The Swiss-Norwegian Beam Lines at ESRF

A NEW MODEL OF CORRELATED DISORDER IN RELAXOR FERROELECTRICS

Alexeï Bosak

Dmitry Chernyshov

Sergey Vakhrushev

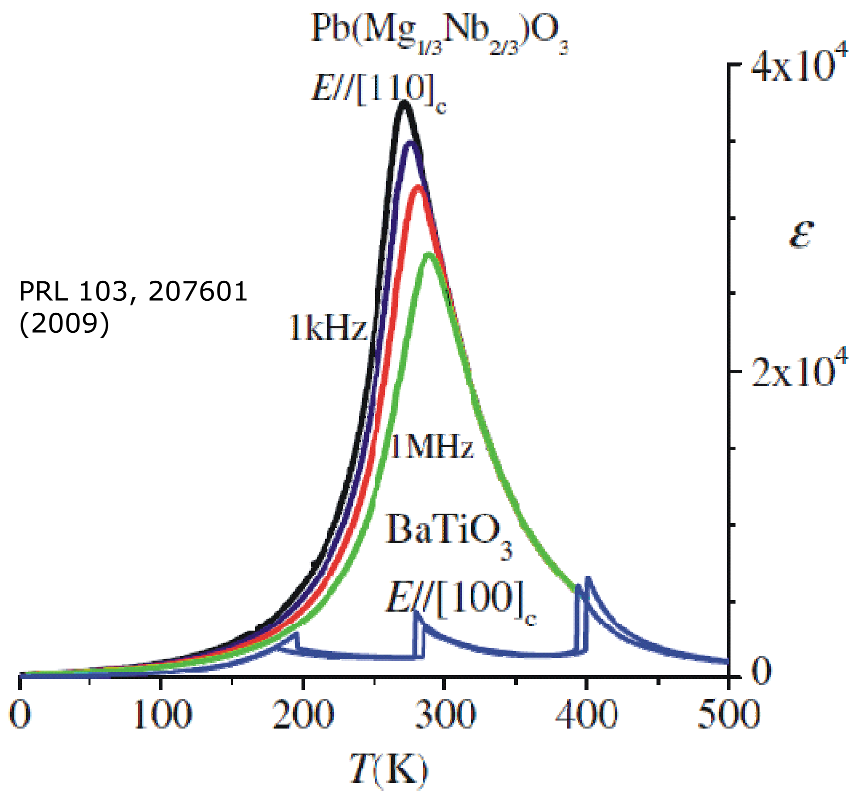
Michael Krisch

Лаборатория нейтронных исследований ФТИ им. А.Ф. Иоффе РАН 2010

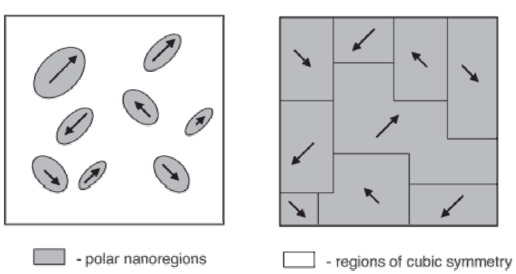
Фонд Дмитрия Зимина

Династия

Why relaxors and diffuse scattering?



PRL 103, 207601 (2009)



Relaxors are interesting

- ❑ Broad frequency-dependent peak of susceptibility
- ❑ No change of the average structure
- ❑ No macroscopic polarization

Relaxors are disordered

Chemically ordered regions (COR)
Static polar nano-regions (PNR)
Polar glass
Soft phonons
Discrete breathers

Disorder is challenging

"Relaxor ferroelectrics were discovered in the 1950s but many of their properties are not understood." AiP 2011

Outline

- Diffuse scattering in relaxors
- What do we measure - the data
- What do we model - PNR
- New parameterization
- Microscopic picture for new model
- Where to move

Well known things - I

- Diffuse scattering in relaxors is well documented

- Diffuse scattering=Relaxor-Specific + TDS + Huang Scattering
- RS component disappears on heating and/or pressure
- Electric field distorts RS component.
- RS scattering has maxima at Bragg nodes and decays as $\frac{1}{q^2}$

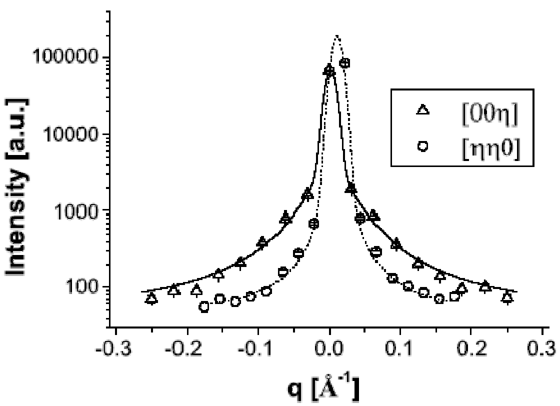
  (in close vicinity of Braggs as $\frac{1}{q^2+k^2}$)

