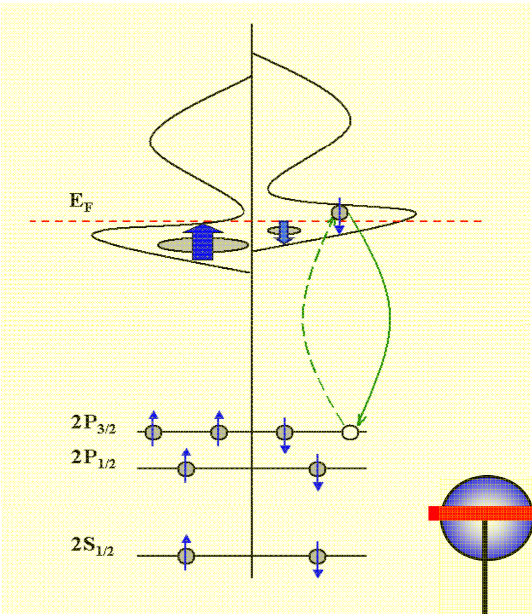
Probe of Orbital order: Resonant X-ray Scattering

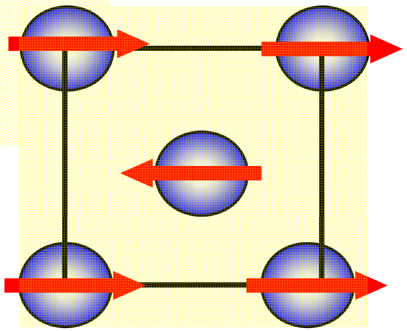
2nd order matrix element

$$\sum_I \frac{\langle f|\mathcal{H}'|I\rangle\langle I|\mathcal{H}'|i\rangle}{E_i - E_I} \quad ; \quad \mathcal{H}' = e\vec{r}\cdot\vec{E}$$

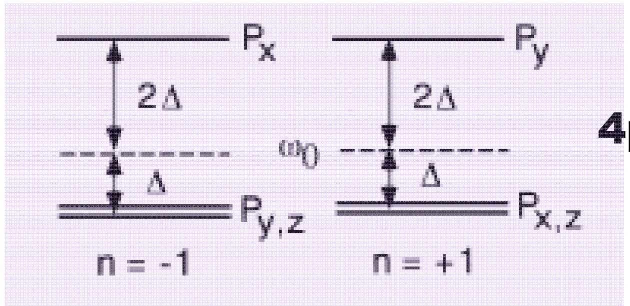
DOS energy

L-edge
2p → *3d*



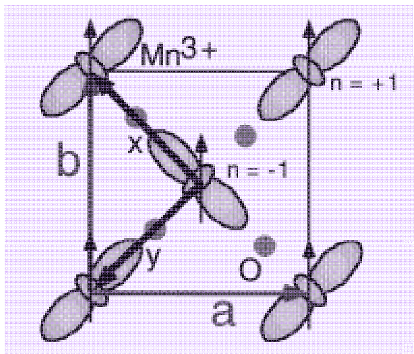


K-edge
1s → *4p*



4p

1s



3d orbital

Scattering Length

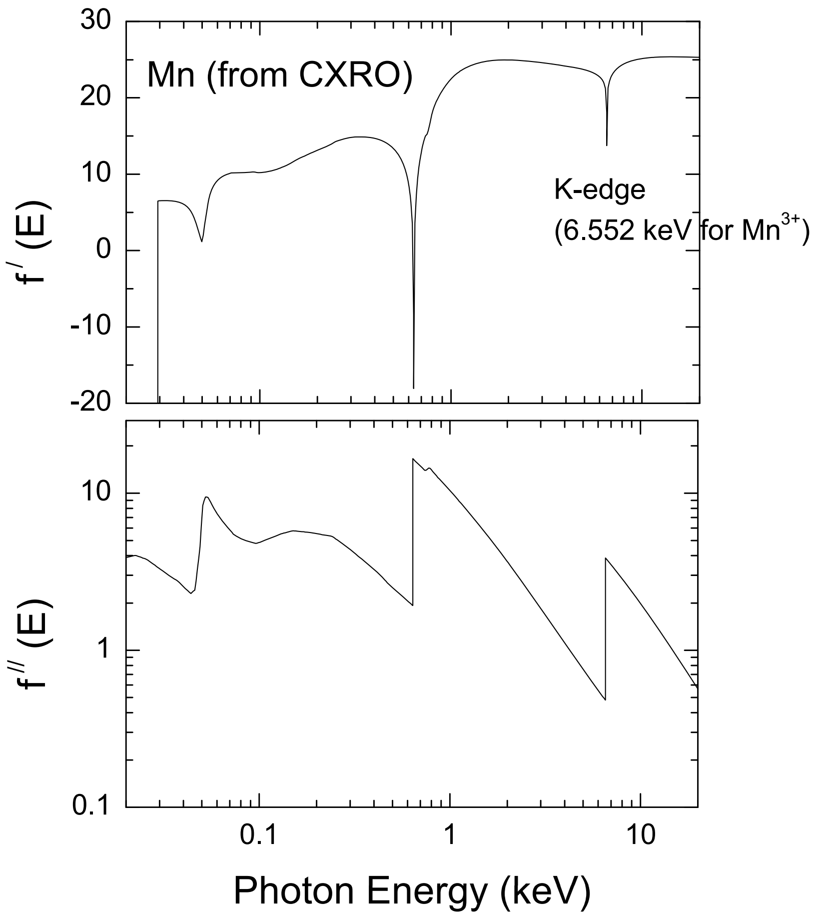
$$f = f^0(q) + f'(E) + i\,f''(E)$$

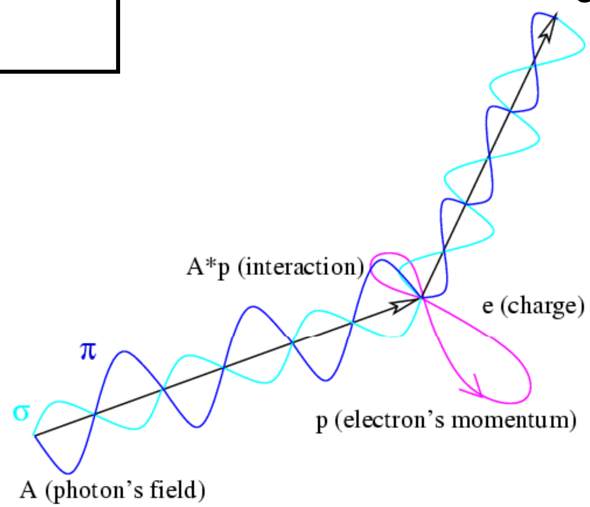
Thomson scattering

$q = 4\pi \sin\theta / \lambda$
$f^0(q)$ is the fourier transform of electric charge density.

Dispersion correction

Resonant, however elastic scattering
Classically, it is similar to the damped harmonic oscillator.
Quantum mechanically, it is second order effect of dipole perturbation.
(photon absorption and emission)
Imaginary part is proportional to photo-absorption cross section and real part can be extracted from Kramers-kronig relation.

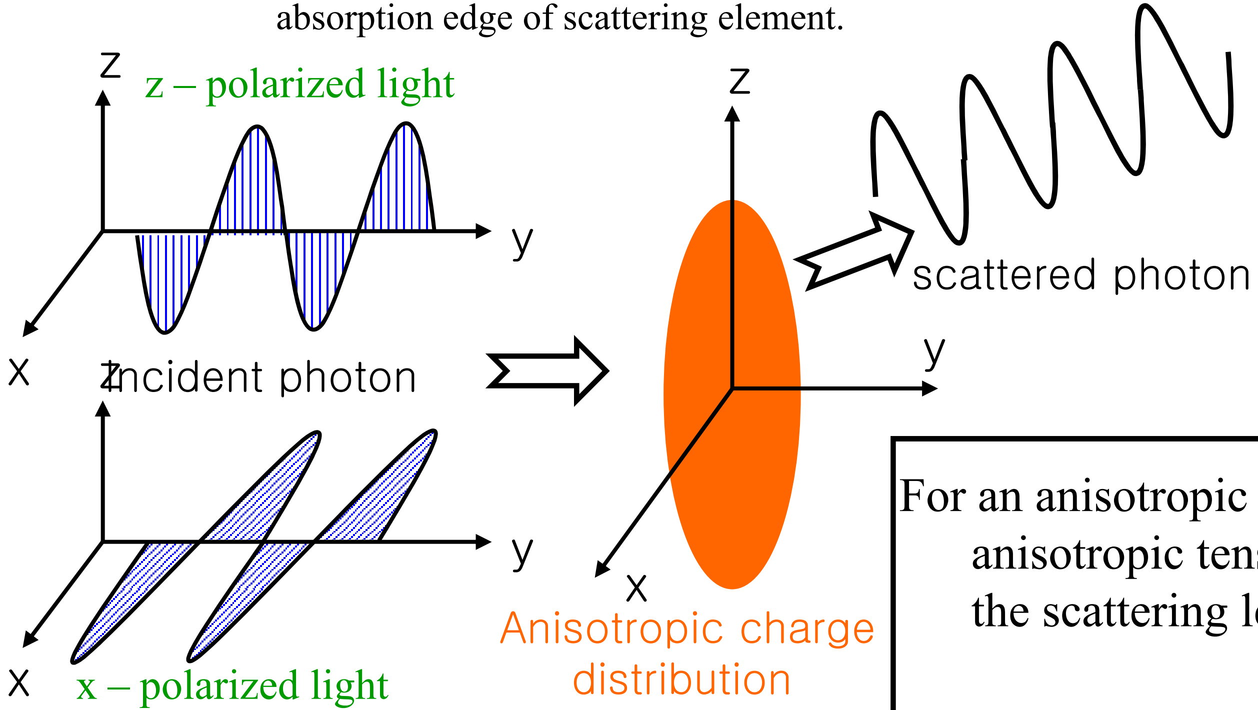




cf) B. E. Warren, X-ray diffraction
Als-Nielsen and McMorrow, Elements of Modern X-ray Physics
X-ray Data Booklet (CXRO)

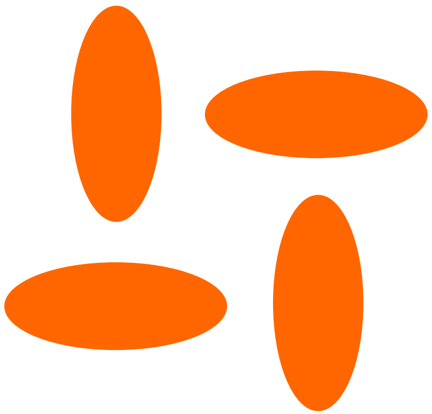
Why resonant scattering ?

