UNIVERSITY of VIRGINIA

CMP Seminar
April 3rd, 2008

Effects of Short-Range Order on the Structure and Dynamics of Relaxor Ferroelectrics

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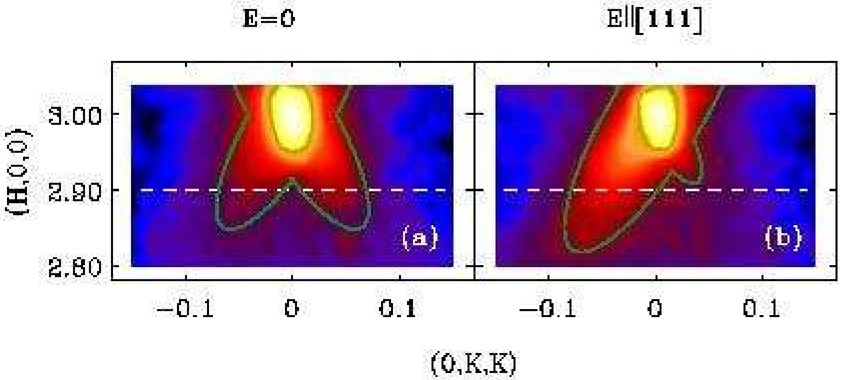
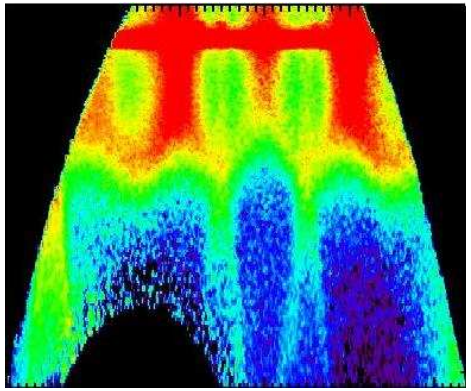
National Institute of Standards and Technology
NIST Center for Neutron Research
Gaithersburg, MD USA





National Institute of Standards and Technology

NIST Center for Neutron Research

Collaborations

National Labs

Brookhaven National Laboratory

NRC, Chalk River Laboratories

Rutherford Appleton Labs, ISIS

Japanese Atomic Energy Agency

NIST (Ceramics Division)

Shanghai Institute of Ceramics

Ioffe Physico Technical Institute

Universities

Virginia Polytechnical University

Johns Hopkins University

Penn State University

University of Illinois

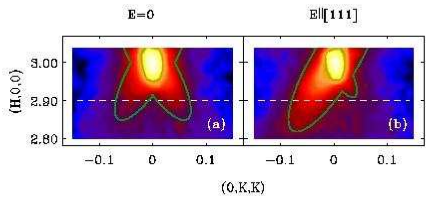
Simon Fraser University

University of Toronto

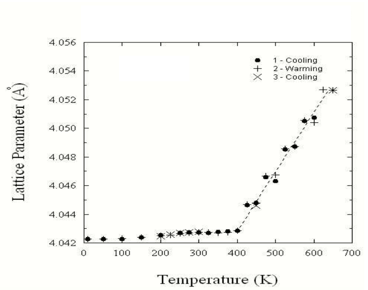
University of Tokyo

Outline:

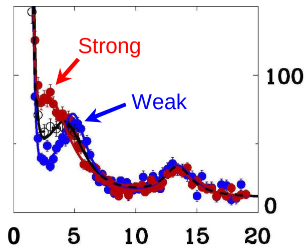
1. Introduction
   - Relaxors
   - Neutron scattering basics



2. Diffuse Scattering
   - Temperature and field dependence
   - Two temperature scales (T_d and T_c)



3. Structure
   - Anomalous thermal expansion
   - Skin effect

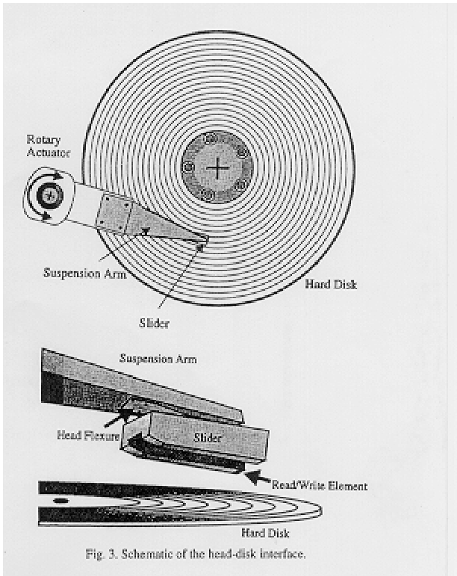


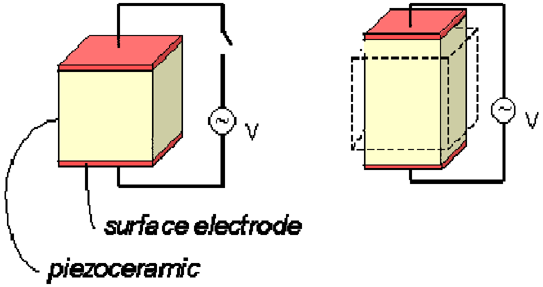
4. Lattice Dynamics
   - Soft modes
   - Phonon coupling

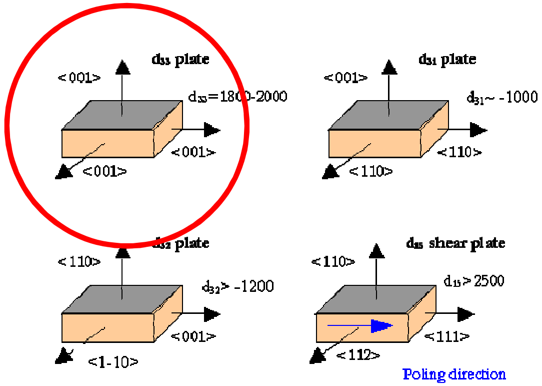
Why Study Relaxors?

Relaxors exhibit exceptional piezoelectric properties.

Numerous device applications: Medical ultrasound, sonar, loudspeakers, automobile air bags, positioning devices, quartz clocks, computer hard drives …







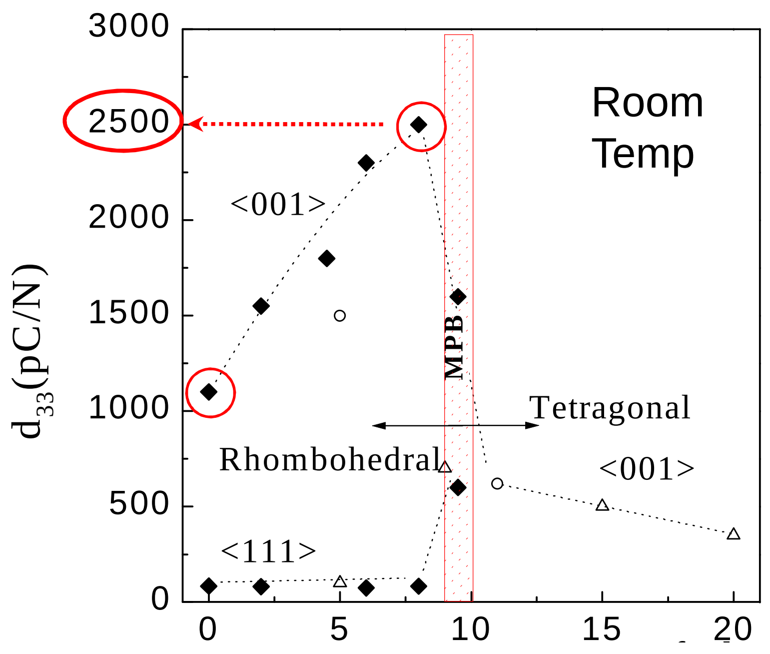
For devices – important quantity is the piezoelectric coefficient d_{33}.

Typical piezoelectrics like SiO_2 (quartz), $LiNbO_3$, $LiTaO_3$: d_{33} < 50 pC/N.

Why Study Relaxors?

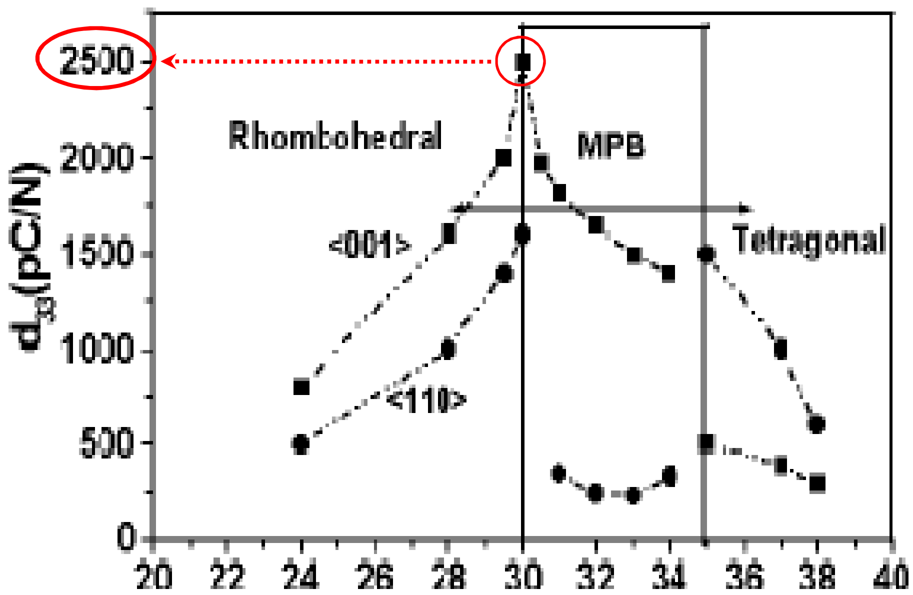
Lead oxide relaxors exhibit record piezoelectric coefficients d_{33}.

S.-E. Park and T. R. Shrout
J. Appl. Phys. **82**, 1804 (1997)



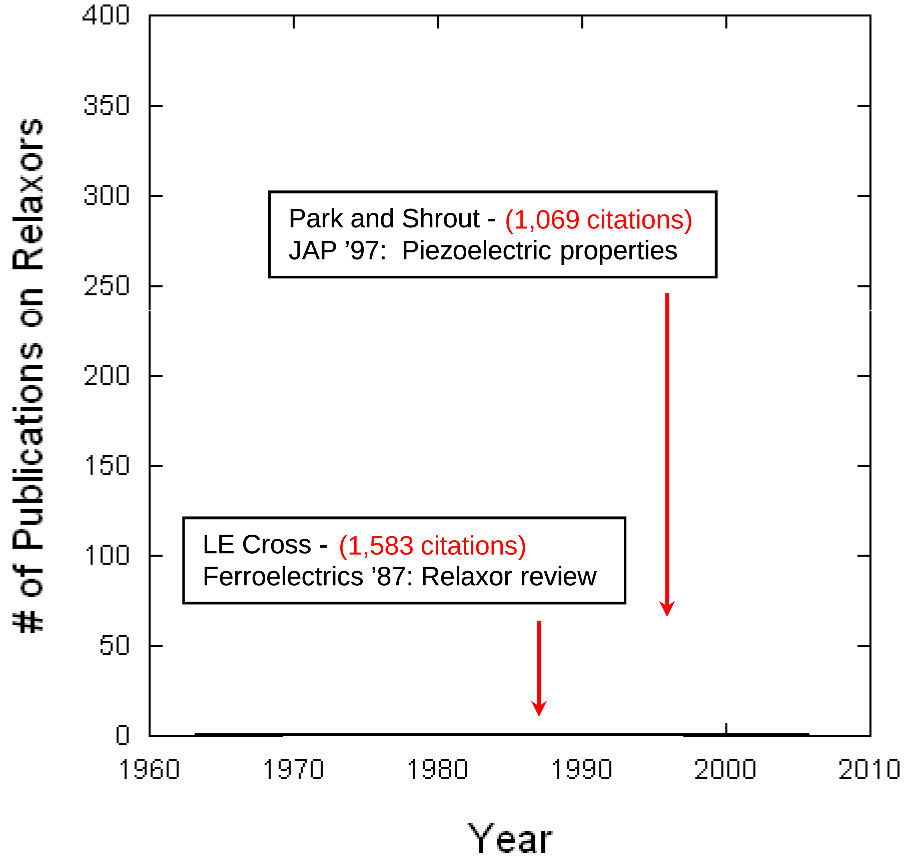
$PbZn_{1/3}Nb_{2/3}O_3$ → %Ti content

Y. Guo et al.,
J. Phys.: Condens. Matter **15**, L77 (2003)



$PbMg_{1/3}Nb_{2/3}O_3$ → %Ti content

Growth of Relaxor Pubs



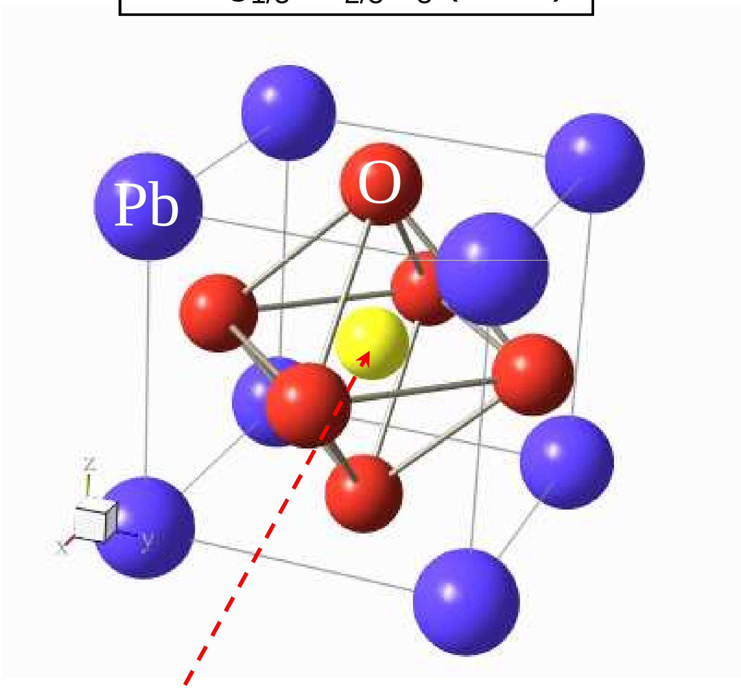
Data from Web of Science

Basic Properties of Relaxors

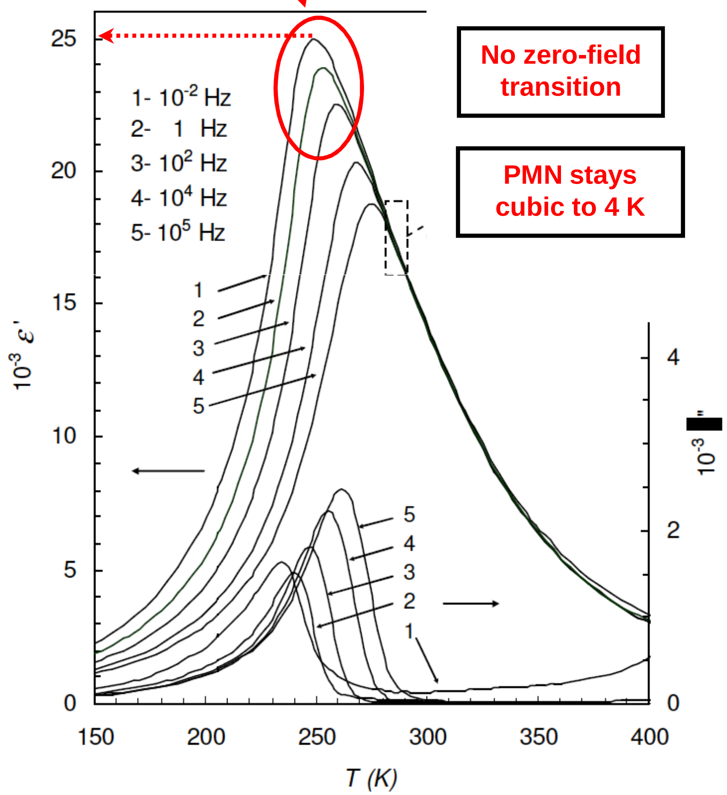
Huge dielectric constant (ε for $PbTiO_3$ ~1000)

Large frequency dispersion – hence "relaxor"

$PbMg_{1/3}Nb_{2/3}O_3$ (PMN)



Mg^{2+} / Nb^{5+}



Z.-G. Ye and A. A. Bokov (Unpublished)