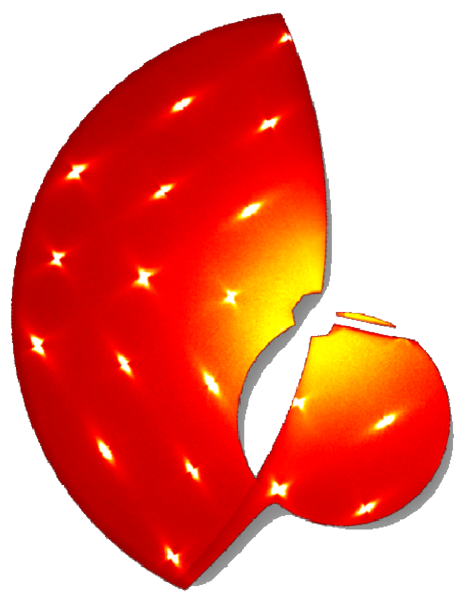
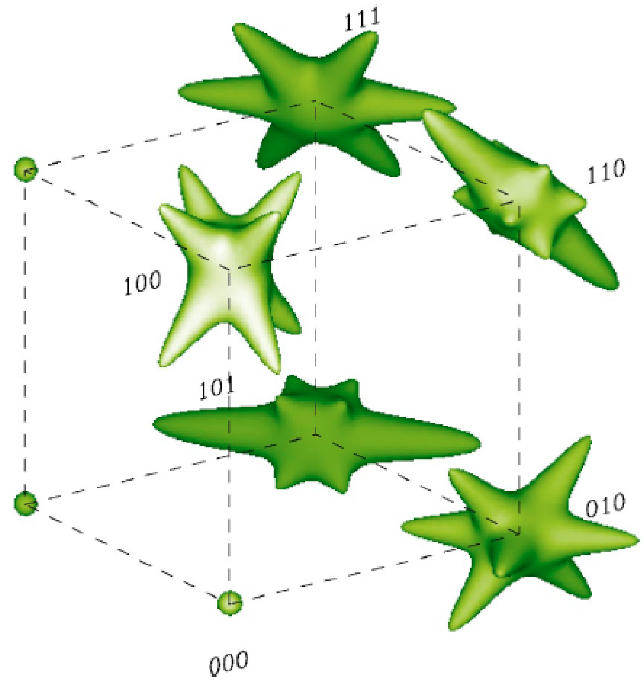
relaxor-specific >> Huang scattering >> thermal diffuse scattering

Gehring et al. PRB 79, 224109 (2009)

Reported DS data

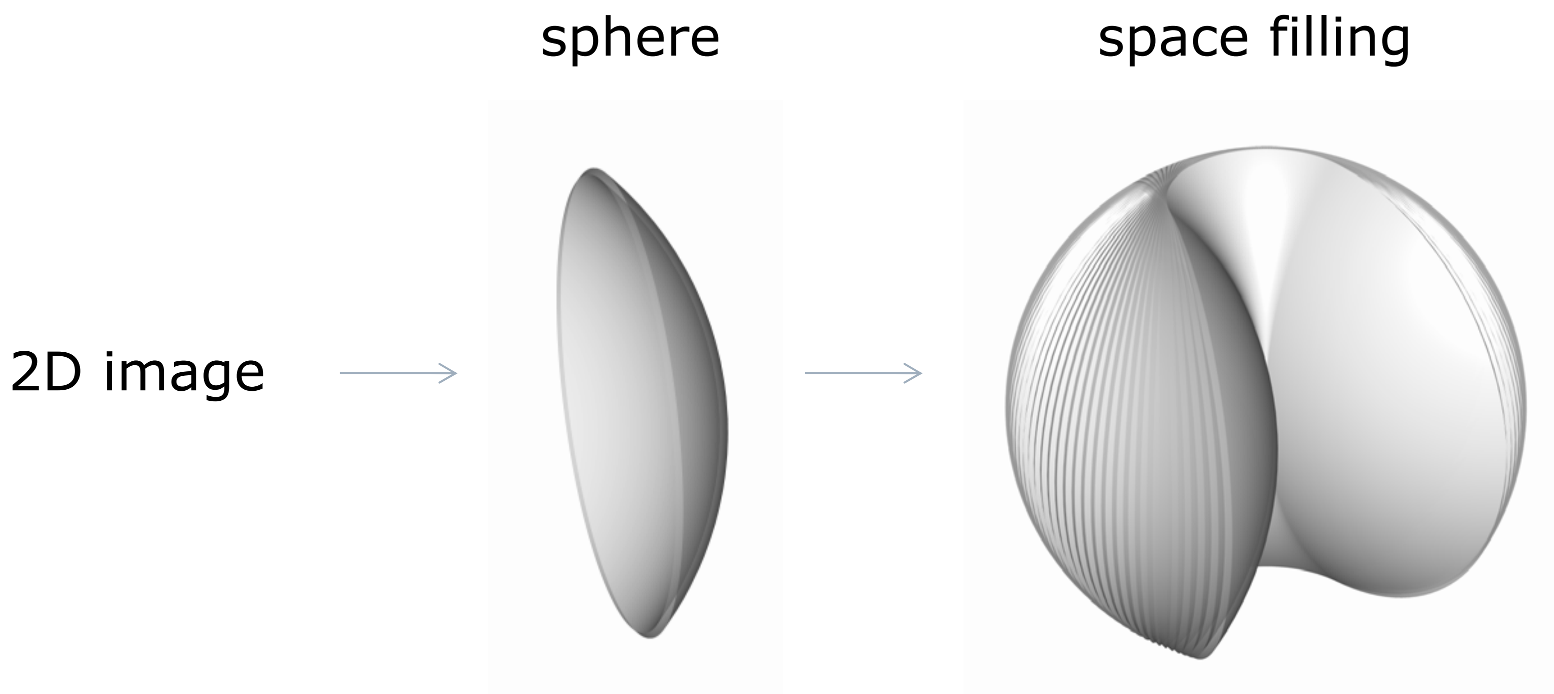
- 1D: line scans
- 2D: flat or curved reciprocal space cuts
- 3D: not yet reported