Say, incident photon energy is tuned to absorption edge of scattering element.



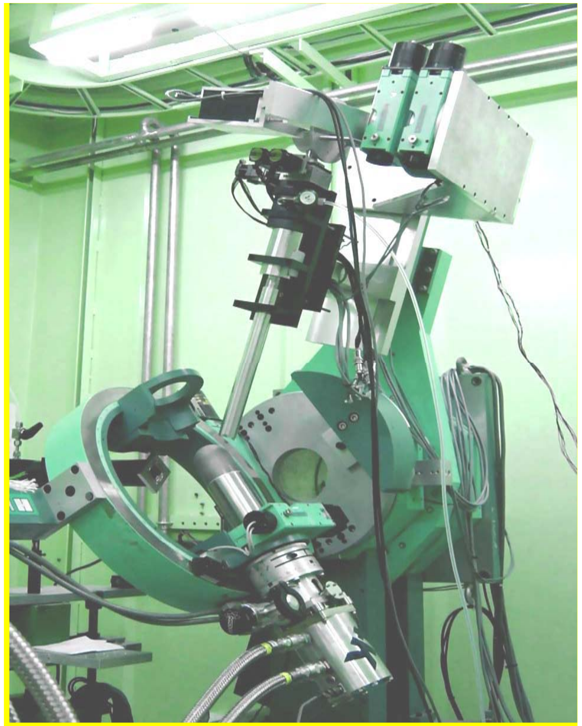
For an anisotropic charge distribution, anisotropic tensor susceptibility (ATS) in the scattering ler

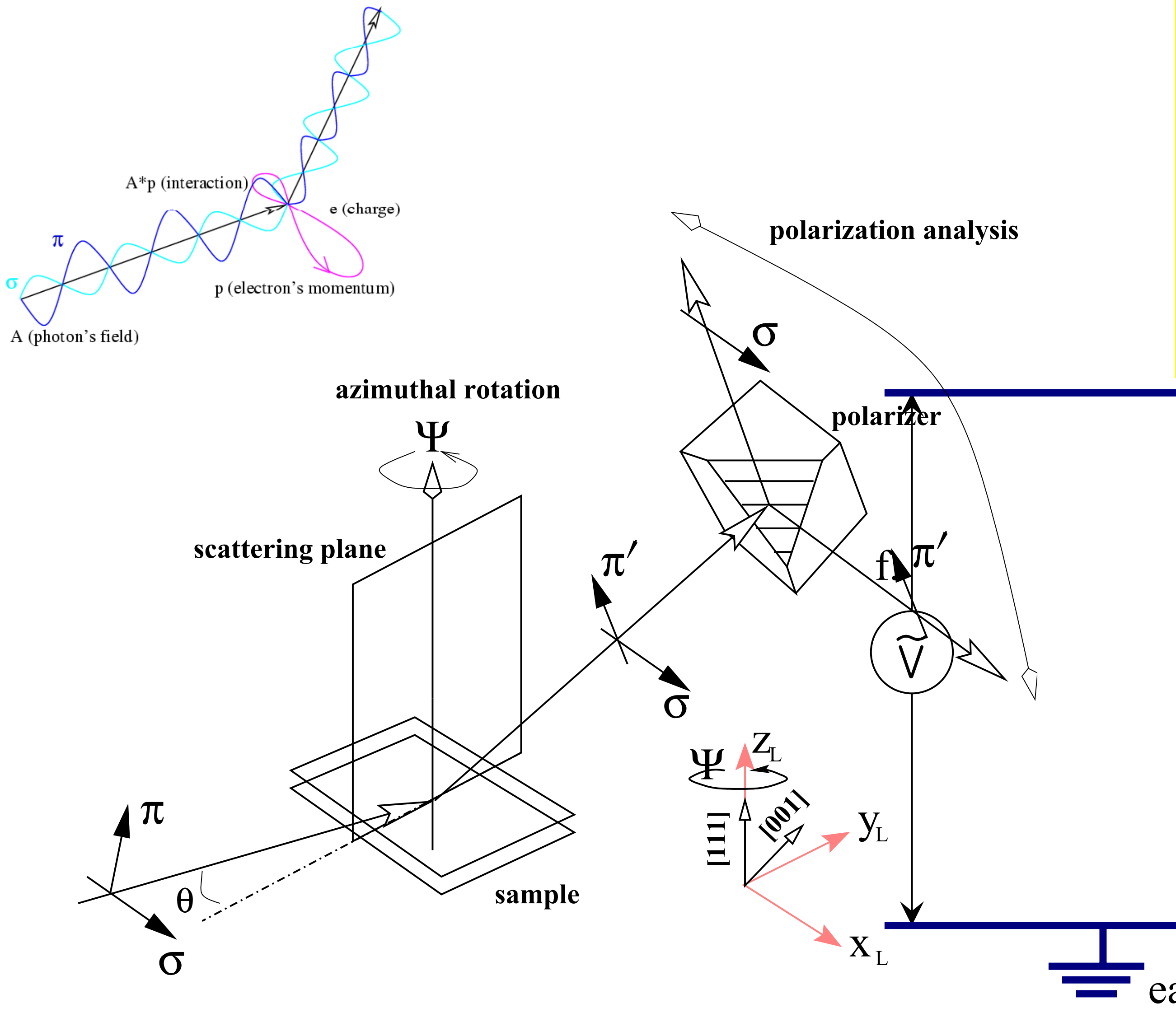
$$\mathbf{F}_{res} = \begin{pmatrix} f_\perp & 0 & 0 \\ 0 & f_\perp & 0 \\ 0 & 0 & f_\parallel \end{pmatrix}$$

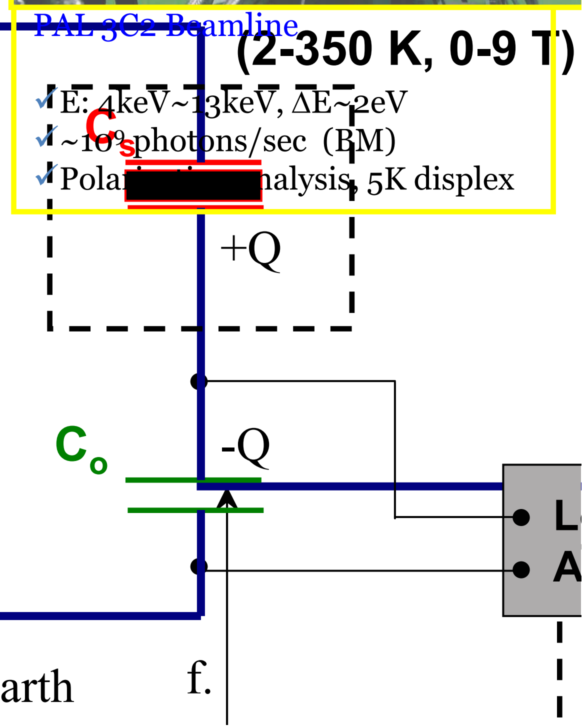


Because of ATS, a superlattice peak may appear at a forbidden reciprocal position. This peak can be largely enhanced when incident photon energy is tuned to the absorption edge.