Ferroelectric Phase Transitions

1st order

2nd order

Diffuse

$PbTiO_3$

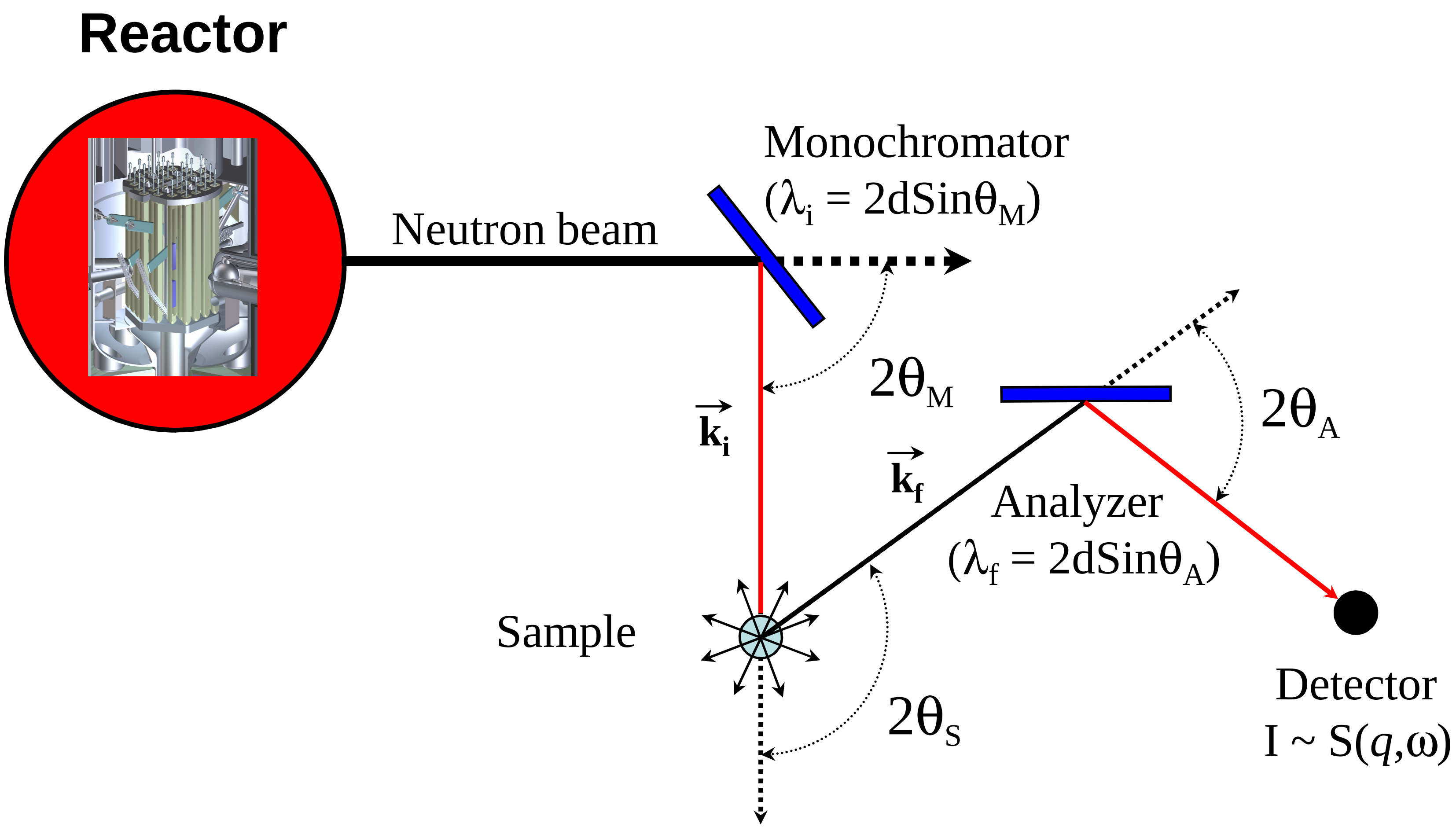
$CdTiO_3$

$PbMg_{1/3}Nb_{2/3}O_3$

From D. Damjanovic, Rep. Prog. Phys. 61, 1267 (1998).

Triple-Axis Spectrometer

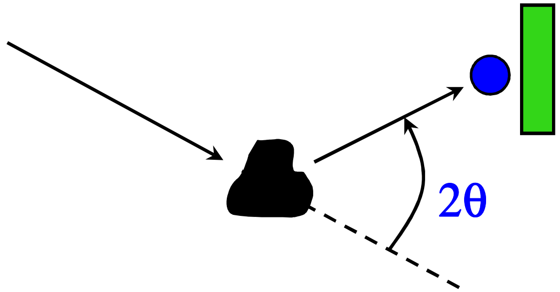
Type of instrument used most commonly during our studies.



Basics of Neutron Scattering

(1) Neutron scattering experiments measure the flux of neutrons scattered by a sample into a detector as a function of the change in neutron wave vector ($\vec{Q}$) and energy ($\hbar\omega$).

$$\Phi(Q,\hbar\omega) = \frac{\text{neutrons}}{\text{sec–cm}^2}$$



<u>Momentum</u>	<u>Energy</u>
$\hbar k = \hbar(2\pi/\lambda)$	$\hbar\omega_n = \hbar^2 k_n{}^2/2m$
$\hbar Q = \hbar\vec{k}_i - \hbar\vec{k}_f$	$\hbar\omega = \hbar\omega_i - \hbar\omega_f$

(2) The expressions for the scattered neutron flux Φ involve the positions and motions of atomic nuclei or unpaired electron spins.

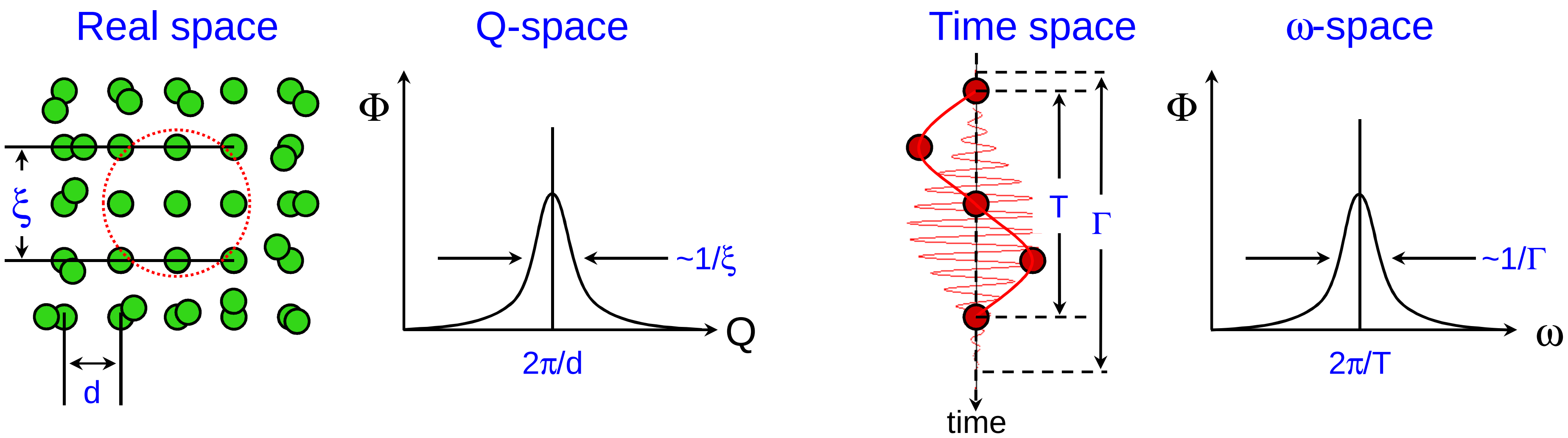
$$\Phi = \mathbb{F}\{\vec{r}_i(t), \vec{r}_j(t), \vec{S}_i(t), \vec{S}_j(t)\}$$

Φ provides information about <u>all</u> of these quantities!

Basics of Neutron Scattering

(3) The scattered neutron flux $\Phi(\vec{Q},\hbar\omega)$ is proportional to the space ($\vec{r}$) and time (t) Fourier transform of the <u>probability</u> $G(\vec{r},t)$ of finding one or two atoms separated by a particular distance at a particular time.

$$\Phi \propto \frac{\partial^2 \sigma}{\partial \Omega \partial \omega} \propto \iint e^{i(\vec{Q}\cdot\vec{r}-\omega t)} G(\vec{r},t)\, d^3\vec{r}\, dt$$

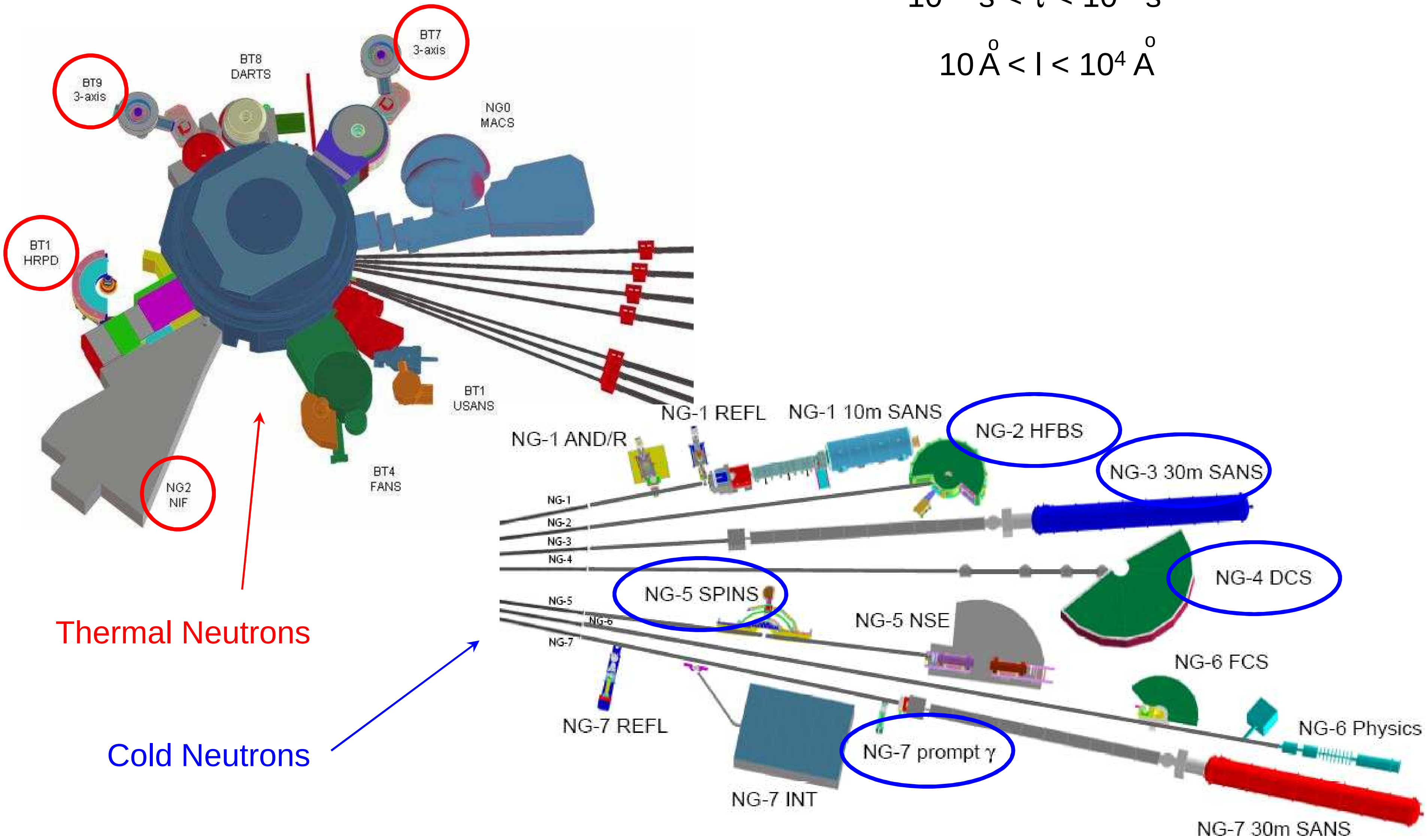


NCNR Facility: Instruments Used

Length Scales and Time Scales

$10^{-12}\ \mathrm{s} < \tau < 10^{-9}\ \mathrm{s}$

$10\ \mathrm{\mathring{A}} < l < 10^{4}\ \mathrm{\mathring{A}}$

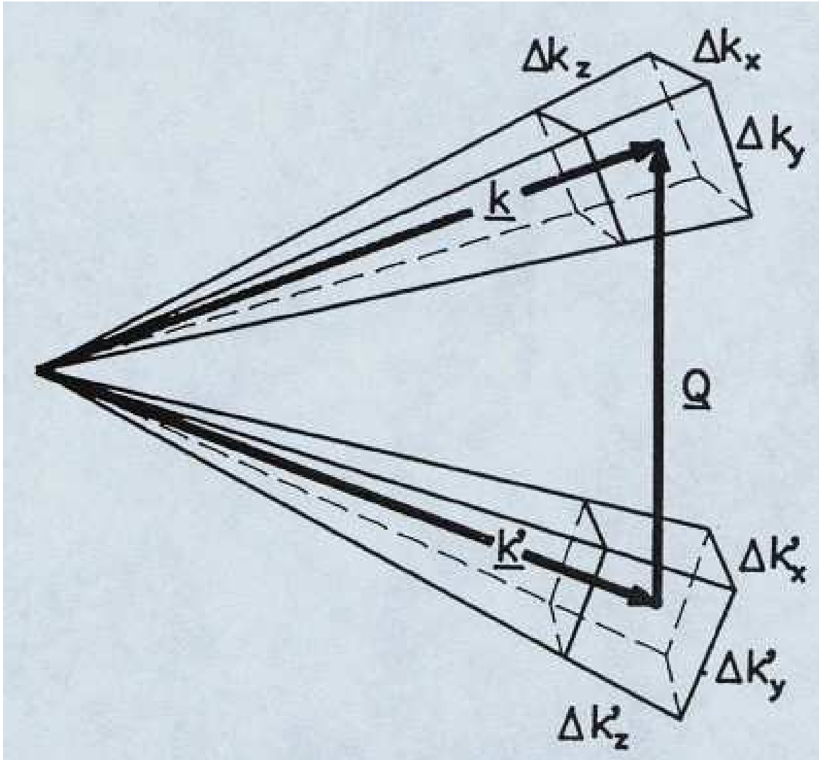


NCNR Facility: Instruments Used

Why use so many spectrometers?

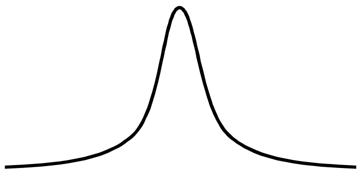
Because neutron scattering is an intensity limited technique. Thus detector coverage and resolution MUST be tailored to the science.

Uncertainties in neutron wavelength and direction imply that **Q** and $\hbar\omega$ can only be defined with finite precision.

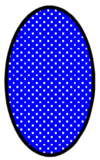


Courtesy of R. Pynn

The total signal in a scattering experiment is proportional to the resolution volume → better resolution leads to lower count rates! One must choose *carefully* …



$\propto$

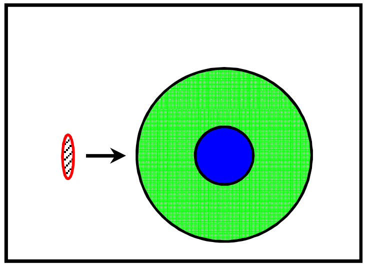


Wave vector (Q) Resolution

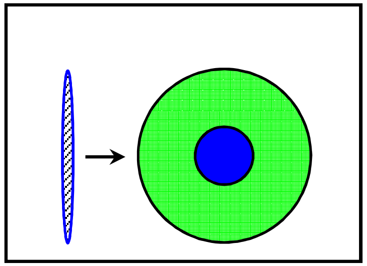
Q-Resolution Matters!

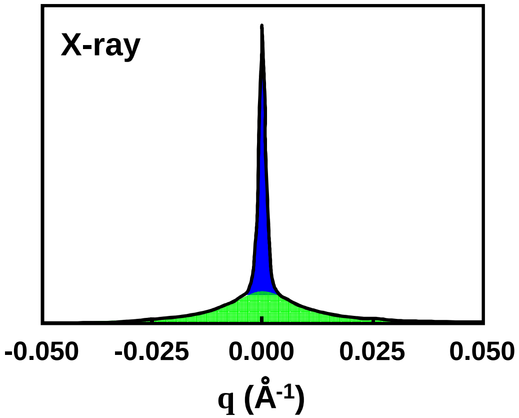
The “right” resolution depends on what you want to study.