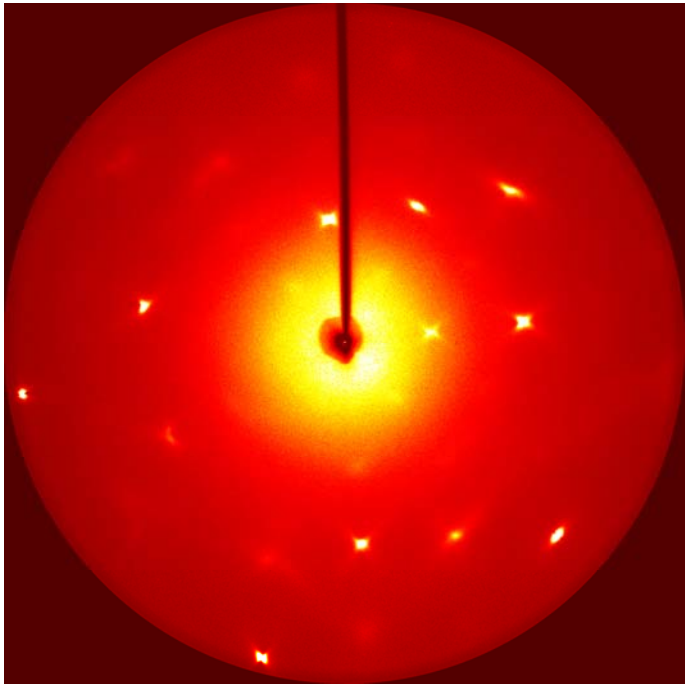
3D mapping

- Laue time-of-flight neutron diffraction
- X-ray area detector data



Experiment

- $PbMg_{1/3}Nb_{2/3}O_3$-$PbTiO_3$ 6%
  50 μm thick needle,
  chemically etched
  SNBL at ESRF / λ = 0.7Å
  MAR345 ImagePlate
  angular step 0.2^0



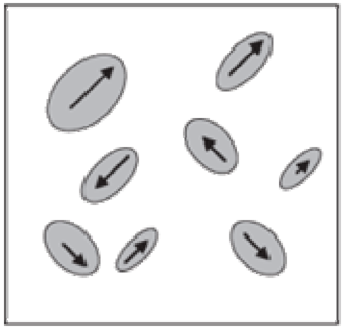
- Data analysis - CrysAlis
- 3D maps – local software
- Visualization – Chimera