The experimental configuration for X-ray scattering



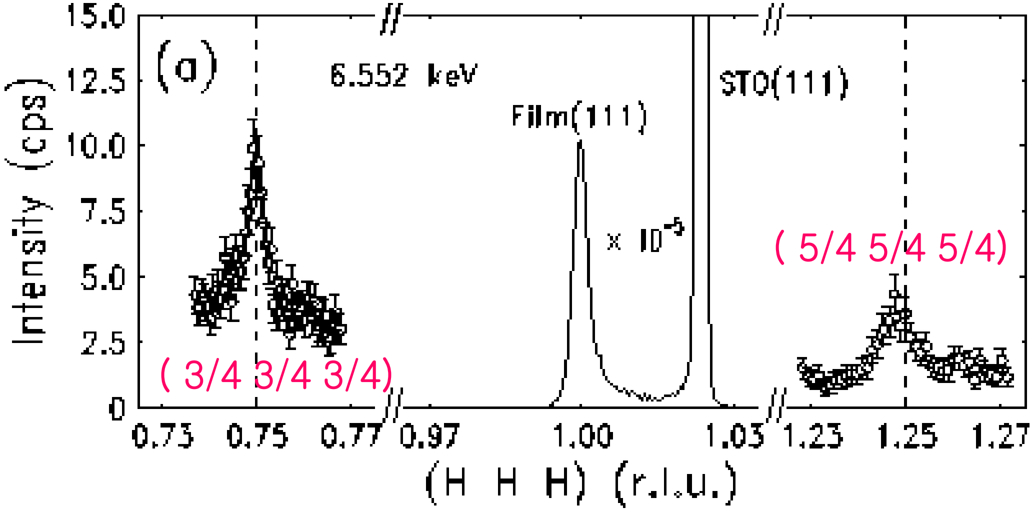


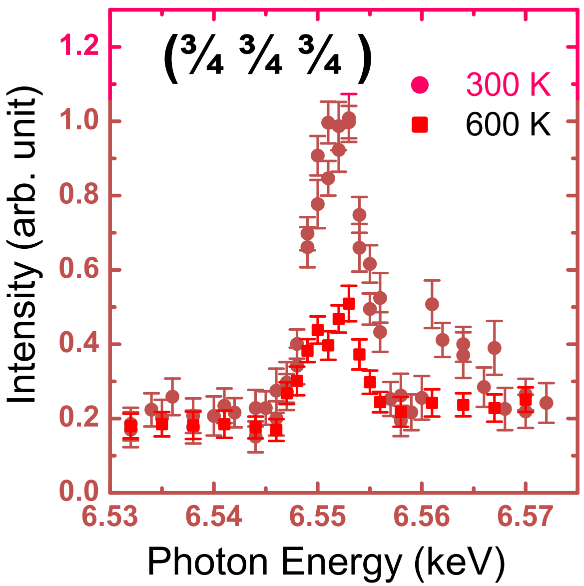


Resonant X-ray Scattering of $BiMnO_3$

grown on .05% Nb-doped $SrTiO_3(111)$ substrate

d = 37 nm

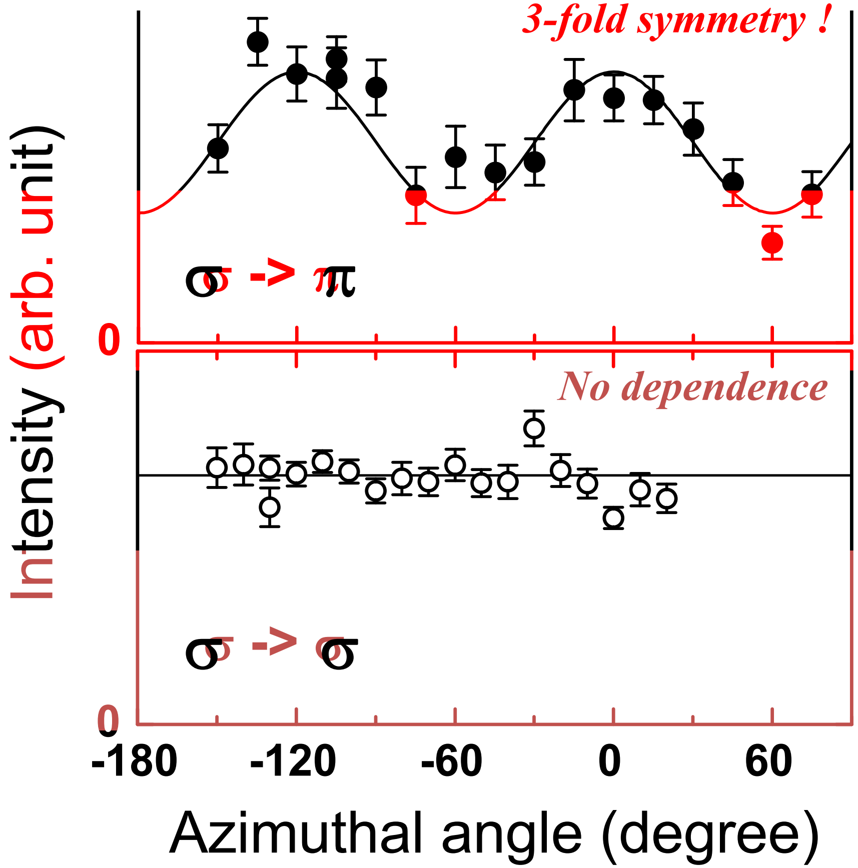




The superlattice peak is enhanced at Mn^{3+} edge 6.552 keV.

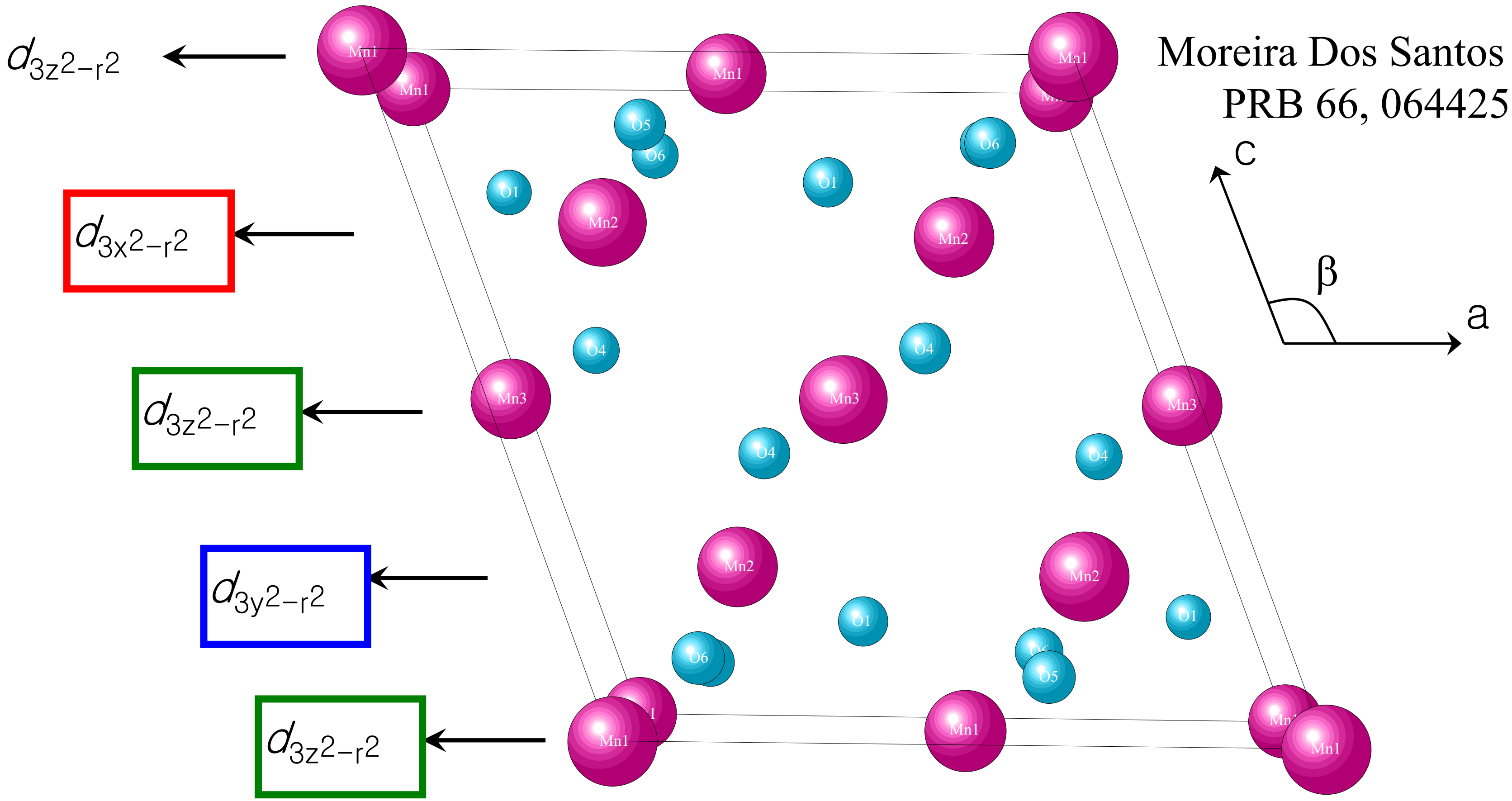
Azimuthal dependence - RXS

(¾ ¾ ¾)



Calculation : azimuthal angle dependence of orbital ordering peak

Space Group ： *C2*



Moreira Dos Santos A., PRB 66, 064425 (2002)

Structure factor for (00L)

$$2f_z e^{0} + 2f_x e^{i2\pi Lz} + 2f_z e^{i2\pi L\frac{1}{2}} + 2f_y e^{-i2\pi Lz} + C(\mathrm{Bi}) + C(\mathrm{O})$$

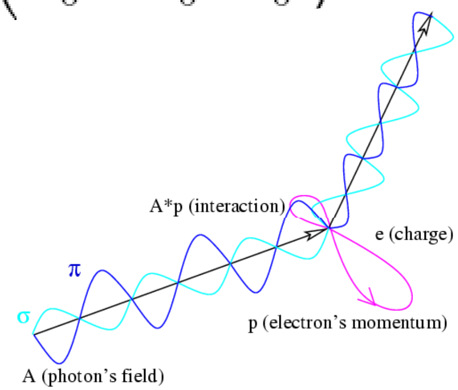
z = ¾ + Δz => Charge scattering + Anomalous scattering

$$2f_z e^0 + 2f_x e^{i2\pi Lz} + 2f_z e^{i2\pi L\frac{1}{2}} + 2f_y e^{-i2\pi Lz} + C(\mathrm{Bi}) + C(\mathrm{O}) \qquad (3.10)$$
$$\simeq \; 2(-1)^{\frac{L+1}{2}} i f_\Delta \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix} + 4(f_{Mn} + f_\perp)\cos 2\pi Lz + C(\mathrm{Bi}) + C(\mathrm{O}),$$

