Frustrations in Relaxors

Neutron and X-ray scattering of PMN-xPT and PIN

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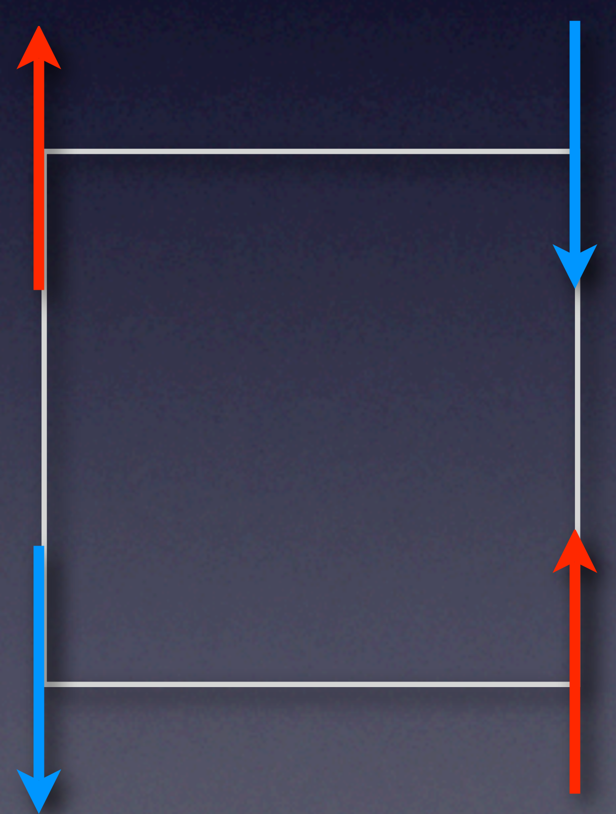
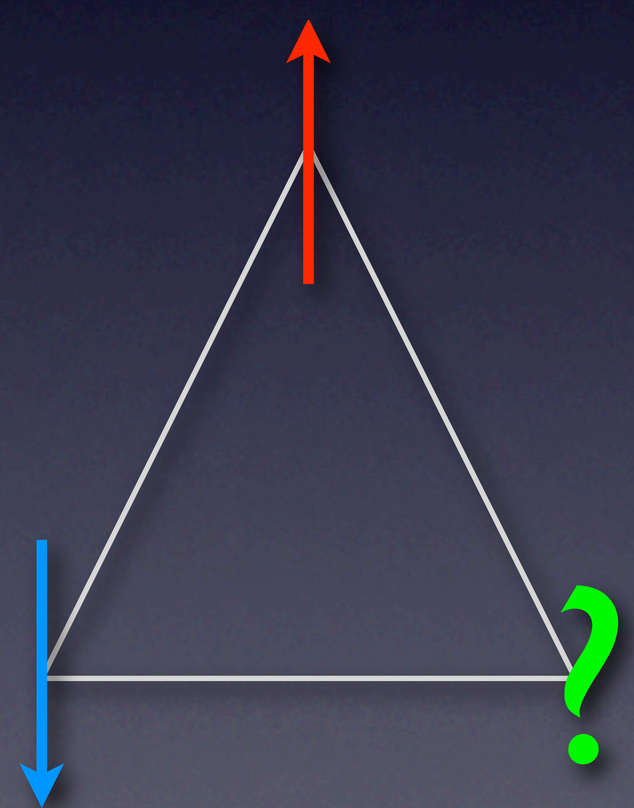
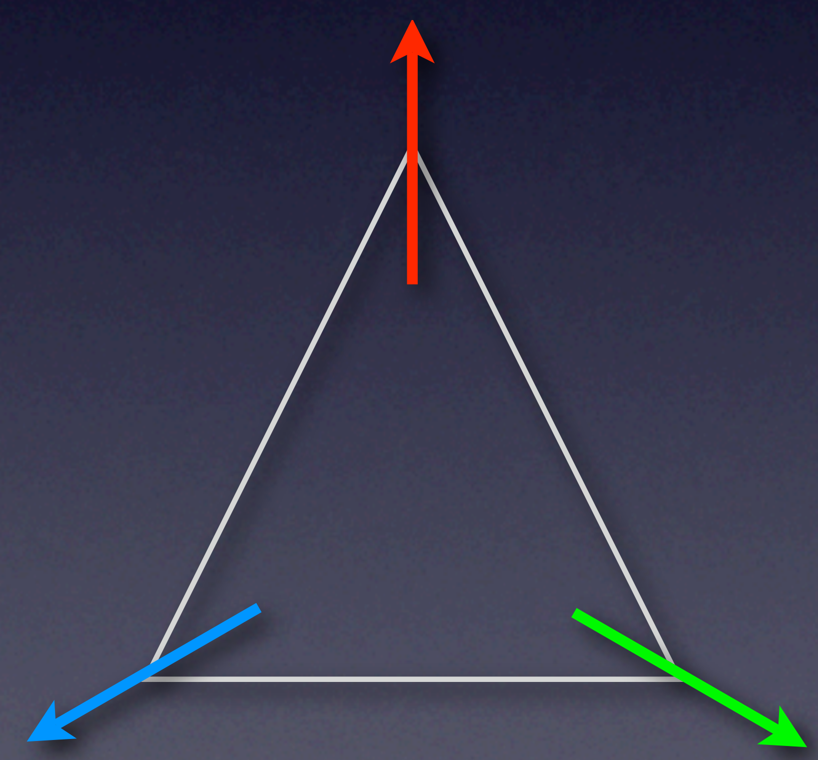
Frustration

- Mutually exclusive ground states
  - *e.g.* Triangular lattice antiferromagnet



Néel state

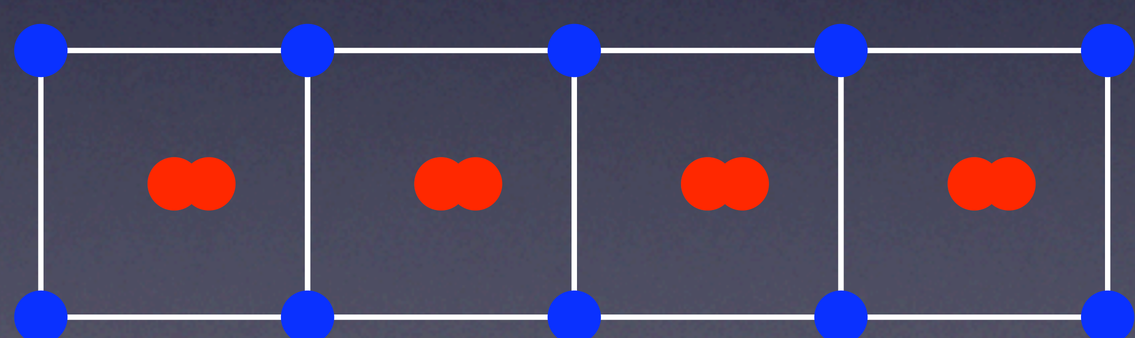


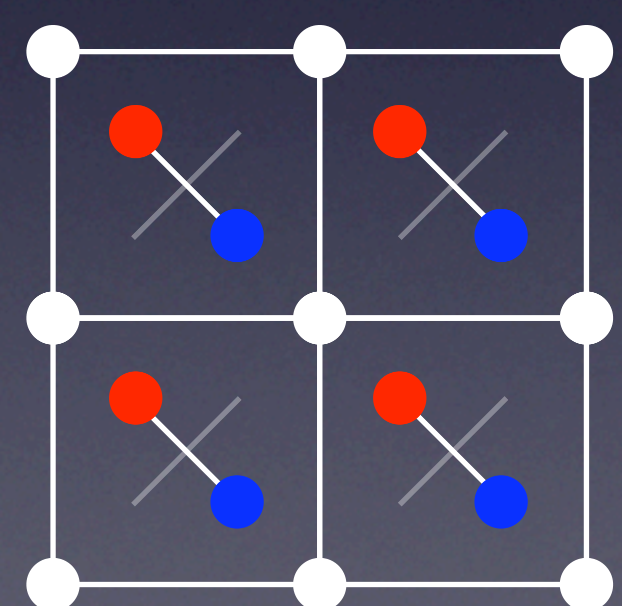


compromize

Ferroelectricity basics

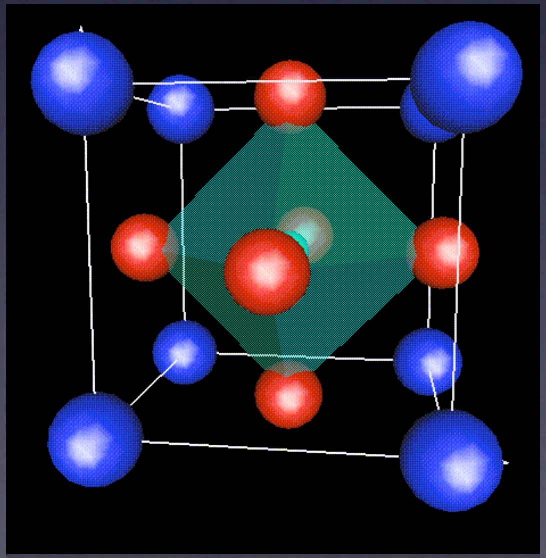
- Ferroelectricity has …
  - Long-ranged order of Spontaneous ***P***
- Displacive type & Order-Disorder type



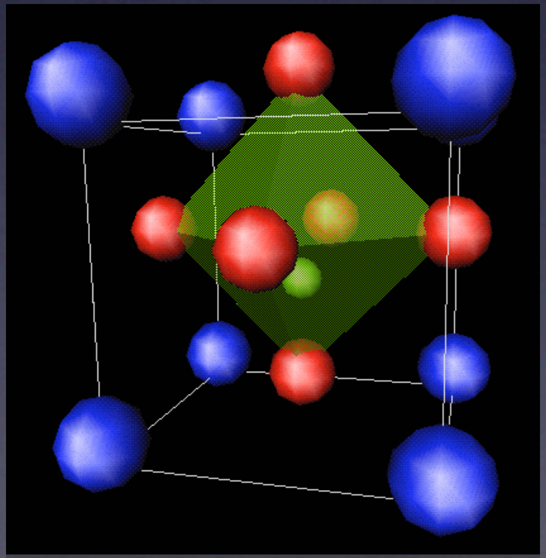


Soft mode

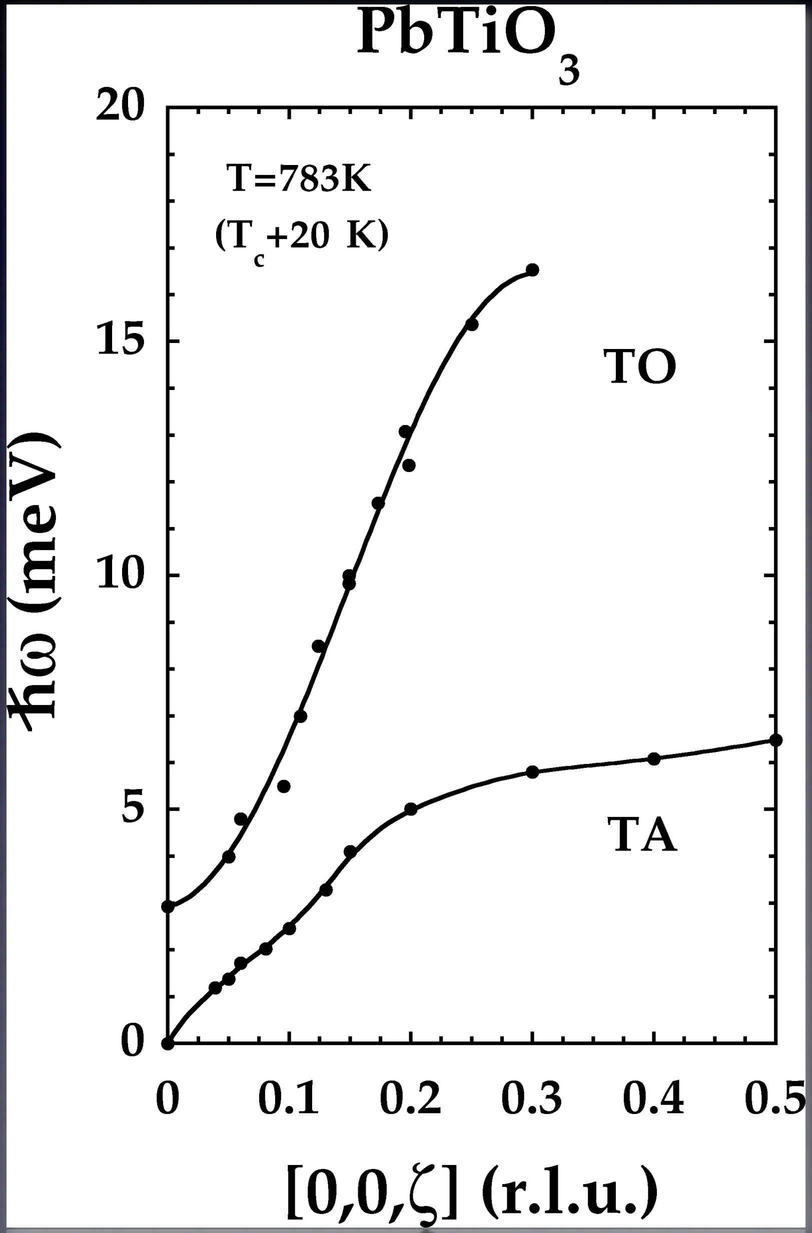
- Displacive type
- Transverse Optic Mode
  - Frozen at $T_C \Rightarrow \boldsymbol{P}$



$\boldsymbol{P} = 0$

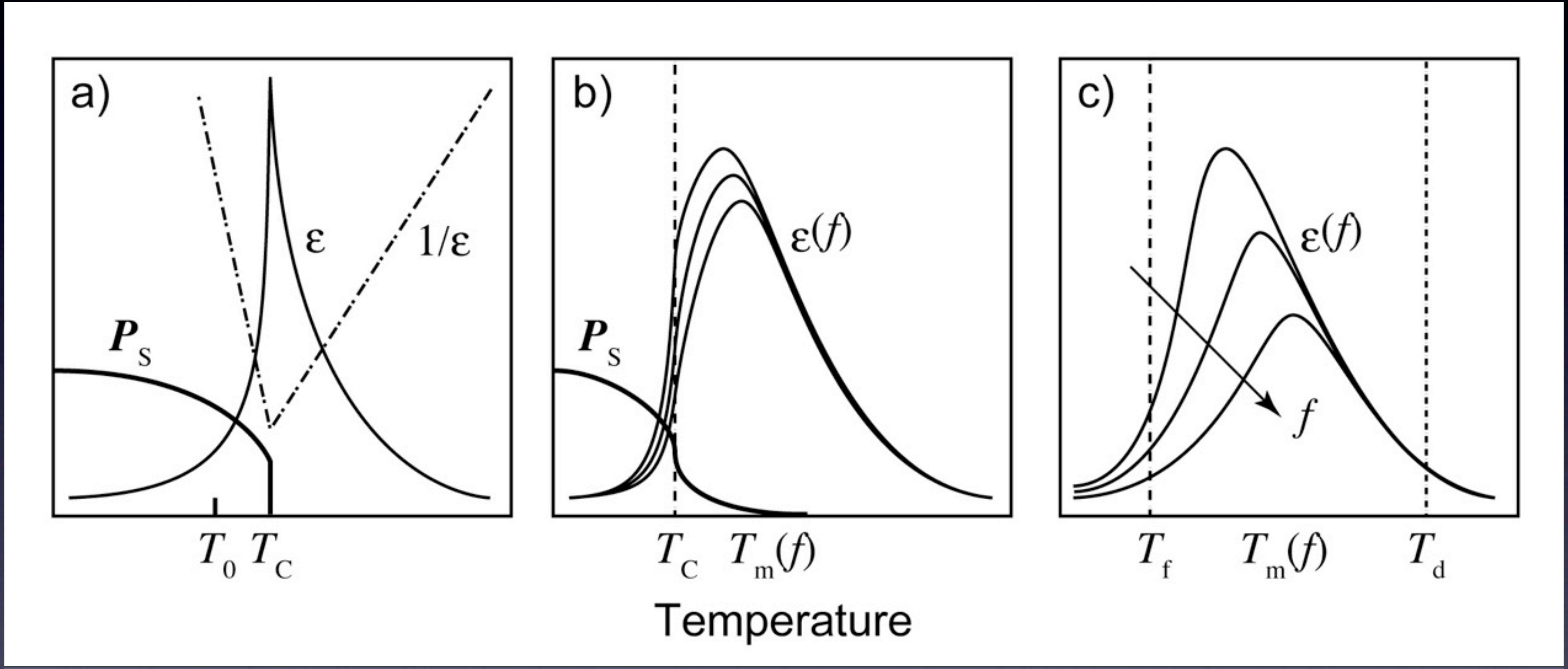


$\boldsymbol{P} \neq 0$



Shirane *et al.* (1972)

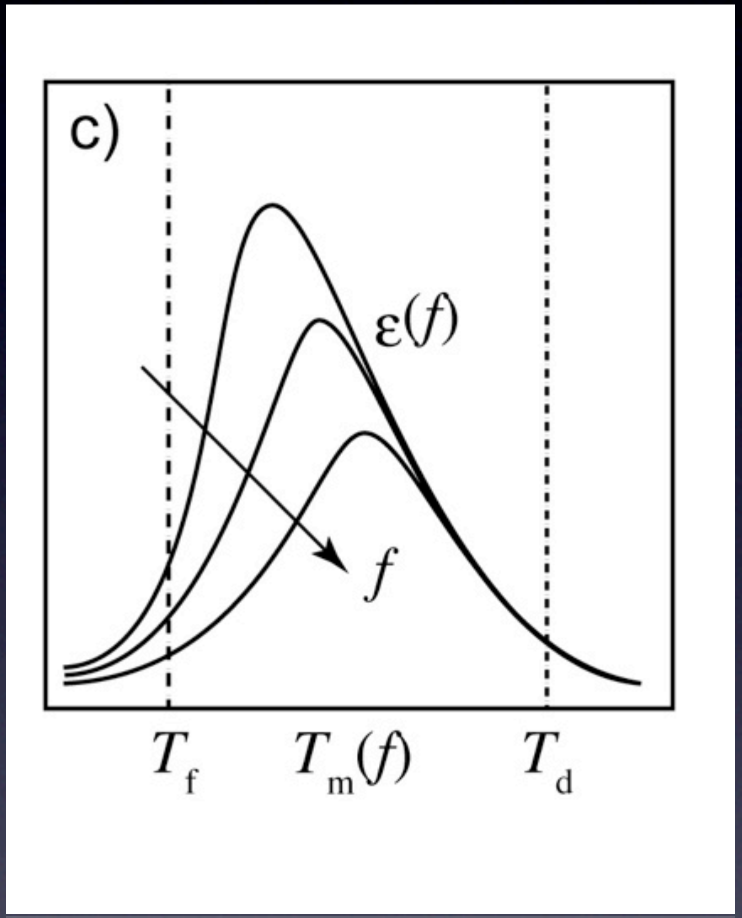
Various ferroelectricities



Normal Diffuse Transition **Relaxors**

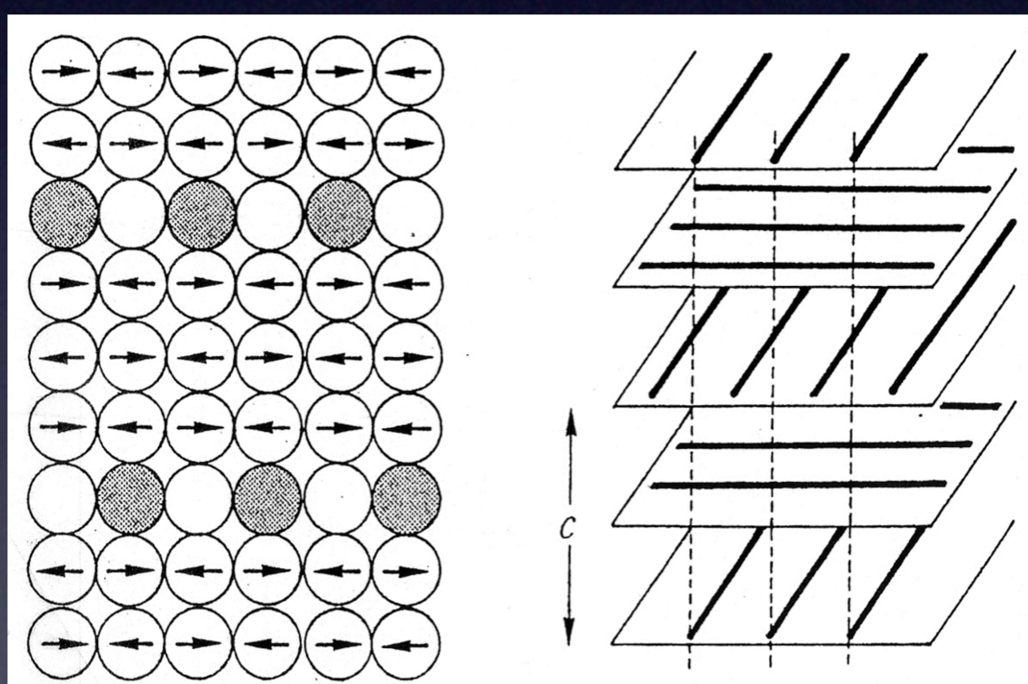
Its importance

- Anomalous ferroelectricity
  - Broad temperature dependence
  - Strong frequency dependence
  - Large ϵ and piezoelectricity
- Intrinsic Heterogeneity