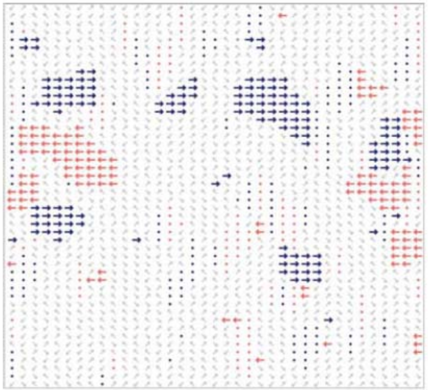
Well known things - II

- Diffuse scattering in relaxors serves as evidence of PNRs

1. Diffuse scattering → parameterization with shaped PRN and local polarization

A. Cervellino et al, J. Appl. Cryst. **44**, 603 (2011)

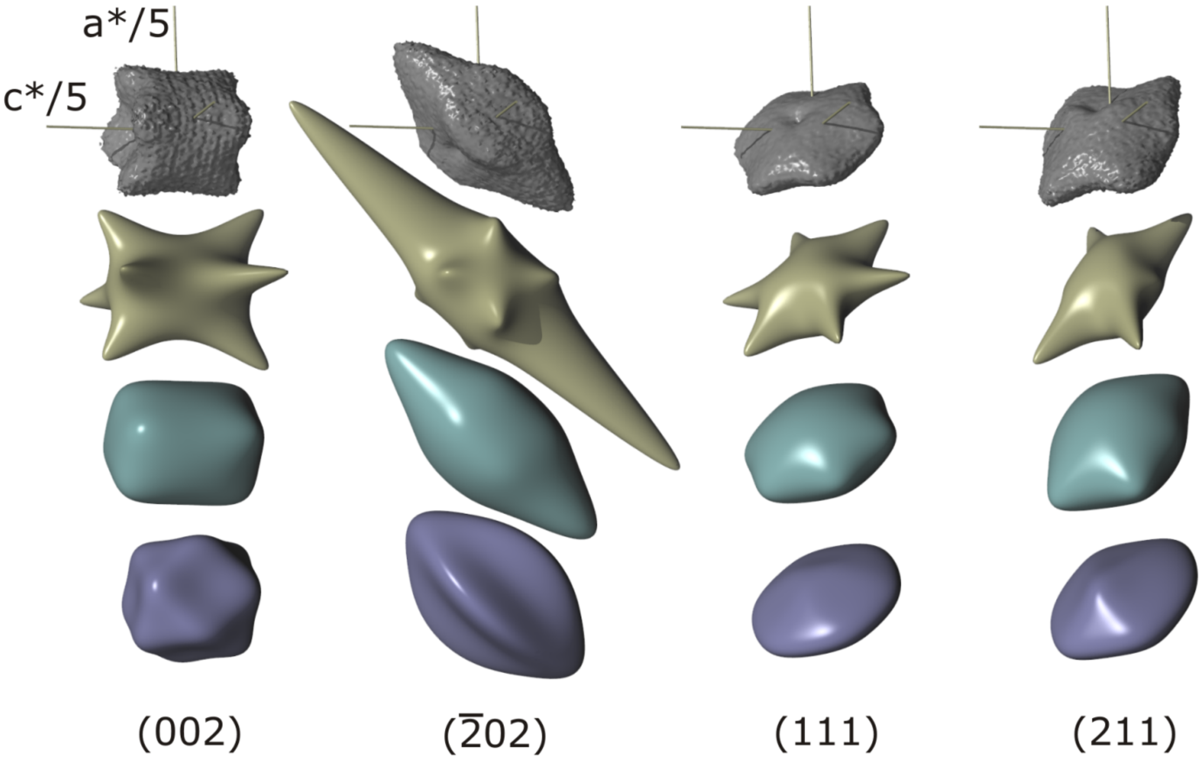




2. Diffuse scattering → MC modeling of polar displacements

M. Pasciak and T.R Welberry, 2011

3D data vs. documented PNR models



experiment

$$G(\mathbf{q}) = \frac{\xi_{//}}{1+q_{//}^2\xi_{//}^2}\,\frac{\xi_{\perp}^2}{\left(1+q_{\perp}^2\xi_{\perp}^2\right)^{3/2}}$$

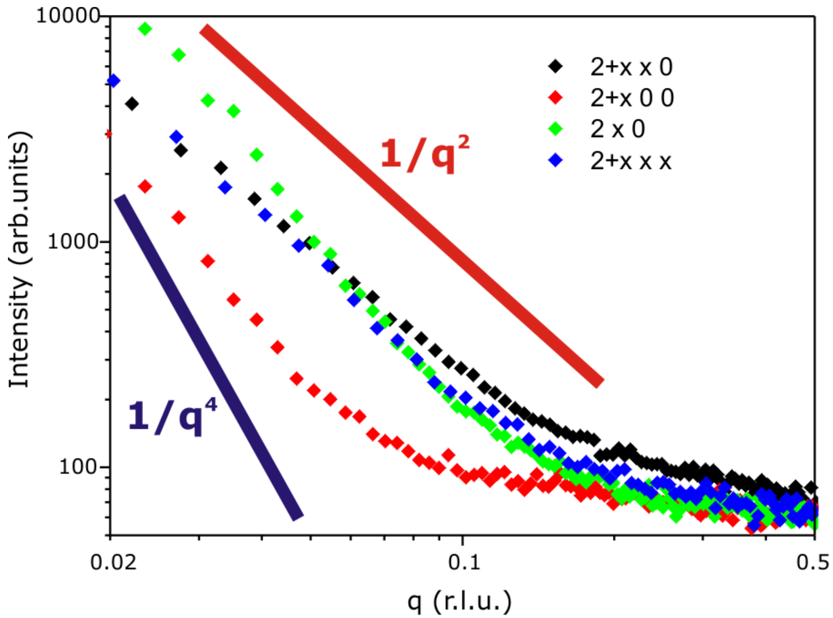
up to 6 parameters

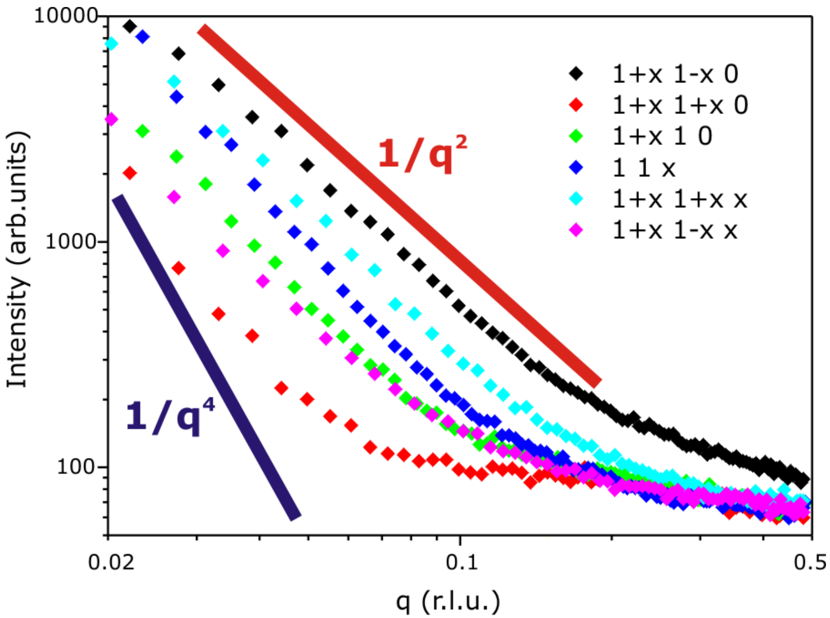
$$G(\mathbf{q}) = \frac{\xi_1\xi_2\xi_3}{\left(1+\left(\xi_1\,\mathbf{w}_1\mathbf{q}\right)^2+\left(\xi_2\,\mathbf{w}_2\mathbf{q}\right)^2+\left(\xi_2\,\mathbf{w}_3\mathbf{q}\right)^2\right)^2}$$

up to 8 parameters

G.Xu, Z. Zhong, H. Hiraka, G. Shirane, Phys. Rev. B **70**, 174109 (2004)
A. Cervellino, S.N. Gvasaliya, O. Zaharko, B. Roessli, G.M. Rotaru, R.A. Cowley, S.G. Lushnikov, T.A. Shaplygina, M.-T. Fernandez-Diaz, J. Appl. Cryst. **44**, 603 (2011)