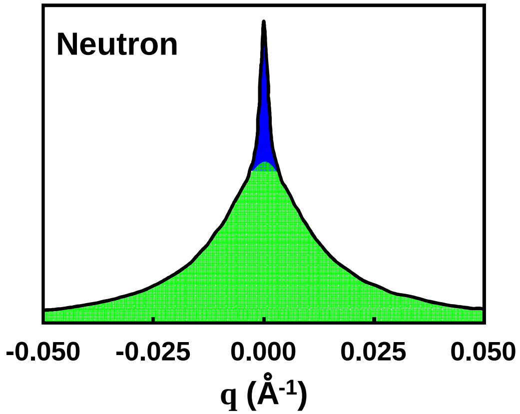
X-ray



Neutron







Energy (ħω) Resolution

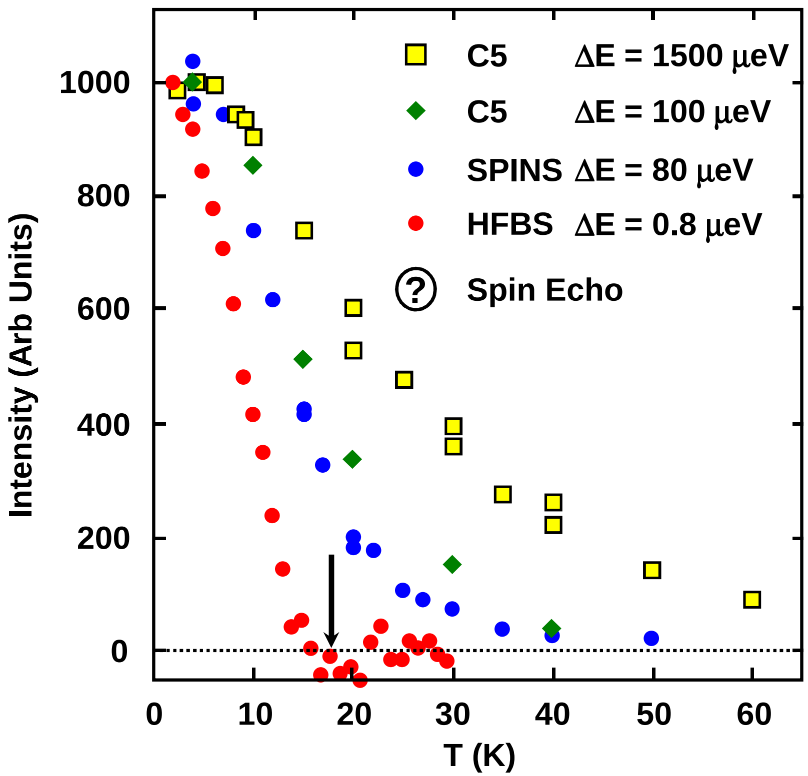
hω-Resolution Matters!

$YBa_2Cu_3O_{6.35}$
T_c = 18K

Magnetic order occurs at Q = (1/2,1/2,2).

But what is T_N?

"Elastic" Bragg Peak Intensity



A "fatter" energy resolution integrates over low-energy fluctuations …

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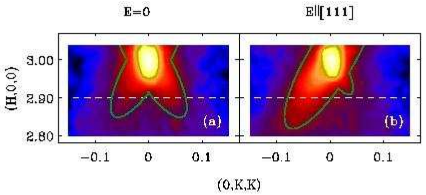

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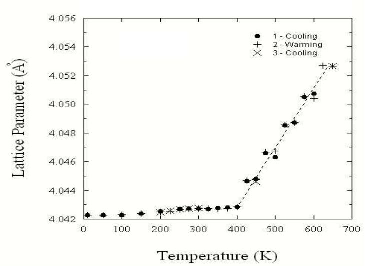

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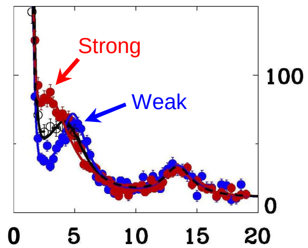
   - Anomalous thermal expansion
   - Skin effect



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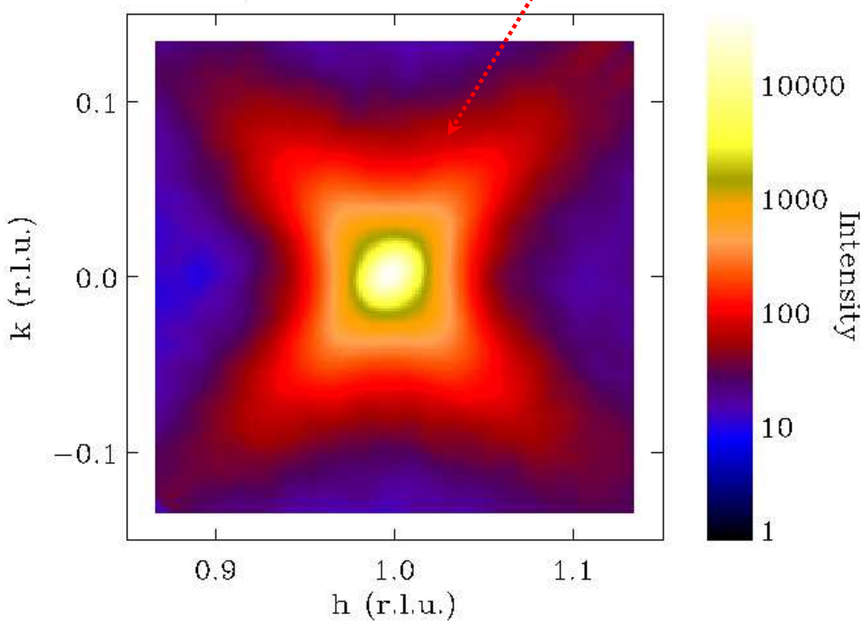
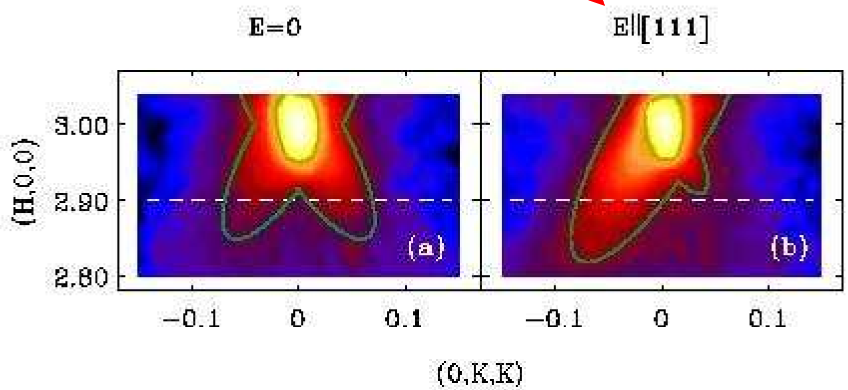
Short-Range Order: Diffuse Scattering

Strong, temperature dependent diffuse scattering.

Responds strongly to electric field → polar in nature.



G. Xu, G. Shirane, J.R.D. Copley, P. M. Gehring,
Phys. Rev. B **69**, 064112 (2004).

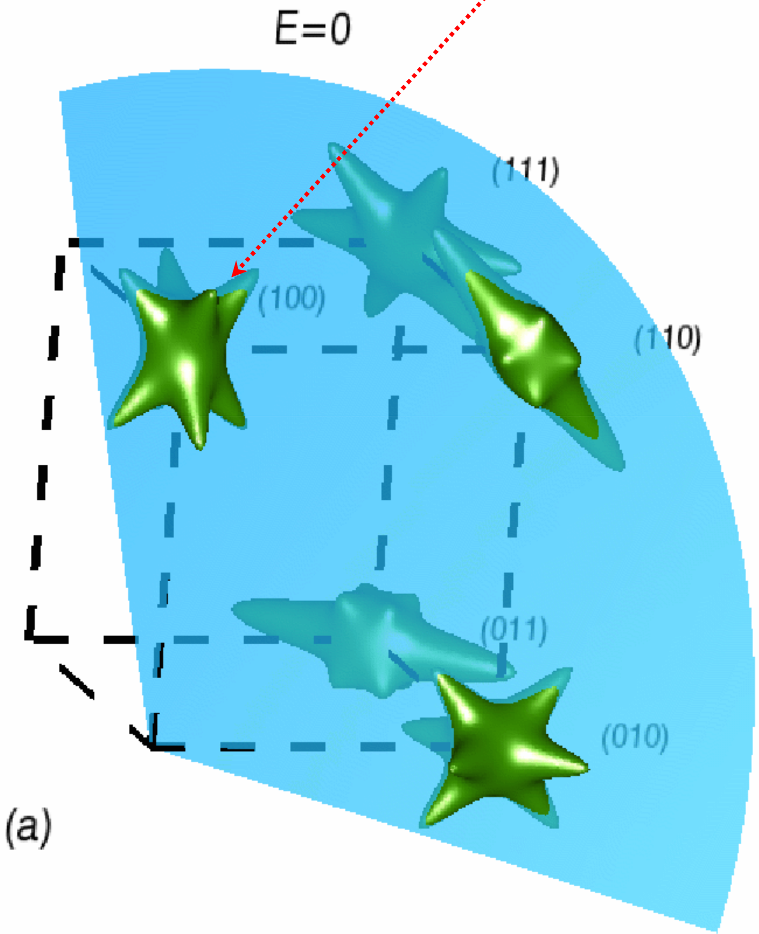


G. Xu, P. M. Gehring, G. Shirane,
Phys. Rev. B **72**, 214106 (2005).

Short-Range Order: Diffuse Scattering

“Butterfly” pattern arises from <110> “rods” in 3D.

Different shapes result from neutron structure factor.



$$I_{diff} \sim |F_{diff}(\mathbf{Q})|^2 \sim |\mathbf{Q} \bullet \varepsilon|^2 \cdot |F_{diff}(\mathbf{G})|^2 \cdot |\mathcal{F}(q)|^2,$$

$$\mathbf{Q} = \mathbf{G} + q,$$

$$|F_{diff}(\mathbf{G})|^2 \sim \left|\sum_j b_j \xi_j e^{i\mathbf{Q}\bullet\mathbf{R}}\right|^2$$

G. Xu, H. Hiraka, Z. Zhong, G. Shirane, Phys. Rev. B **70**, 174109 (2004).
T.R. Welberry *et al*. Appl. Cryst. (2005).

G. Xu, G. Shirane, J.R.D. Copley, P. M. Gehring, Phys. Rev. B **69**, 064112 (2004).
H. Hiraka, S.-H. Lee, P. M. Gehring, G. Xu, G. Shirane, Phys. Rev. B **70**, 184105 (2004).

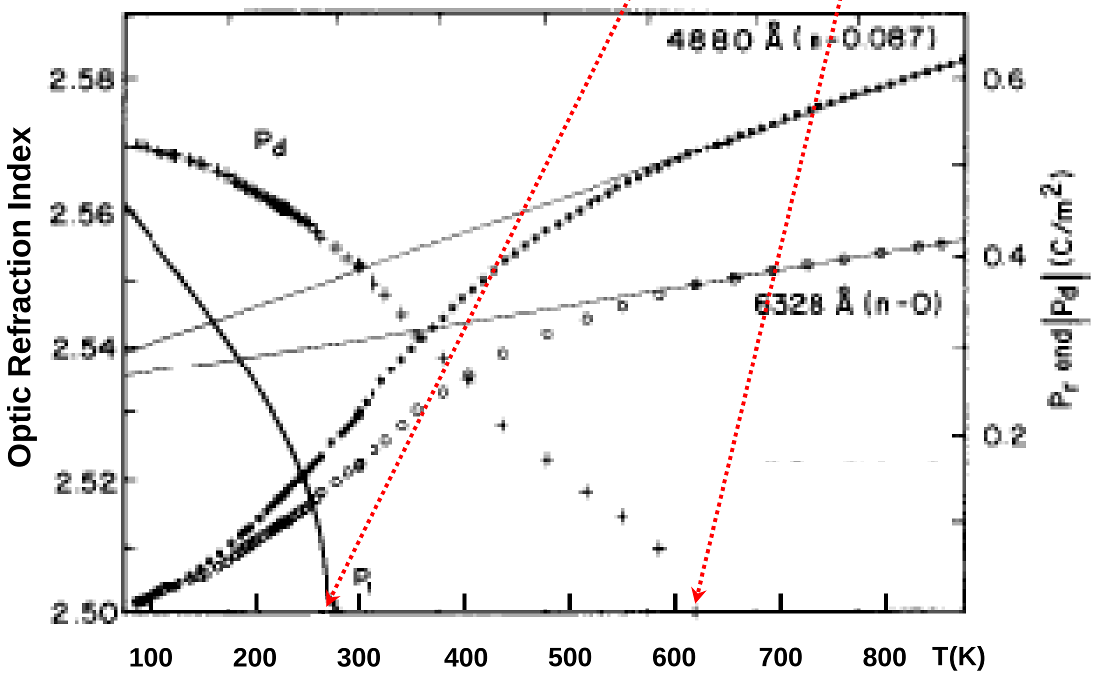
Temperature Scales in $PbMg_{1/3}Nb_{2/3}O_3$

T_c = Curie Temperature

T_d = Burns Temperature

G. Burns and F. H. Dacol,
Solid State Commun. 48, 853 (1983).

Light



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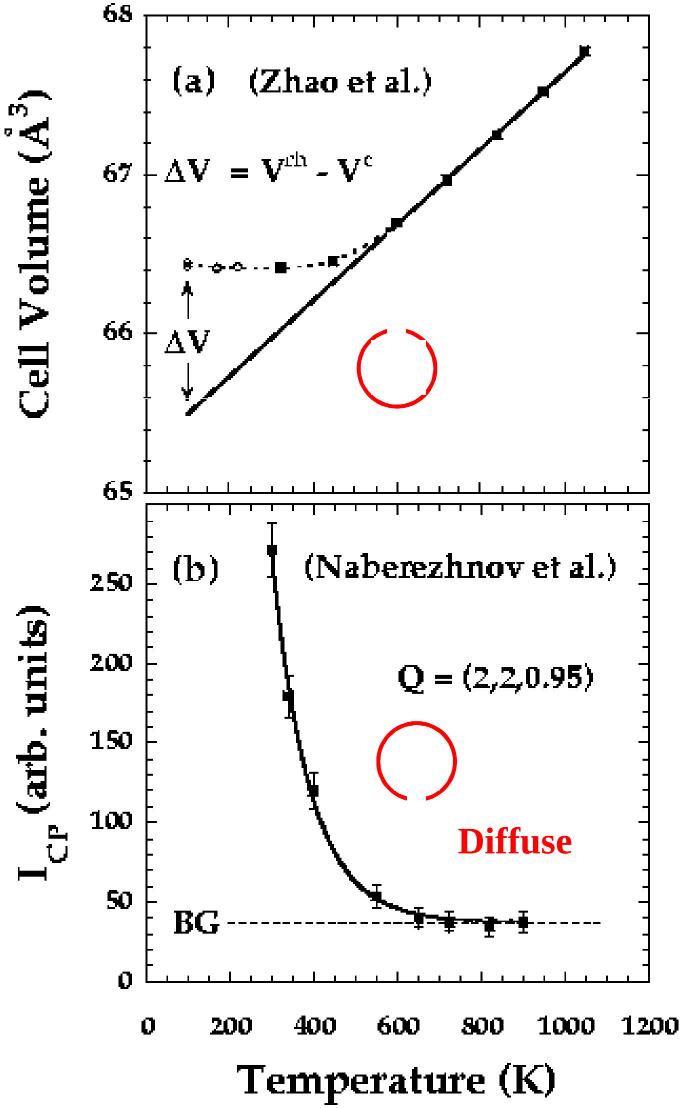
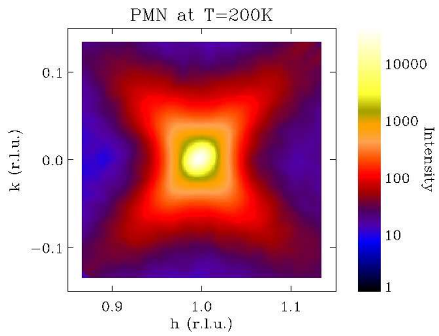


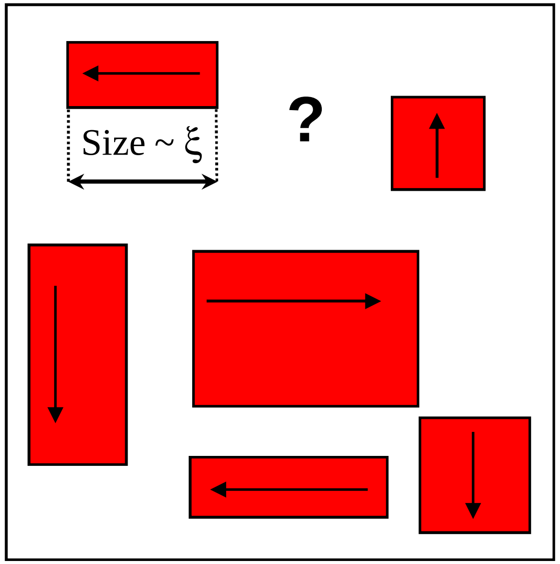
Temperature Scales of Relaxors

Two characteristic temperature scales in relaxors.

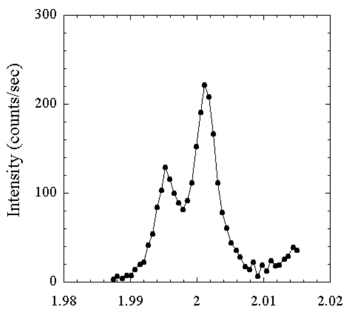
Burns temperature T_d – onset of short-range, polar correlations, aka “Polar Nanoregions” (PNR).