Heterogeneity everywhere

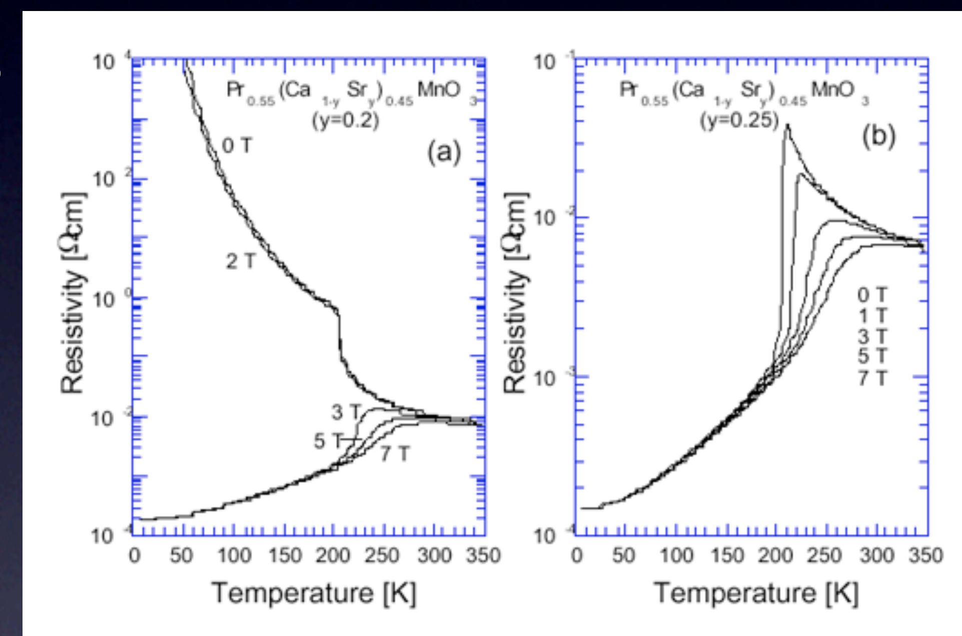
- Stripe model

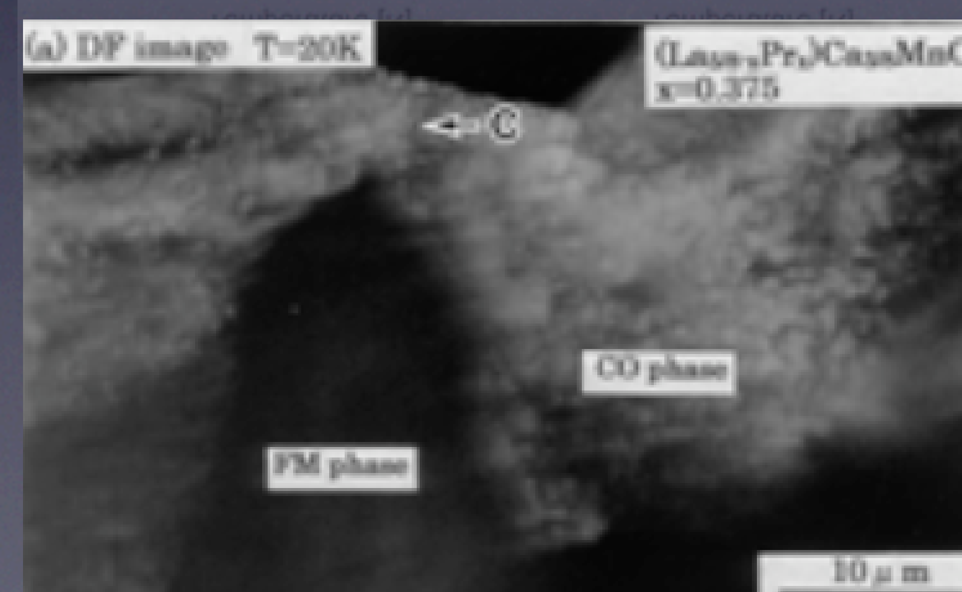


Tranquada *et al*. 1995

- CMR Mn Oxides

Tokunaga *et al*. 1998





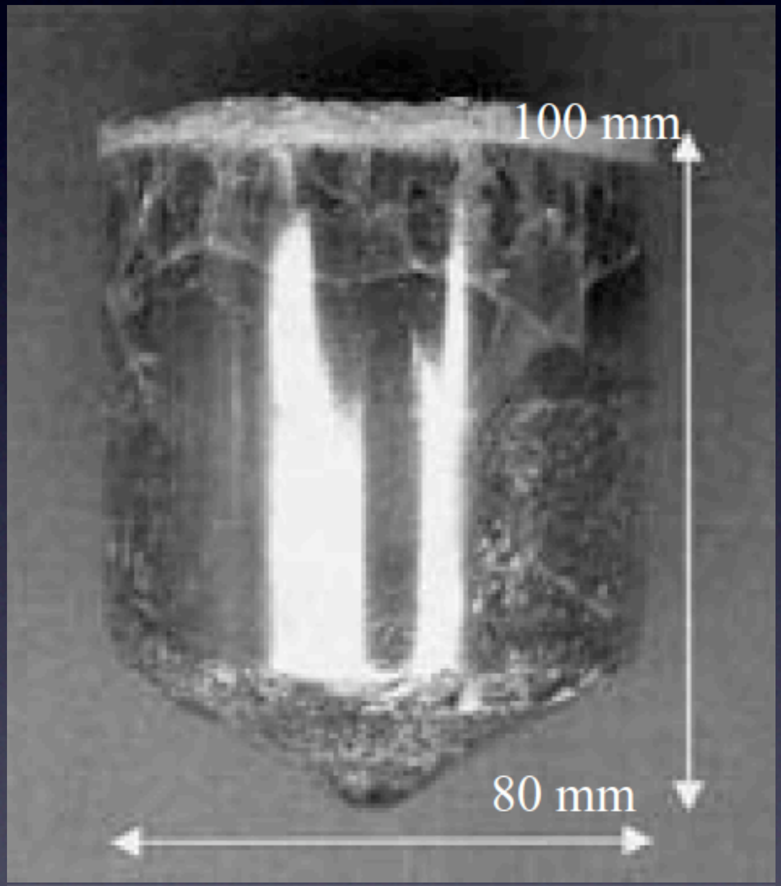
Mori *et al*. 2002

Aims

- Understanding & describing various properties specific to Relaxors
- Heterogeneity due to ***Frustrations*** between charge and structure
- Writing a Hamiltonian for ferroelectricity ~ applying concepts of magnetism

Canonical relaxors

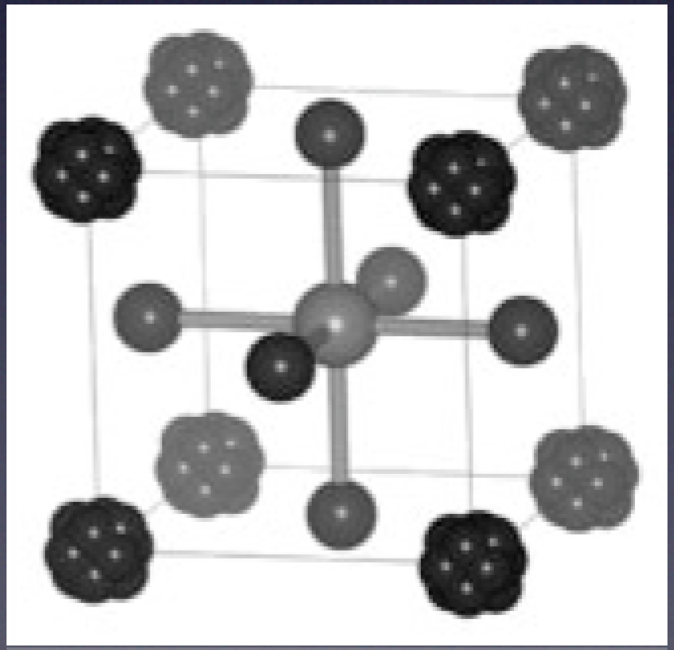
- ABO_3 type Perovskite
  - B-site substitution
  - PMN: $Mg^{2+}{}_{1/3}Nb^{5+}{}_{2/3} = B^{4+}$
  - PIN : $In^{3+}{}_{1/2}Nb^{5+}{}_{1/2} = B^{4+}$
  - Stoichiometric growth



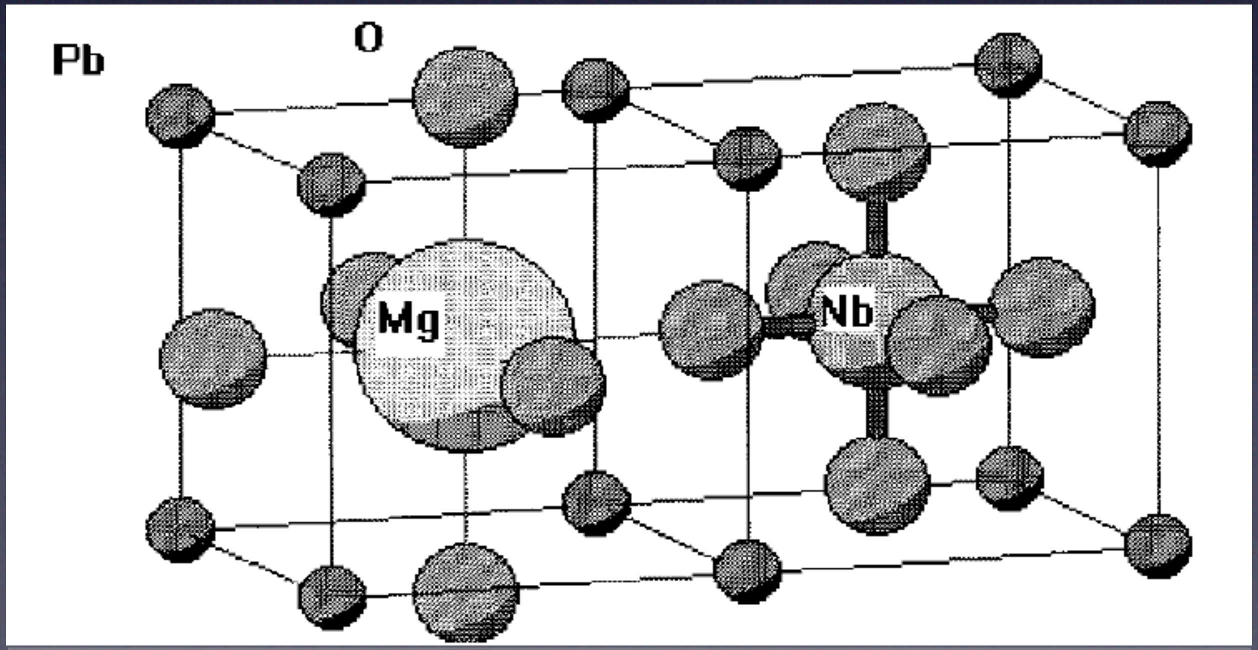
PMN by JFE

Structures

- ABO_3-type Perovskite
  - A site: Off-center of Pb^{2+}
  - B site: Randomness / Frustration

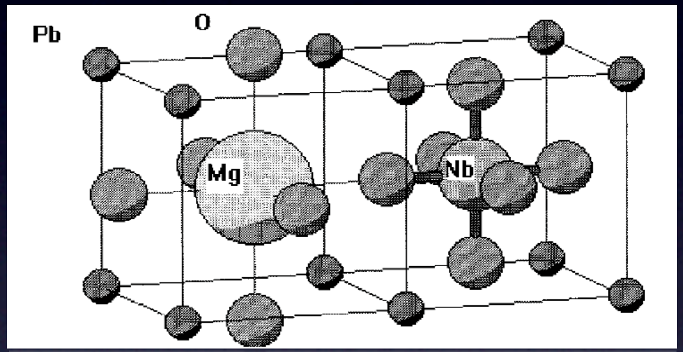


Terado *et al.* 2006

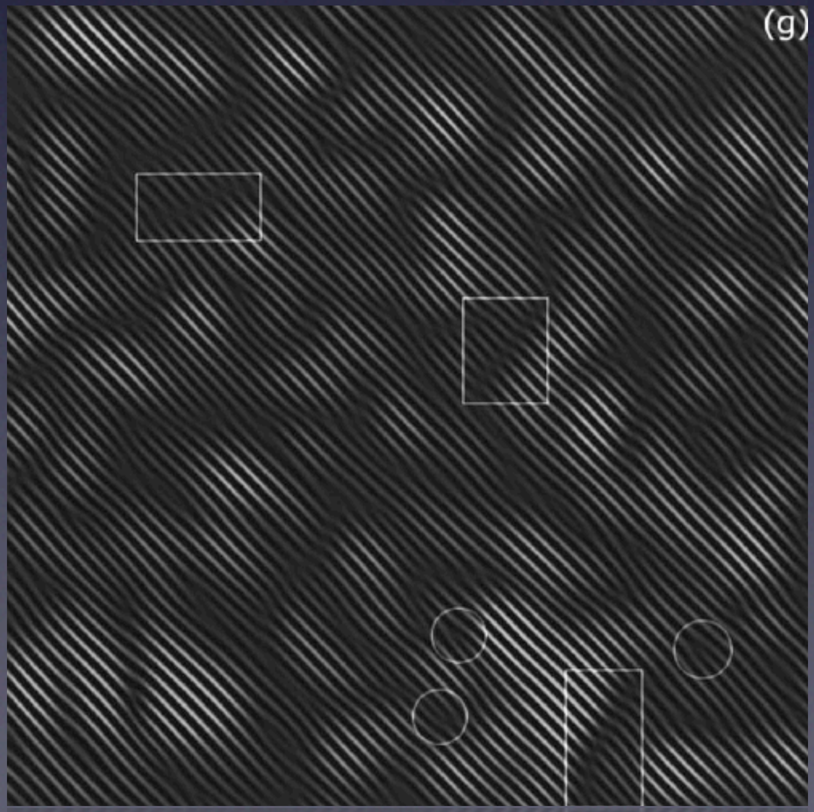


Frustrations in Relaxors

- Structural stability vs. Charge neutrality
  - $Mg^{2+}_{1/3}Nb^{5+}_{2/3} = B^{4+}$
  - Lattice → Mg : Nb = 1:1
  - Coulomb → Mg : Nb = 1:2

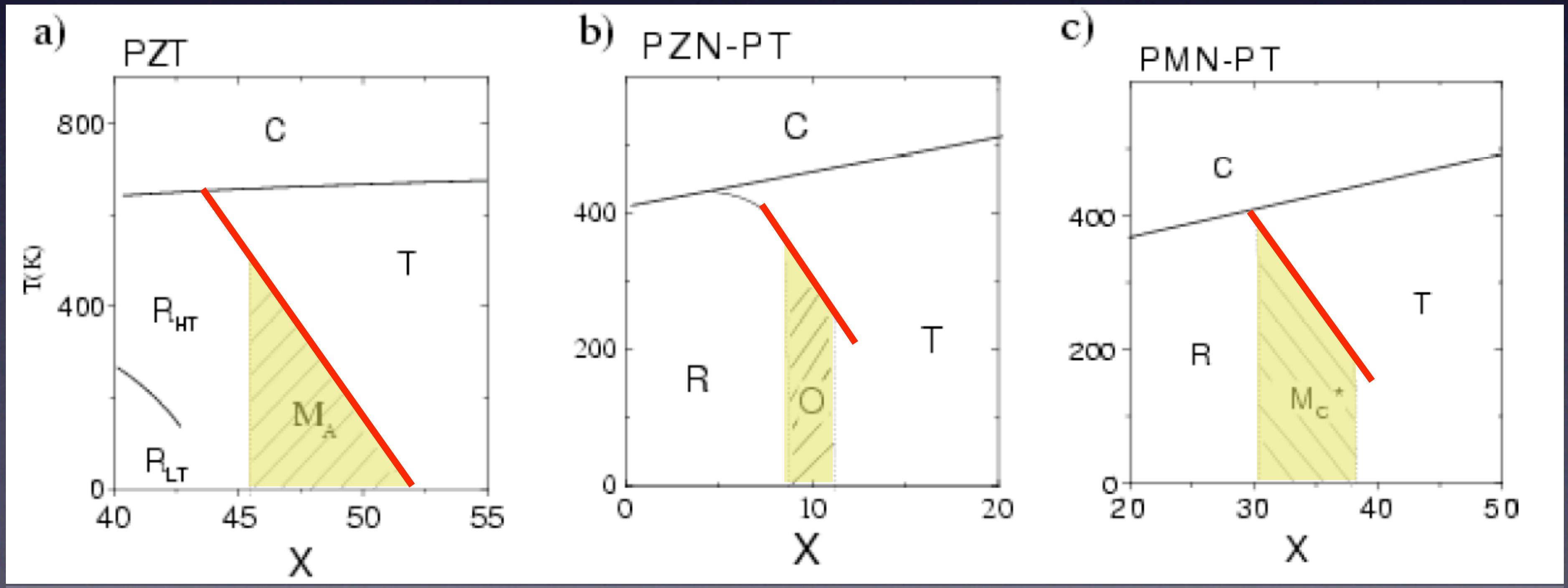


- Heterogeneity
  - HRTEM (Jin *et al.* 2001)

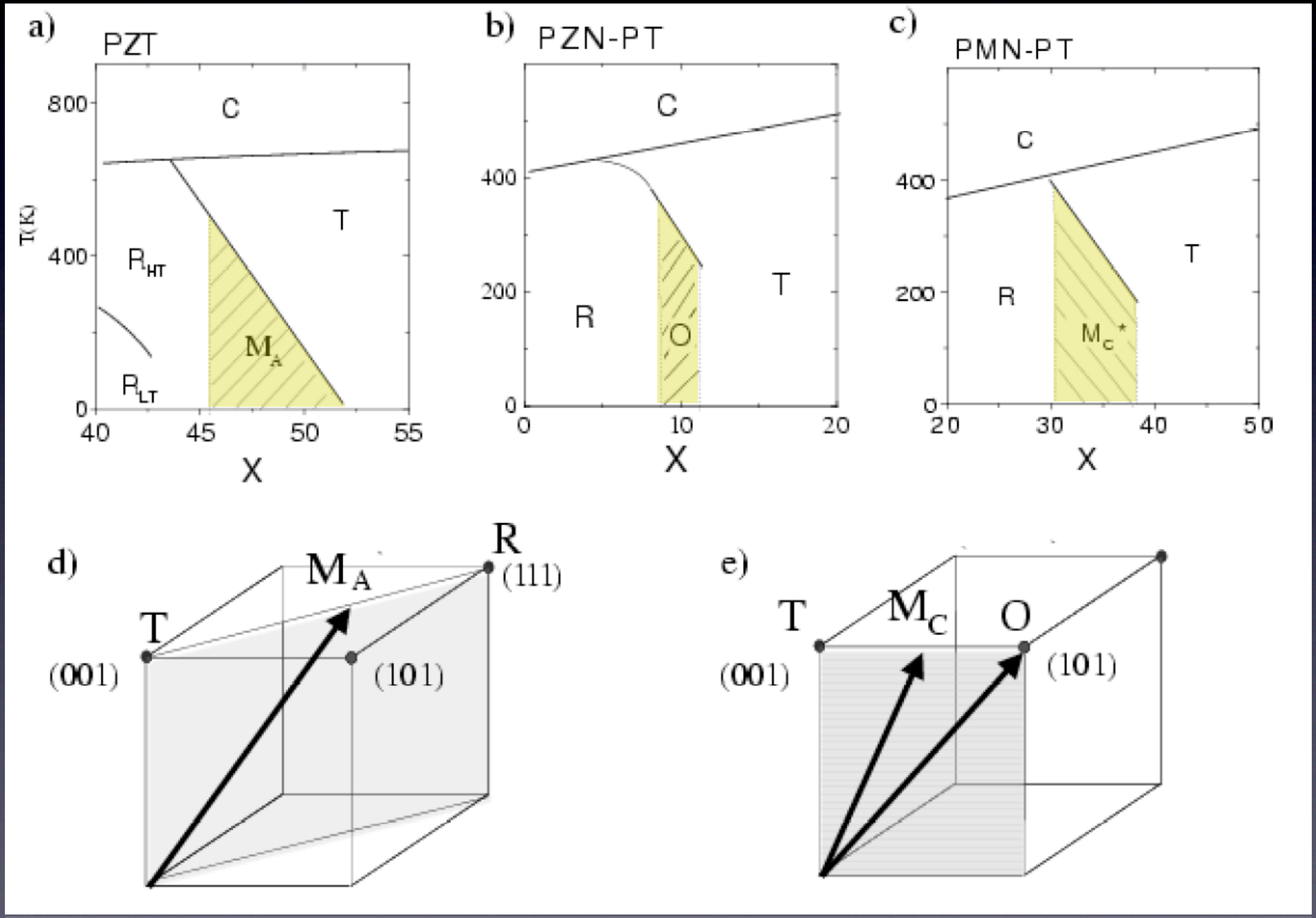


Why is ϵ so large?