1D data vs. PNR models





typically decays as ~q^{-2}; never reaches q^{-4}

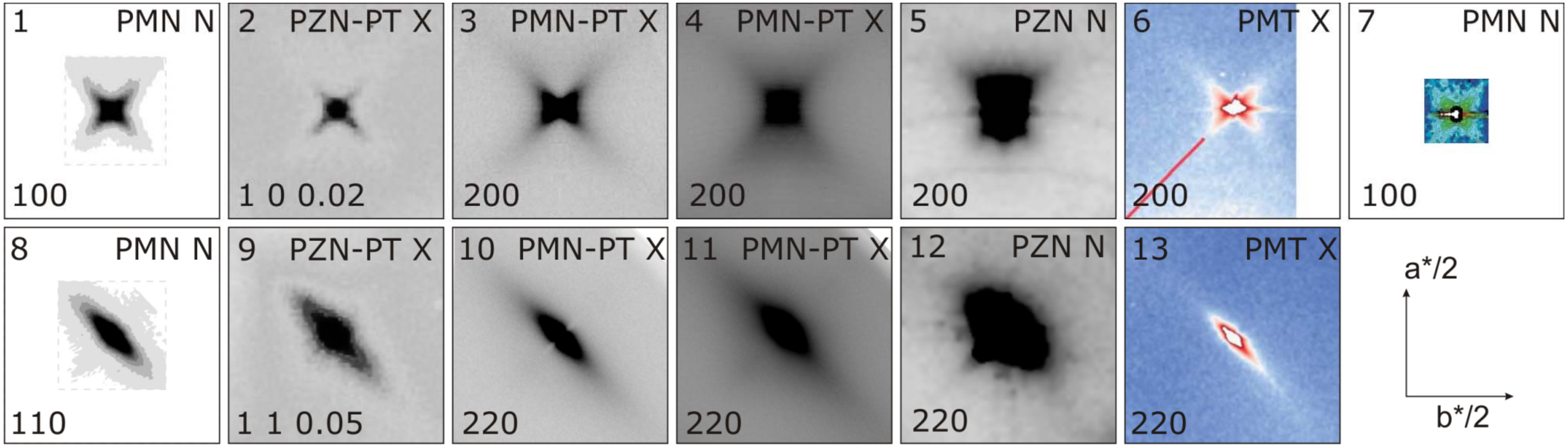
$$G(\mathbf{q}) = \frac{\xi_{//}}{1+q_{//}^2\xi_{//}^2}\frac{\xi_{\perp}^2}{\left(1+q_{\perp}^2\xi_{\perp}^2\right)^{3/2}}$$

$I \sim q^{-2}$ to $I \sim q^{-5}$

$$G(\mathbf{q}) = \frac{\xi_1\xi_2\xi_3}{\left(1+\left(\xi_1\,\mathbf{w}_1\mathbf{q}\right)^2+\left(\xi_2\,\mathbf{w}_2\mathbf{q}\right)^2+\left(\xi_2\,\mathbf{w}_3\mathbf{q}\right)^2\right)^2}$$