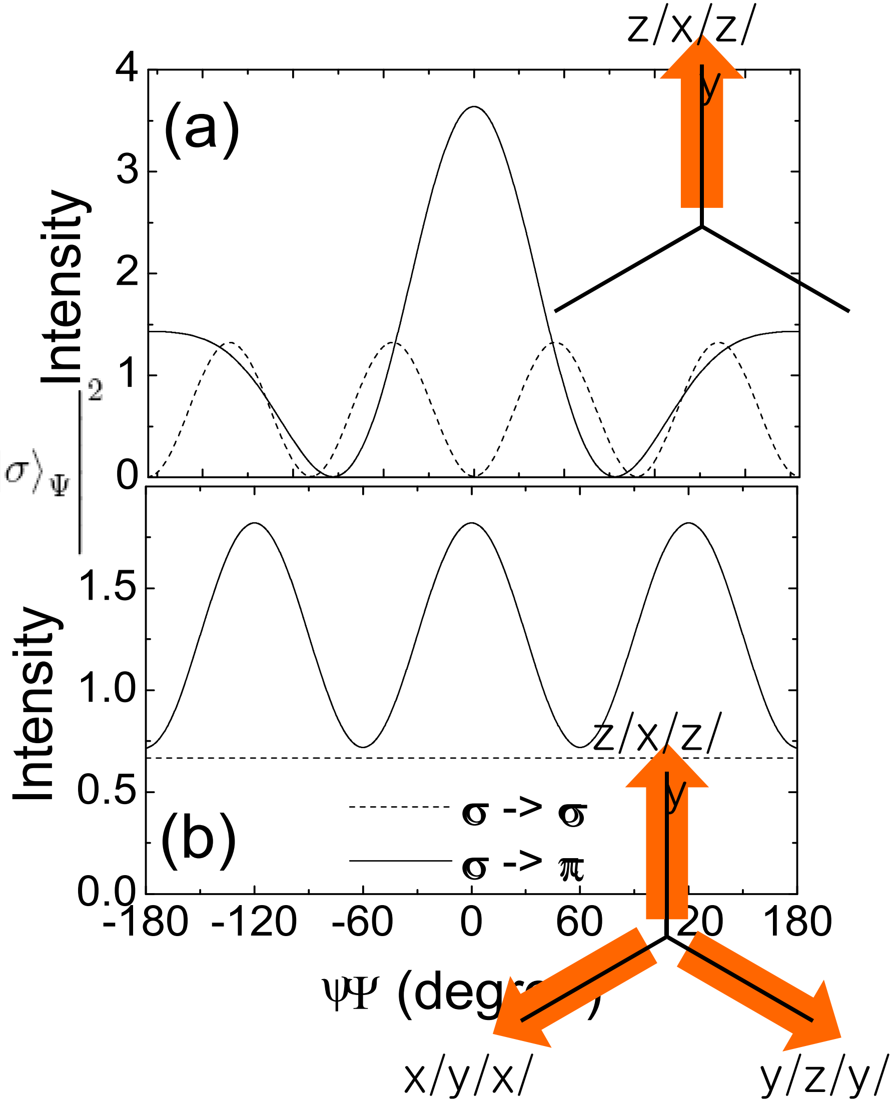
$$\mathcal{F}^{\alpha\beta}_{res} = \sum_{m=x,y,z} \frac{< 1s|P^\alpha|4p_m >< 4p_m|P^\beta|1s >}{\omega - \omega_0 - \delta\omega_m + i\Gamma/2}$$

$$\mathbf{F}_{res} = \begin{pmatrix} f_\perp & 0 & 0 \\ 0 & f_\perp & 0 \\ 0 & 0 & f_\parallel \end{pmatrix}$$

$$I_{\sigma\to\sigma,\pi} = \left| \langle \sigma, \pi|_\Psi \mathcal{M}^\dagger_{L\to B} \begin{pmatrix} 2f_\Delta & 0 & 0 \\ 0 & -2f_\Delta & 0 \\ 0 & 0 & 0 \end{pmatrix} \mathcal{M}_{L\to B} |\sigma\rangle_\Psi \right|^2$$

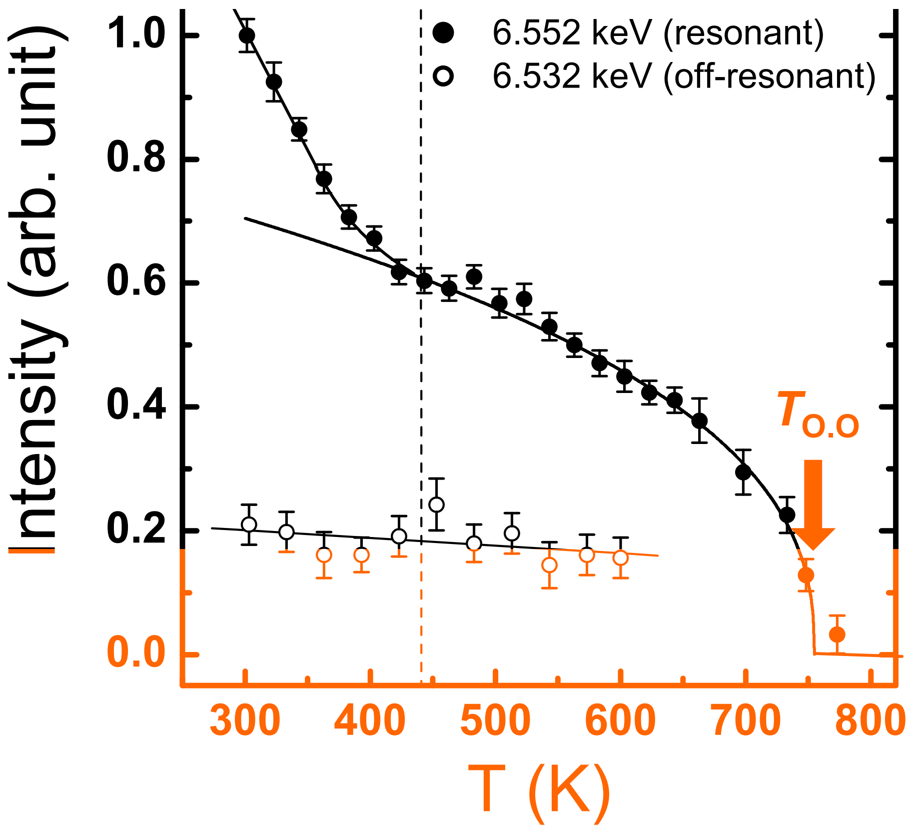


$$I_{\sigma\to\sigma} = \frac{4}{3} f_\Delta^2 \sin^2 2\Psi,$$
$$I_{\sigma\to\pi} = \frac{4}{3} f_\Delta^2 (\sqrt{2}\cos\theta\cos\Psi + \cos 2\Psi \sin\theta)^2$$



Temperature dependence of orbital order

(¾ ¾ ¾)



The peak persists up to 770 K and shows an anomaly around 440 K.

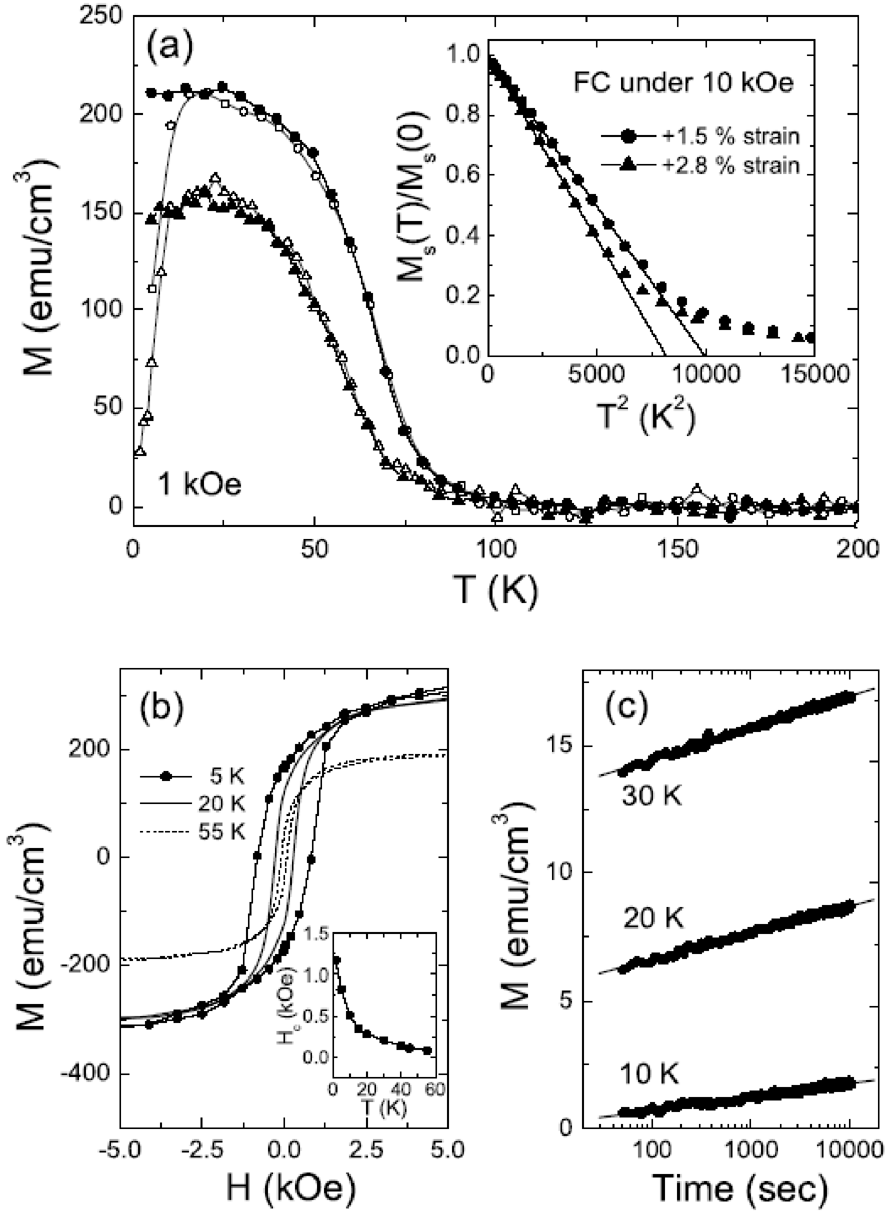
Magnetic consequences

Unusual magnetic properties

"cluster glass like behaviors"

- FC & ZFC M(T)
- Hc
- relaxation
- T^2 law

caused by frustration stemming from peculiar Orbital Ordering in BMO.