- Morphotropic Phase Boundary (MPB)
- Monoclinic Phase (Noheda *et al.* 2001)



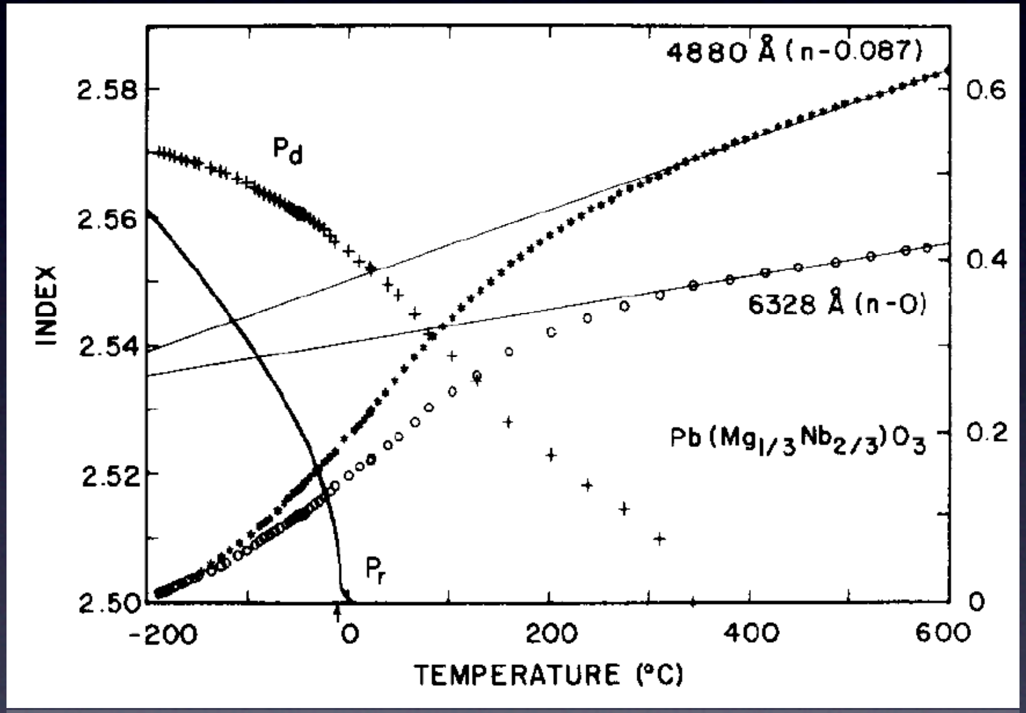
P rotation



a)
PZT
T(K)
800
400
0
40
45
50
55
X
C
T
R_{HT}
R_{LT}
M_A
b)
PZN-PT
400
200
0
0
10
20
X
C
R
O
T
c)
PMN-PT
400
200
0
20
30
40
50
X
C
R
T
M_C*
d)
R
M_A
T
(111)
(001)
(101)
e)
T
M_C
O
(001)
(101)

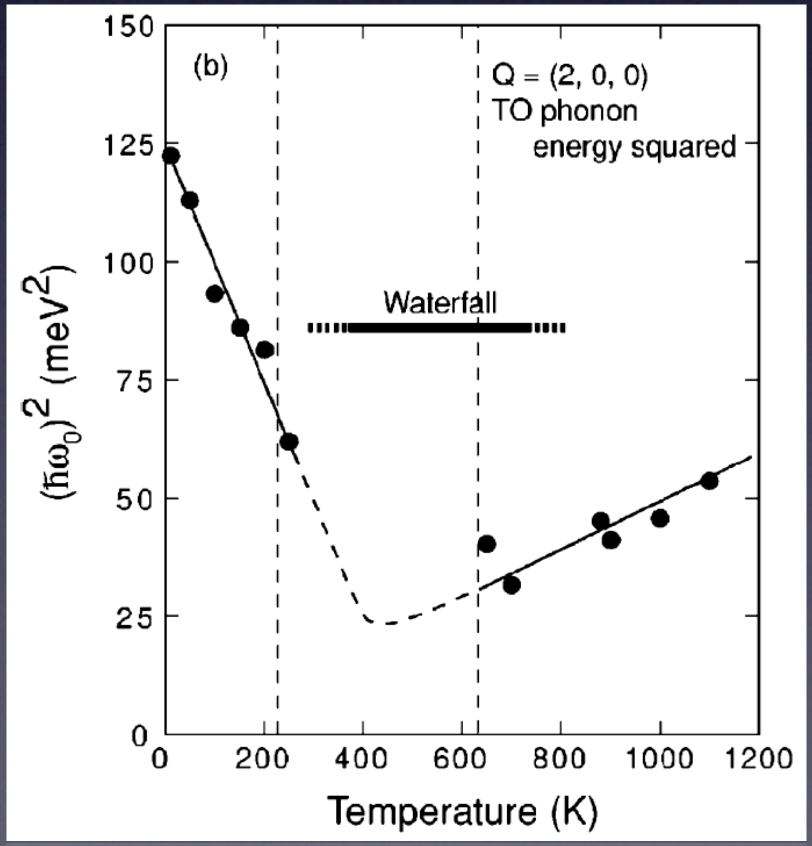
Polar nanoregions

- Burns & Dacol 1983
  - T_d : $n(T)$ deviation
  - $T_d >> T_{max}$
- PNR
  - local polar regions
  - randomly oriented
  - no macroscopic polarization

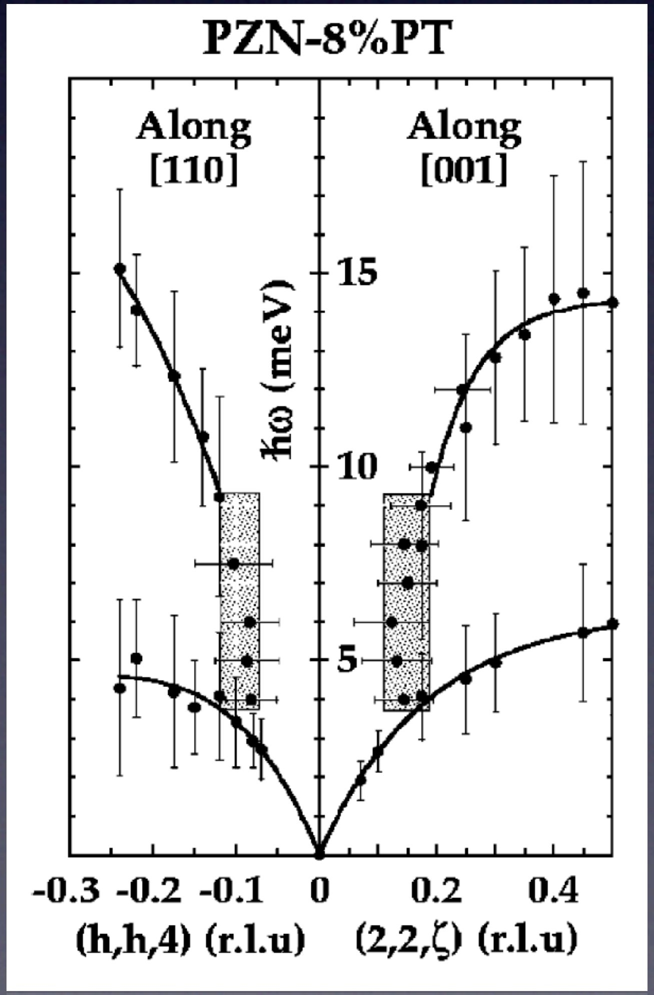


Dynamics

- Soft mode or not?
  - Softening ($T > T_d$)
  - Waterfall ($T < T_d$)



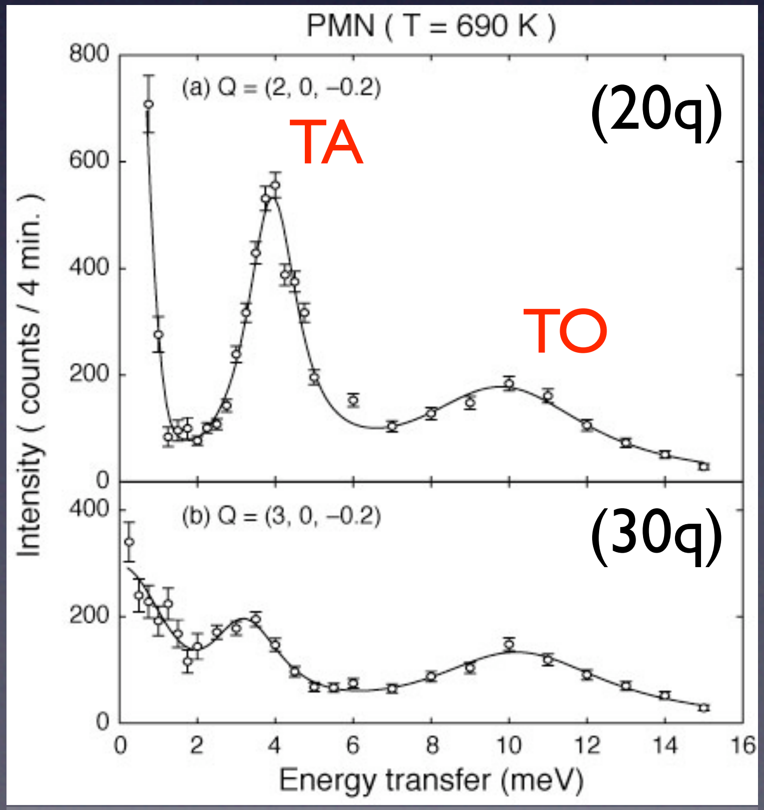
Wakimoto *et al.*



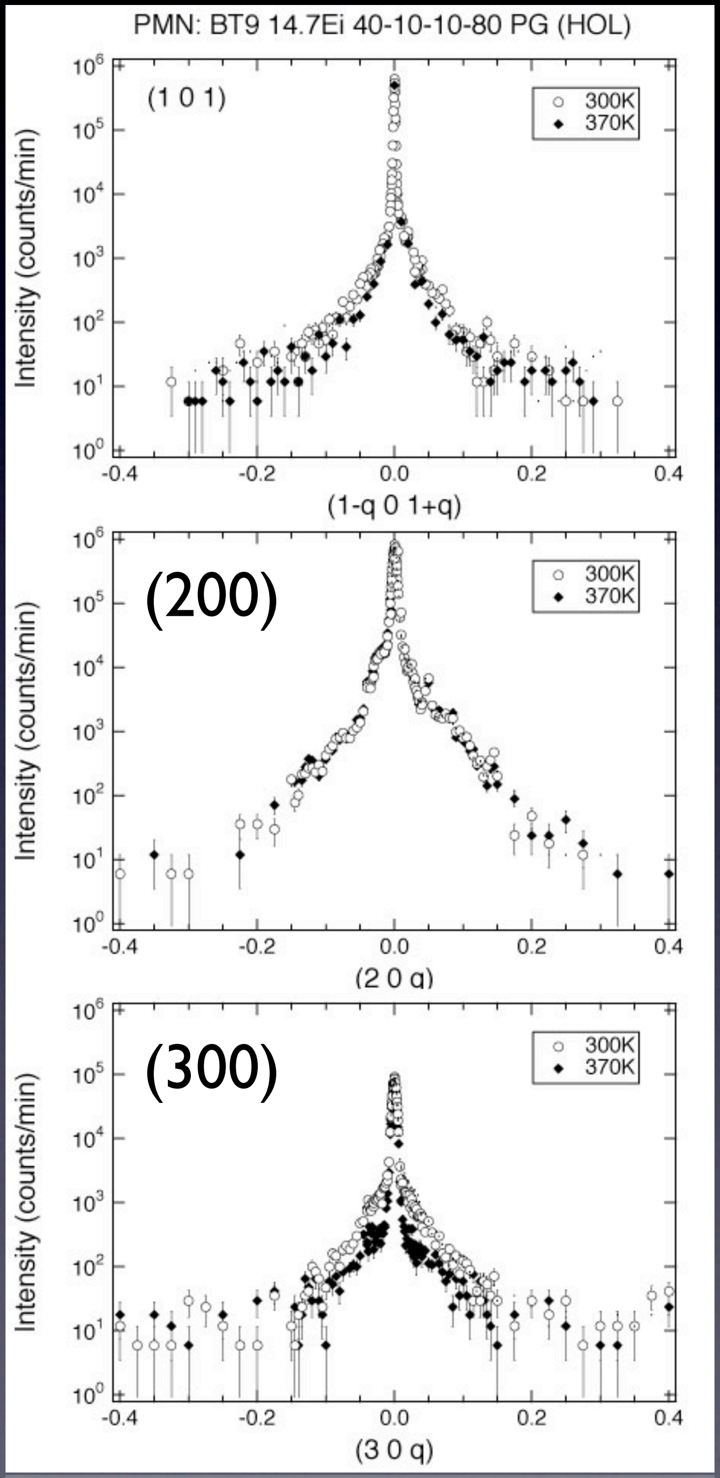
Gehring *et al.*

Diffuse scattering

- Inconsistency
  - Diffuse: (200) << (300)
  - TO phonon: (200)/(300) = 1.24



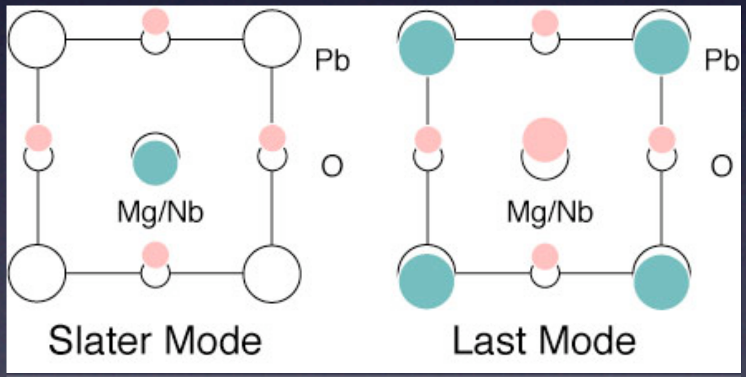
Hirota *et al.* 2002



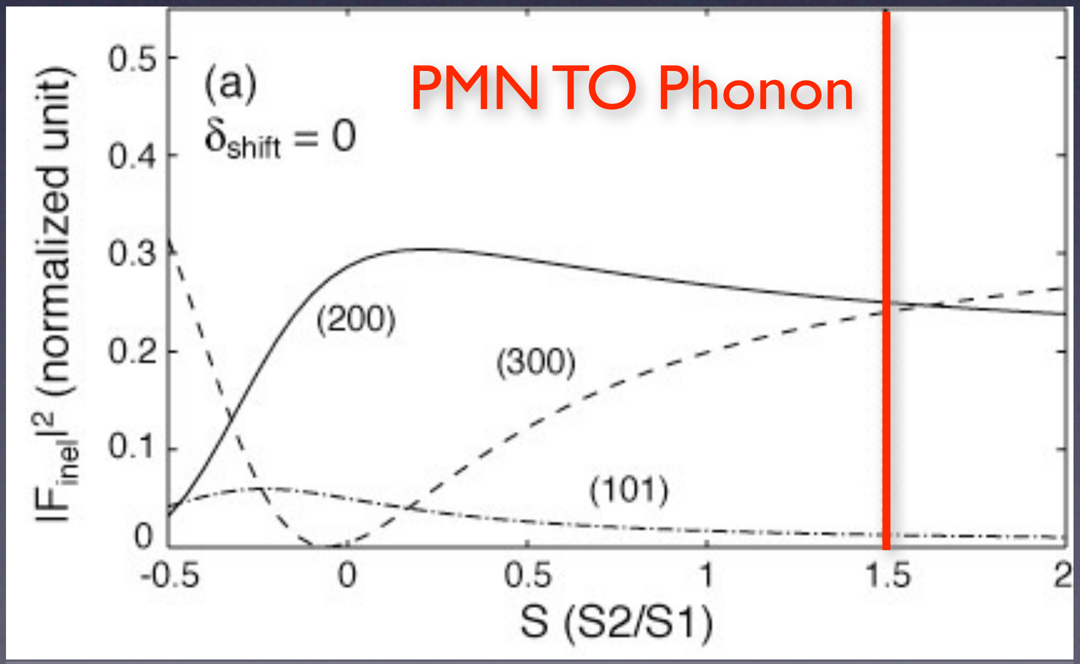
Hirota *et al.* 2002

Phonon intensities

- Normal mode expansion (Harada 1970)
  - Perovskite: Slater mode & Last mode
  - Needs only <u>Ratio</u> $S = s_2/s_1$ & <u>Center of Mass</u>

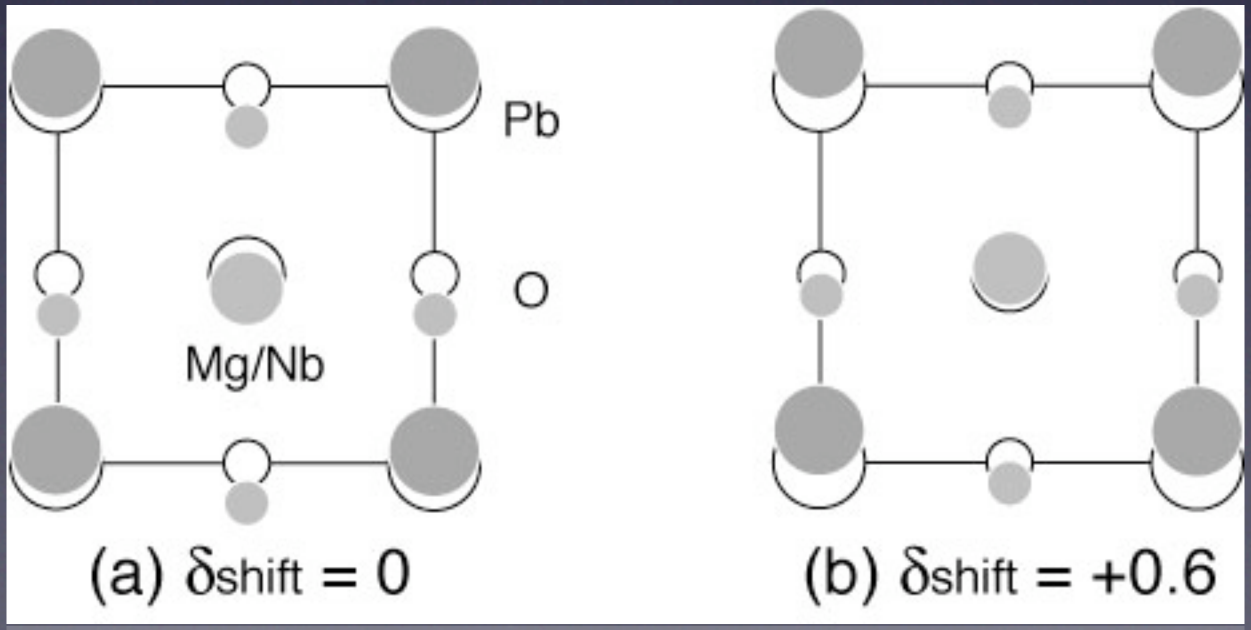


Atom	Position	s_1	s_2
A	$(0, 0, 0)$	0	$-k'$
B	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	$-k$	1
X_1	$(\frac{1}{2}, 0, \frac{1}{2})$	1	1
X_3	$(0, \frac{1}{2}, \frac{1}{2})$	1	1
X_3	$(\frac{1}{2}, \frac{1}{2}, 0)$	1	1



A new model

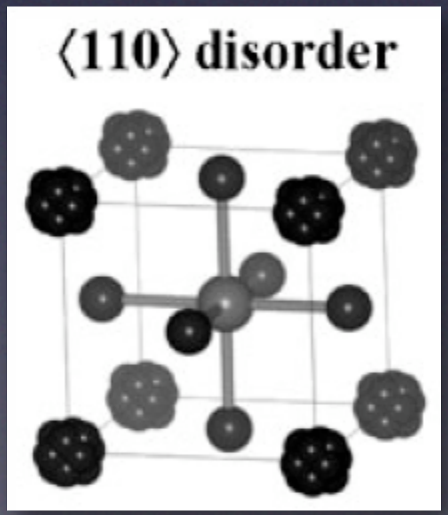
- Uniform Phase Shift model
  - Separate atomic shift: $\delta(k) = \delta_{CM} + \delta_{shift}$
  - TO phonons: δ_{CM} only
  - Diffuse scattering: $\delta_{shift} \parallel \text{local}\nabla E$



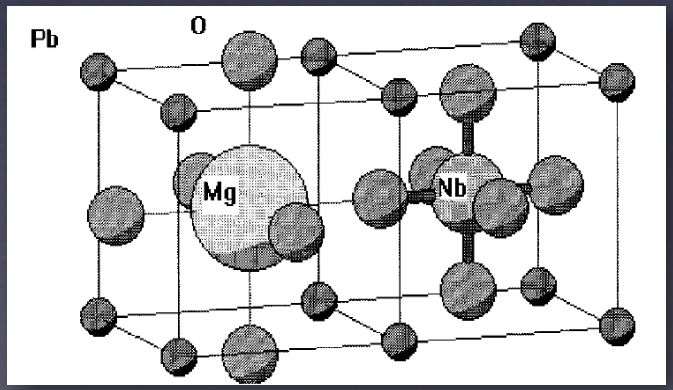
Hirota *et al*. 2002

Current understanding

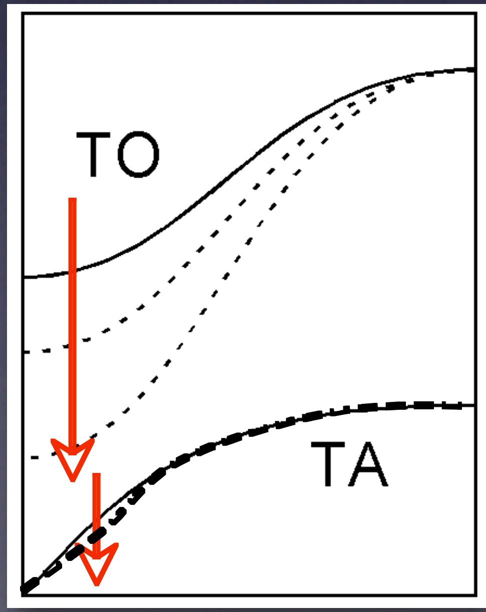
- Large ϵ & piezoelectricity
  - Monoclinic: ***P*** rotates more freely
- *Off-centered* Pb & B-site randomness
- PNR via soft TO mode