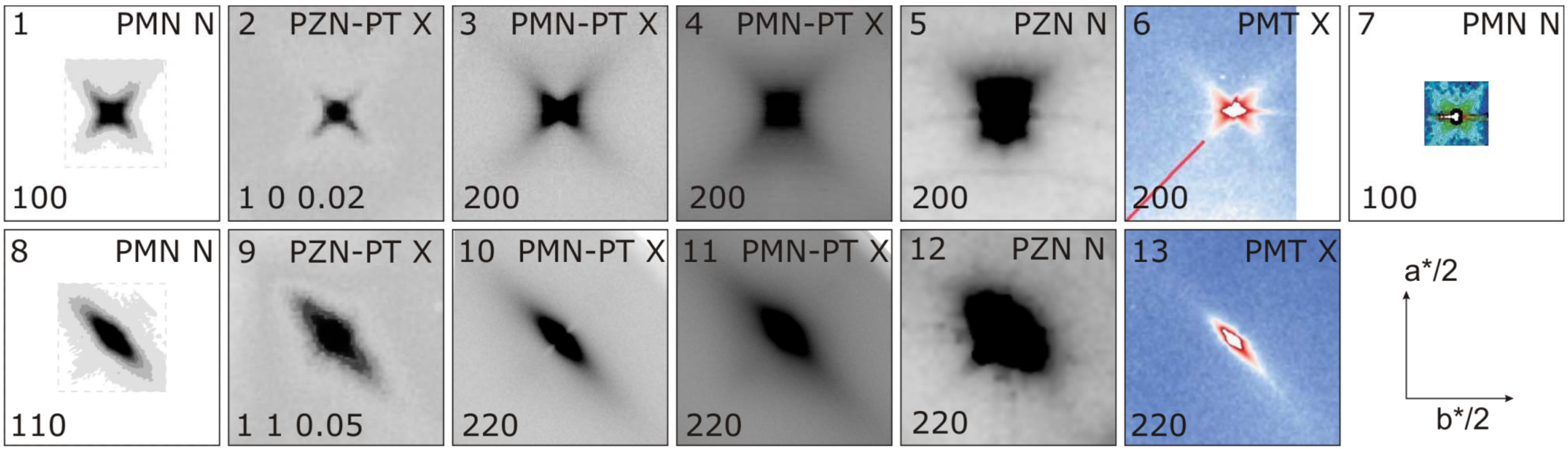
$I \sim q^{-4}$

Comparing 2D data…



Hiraka et al. 2004 | Xu et al. 2004 | this work *thin cut* | this work *thick cut* | Welberry et al. 2008 | Cervellino et al. 2011 | Vakhrushev et al. 2005

Comparing 2D data

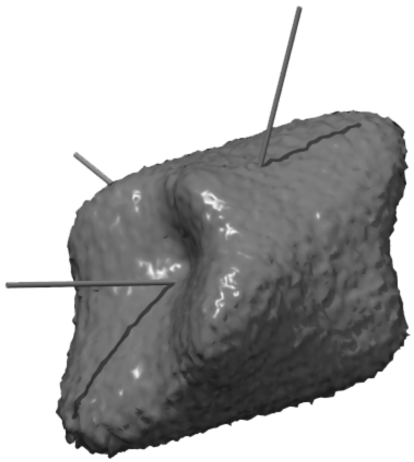


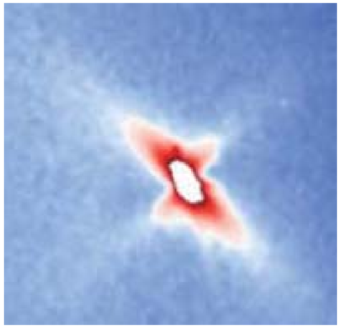
ΔQ_z? misalignment

thick layer?

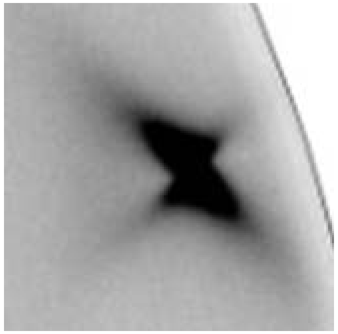
damaged surface
(known)