Polar Nanoregions (PNR)



Curie temperature T_c – onset of long-range, polar correlations → change of crystal symmetry.

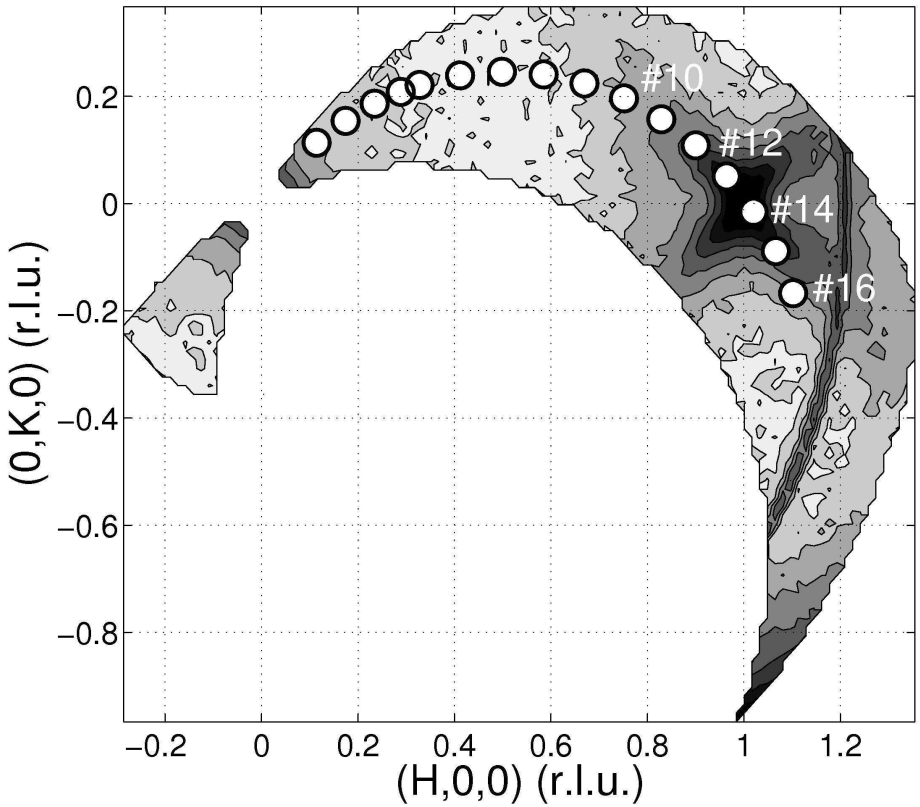


Different values of T_d and opinions of the number of relevant temperature scales → reassess T_d …

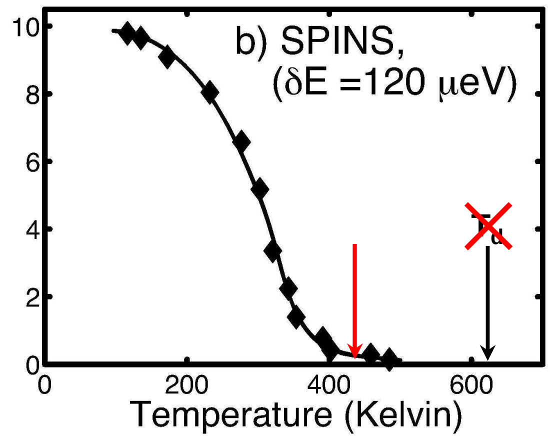
Reassessment of Burns Temperature

Examined diffuse scattering with high energy resolution.

Found that T_d = 420 K (not 620 K).

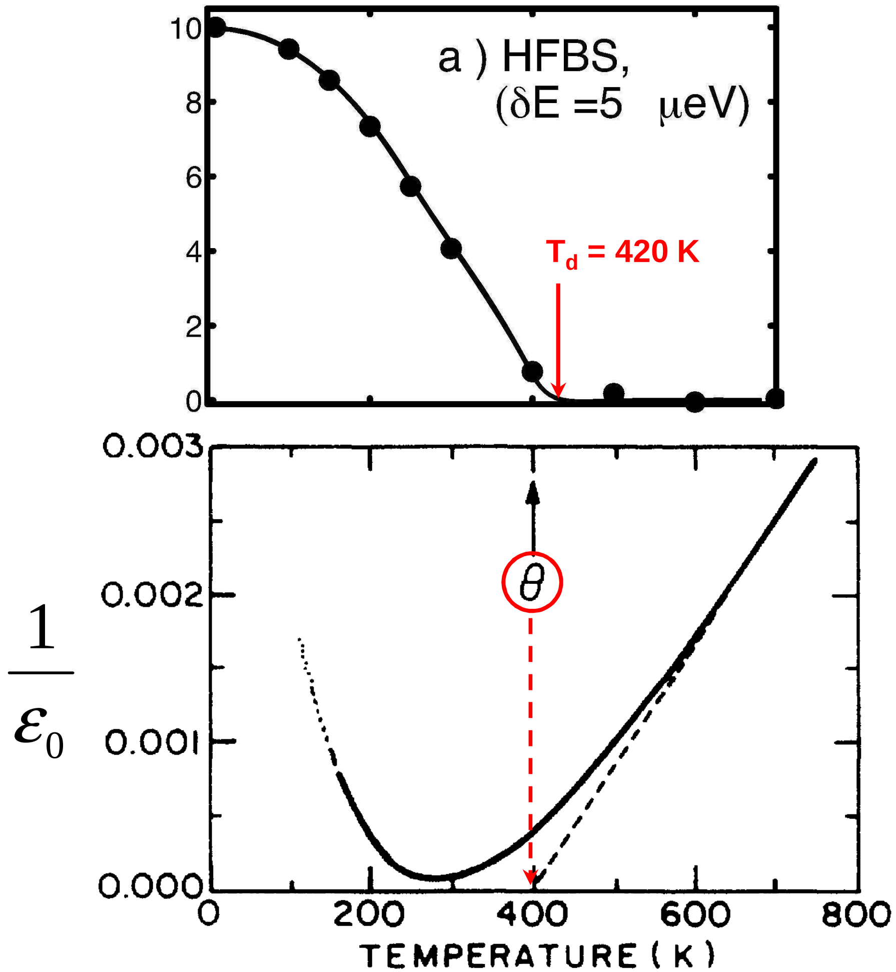


P. M. Gehring *et al.*,
(submitted to Phys. Rev. B)



Comparison with Dielectric Constant

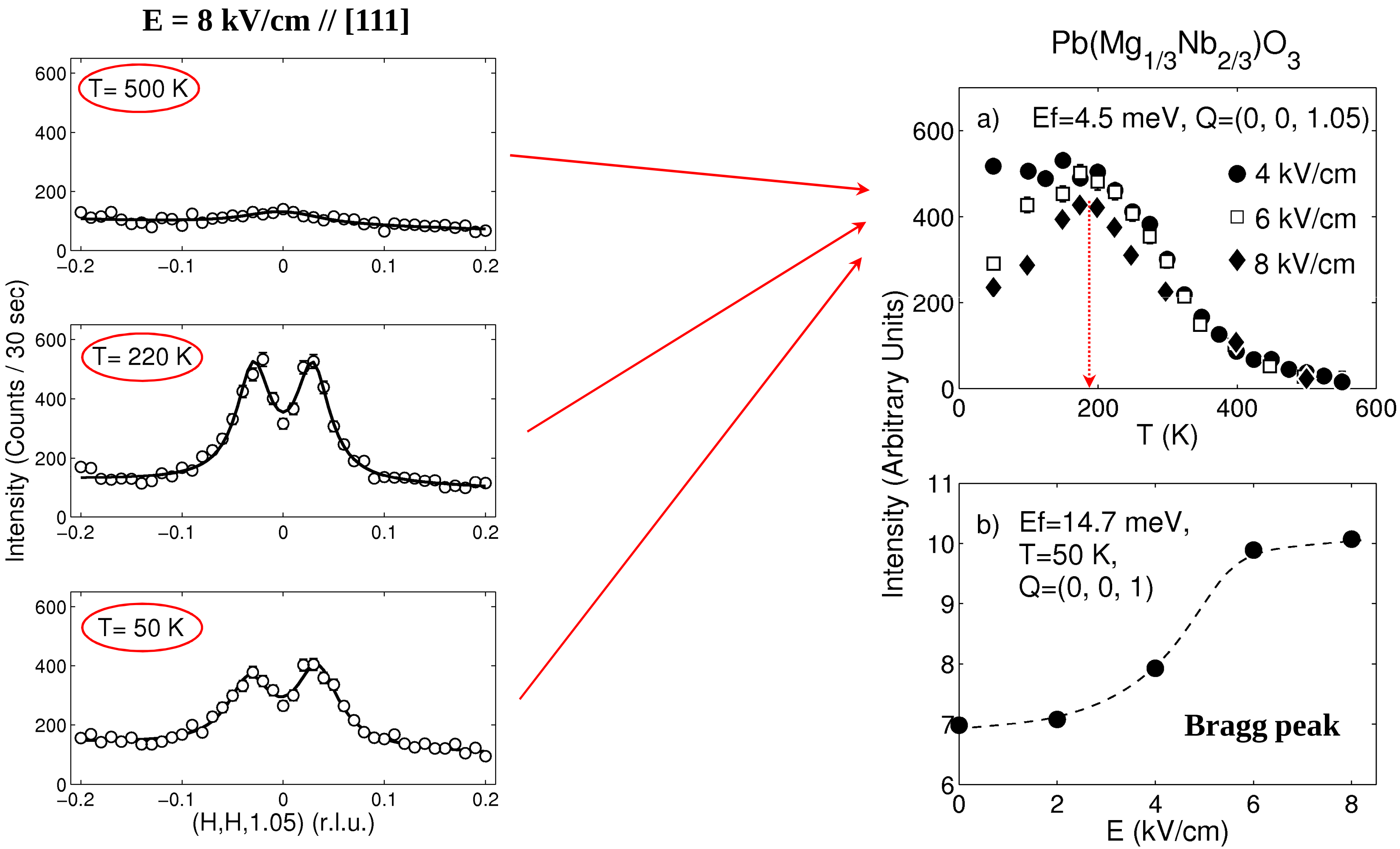
Revised T_d is in excellent agreement with Curie-Weiss temperature .



D. Viehland et al.,
Phys. Rev. B **46**, 8003 (1992).

Does Diffuse Reflect T_c?

The Curie temperature is reflected in the diffuse scattering response to an electric field.



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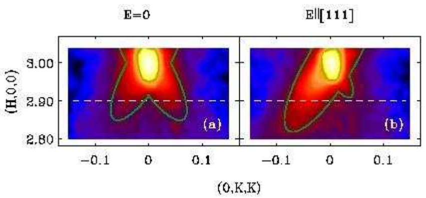

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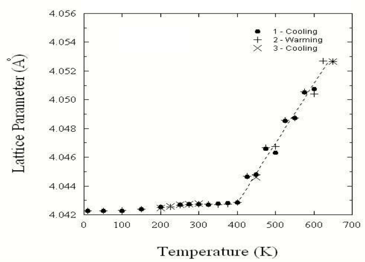

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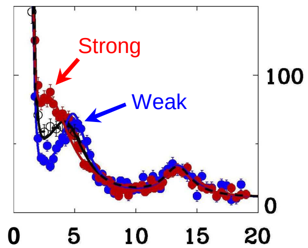

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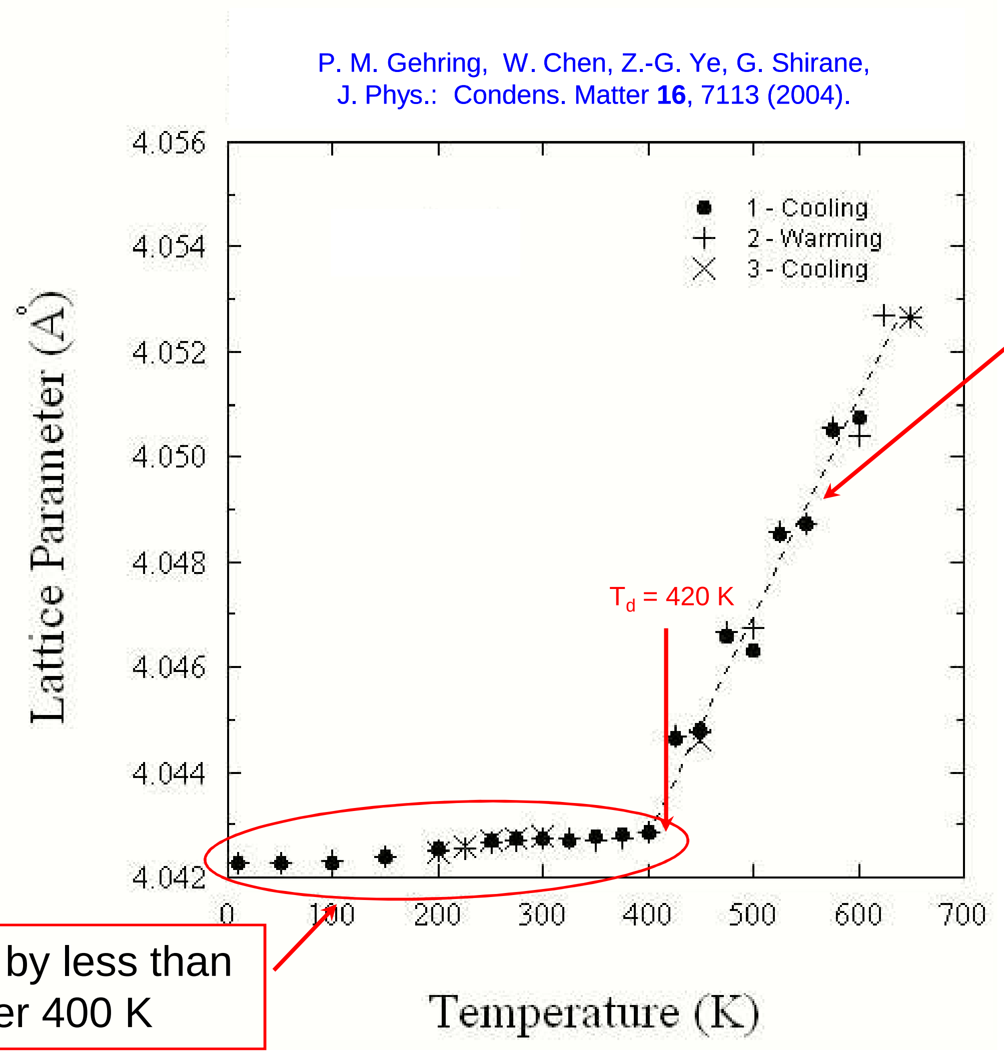
   - Soft modes
   - Phonon coupling

Effect of Diffuse on Thermal Expansion

Strong thermal expansion is seen above T_d.

Anomalous Invar-like effect is seen below T_d.



Thermal expansion is ~ 10^{-5} 1/K.

Why does this happen?

d-spacing changes by less than 0.001 Angstrom over 400 K

Real Space Structure of Short Range Order

Key Concept: PNR are <u>shifted</u> wrt non-polar (cubic) lattice.