×



×

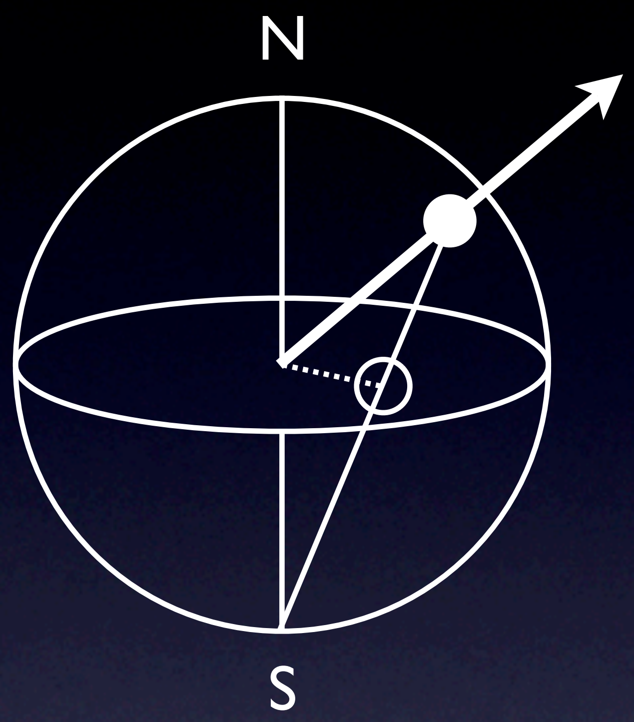


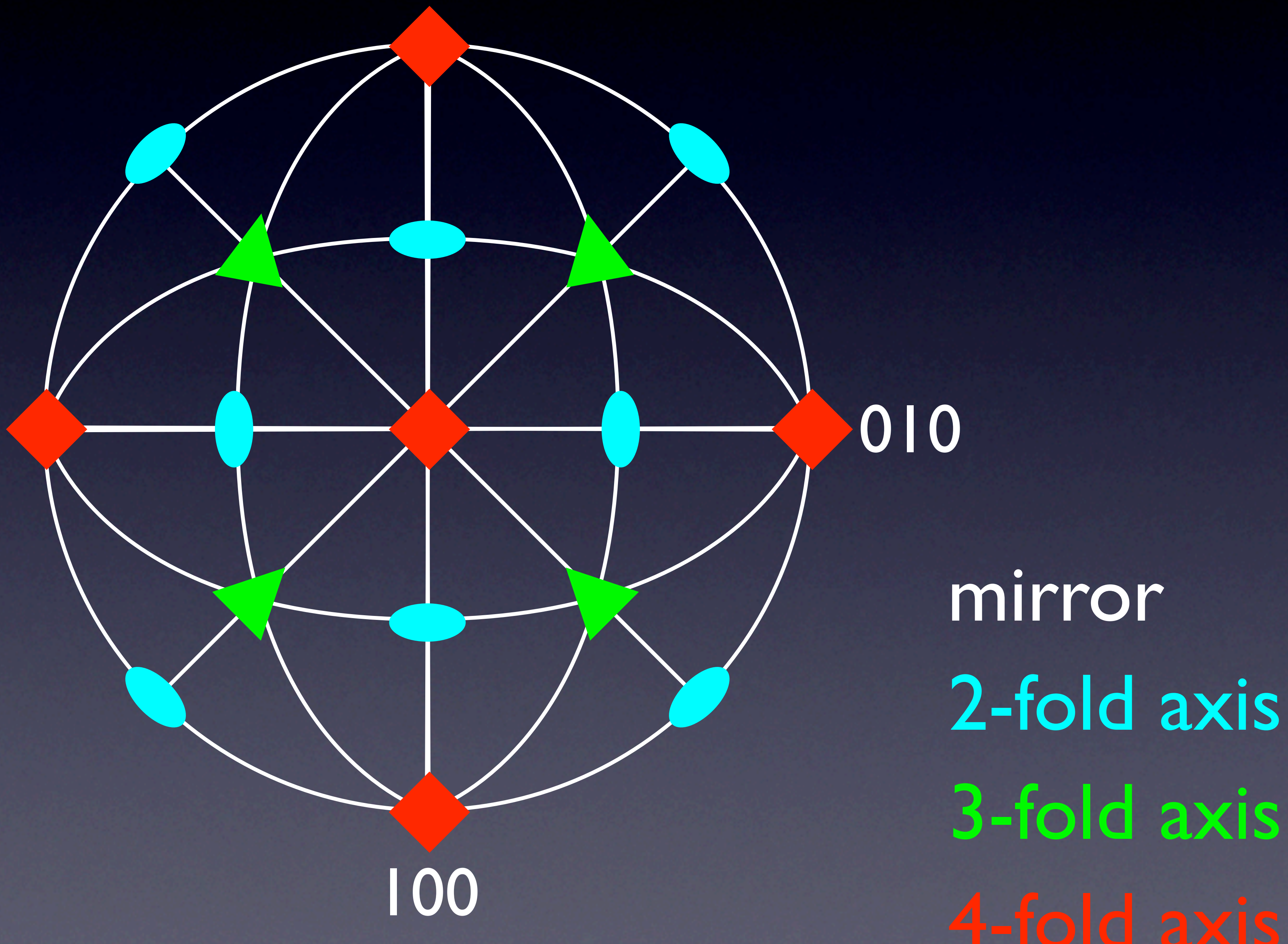
= Relaxor!

Remaining issues

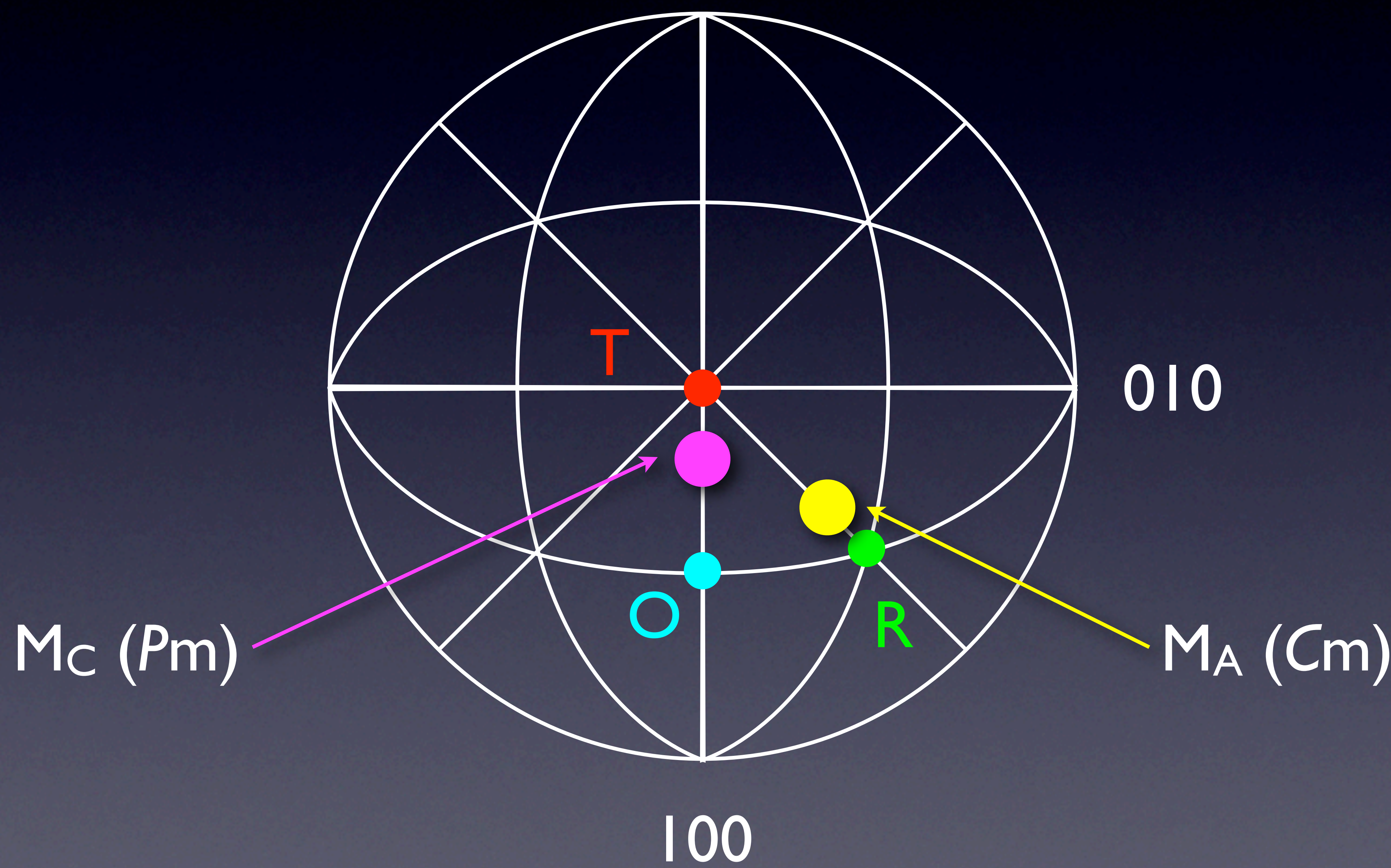
- How does PNR develop below T_d ?
- Relation among different spatial scales
  - micro: PNR through soft TO mode
  - meso: heterogeneity
  - macro: *R* or *M* or *T* phase
- What does heterogeneity do?

Stereographic Projection



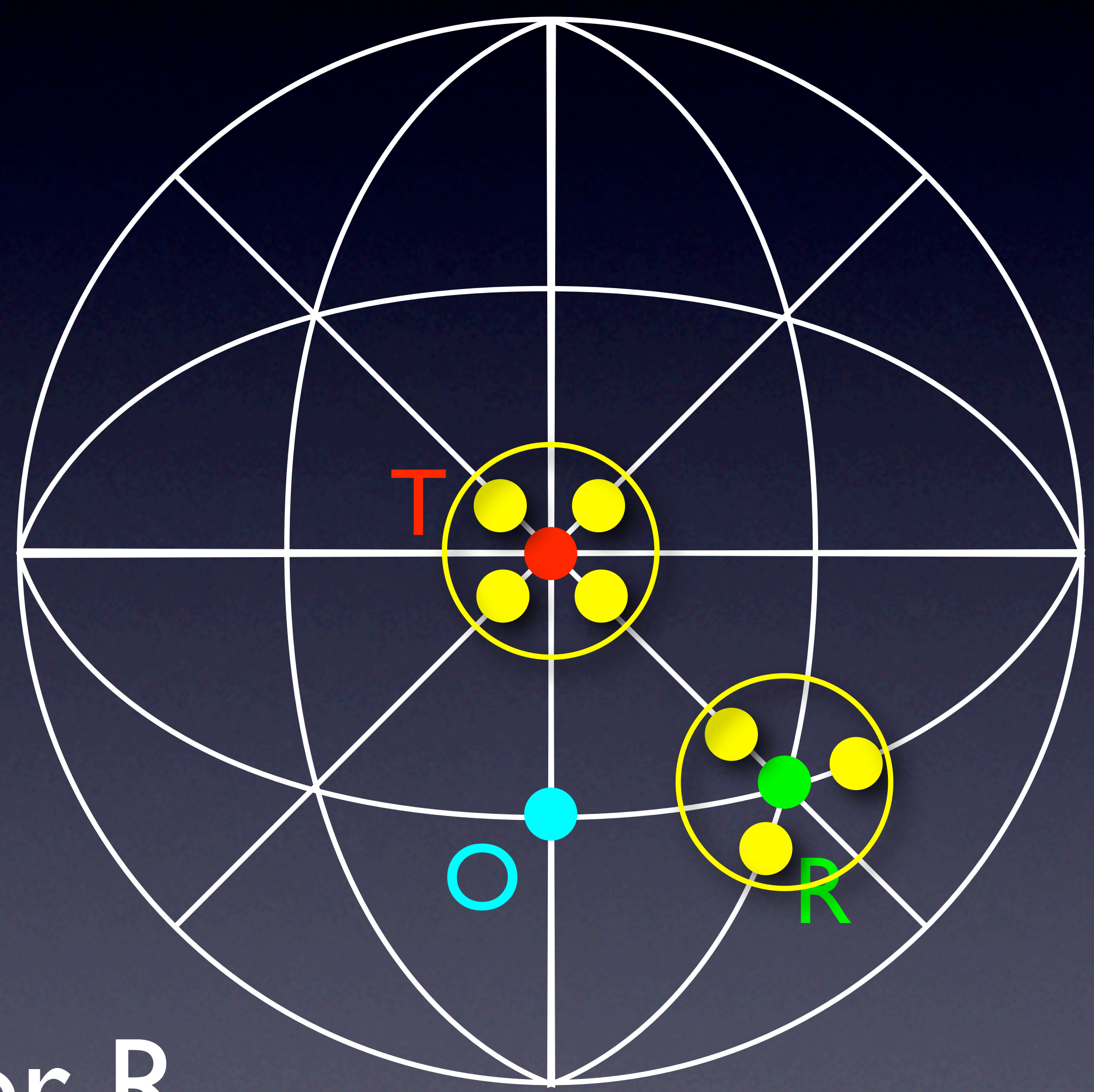


Stereographic Projection



Pb Local Structure

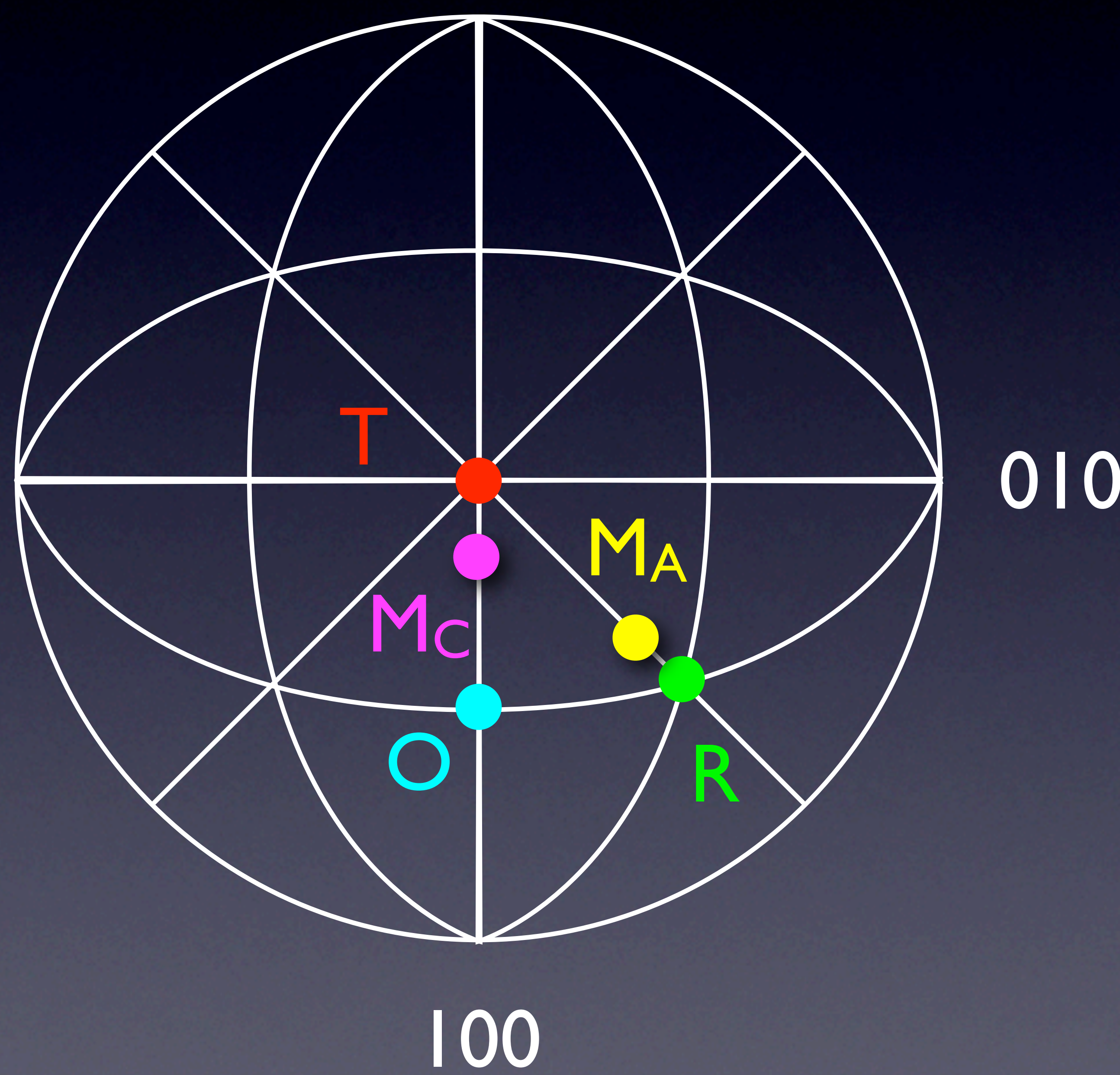
Diffuse Scattering ~ Glazer *et al*. PRB 2004