Modifying $BiMnO_3$

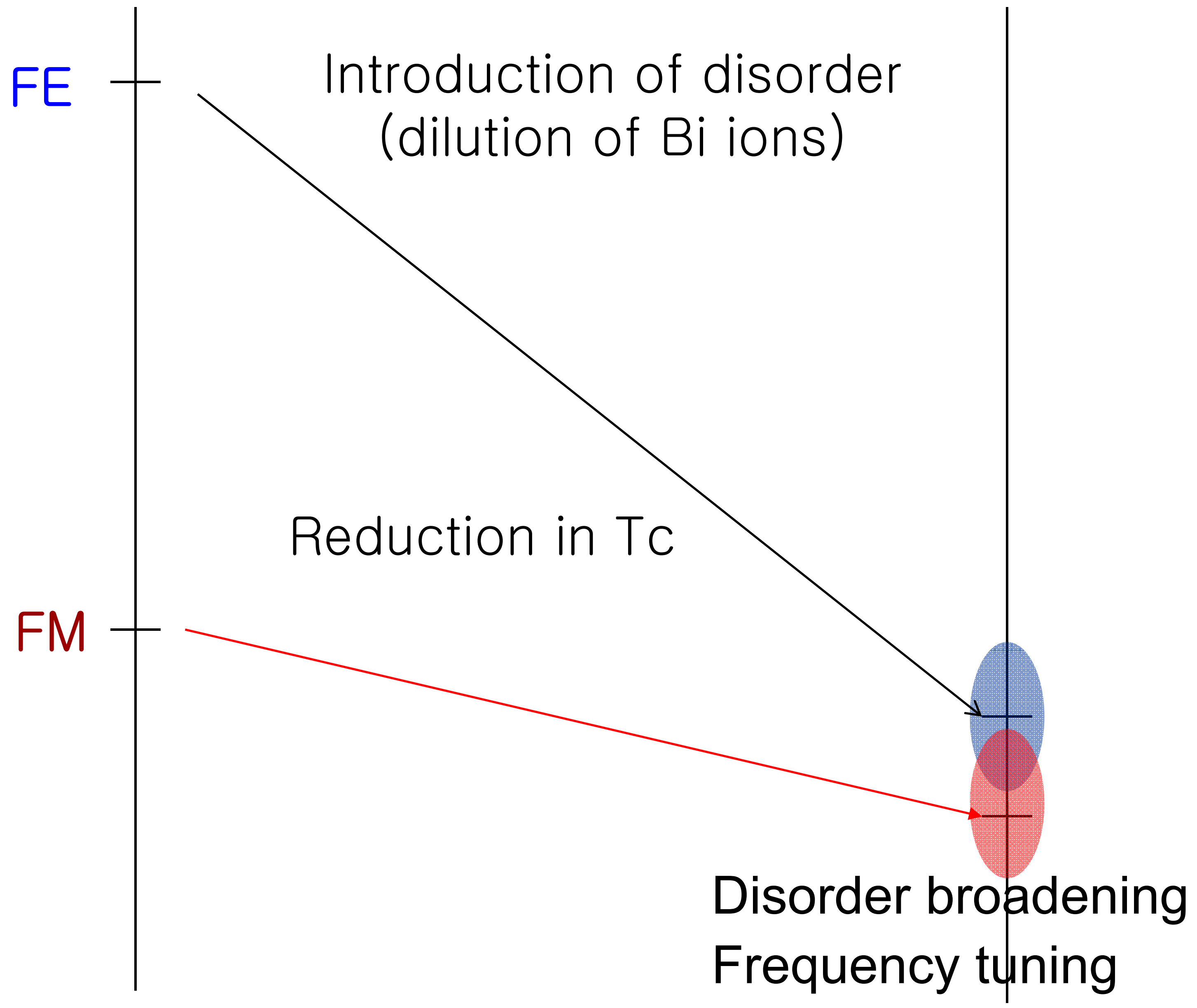
Two observations:

- The transition temperatures are in strong disparity.

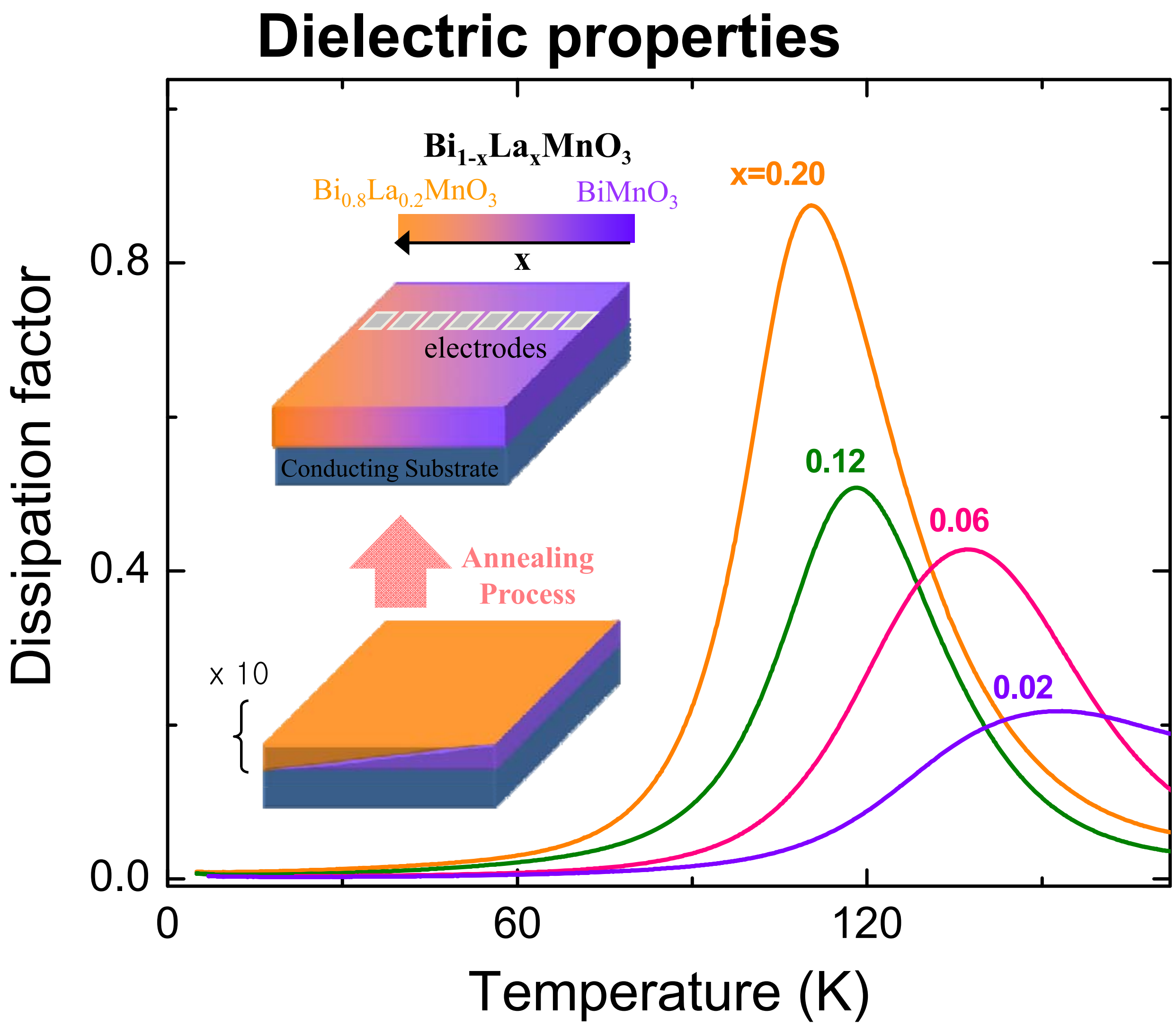
  One type of order develops in the presence of the other order already fully saturated.

- Susceptibilities become large in transition regions.