310 node – 2D and 3D





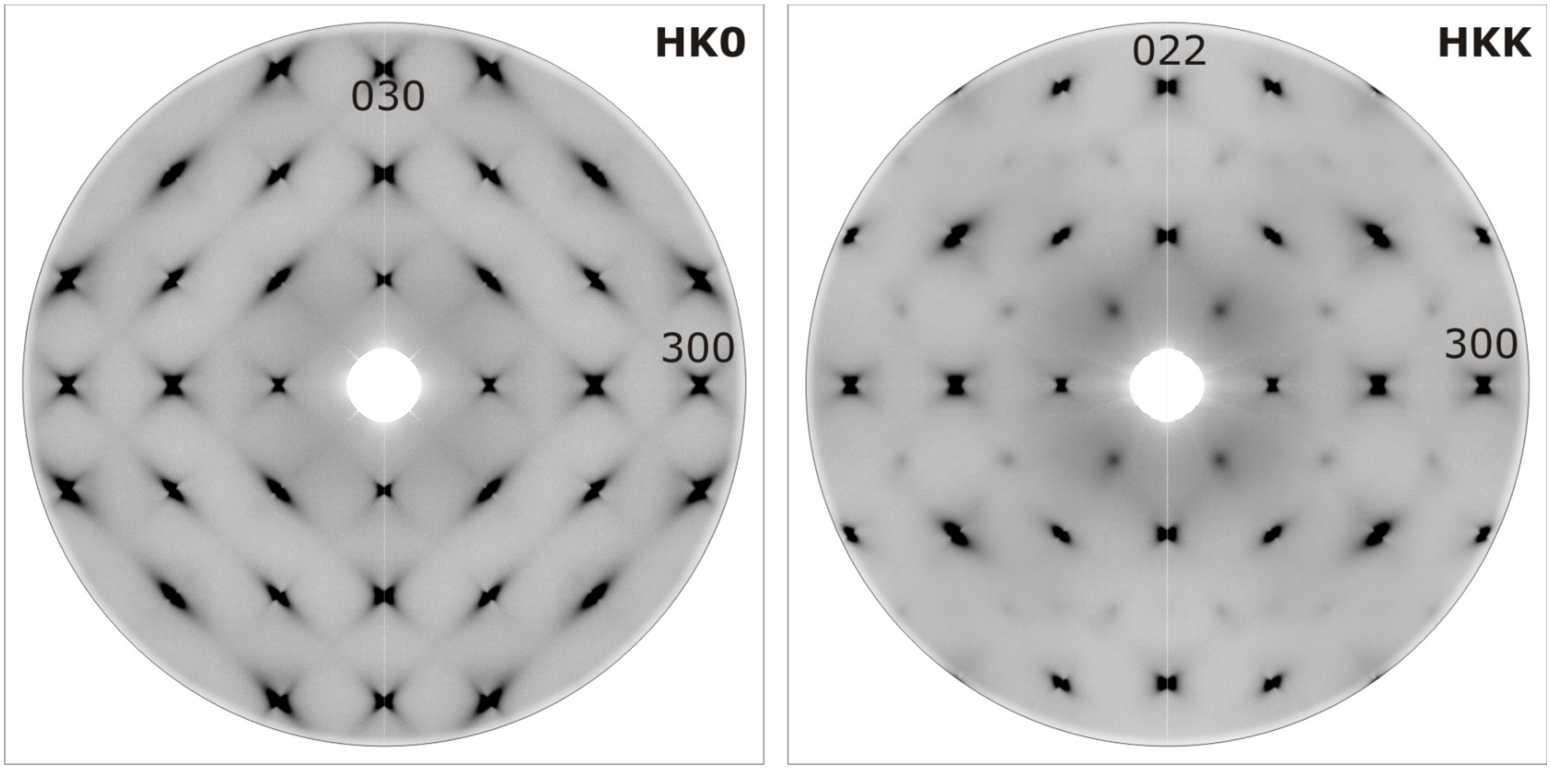
Cervellino et al.
2011



this work
thin cut

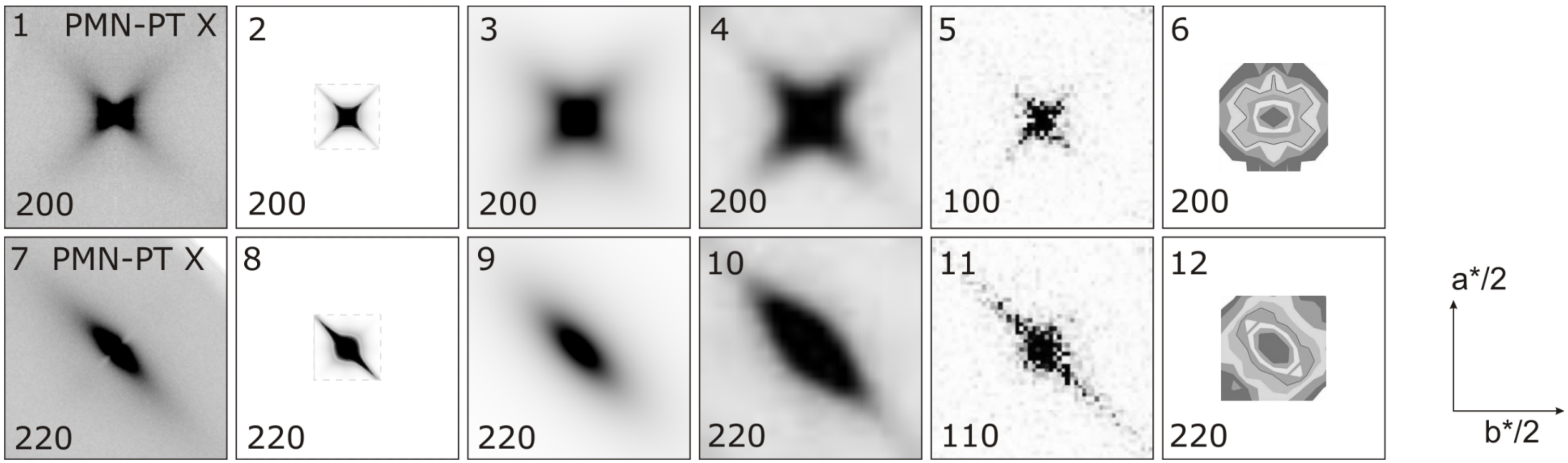
Welberry et al.
2008

Do we care about this difference?



directional minima along τ = **Q** − **q**: *not noted before*
asymmetry of spots out of high symmetry directions: *not noted before*

Incomplete input for modeling



this work *thin cut*	Xu et al. 2004	Cervellino et al. 2011	Welberry et al. 2008	Paściak et al. 2007	Ganesh et al. 2010
experiment	PNR “pancake”	PNR “baguette”	Monte-Carlo	Monte-Carlo	molecular dynamics

directional minima along τ = **Q** – **q**: *never predicted*
asymmetry of spots out of high symmetry directions: *never predicted*

- reverse MC modeling cannot reproduce features not present in the input
- <u>existing phenomenological models have poor descriptive and predictive power</u>

Too complex for simple models?

<u>phenomenological PNR models introduce low-symmetry objects embedded in cubic matrix</u>

- 3 parameters: characteristic lengths ($\xi_\alpha \sim 10$ nm)
- 3 parameters: basis orientation
- 2 parameters: Pb displacement direction

<u>still not enough to reproduce the experimental data</u>

- Wrong q-dependence
- Does not reproduce 2D maps
- Wrong shape in 3D

Is something wrong with the structure of models?
How can one model diffuse scattering in relaxor without having PNRs?