S. Vakhrushev *et al*.,
Phys. Solid State 37, 1993 (1995).

Determined ionic displacements in PMN from room temp. diffuse scattering measurements:

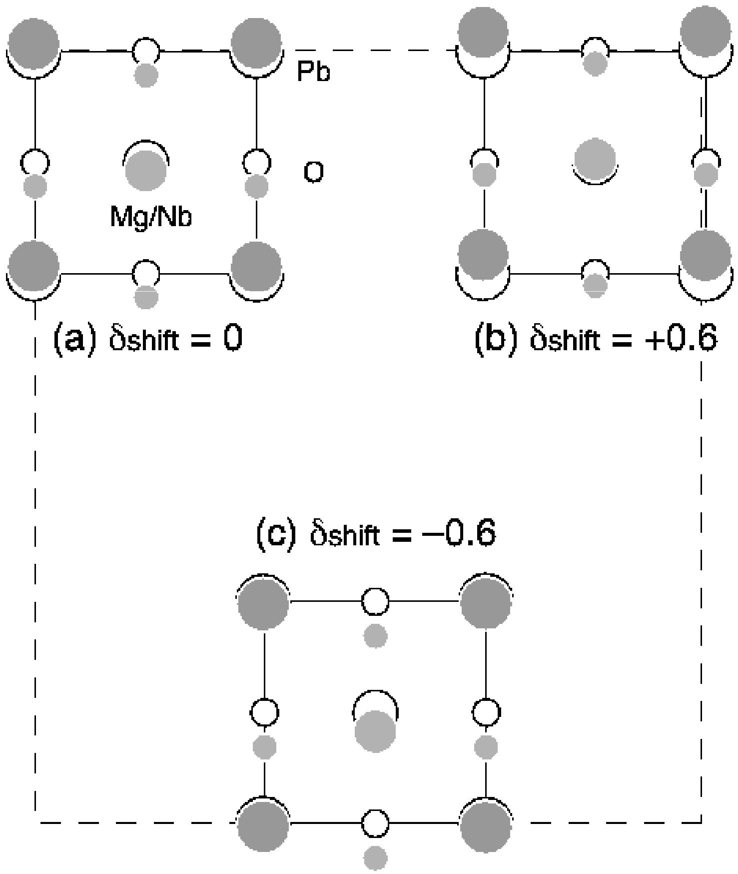
$$\delta_{Pb} = 1.00,\ \delta_{MN} = 0.18,\ \delta_{O} = -0.64$$

If these result from the soft transverse optic phonon, they must conserve the unit cell center-of-mass. But:

$$\Sigma\, m_i\, \delta_i \neq 0$$

Hirota *et al*. proposed an elegant model:

$$\delta_i = \delta_\iota^{CM} + \delta_{shift},\ \delta_{shift} = 0.58$$

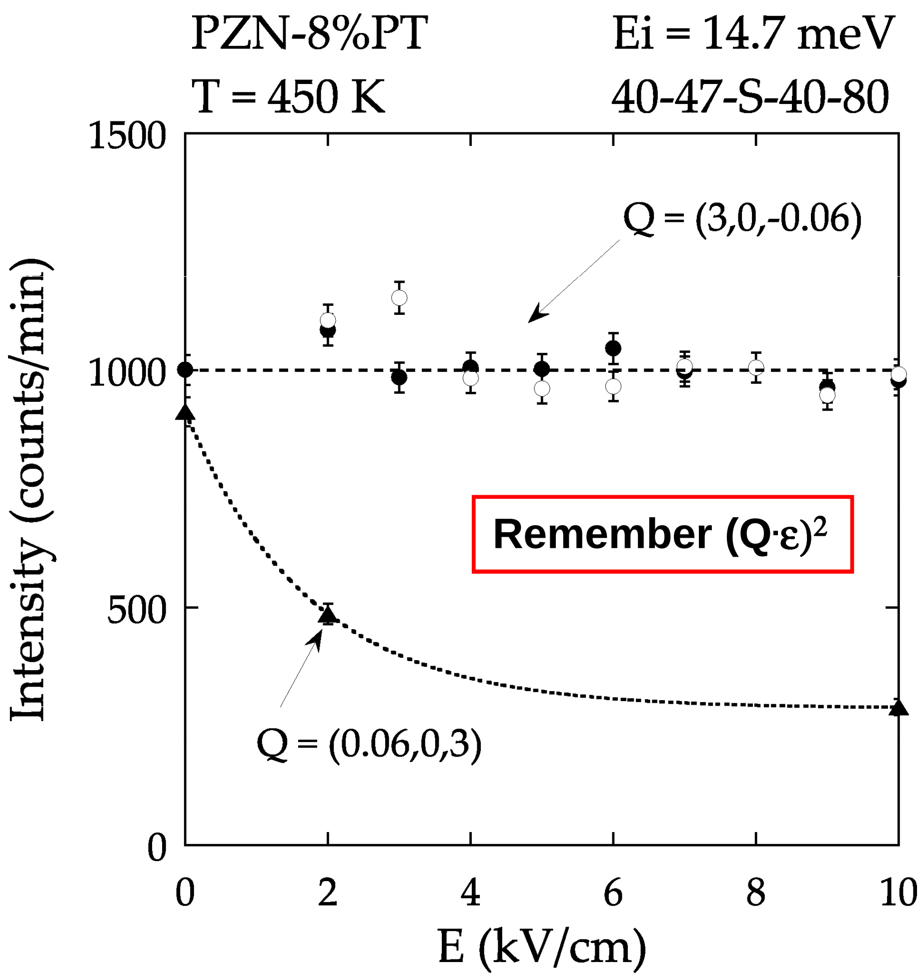


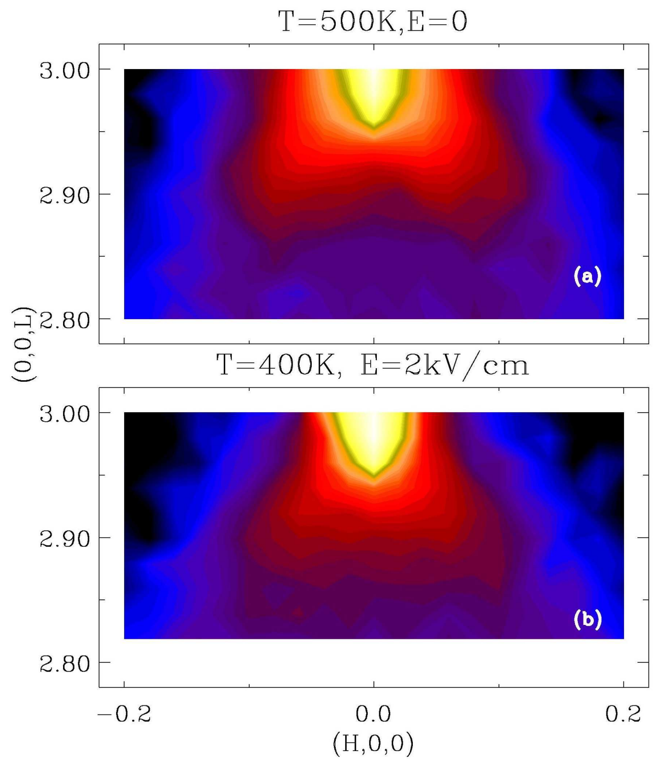
Hirota *et al*., Phys. Rev. B 65, 104105 (2002).

PNR Response to E // [001]

Diffuse scattering is robust against strong fields.

But the response is anisotropic → no uniform polar phase.





Gehring *et al.*, Phys. Rev. B **70**, 014110 (2004).

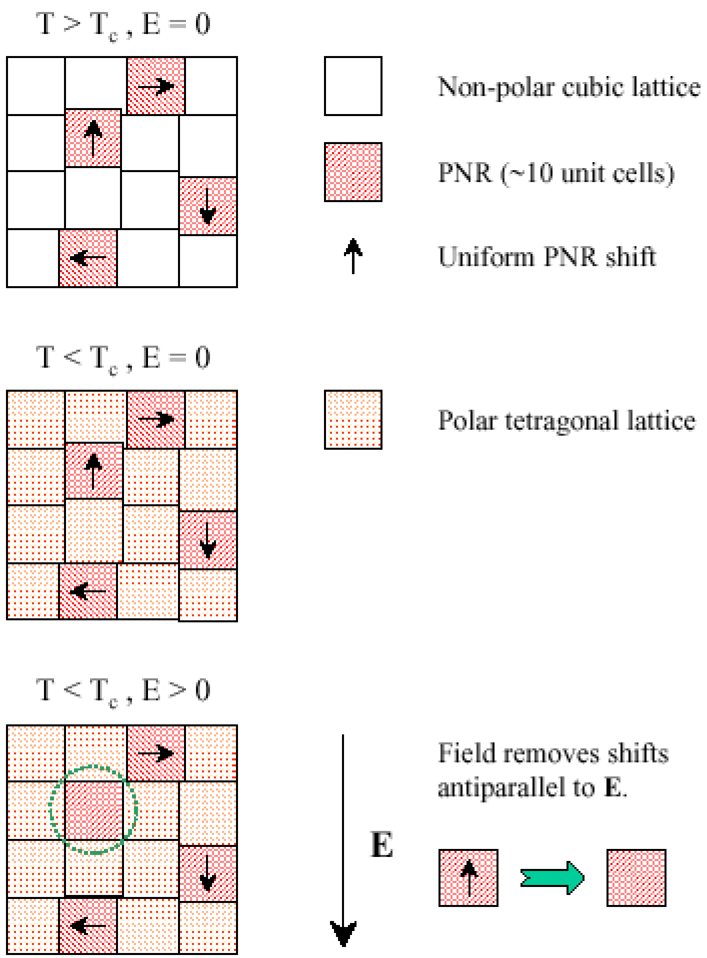
Shifted Polar Nanoregions

Shift of PNR is able to explain the anisotropic response to an electric field.

Above T_c

Zero-field cooled

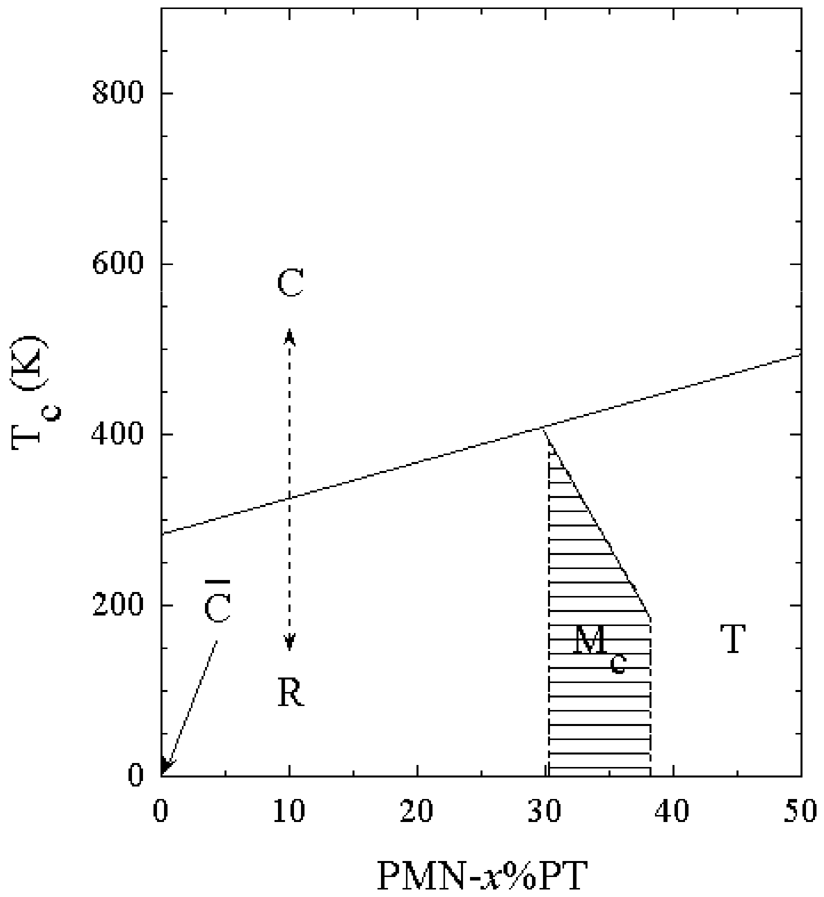
Field cooled

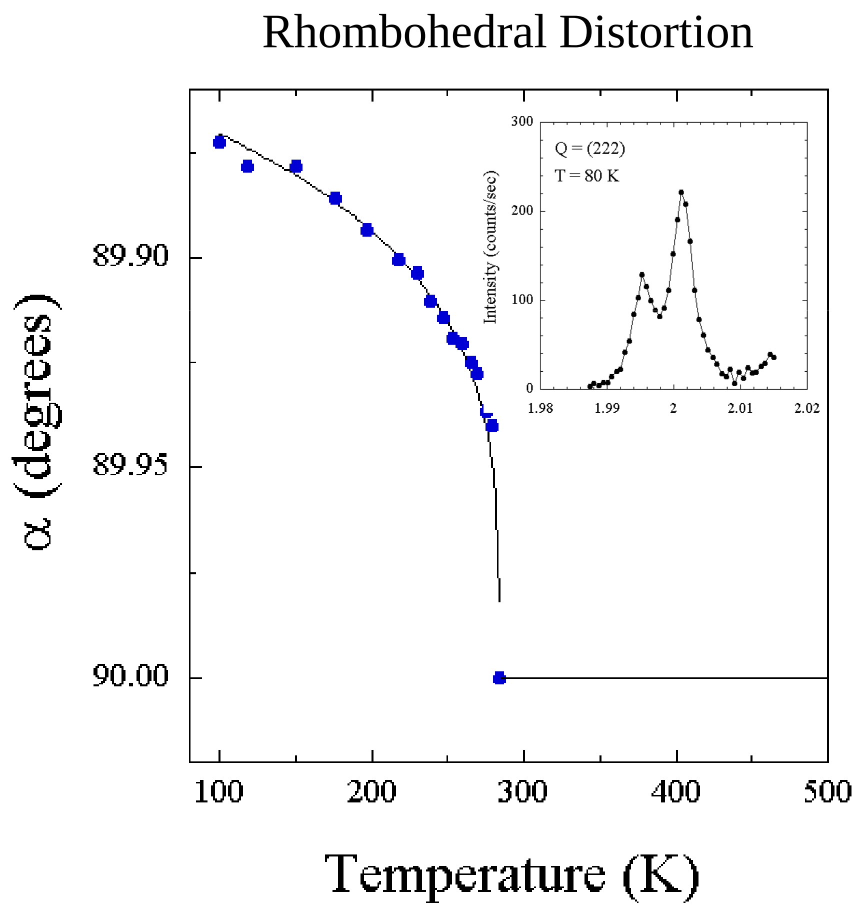


The shifted PNR concept also provides a plausible explanation for the anomalous thermal expansion.

Phase Diagram for PMN-xPT

X-rays observe a cubic to rhombohedral distortion for PMN-10%PT.

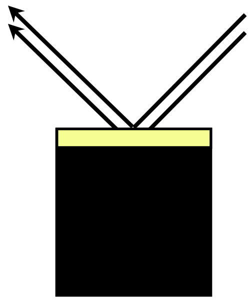




B. Dkhil *et al.*, Phys. Rev. B **65**, 024104 (2001)

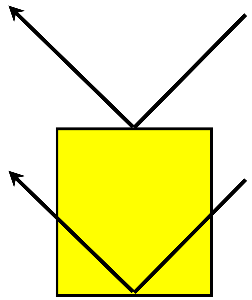
Effect of PNR on Crystal Structure

Only outermost "skin" region of the crystal is distorted. Bulk remains cubic!



X-rays:

λ= 1.39 Å
E = 8.9 keV
t ~ 10 μm



Neutrons:

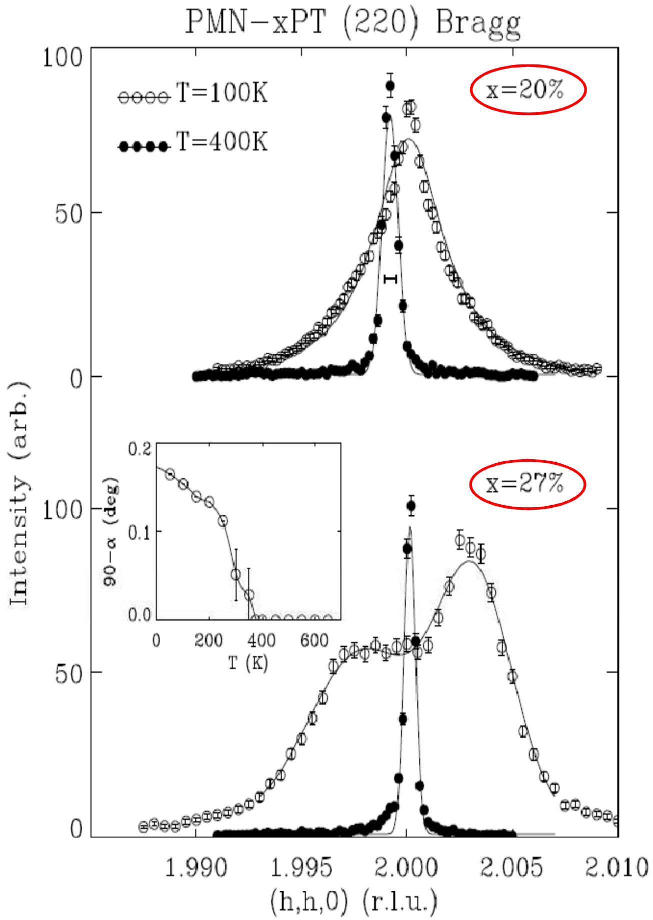
λ= 3.10 Å
E = 8.5 meV
t ~ 1 cm

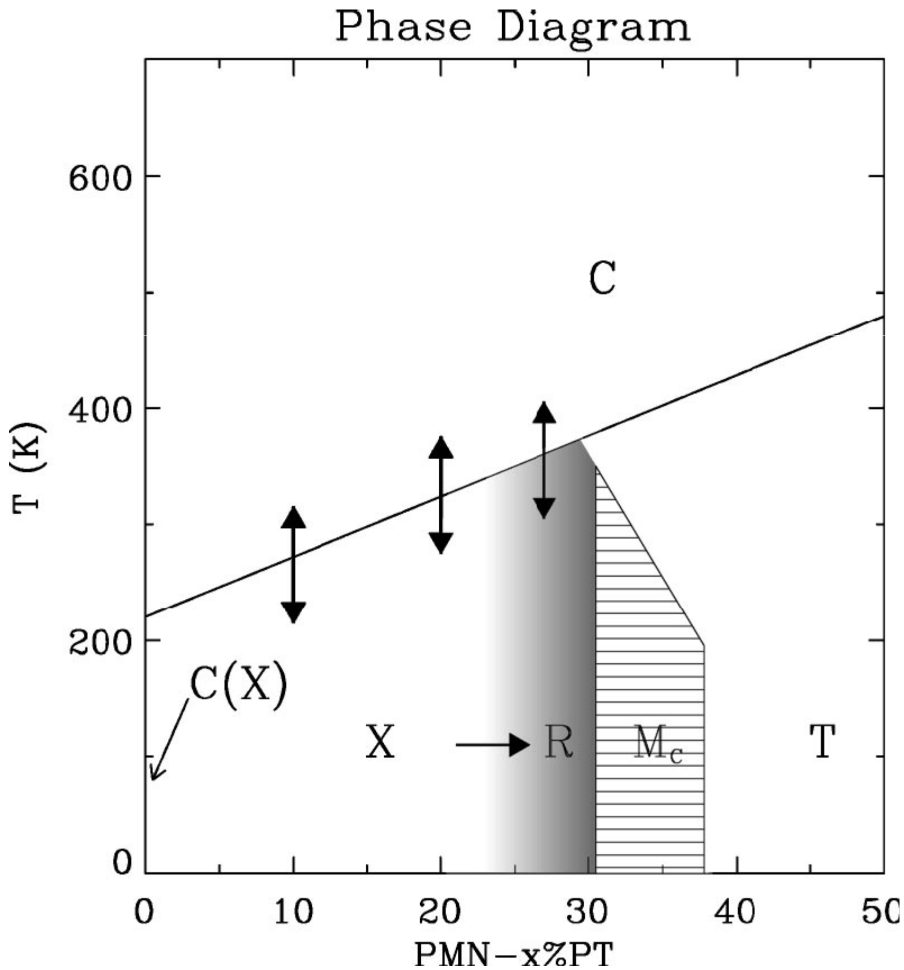
P. M. Gehring, W. Chen, Z.-G. Ye, G. Shirane, J. Phys.: Condens. Matter **16**, 7113 (2004).