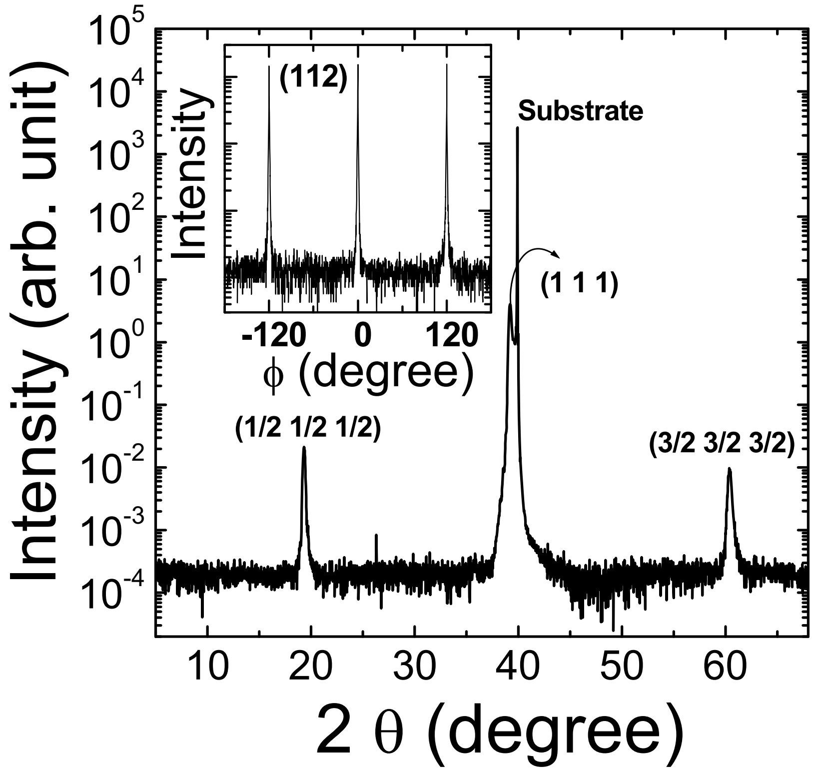
  Overlapping of the two transitions would lead to amplification effects.

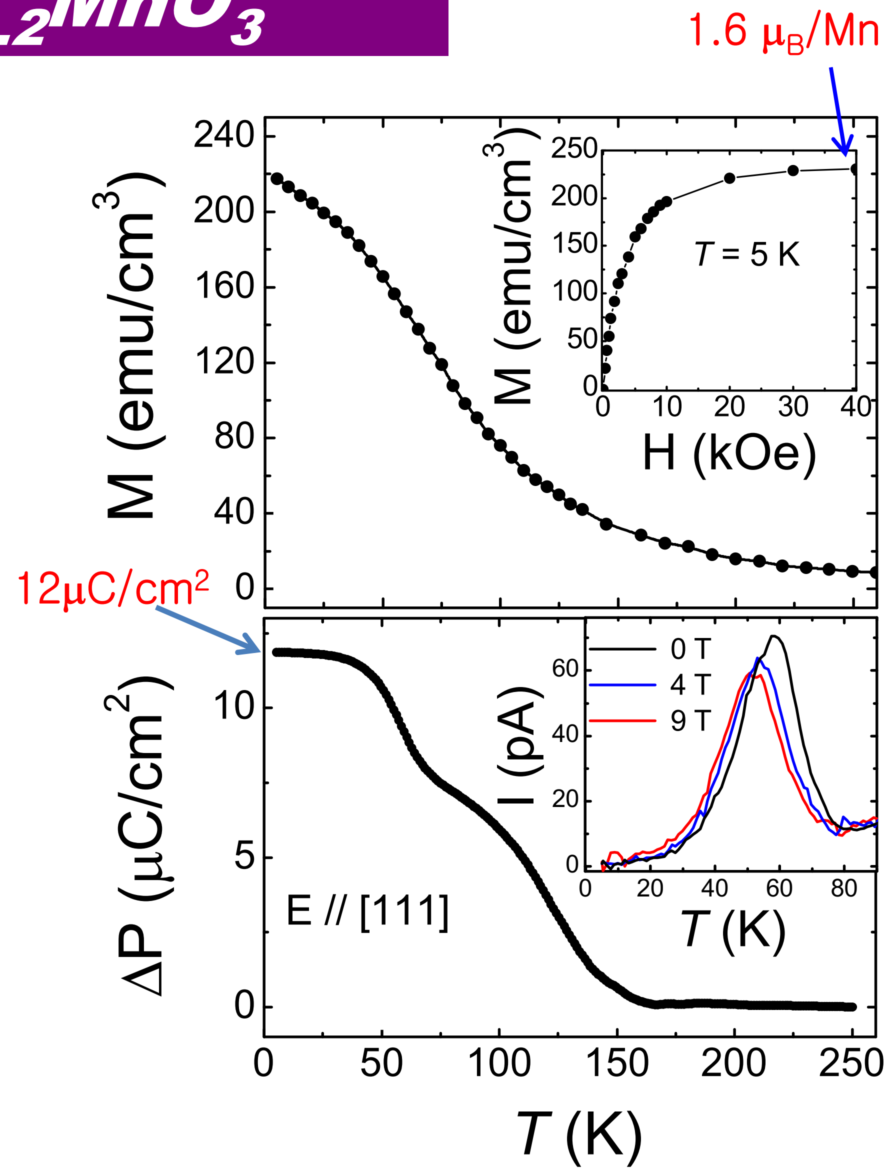

FE
Introduction of disorder
(dilution of Bi ions)
Reduction in Tc
FM
Disorder broadening
Frequency tuning