LRO ~ T or R

SRO ~ M_A

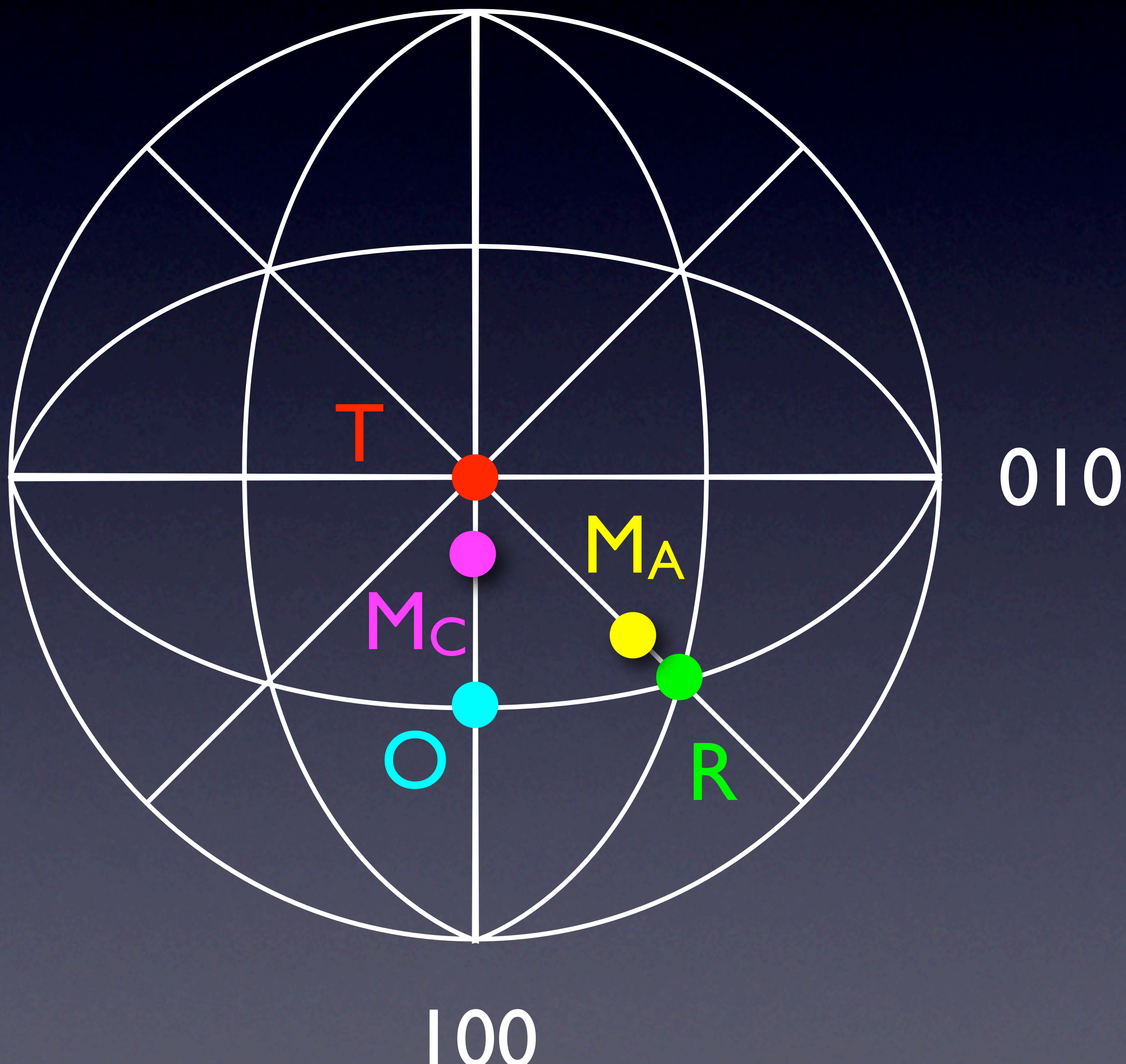
Morphotropic Phase Boundary

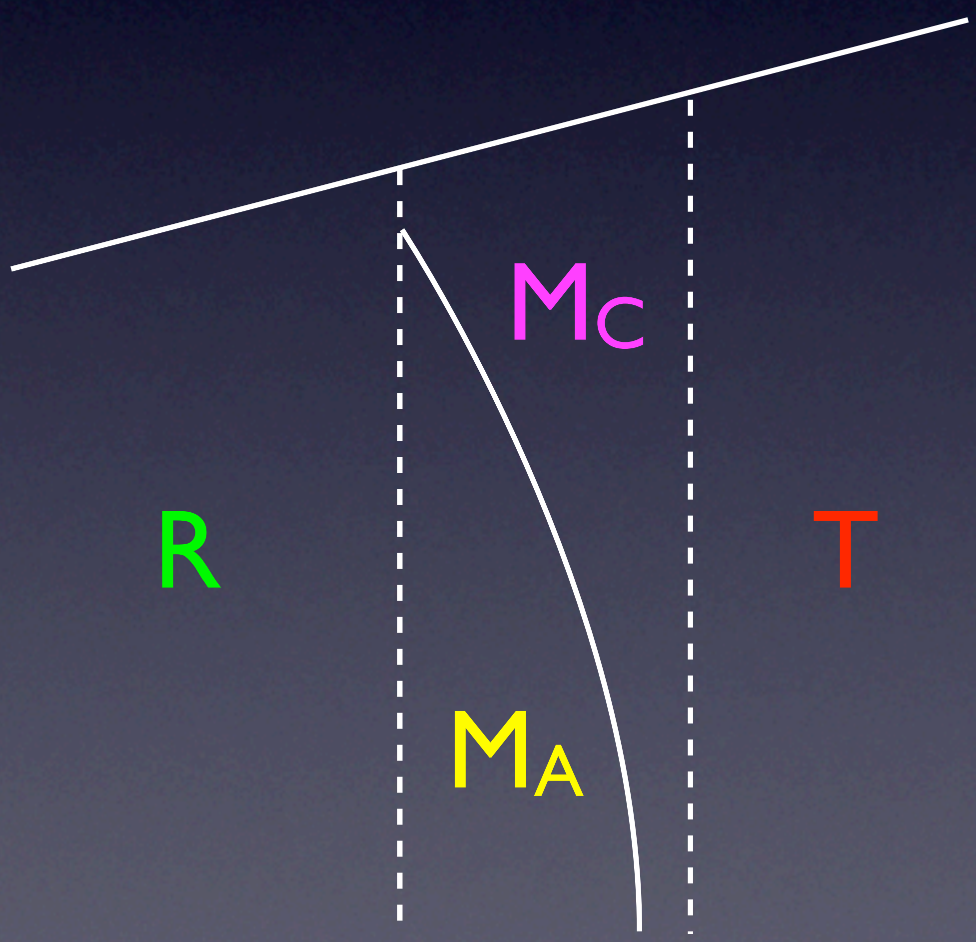


Morphotropic Phase Boundary

PZT: R→M_A→T

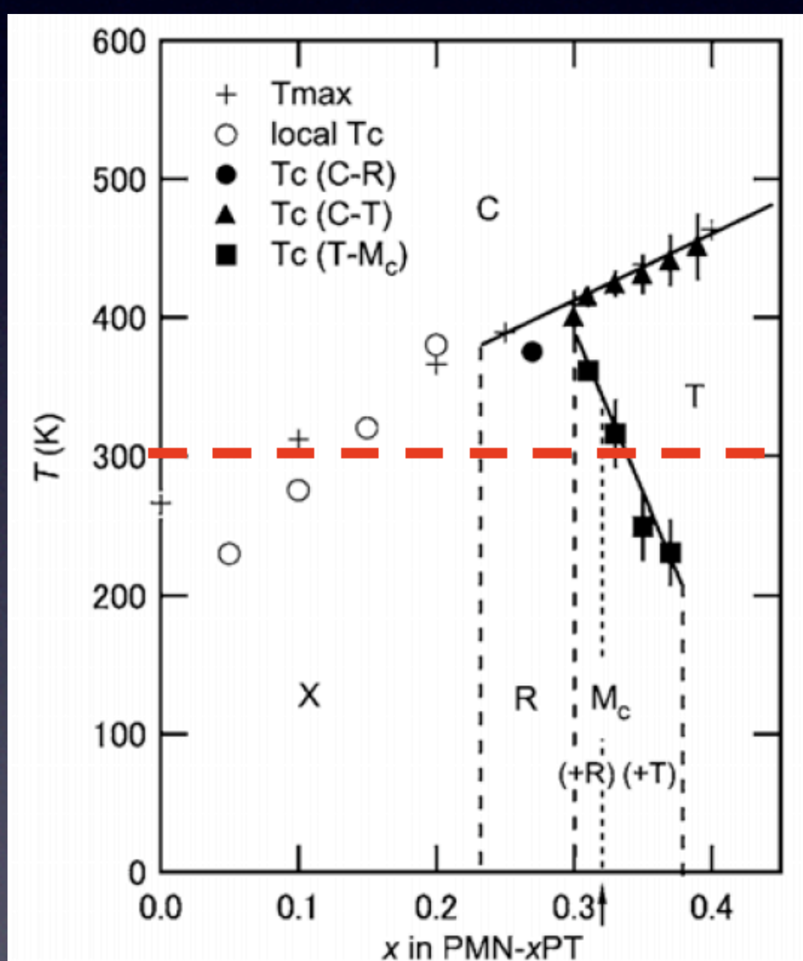
PMN-xPT: R→M_C→T ???

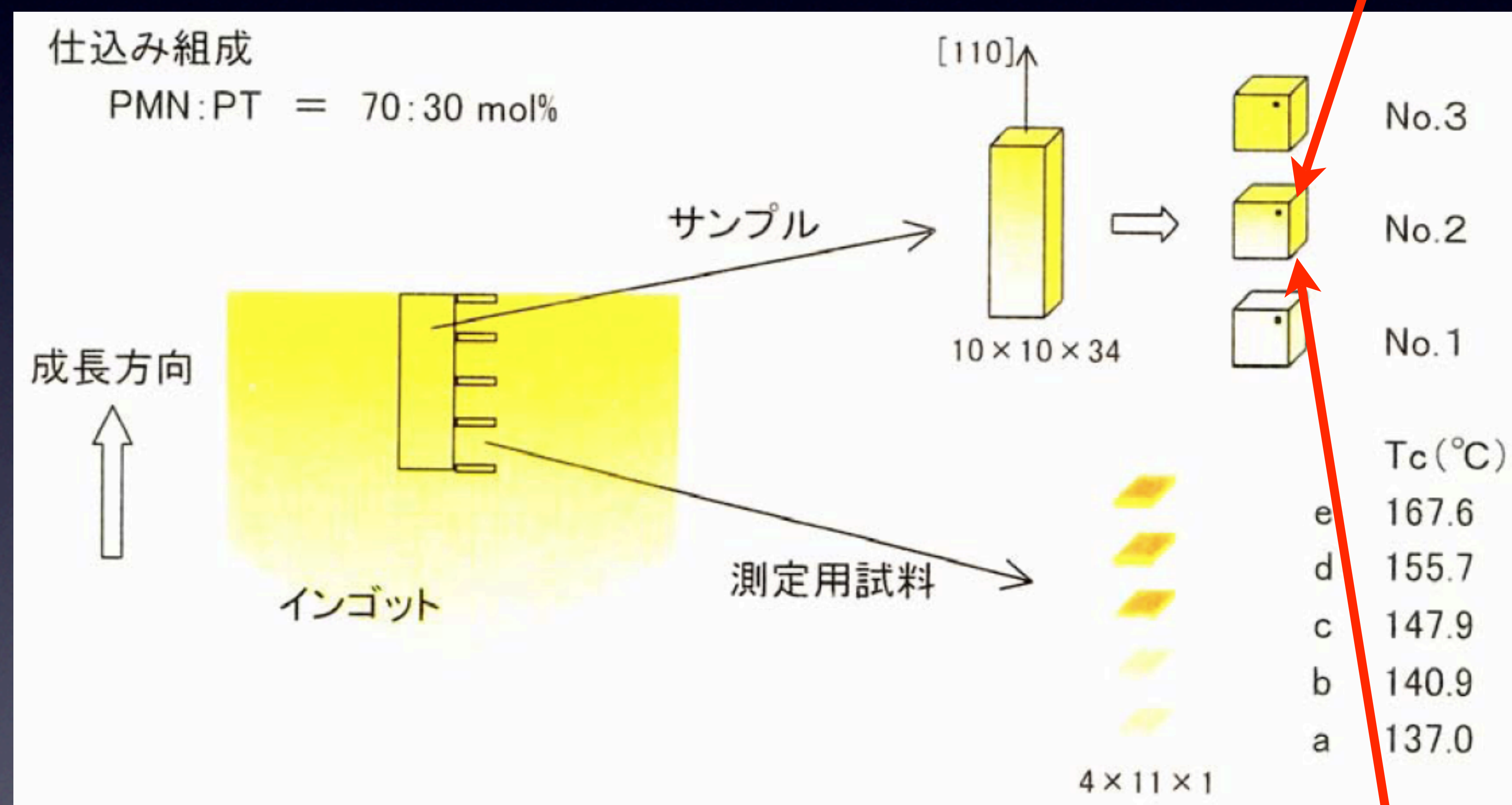




PT Gradient Samples

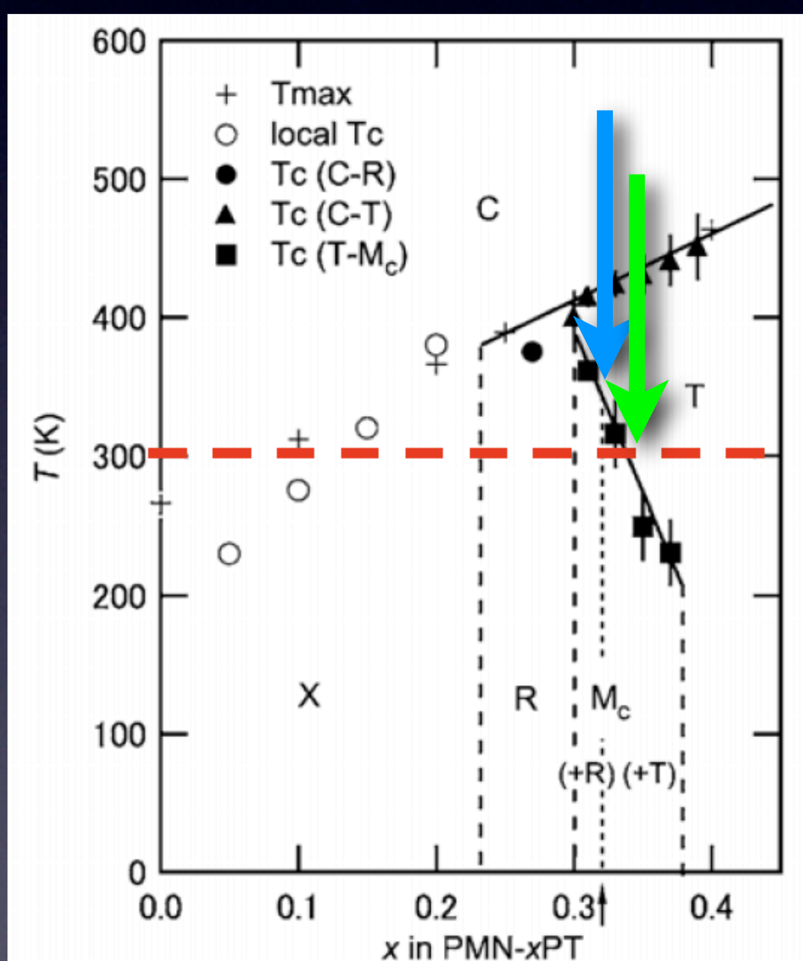
35%

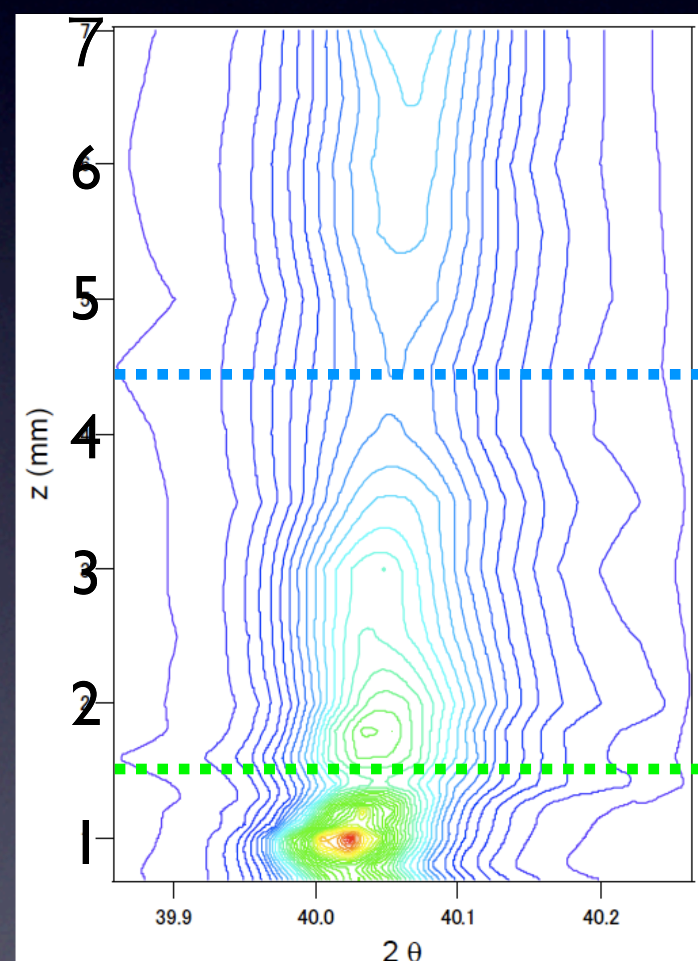


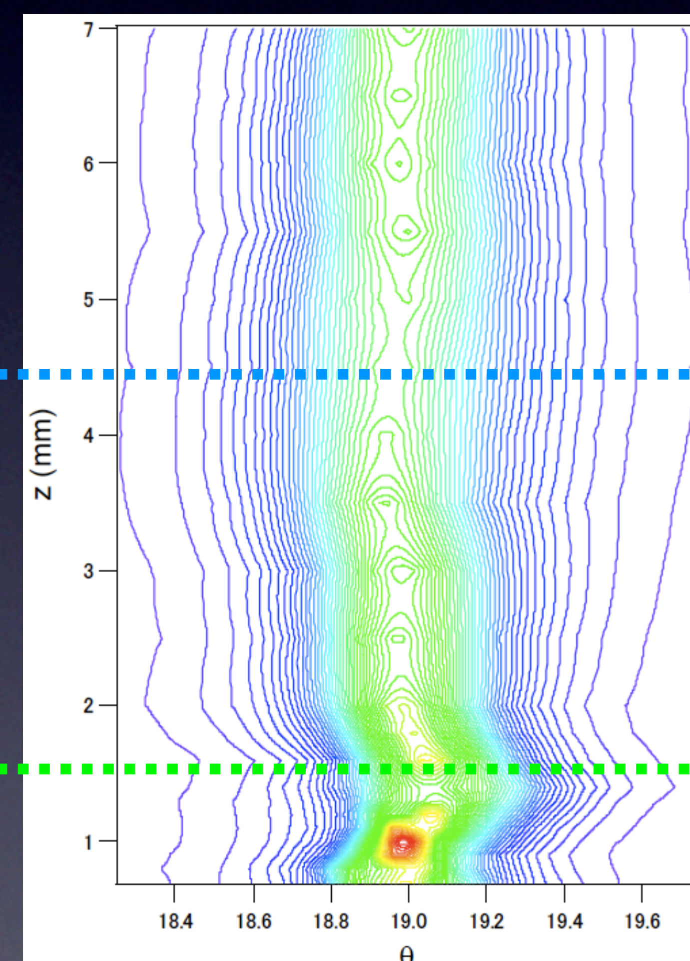


31%

PT Gradient Samples







33.4%

34.6%

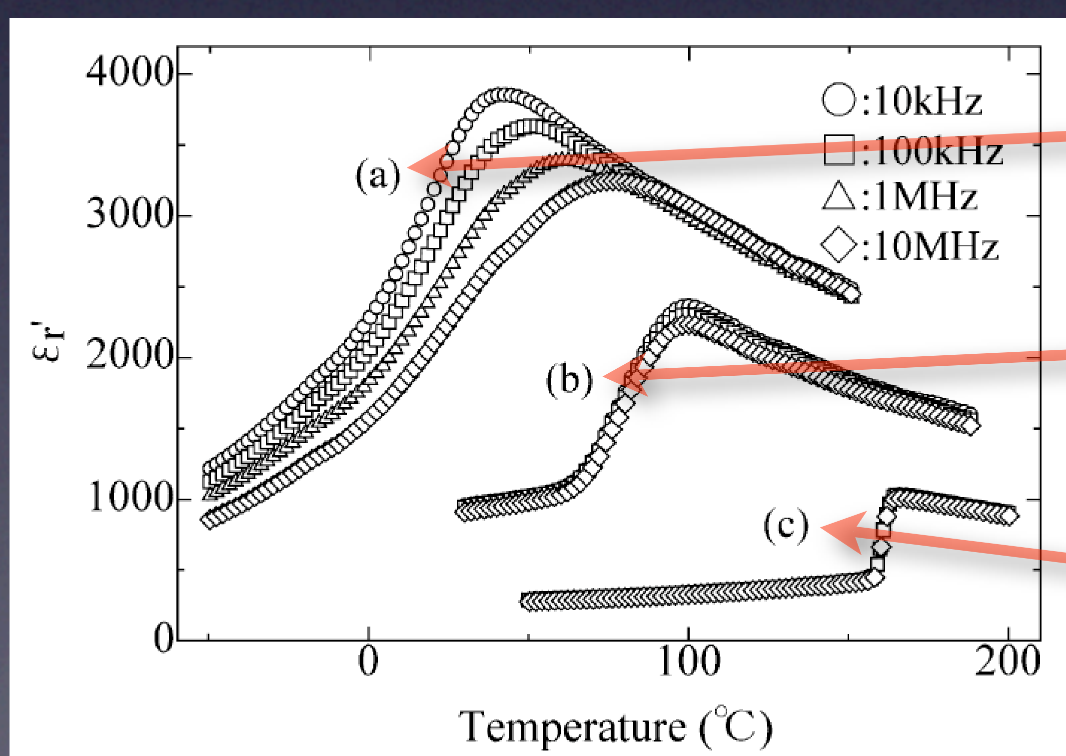
2θ

ω

K. Ohwada *et al.* 2008

Controlling heterogeneity

- $Pb(In^{3+}{}_{1/2}Nb^{5+}{}_{1/2})O_3$
  - Control B site randomness (Ohwa *et al.* 2000)
  - Chemical order $S_2 = (I_{\frac{1}{2}\frac{1}{2}\frac{1}{2}}/I_{111})_{obs.}/(I_{\frac{1}{2}\frac{1}{2}\frac{1}{2}}/I_{111})_{cal.}$



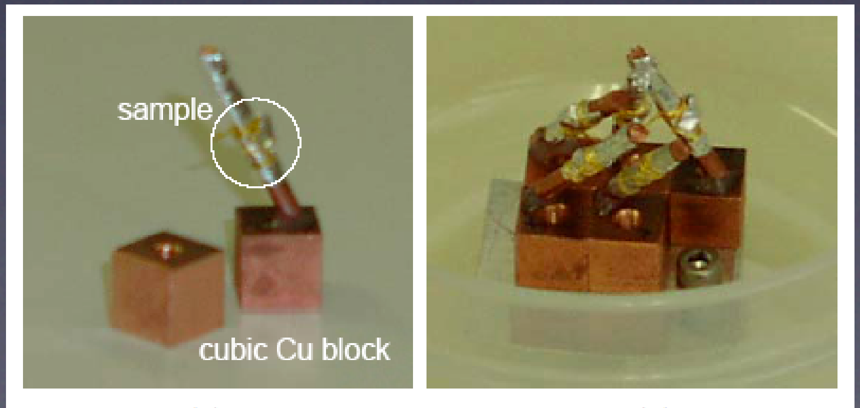
(a) Relaxor (S_2<0.4)

(b) FE (0.4<S_2<0.7)