Effect of PNR on Crystal Structure

Phase diagrams for both PMN-xPT and PZN-xPT have since been revised.

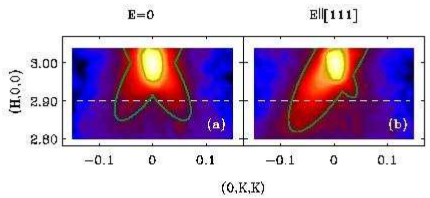
Xu *et al.*, Phys. Rev. B (2004)



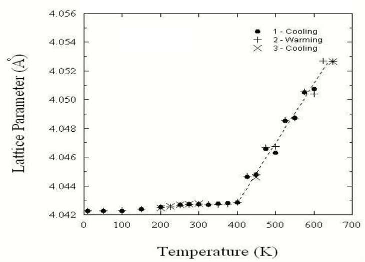


Outline:

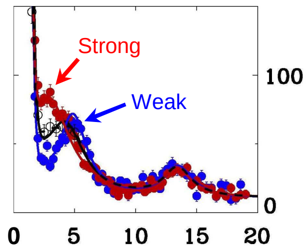
1. Introduction
   - Relaxors
   - Neutron scattering basics



2. Diffuse Scattering
   - Temperature and field dependence
   - Two temperature scales (T_d and T_c)



3. Structure
   - Anomalous thermal expansion
   - Skin effect



4. Lattice Dynamics
   - Soft modes
   - Phonon coupling

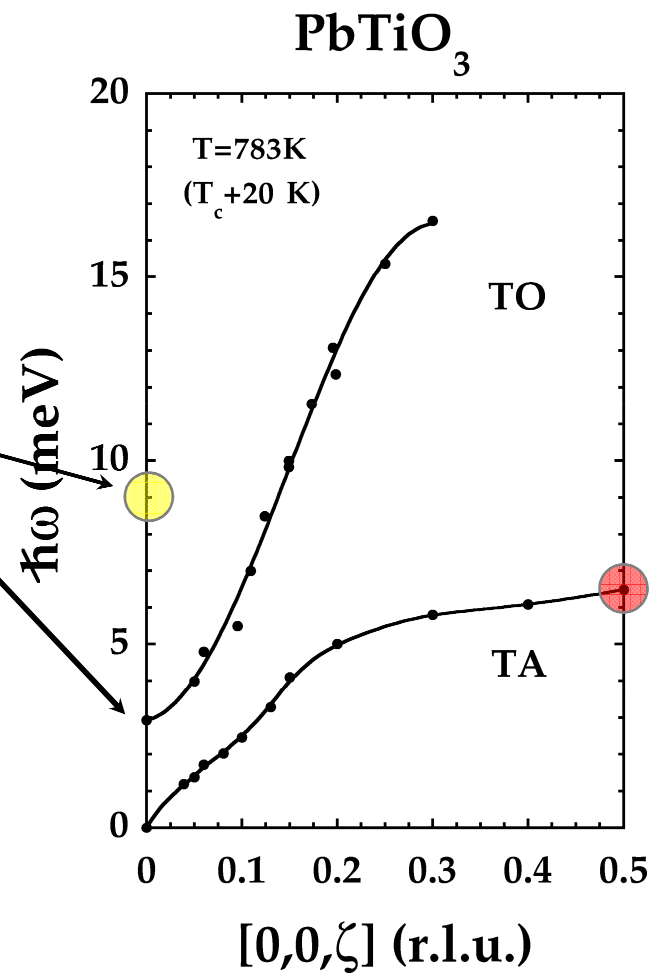
Displacive Transition: Soft Modes

In $PbTiO_3$ a cubic to tetragonal structural phase transition takes place at T_c = 763K.

The lowest-lying TO phonon frequency $\hbar\omega_{TO} \rightarrow 0$ as $T \rightarrow T_c$.

This is a phonon instability known as a "soft mode," and is typical of displacive ferroelectrics.

For an antiferroelectric, the zone boundary phonon goes soft.



Shirane *et al.*,
Phys. Rev. B **2**, 155 (1970)

Lyddane-Sachs Teller (LST) Relation:

Signature of displacive ferroelectricity …

Curie-Weiss:

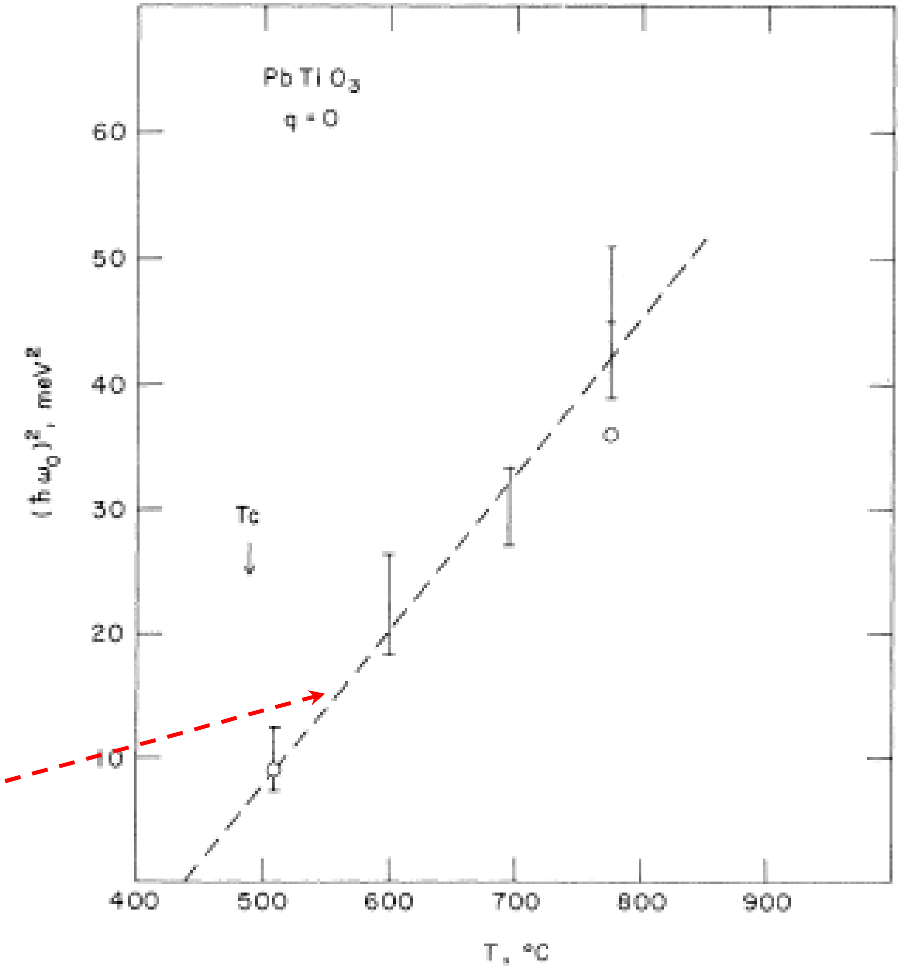
$$\frac{1}{\varepsilon_0} \propto (T - T_c)$$

LST:

$$\frac{\varepsilon_0}{\varepsilon_{oo}} \propto \left(\frac{\omega_L}{\omega_T}\right)^2$$

$$\Rightarrow (T - T_c) \propto (\hbar \omega_T)^2$$

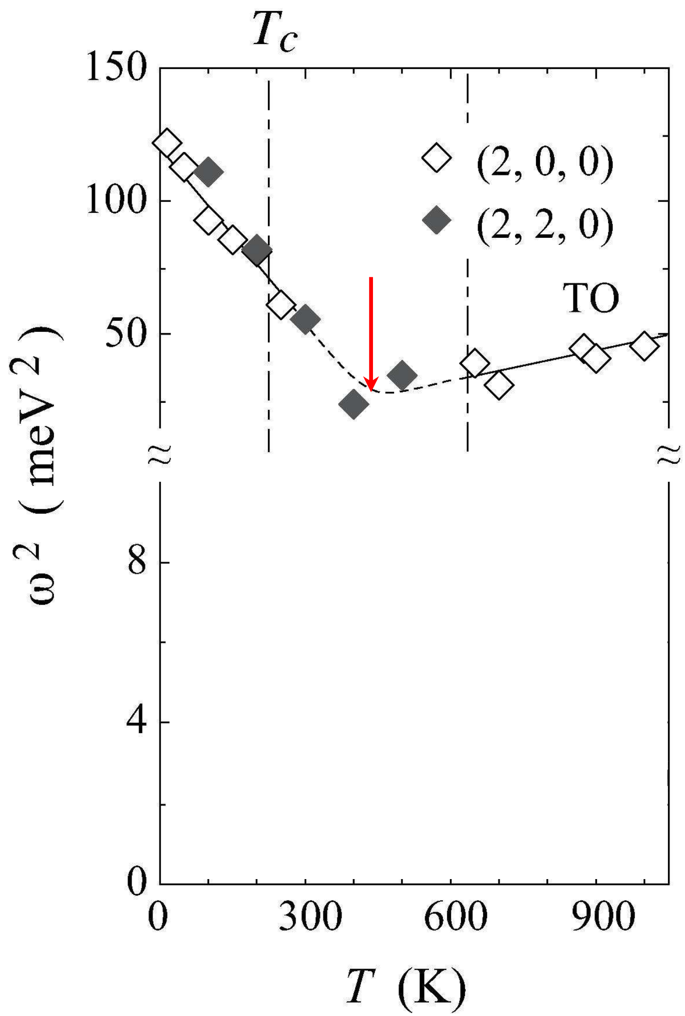
Shirane *et al.*,
Phys. Rev. B **2**, 155 (1970)

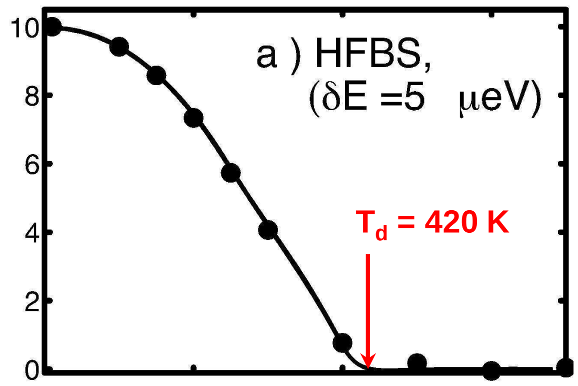


Effect of PNR on TO or TA Phonons

Minimum TO energy occurs at T_d.

Minimum TA energy occurs at T_d.





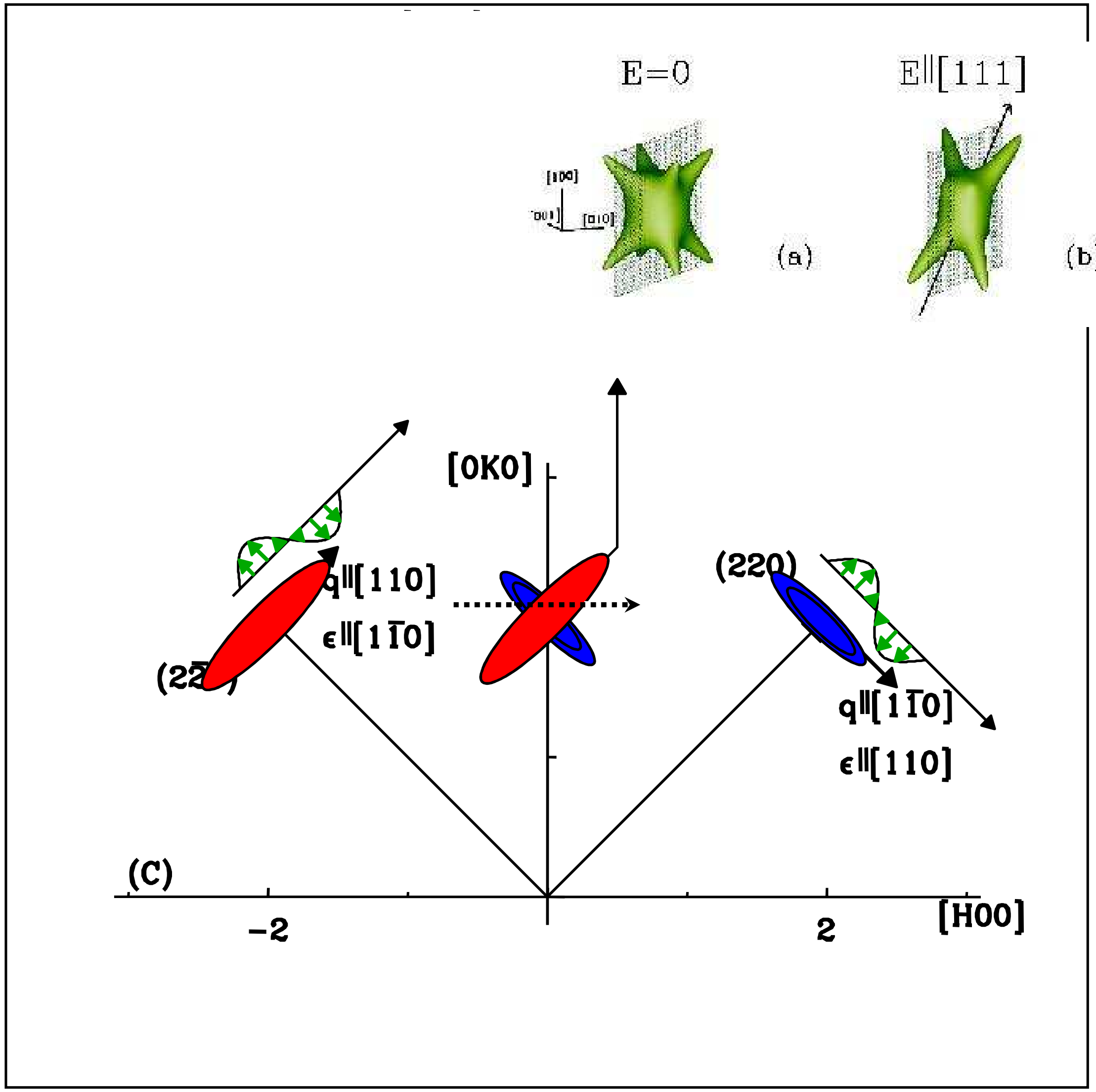
Suggests coupling is present. What kind?