La doping via combinatorial chemistry

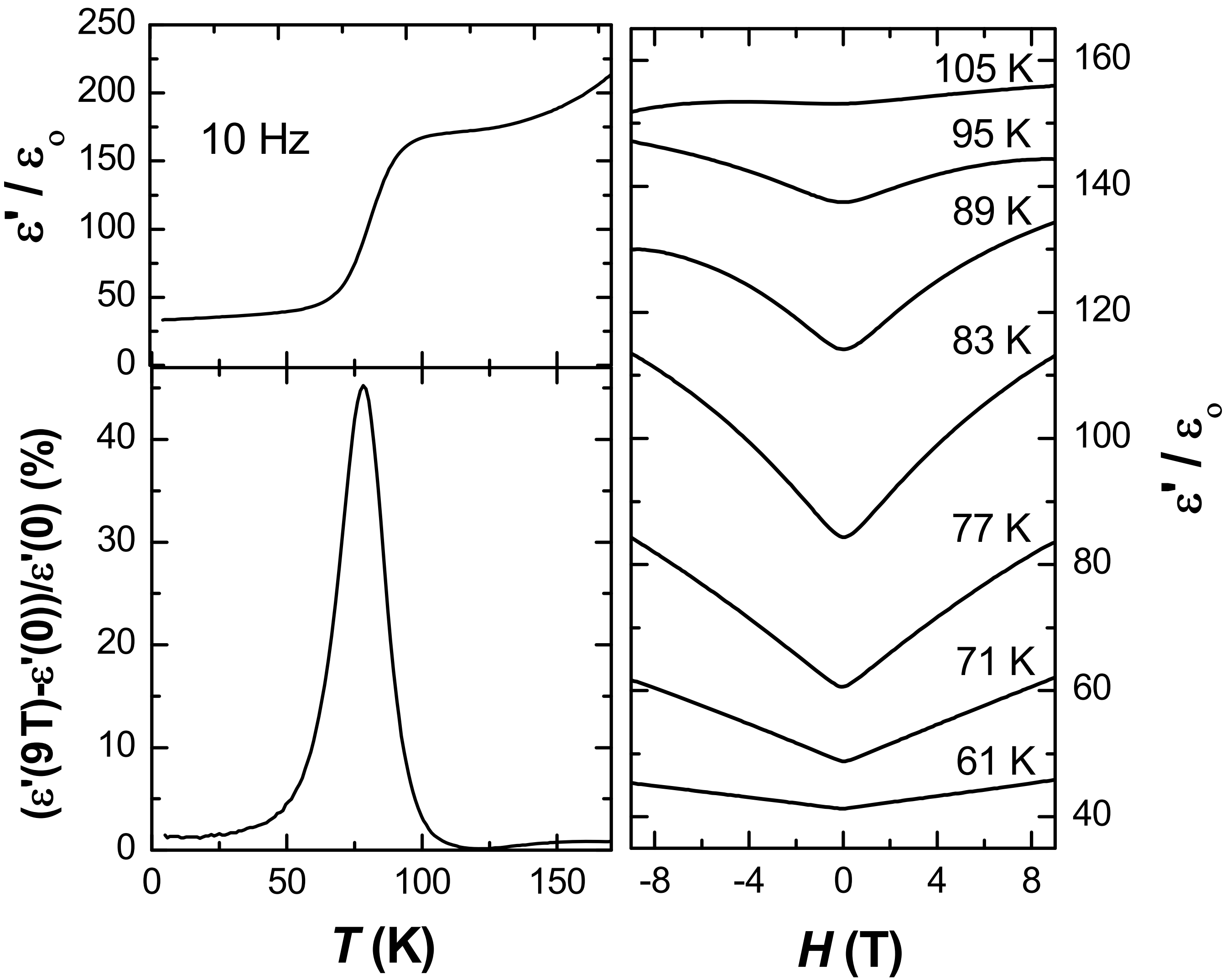


Structure and Magnetization & Polarization of $Bi_{0.8}La_{0.2}MnO_3$



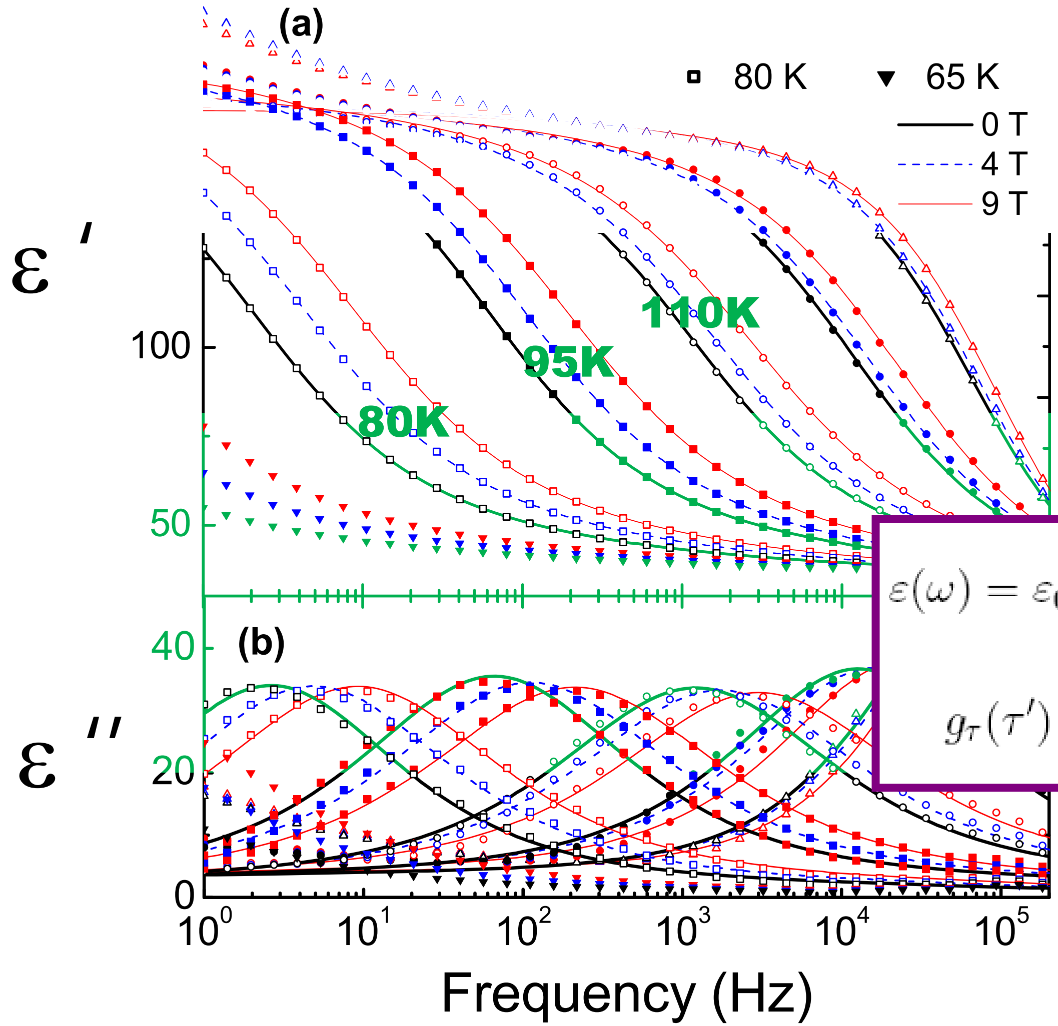


Large Magnetodielectric Effect



Δε/ε = 45 % at 80 K is a 70-fold increase from -0.6% of $BiMnO_3$

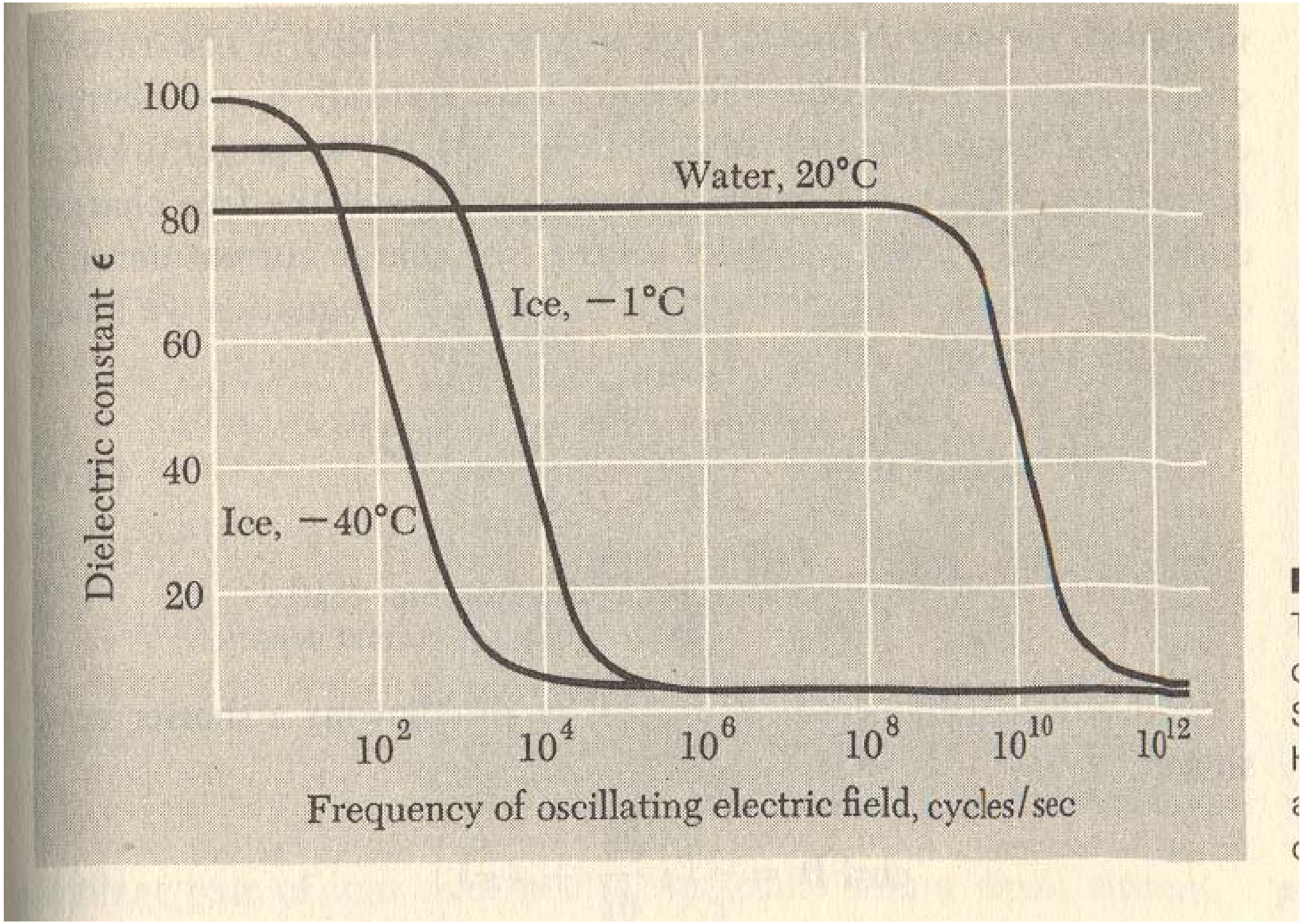
Controlling electric relaxation with a magnetic field



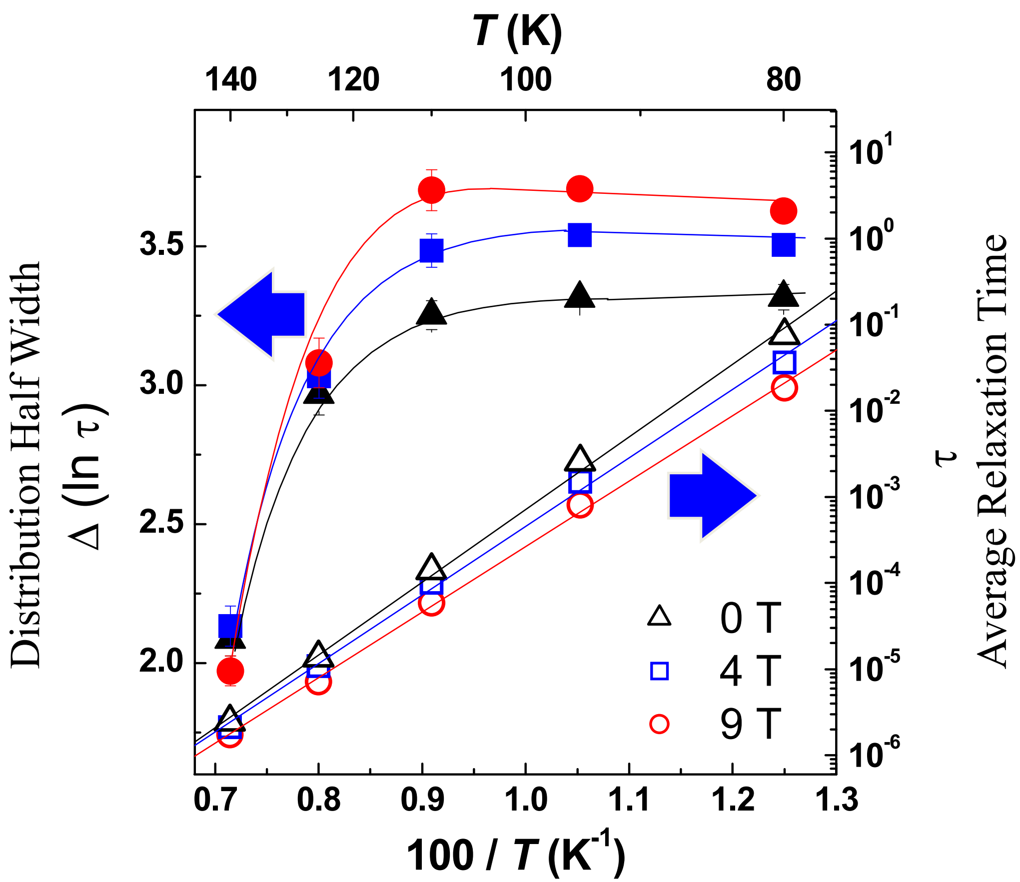
$$\varepsilon(\omega) = \varepsilon_0 + (\varepsilon_\infty - \varepsilon_0) \int \frac{1}{1 + i\ \omega\tau'} \frac{g_\tau(\tau')}{\tau'} d\tau',$$