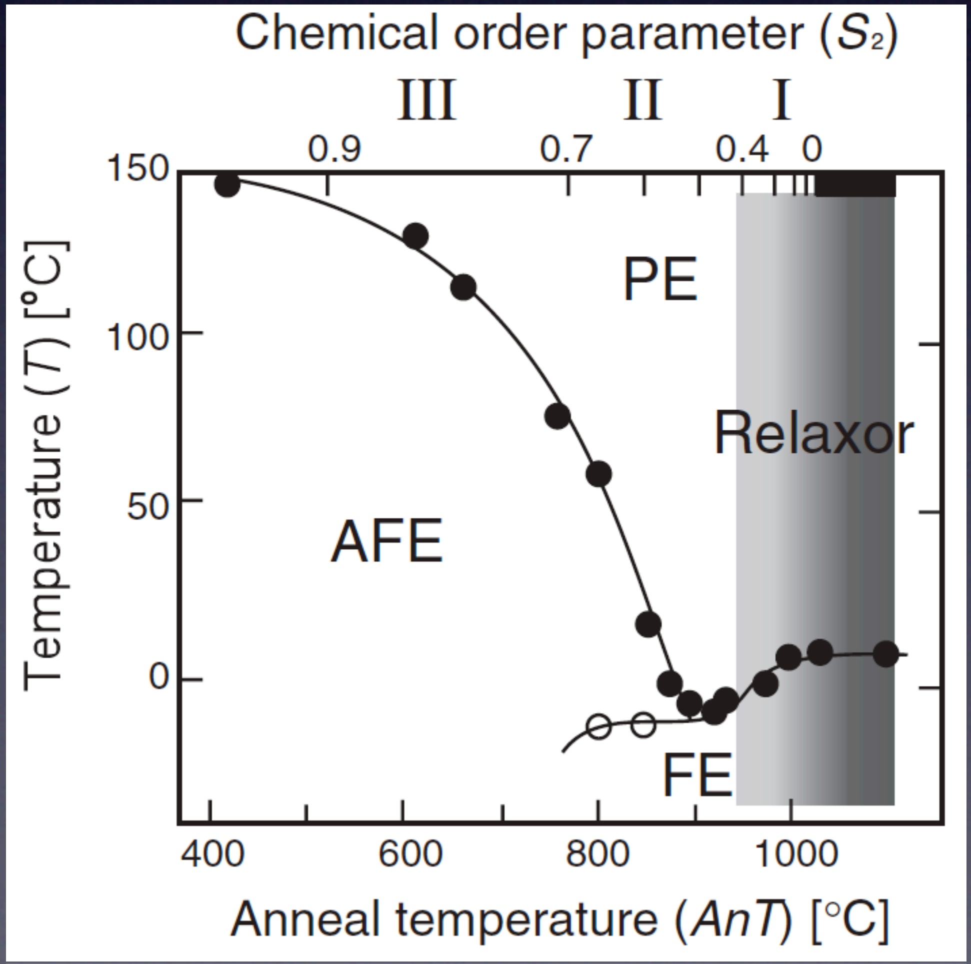
(c) AFE (S_2>0.7)

$Pb(In_{1/2}Nb_{1/2})O_3$

- PROs
  - In/Nb order is controllable by heat treatment
  - AFE → FE → Relaxor
- CONs
  - difficult to grow
  - In absorbs neutrons

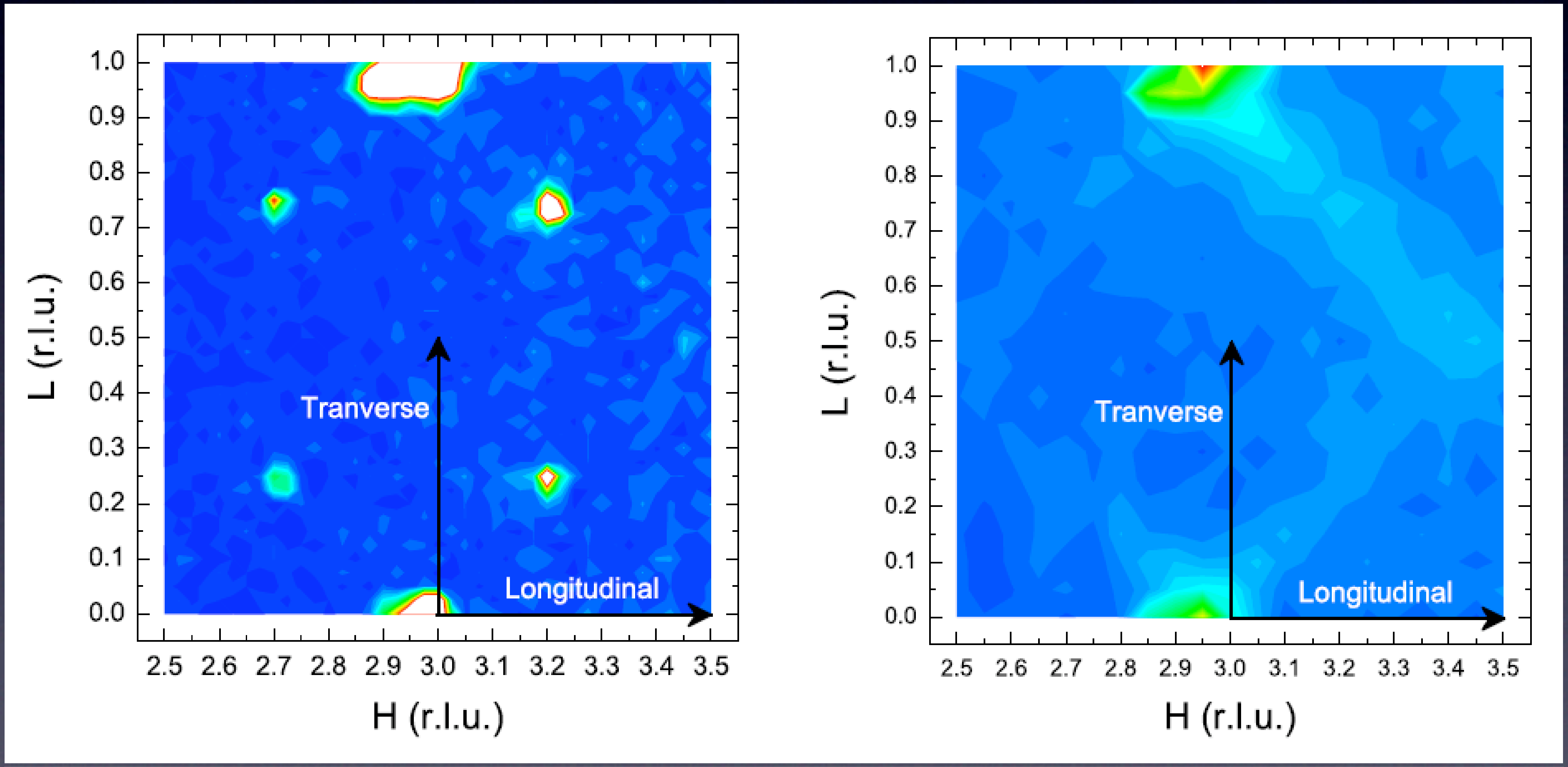


(a) (b)



Chemical orderness

- Diffuse scattering at room temperature



Ordered PIN
h/4 k/4 0 (AFE)

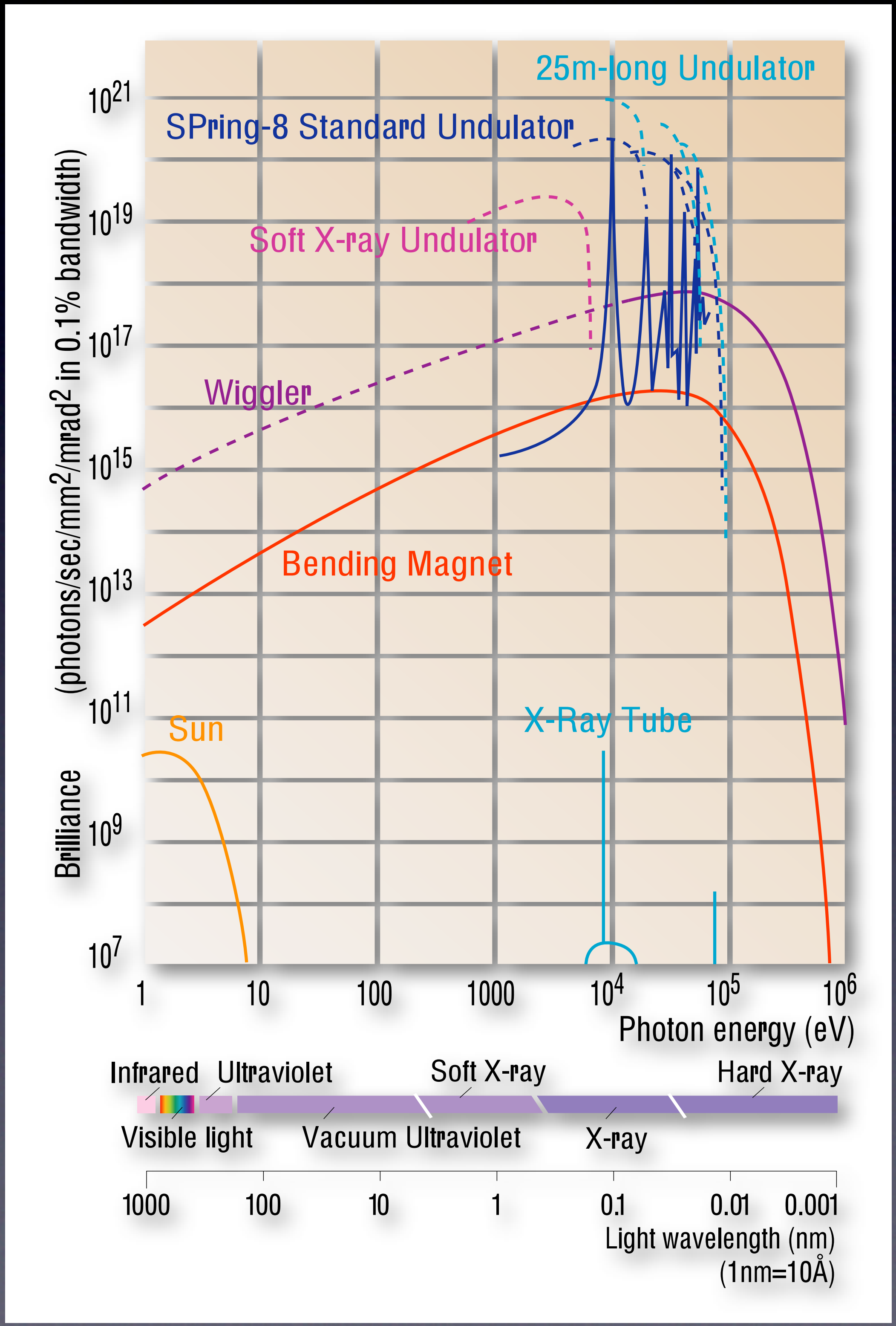
Disordered PIN
diffuse (Relaxor)

3rd Generation Rings

SPring-8	APS	ESRF
RIKEN / JAEA Harima, Japan	DOE Argonne Nat'l Lab.	18 European countries Grenoble
8 GeV / 1436 m 62 lines	7 GeV / 1104 m 68 lines	6 GeV / 844 m 56 lines
1997	1996	1994

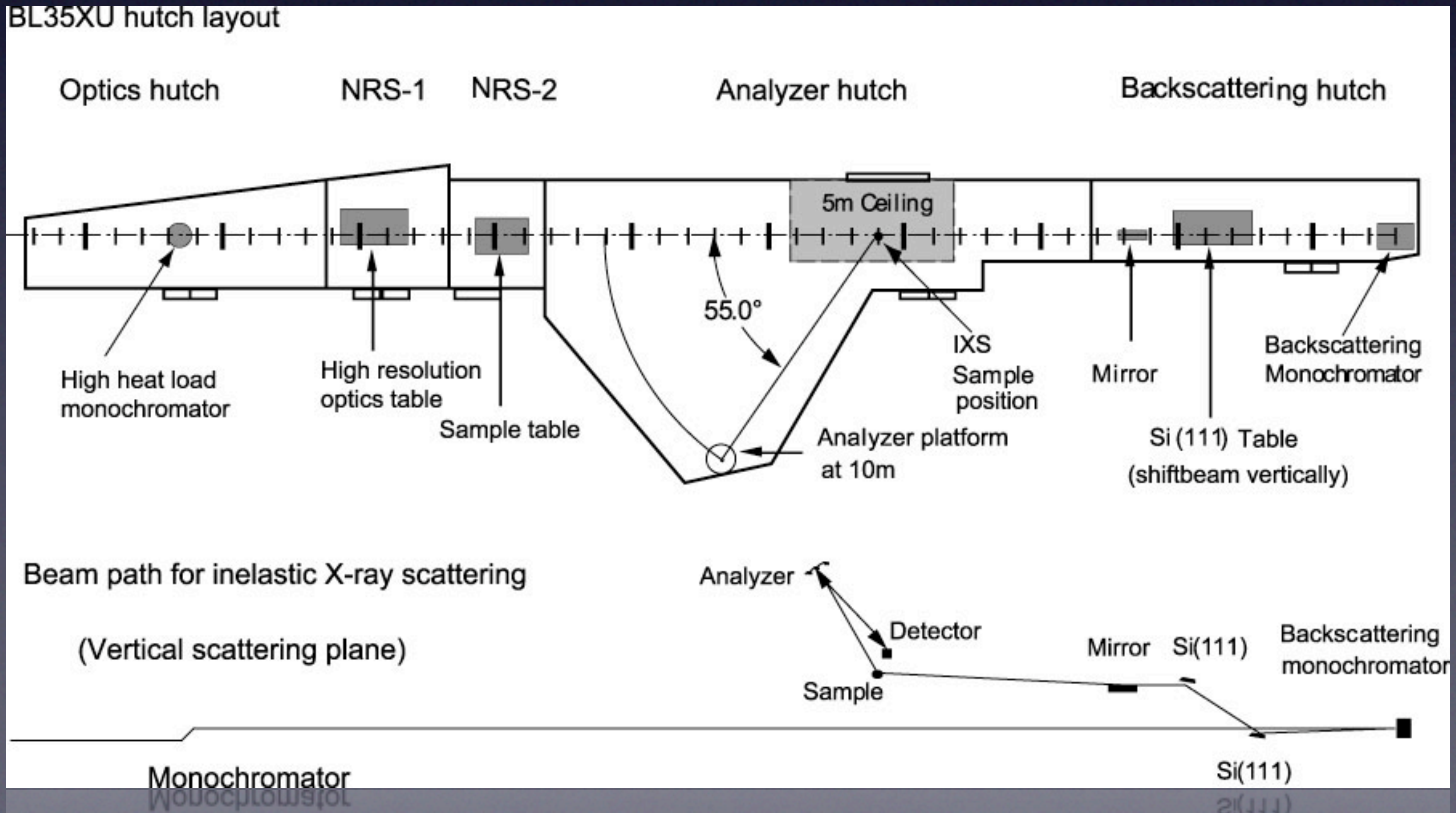
SPring-8

- 8 GeV
  - 100mA top up
  - good at 300 keV – 300 eV
- 38 Undulators
- Insertion 4.5 – 25 m
- 49 working beam lines



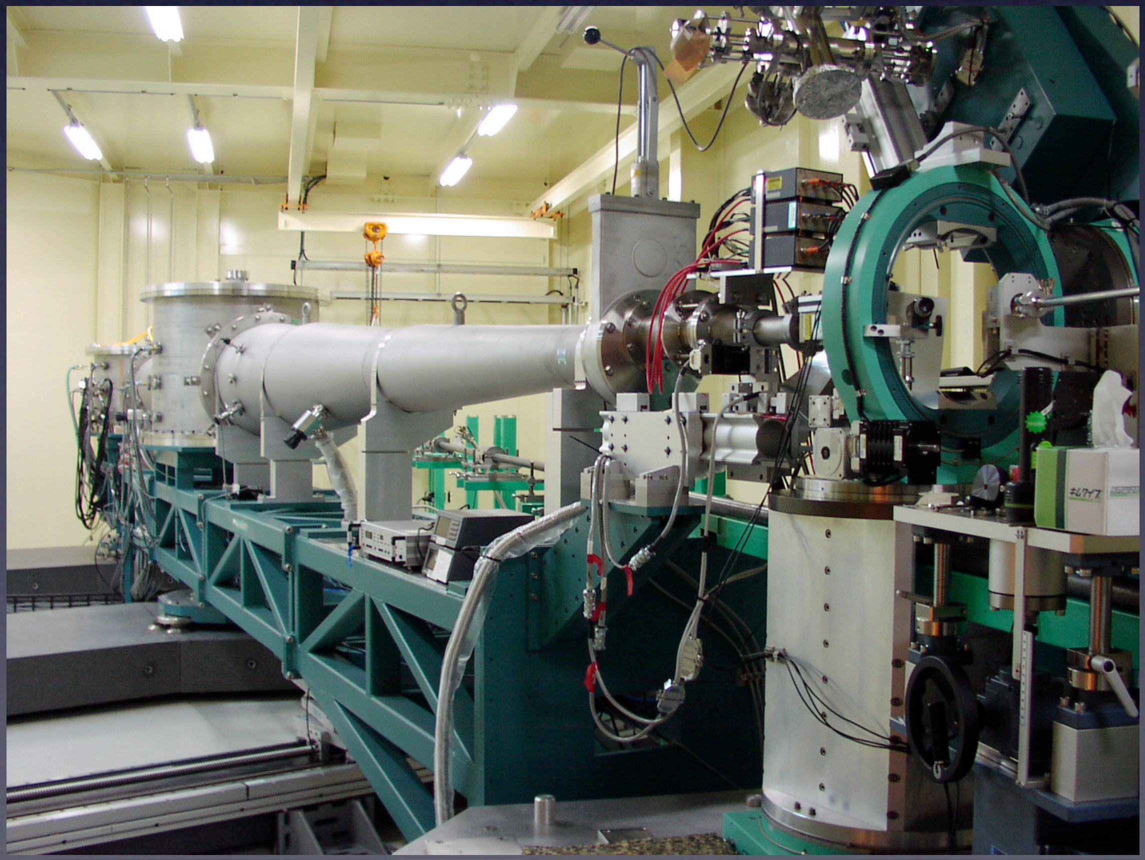
BL35XU @ SPring-8

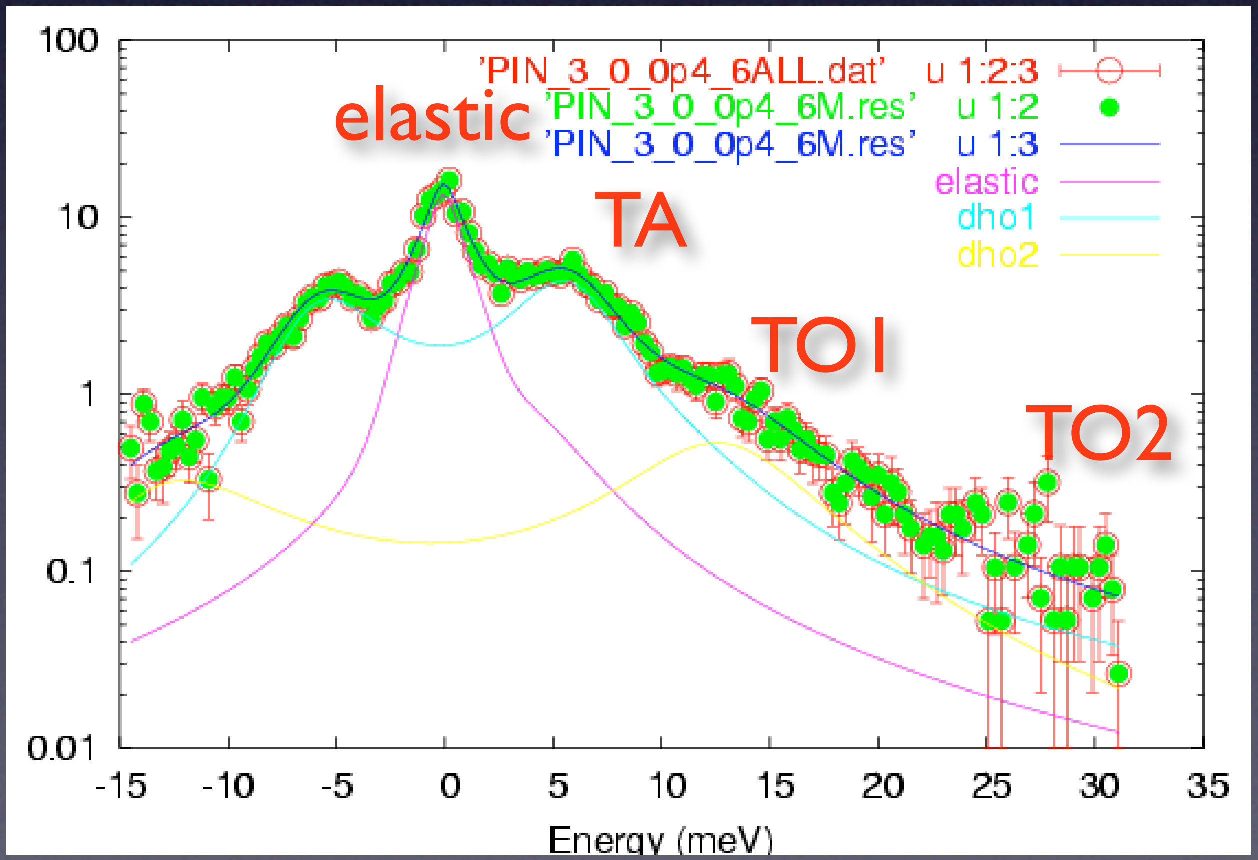
- Si(11 11 11) monochromator (21.7keV)
- Multiple analyzers: 4L×3T
- ΔE~1.5meV, ΔQ~0.05rlu (4.1Å cubic)