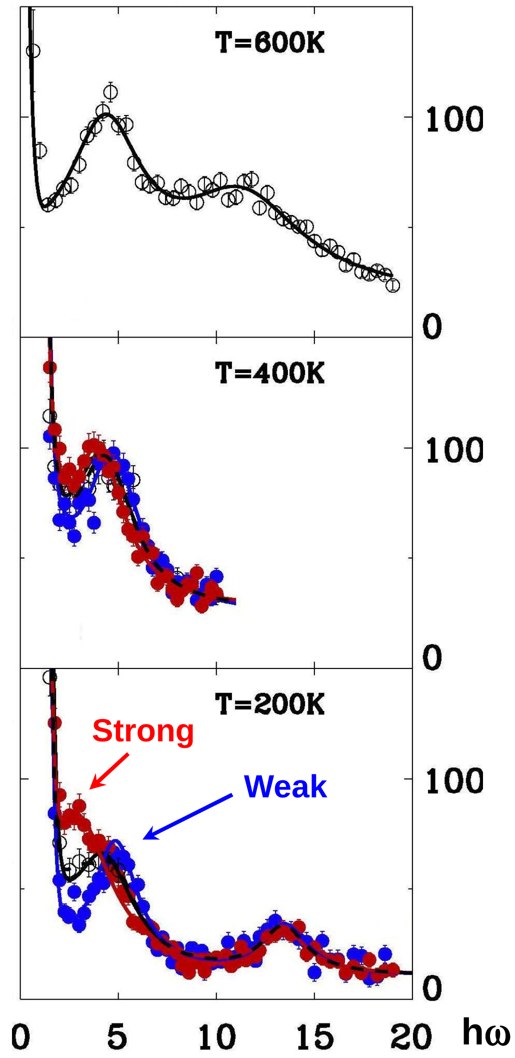
P. M. Gehring *et al.*,
(submitted to Phys. Rev. B)

Coupling Effects: PNR - TA Phonon

Field cooling creates single domain state.

TA phonon is strongly affected where diffuse is strong.

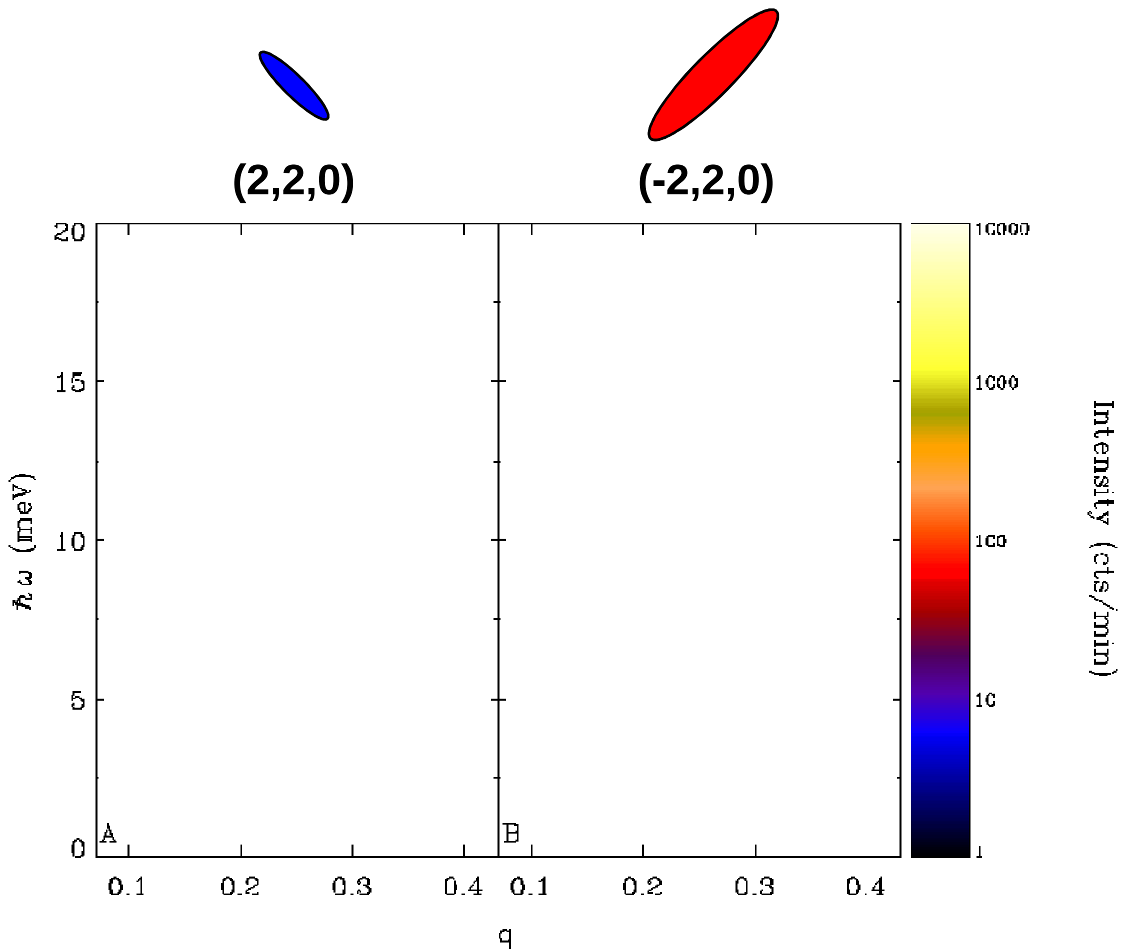




Effect of PNR on Phonon Dispersion

TO phonons are unaffected by PNR.

TA phonons are softer and broader.

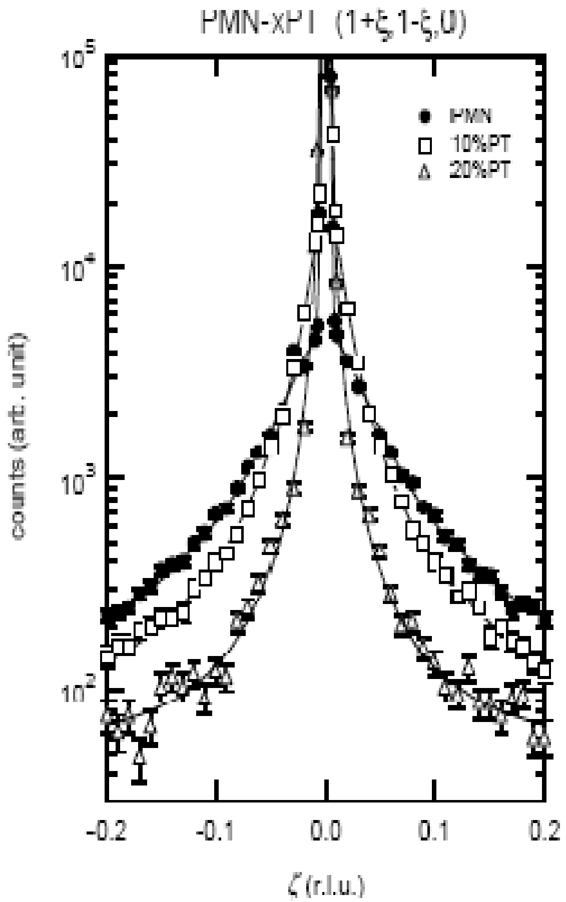


These data indicate the presence of a phase instability (soft TA mode).

These data further suggest PNR-phonon coupling could provide a plausible origin for the exceptional piezoelectric properties of relaxors …

G. Xu, J. Wen, C. Stock, and P. M. Gehring, Nature Materials (submitted).

Correlation Between Diffuse and d_{33}?



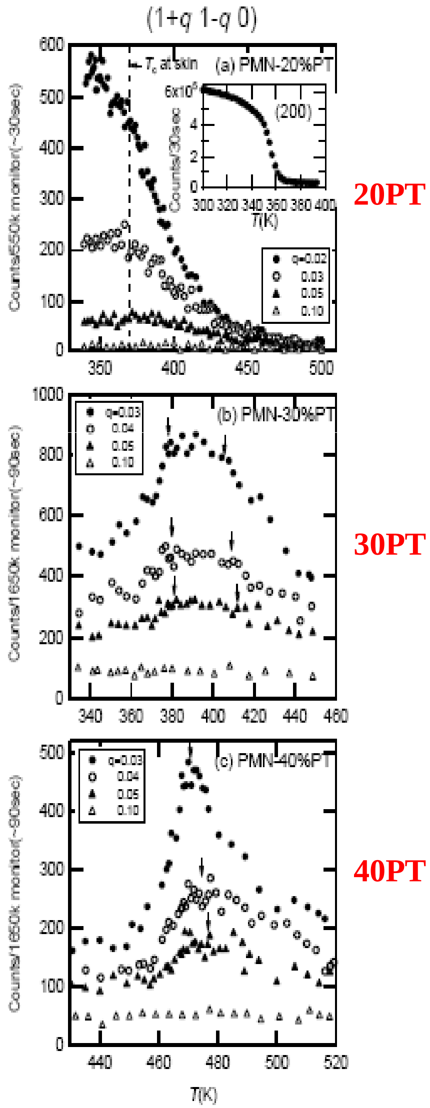
Intensity profiles of the diffuse scattering measured along (110).

Width narrows with increasing PT → increasing correlation lengths; but the integrated diffuse intensity <u>increases</u>.

Data are consistent with a maximum of the integrated intensity near the MPB (~32%).

Diffuse scattering is essentially absent for compounds with PT beyond the MPB.

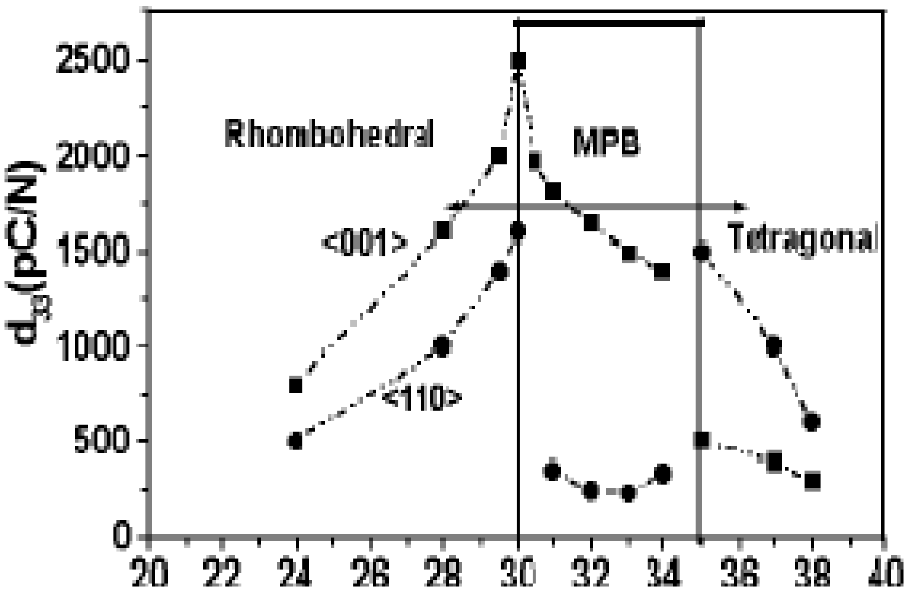
Recover <u>critical behavior</u> for 30% and 40%.



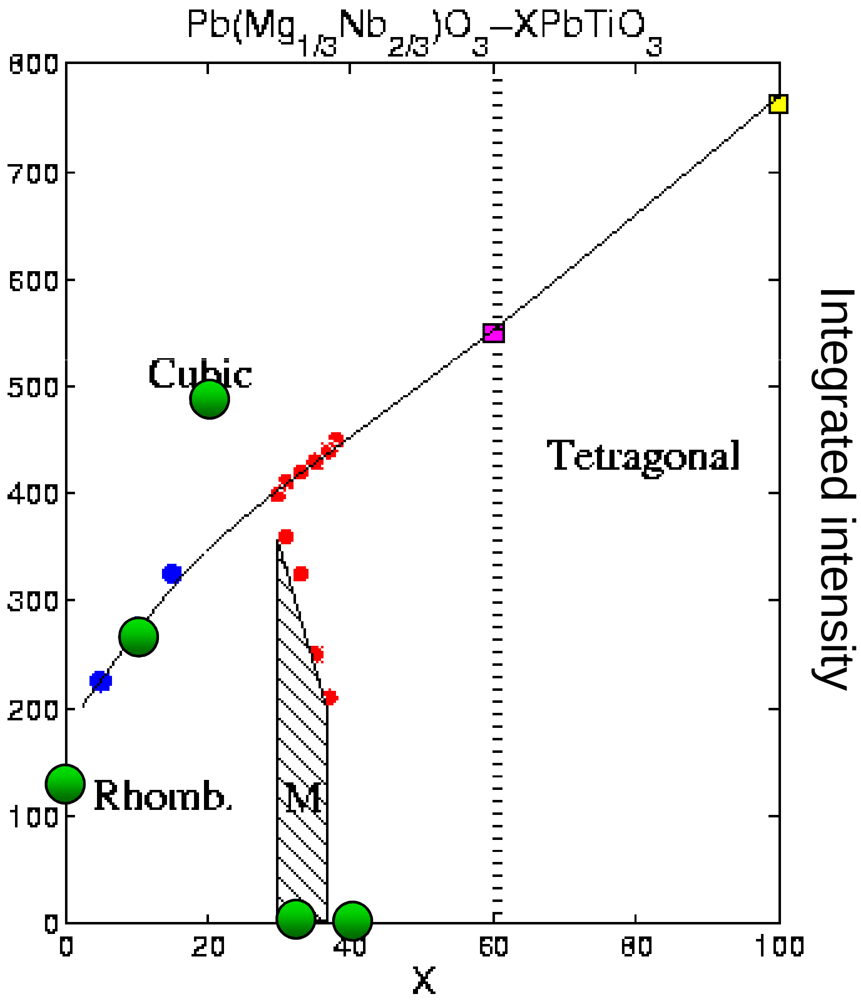
Correlation Between Diffuse and d_{33}?

= q-integrated diffuse scattering

Y. Guo et al.,
J. Phys.: Condens. Matter **15**, L77 (2003)



$PbMg_{1/3}Nb_{2/3}O_3$ → %Ti content



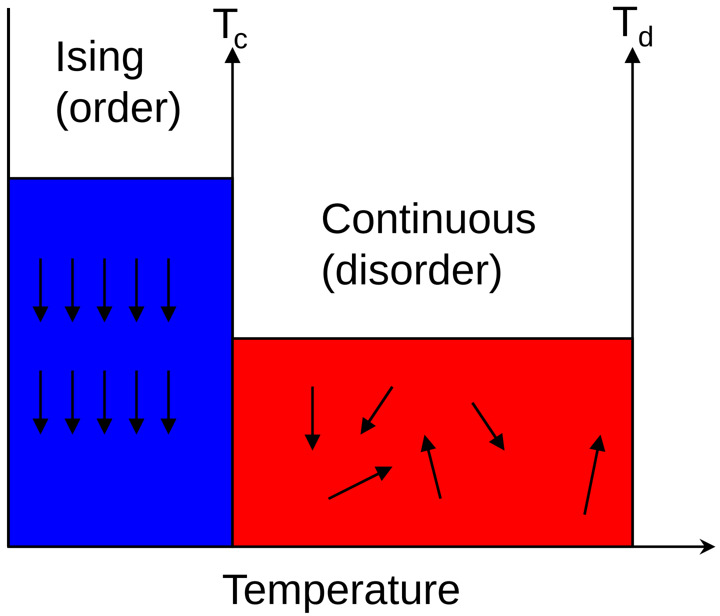
Random Field Model: Two Temp. Scales

Suppose that $H_{Heisenberg} > H_{RF} > H_{cubic}$

At high T the polarization vectors (spins) would look like a continuous symmetry model in a random field

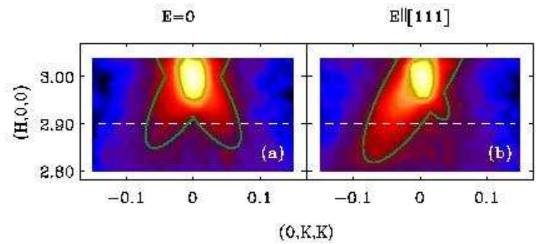
At low T the "spins" would behave more like an Ising model

→ Two temperature scales

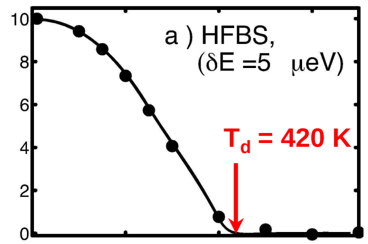


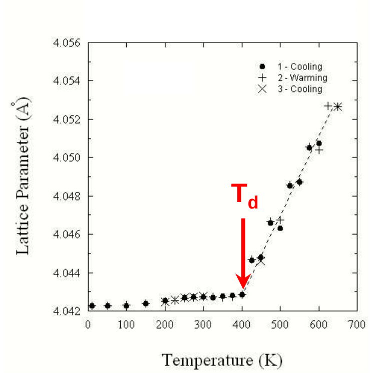
Conclusions and Summary

- $PbBO_3$ perovskite relaxors exhibit strong diffuse scattering that is polar in nature.

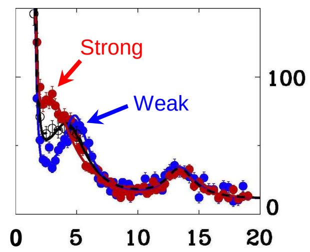


- Onset of diffuse scattering correlates with anomalous invar-like effect.