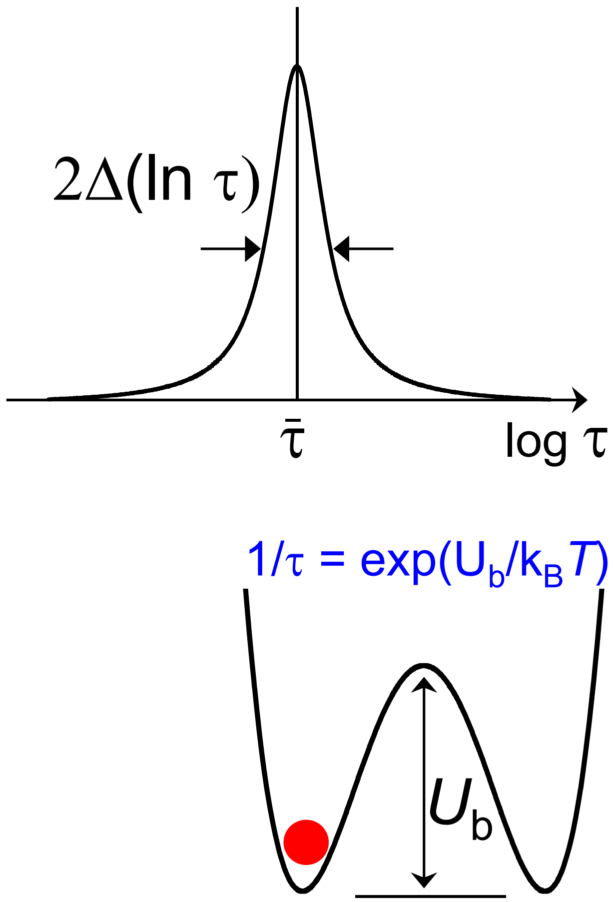
$$g_\tau(\tau') = \frac{\Delta(\ln(\tau))/2\pi}{(\ln(\tau') - \ln(\tau))^2 + \Delta(\ln(\tau))^2},$$

Dielectric relaxation in water



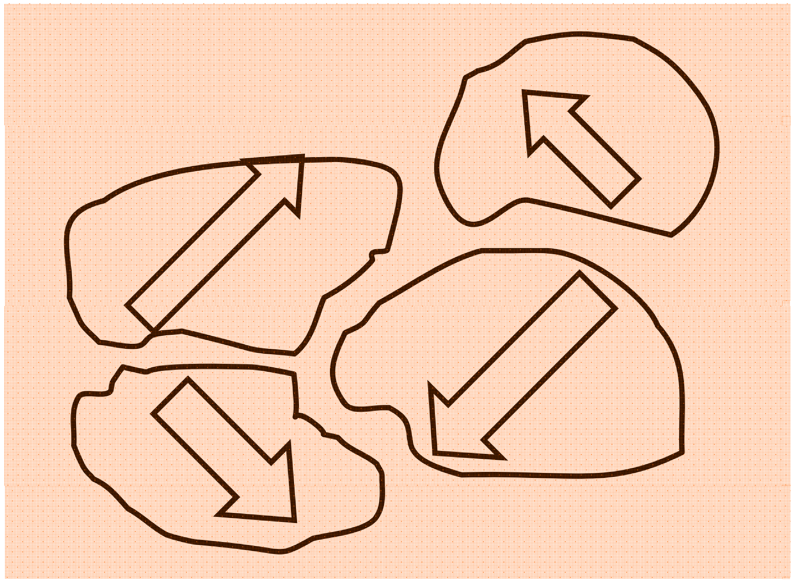
Berkeley physics vol. 2





U_b depends on H field.

- 162 meV for 0T
- 153 meV for 4T
- 146 meV for 9T



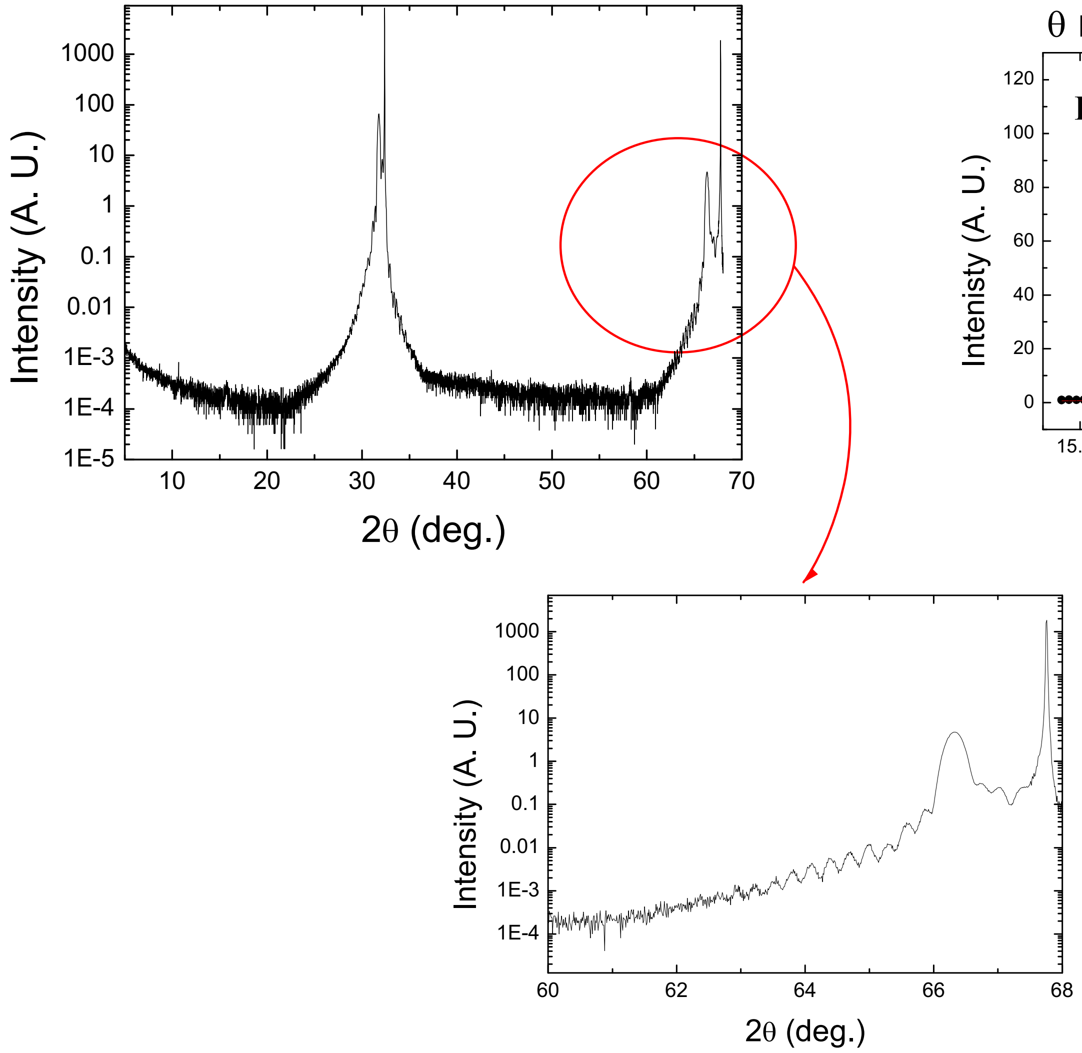
Conclusions and outlook

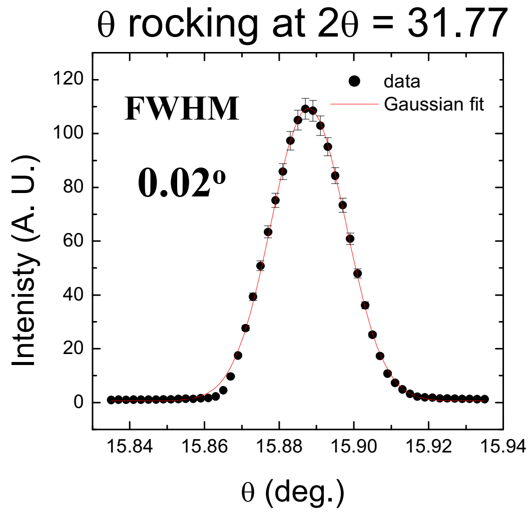
We have revealed the orbital order and its magnetic consequences in pure BiMnO3,

and also demonstrated the possibility of tailoring the properties of BiMnO3 compounds.

Currently work is in progress:
(1) elucidation of low temperature FM and FE structures
(2) development of multiferroic materials with room temperature or higher transition temperatures.

No impurities and high crystallinity





JKT-7 Spring8