IXS results

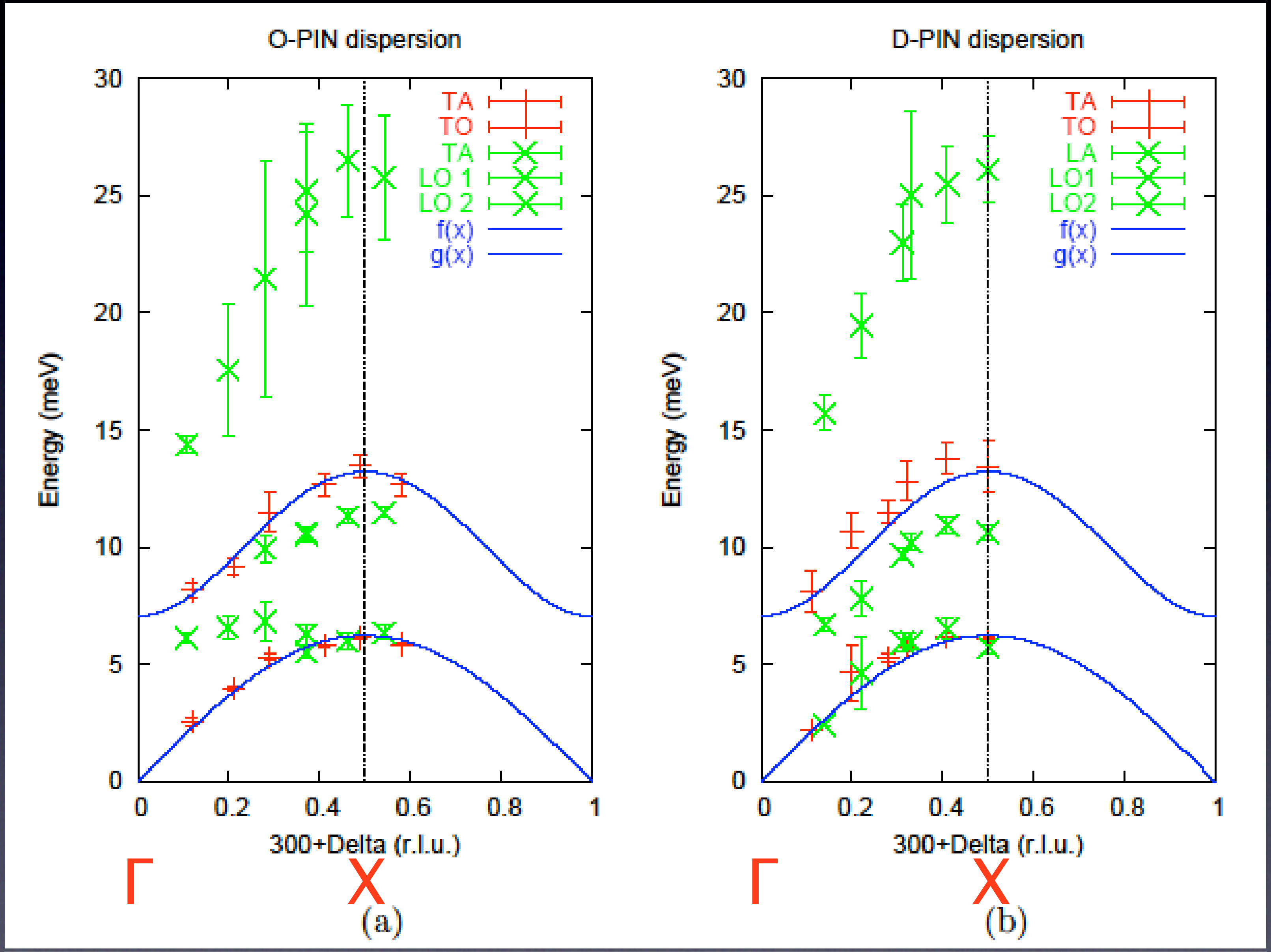
- Constant-Q at room T
  - Mono temp: 10mK→1meV
  - 3 0 q (T), 3+q 0 0 (L)





Dispersion relations

Ordered



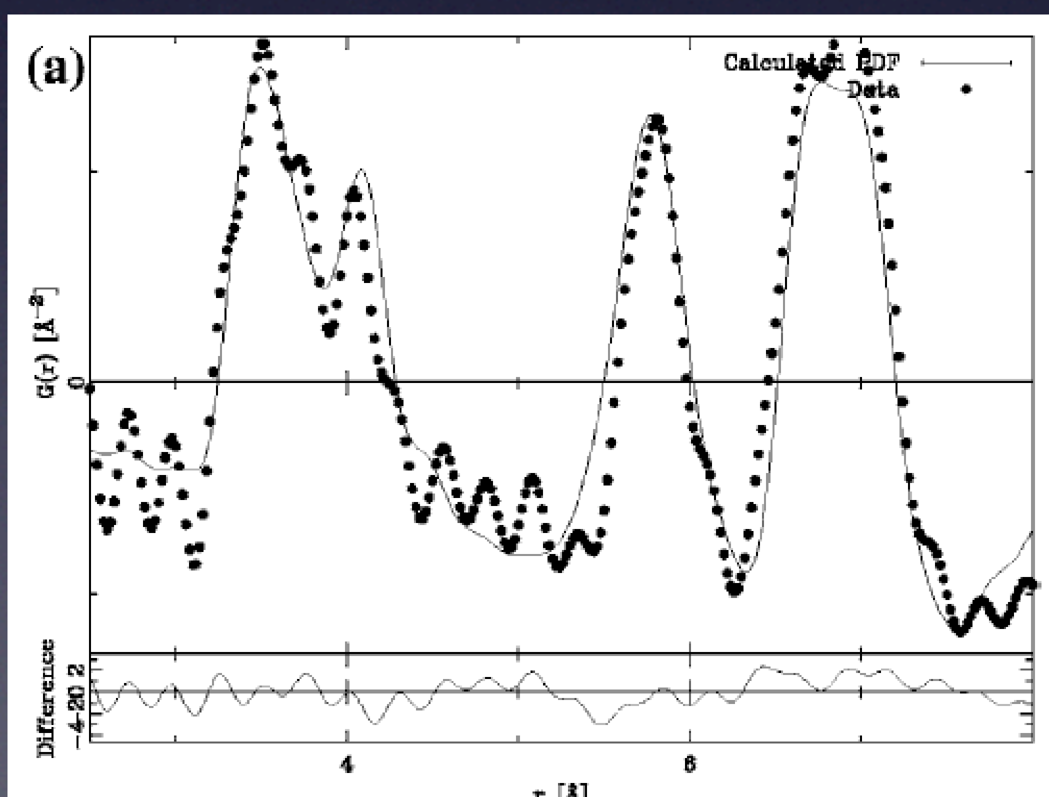
Disorderd

Strong instability toward ferroelectricity

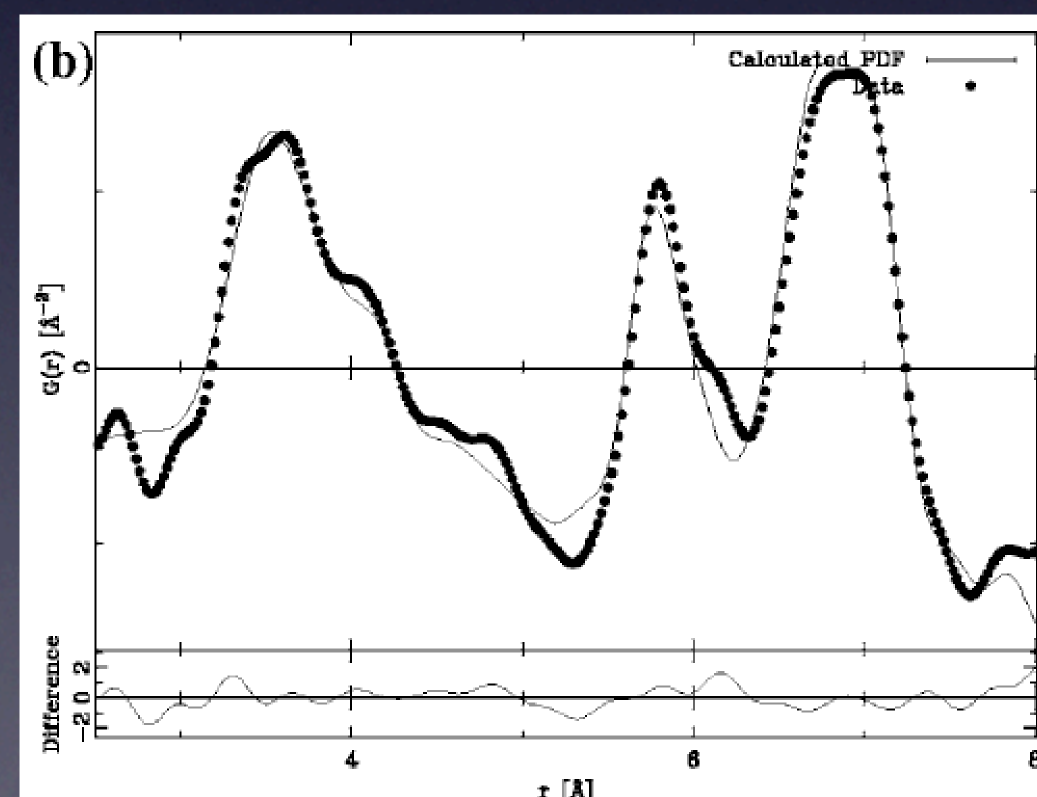
Similar local structures

- X-ray PDF (Yoneda *et al*. 2006)

	Disorderd (avg.)	Disorderd (local)	Ordered (local)
Pb x	0.750	0.720	0.724
Pb y	0.125	0.125	0.122



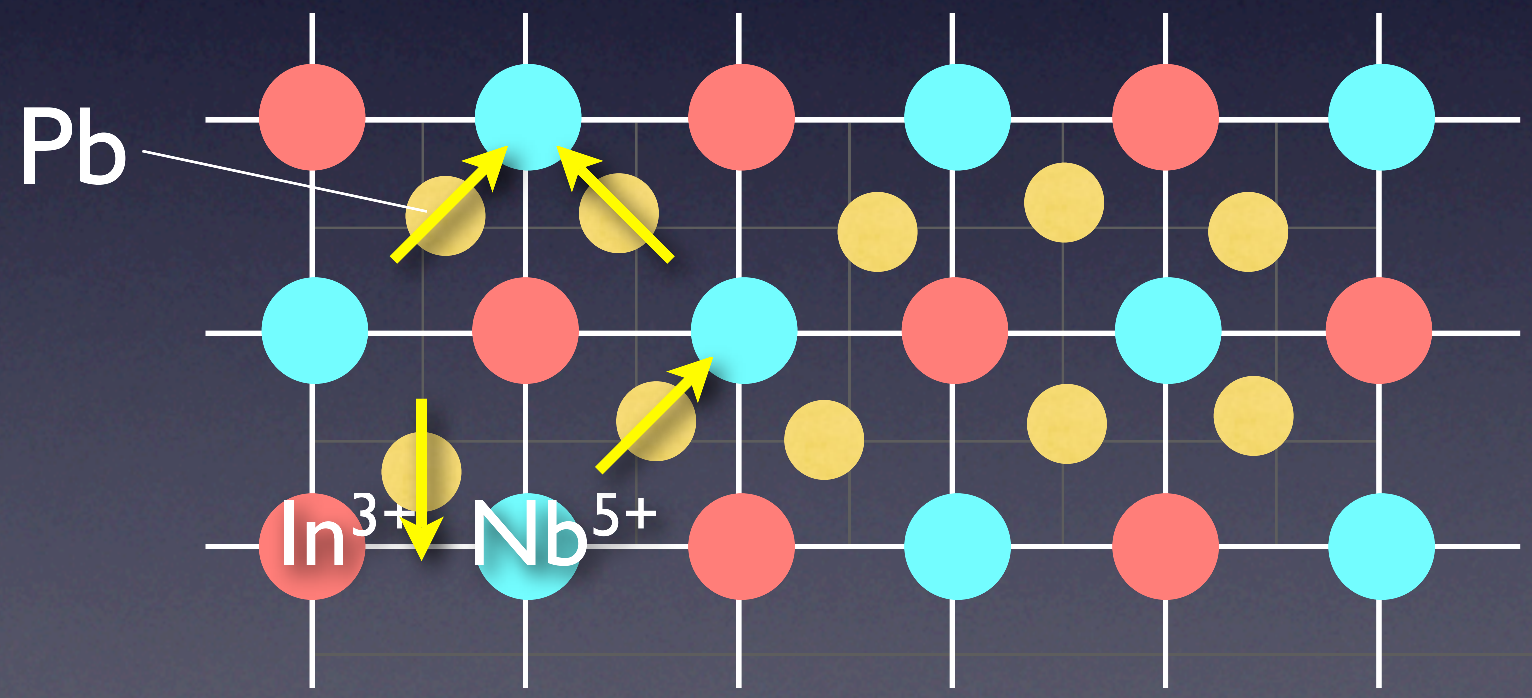
Ordered



Disordered

Modeling PIN

- Pb dipole-dipole interaction ~ J
- Coulomb from B site to Pb ~ H

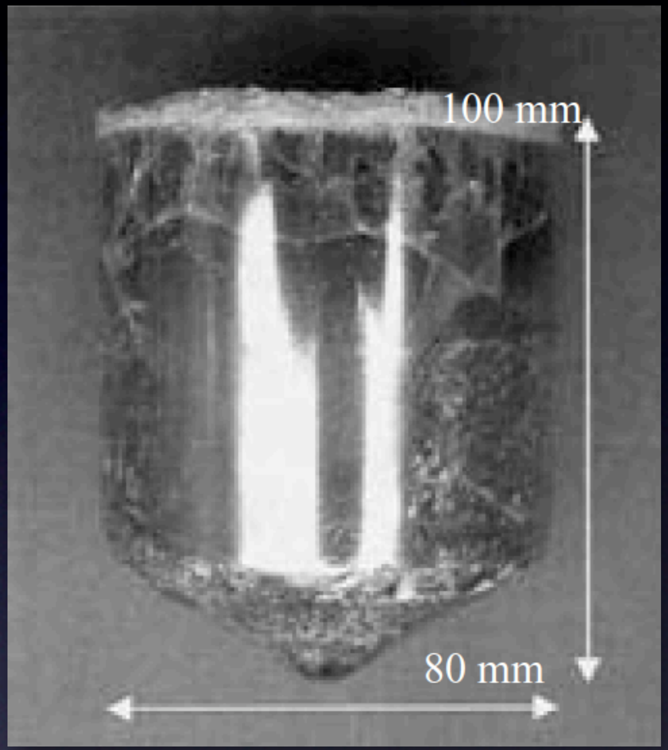


Summary of PIN

- Intrinsic instability toward FE
  - Off-center Pb ~ Driving force of polarization
- Control by B-site orderness/randomness
  - Order ⇒ Stabilize AFE
  - Partial order ⇒ FE appears
  - Disorder ⇒ Relaxor due to suppression of LRO

Quo vadis?

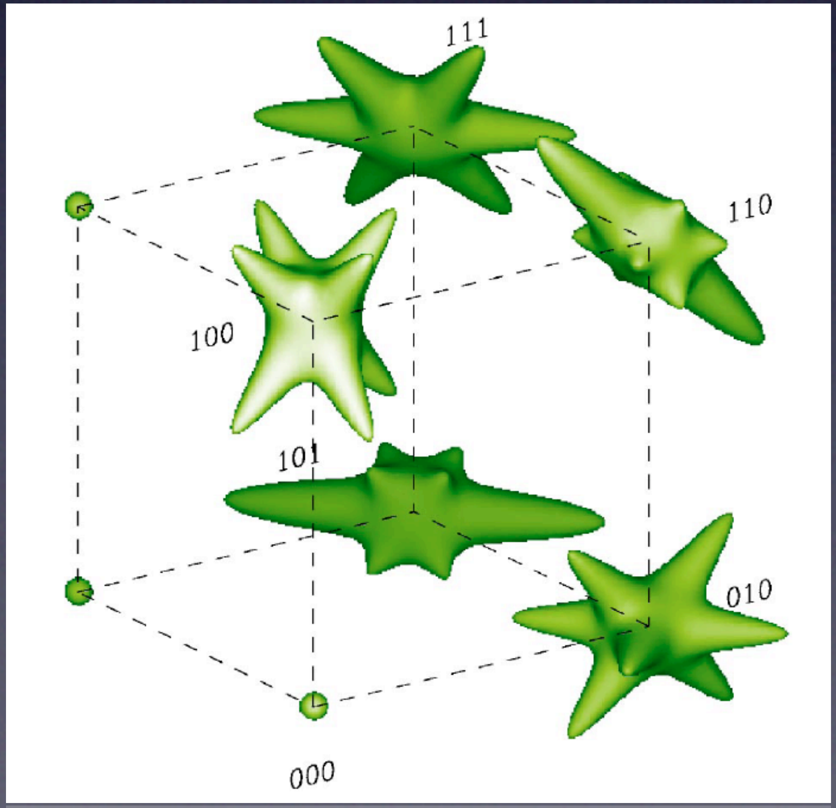
- Intrinsic Heterogeneity
  - PMN-*x*PT: *x*-gradient single crystal
  - Synchrotron x-rays
    - beam size ~ 0.01 mm
    - diffraction, diffuse, inelastic
    - real space information needed
    - PDF, XAFS, DAFS, …
- Apply to high T_c and CMR systems

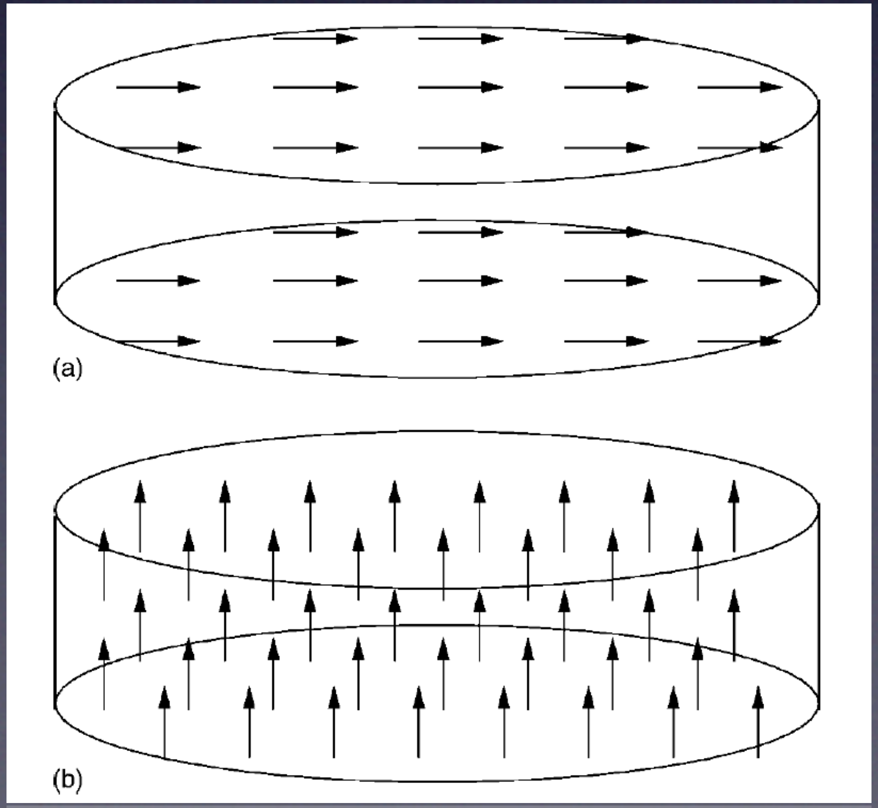


PMN-*x*PT by JFE

PNR shape for PMN

- scattering || [110] → $(1\bar{1}0)$ planar correlation
- appearing only for Q⊥ → [110] polarization
  - $I \propto (Q \cdot e)^2$: e ~ polarization