- Neutron measurements reveal a strong coupling between the diffuse scattering and TA phonon → relationship between SRO and piezoelectricity



Collaborators

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D. Viehland

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Penn State Univ:

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P. Rehrig

Simon Fraser Univ:

Z. –G. Ye

W. Chen

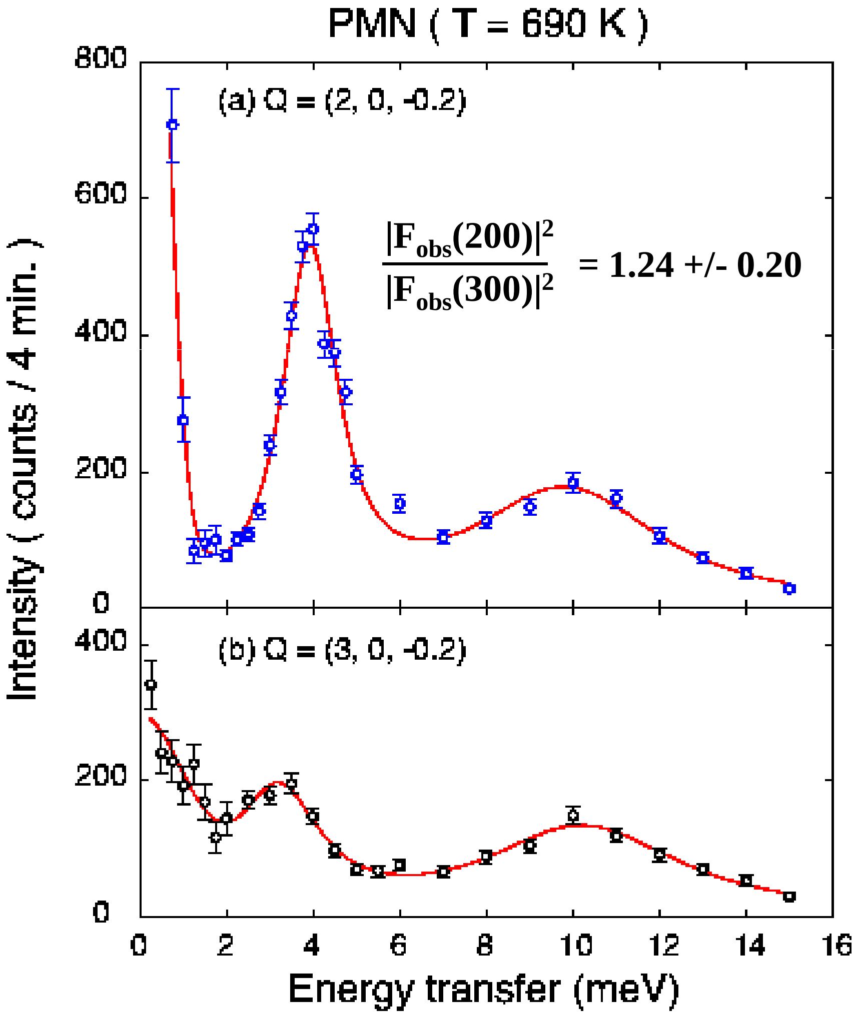
Shanghai Inst Ceramics:

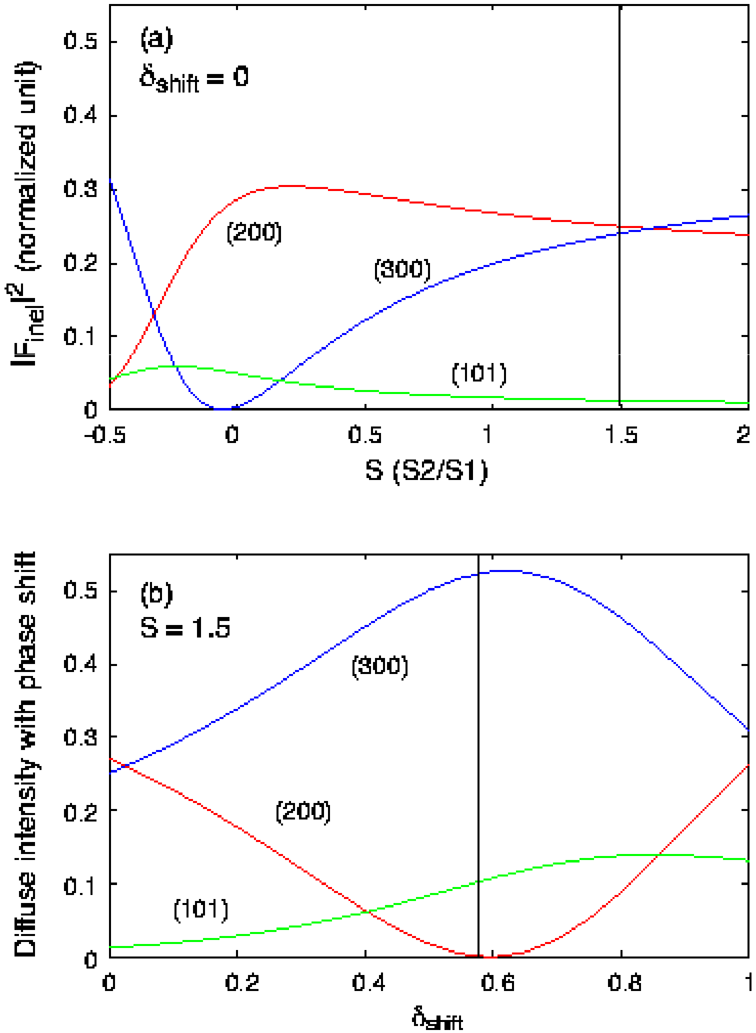
H. Luo

H. Wang

(Provided high quality single crystal samples)

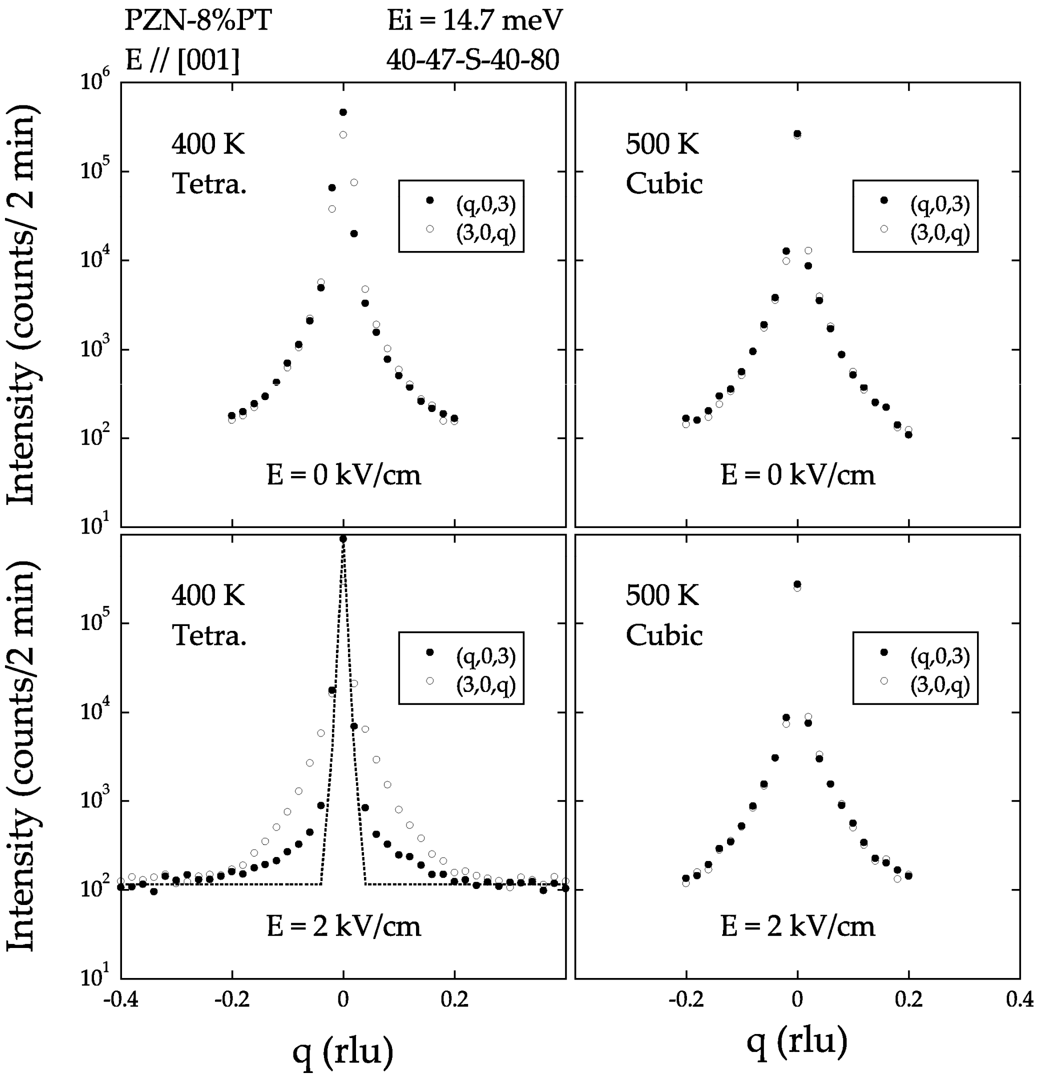
Dynamic Structure Factors for TO mode





Effects of E//[001] on Diffuse

Anistropy: (300) vs (003) …



Gehring *et al.*, Phys. Rev. B **70**, 014110 (2004).

The neutron scattering cross section depends on $(\mathbf{Q}\cdot\mathbf{u})^2$, where **Q** is the scattering wave vector, and **u** is the atomic displacement.

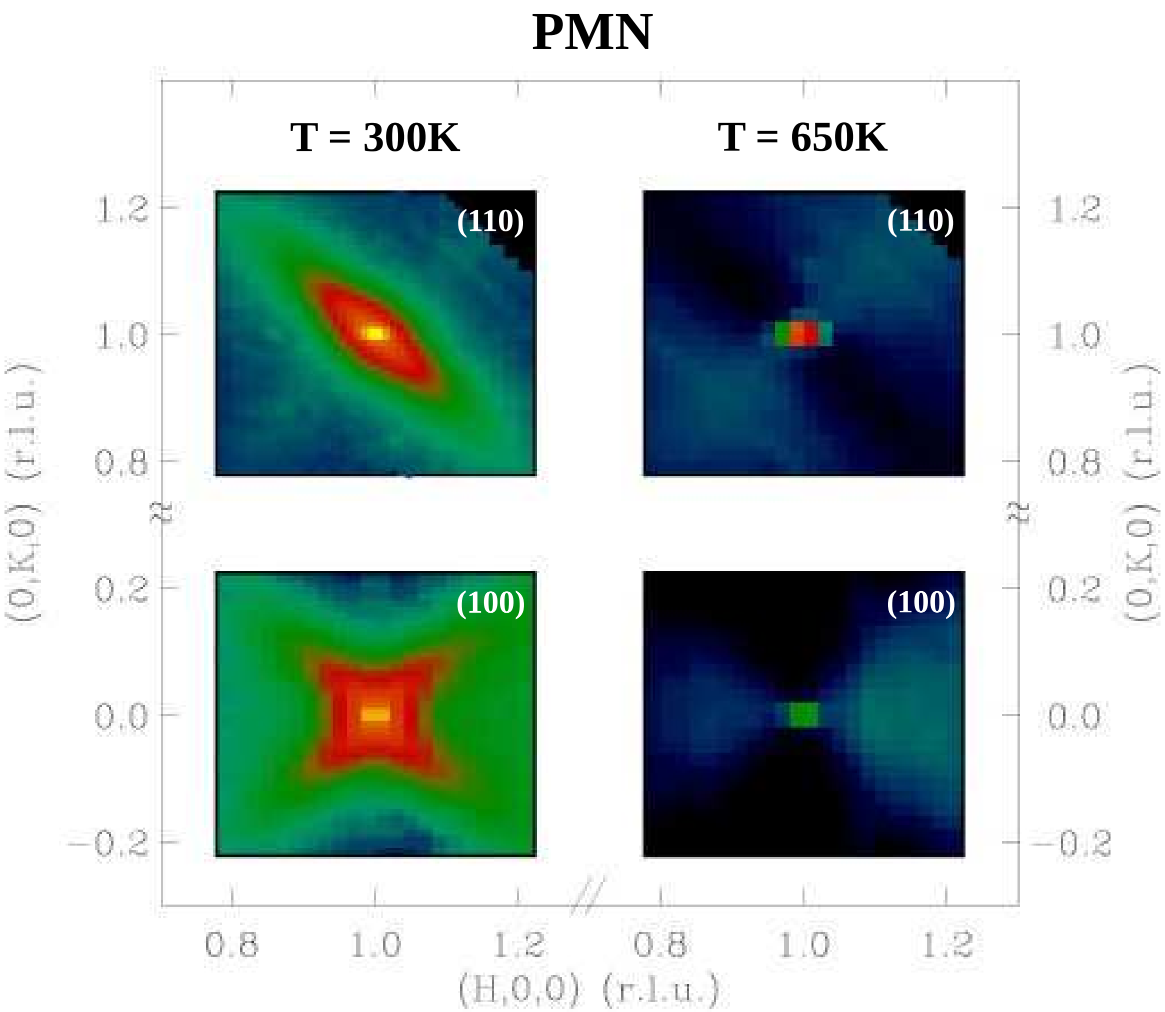
In the cubic phase, no changes are observed. (No energetic incentive.)

In the tetragonal phase, the diffuse scattering along (003) decreases, i.e. the net atomic displacements along E // [001] diminish as expected.

However, the diffuse scattering along (300) is unaffected, i.e. the net atomic displacements perpendicular to E // [001] don't change.

Short-Range Order: Diffuse Scattering

High Temperature Diffuse Scattering for $T > T_d$.



Polar diffuse scattering vanishes above T_d ~ 420K.

Measurements above Td show the presence of weak diffuse scattering.

We attribute this to the short-range chemical disorder.

Hiraka *et al*., Phys. Rev. B **70**, 184105 (2004).

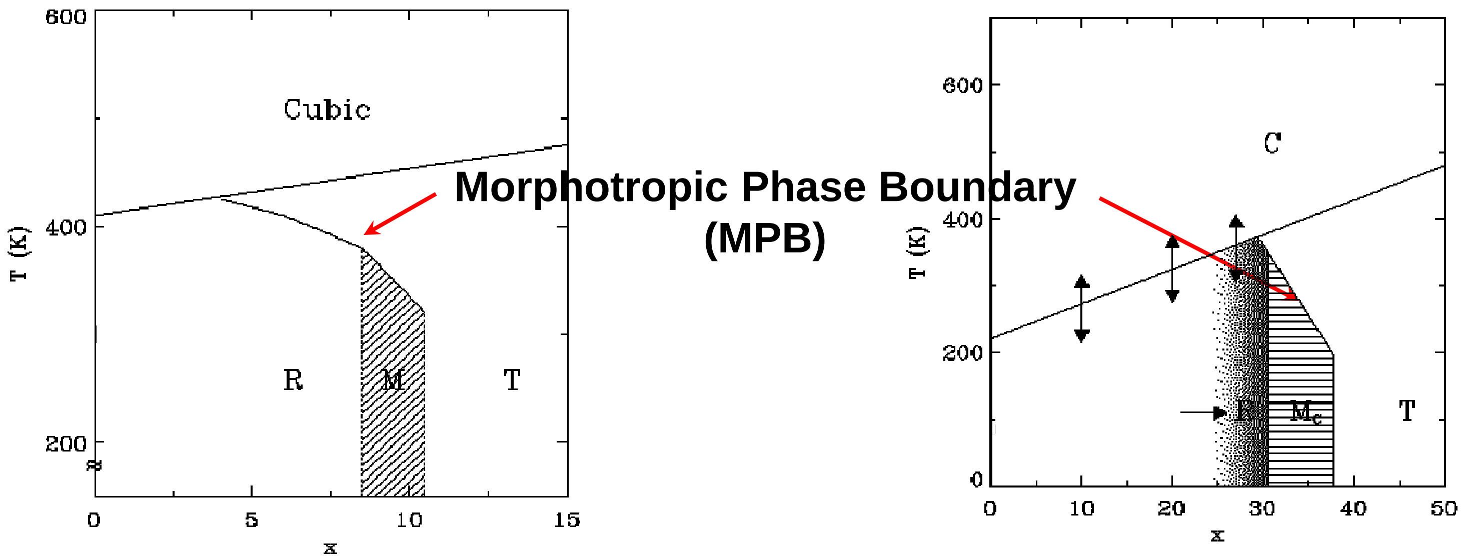
Phase Diagram and Notation

$PbZn_{1/3}Nb_{2/3}O_3$ → PZN

(1-x) PZN + x $PbTiO_3$ → PZN-xPT

$PbMg_{1/3}Nb_{2/3}O_3$ → PMN

(1-x) PMN + x $PbTiO_3$ → PMN-xPT



Energy (ħω) Resolution

ħω-Resolution Matters!