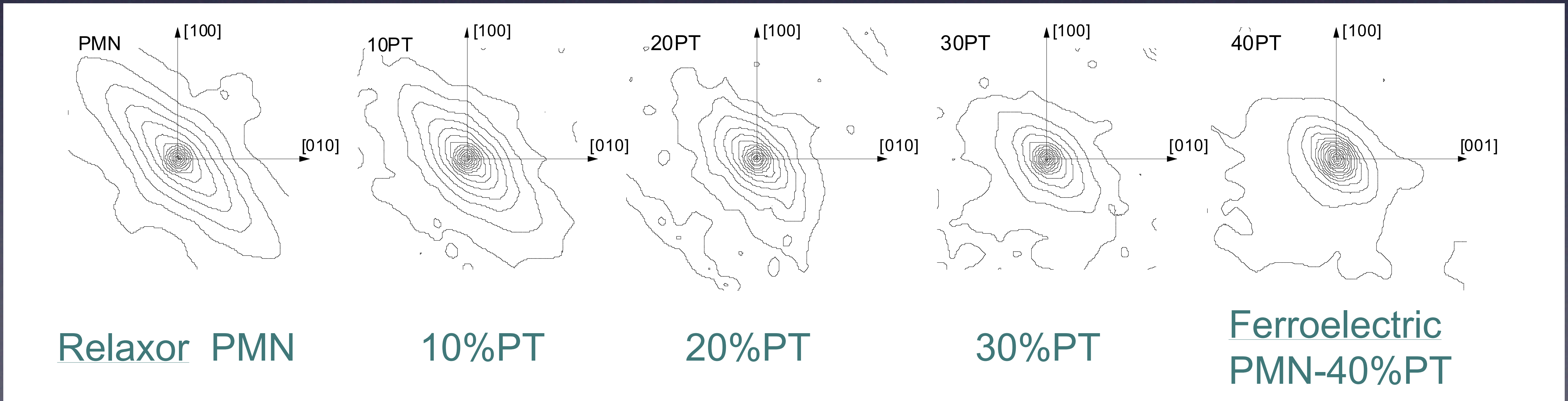
☺

☹

Xu *et al.* 2004

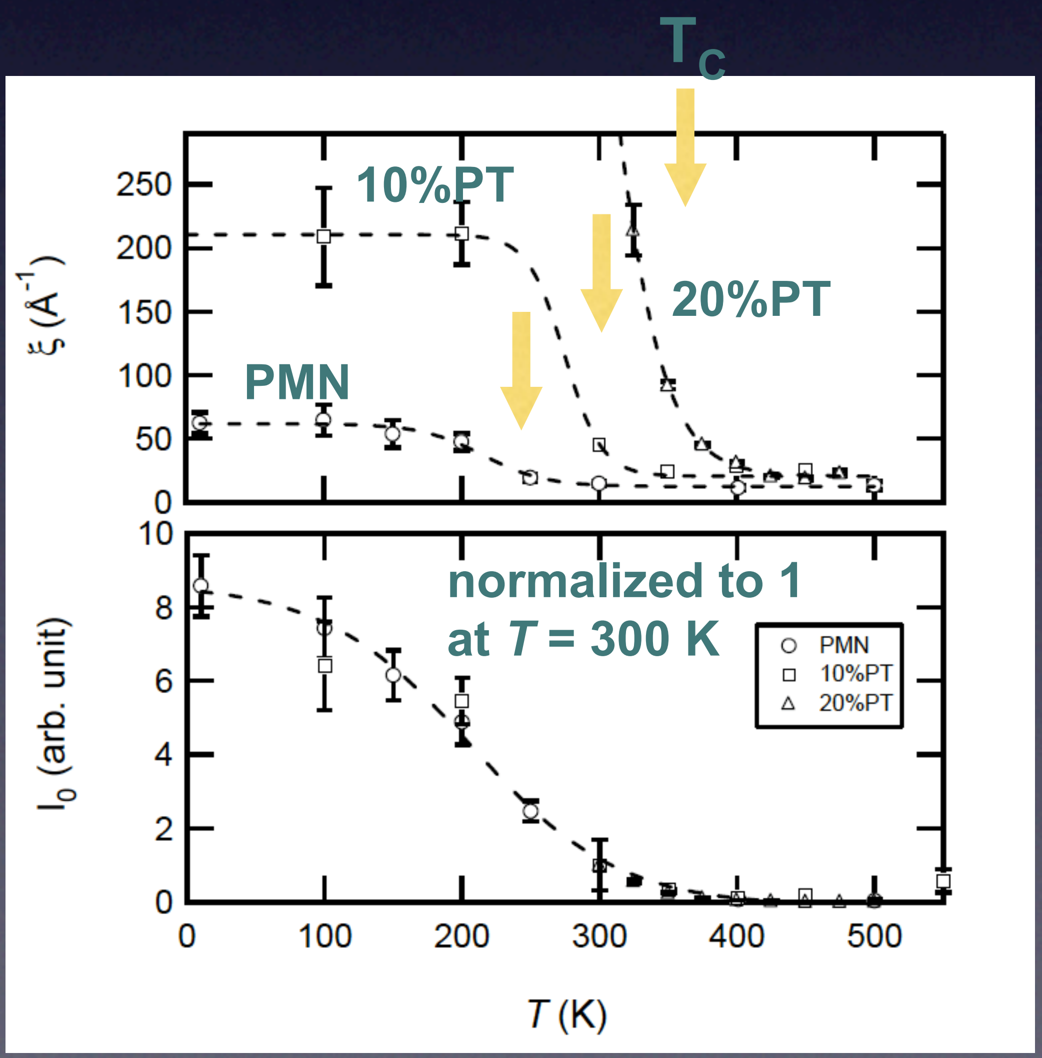
PMN-xPT

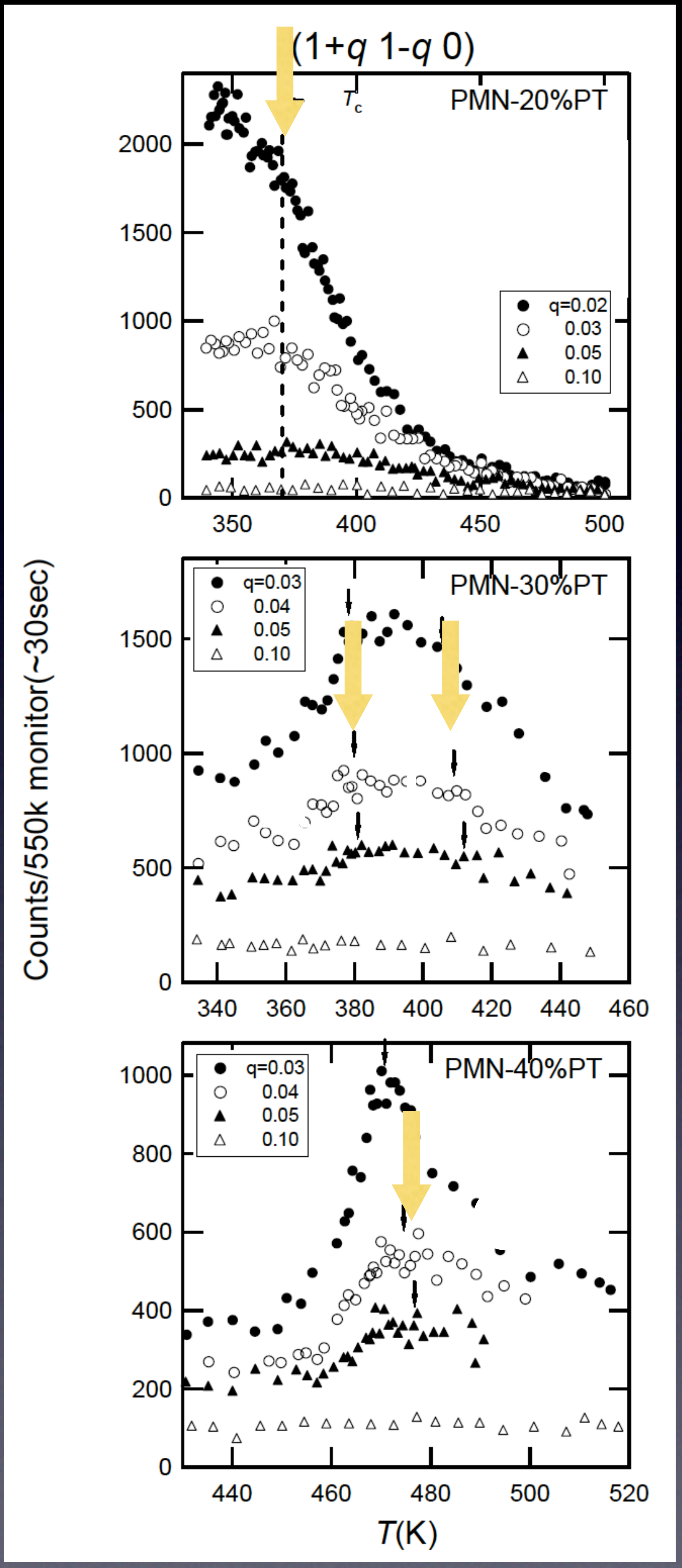
- x dependence of diffuse (Matsuura 2006)
  - ξ: 12.6 Å (x=0) ⇒ 350 Å (x=0.2) at 300K
  - more isotropic with x
  - no diffuse at x > 0.3 (MPB)



PMN-xPT

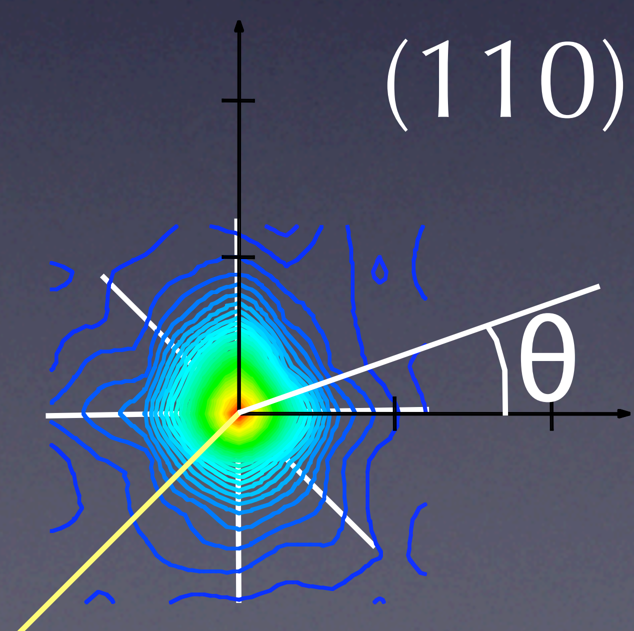
- T dependence and I scaling
- Critical behavior for x>30%

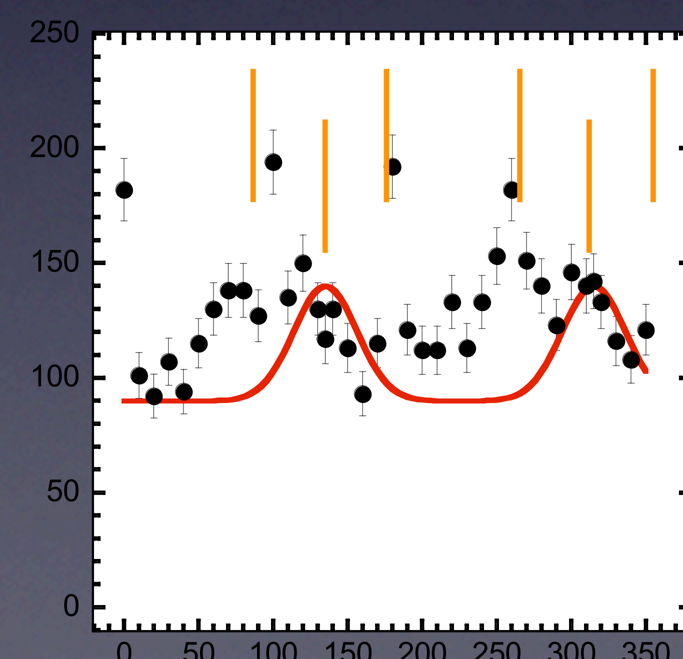


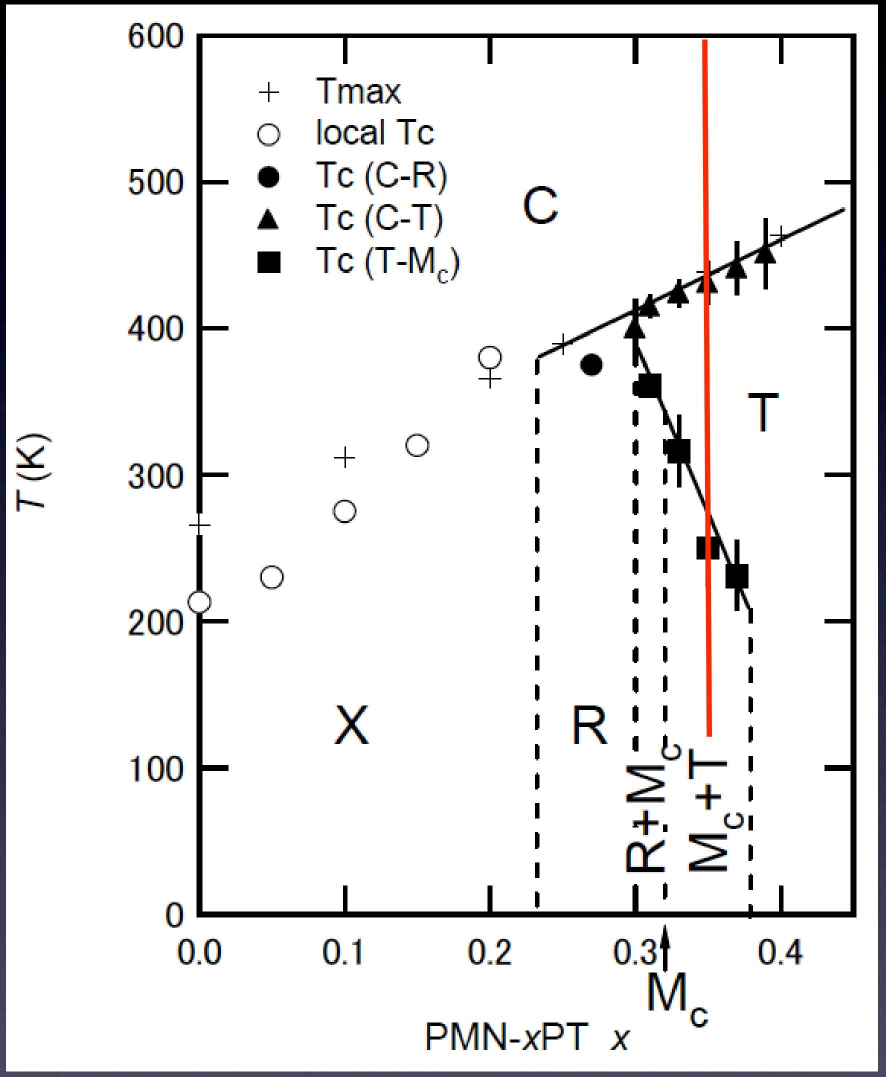


PMN-34%PT

- on MPB
  - successive: C → T → M
  - various diffuse scattering
- analysis using a polar plot







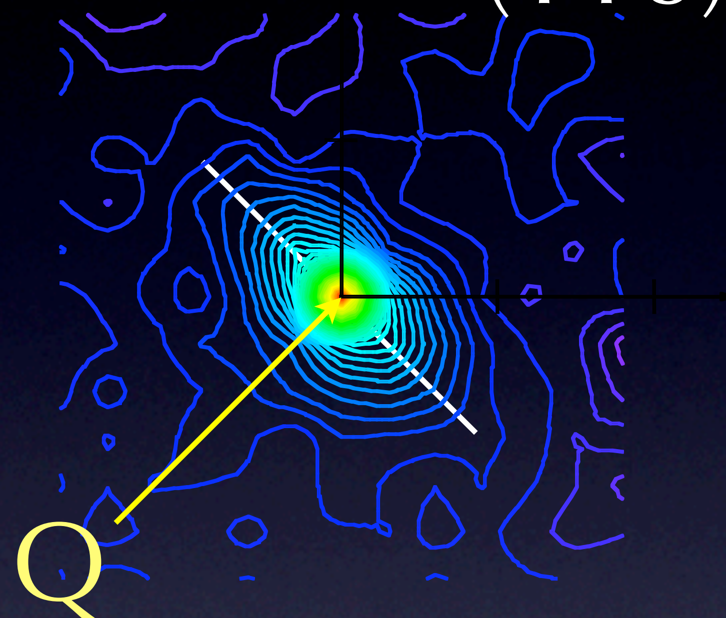
PMN-34%PT

C phase

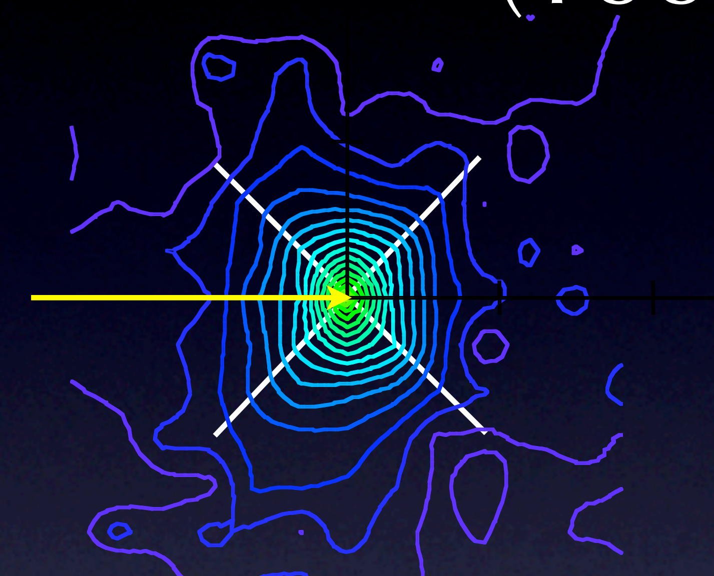
〈110〉 type

with Q⊥

(110)



(100)



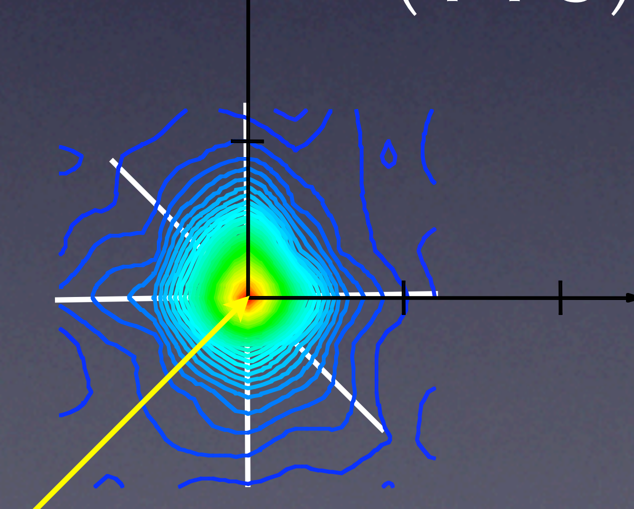
T phase

〈110〉 type

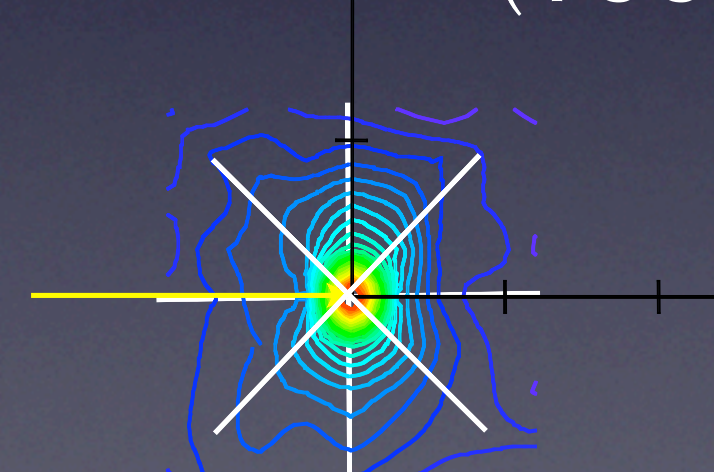
& 〈100〉 type

with Q⊥

(110)

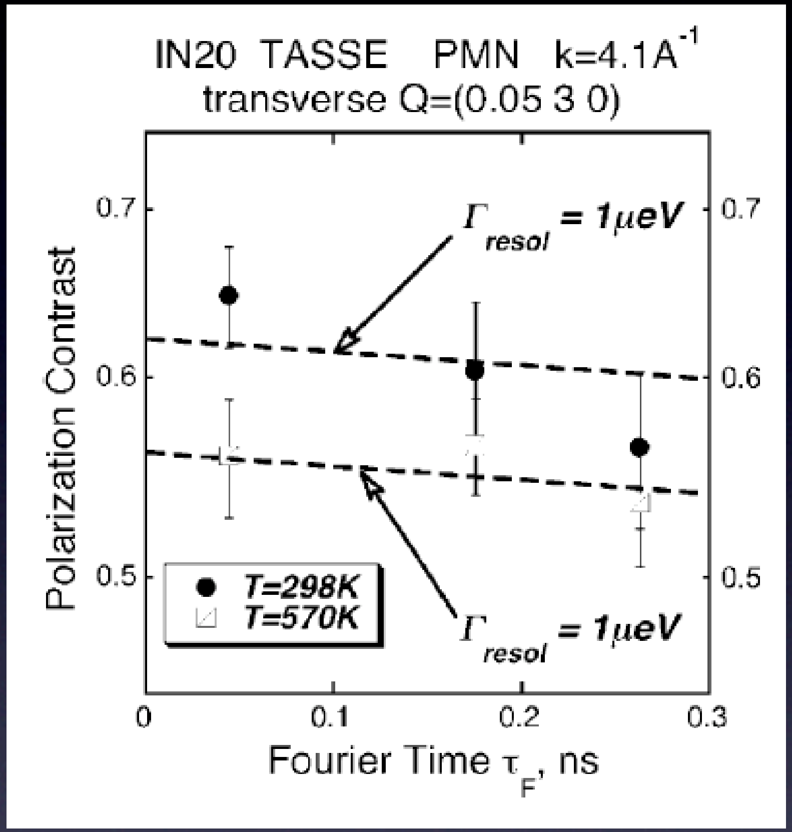


(100)



Diffuse scattering

- Static ?
  - Huang scattering ?
  - 1 μeV ~ 0.24 GHz
- Dynamic?
  - Soft TO mode / Waterfall ?
- Interpreting PMN-xPT
  - 〈110〉diffuse in the C phase
  - How〈100〉diffuse added in the T phase ?



Vakhrushev et al.