New parametrization

hint: use the analogy with thermal diffuse scattering
average symmetry: cubic
Pb position: delocalized over sphere

$$\boxed{I \propto f_{Pb}^{2}(\mathrm{Q})\exp(\text{-}2\mathrm{W}_{Pb}(\mathrm{Q}))\frac{\sin^2(2\pi r_0 Q)}{\mathrm{Q}^2}\cdot \boldsymbol{Q}^T \cdot \Sigma(\boldsymbol{Q})^{-1}\cdot \boldsymbol{Q}}$$

$$\Sigma_{\alpha\alpha}(\mathbf{Q}) = (1-\mu)\Sigma_{\alpha\alpha}^{pc}(\mathbf{Q}) + \mu\Sigma_{\alpha\alpha}^{fcc}(\mathbf{Q})$$

$$\Sigma_{\alpha\alpha}^{pc}(\mathbf{Q}) = 2\Psi_{11}(1-\cos(2\pi Q_\alpha)) + 2\Psi_{44}(2-\cos(2\pi Q_\beta)-\cos(2\pi Q_\gamma))$$

$$\Sigma_{\alpha\alpha}^{fcc}(\mathbf{Q}) = \Psi_{11}(2-\cos(2\pi Q_\alpha)(\cos(2\pi Q_\beta)+\cos(2\pi Q_\gamma))) + (2\Psi_{44}-\Psi_{12})(1-\cos(2\pi Q_\beta)\cos(2\pi Q_\gamma))$$

$$\Sigma_{\alpha\beta}(\mathbf{Q}) = (\Psi_{44}+\Psi_{12})\sin(2\pi Q_\alpha)\sin(2\pi Q_\beta)$$

Ψ_{ijkl} is of cubic symmetry: 3 invariants

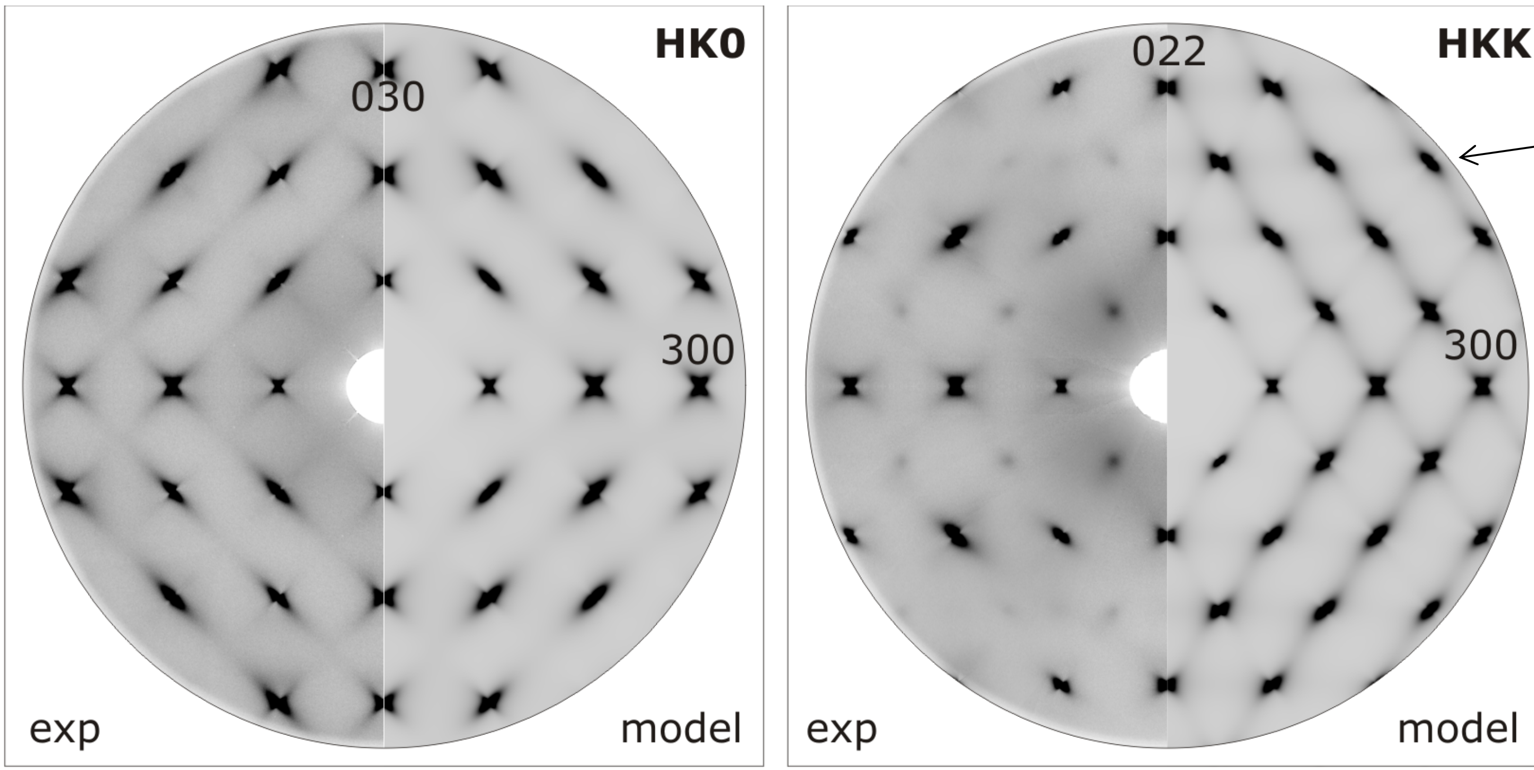
analogy with $\boldsymbol{D}(\mathbf{Q})$
for monoatomic lattice

Ψ is **not** elastic tensor

2 adjustable parameters: i.e. Ψ_{11}/Ψ_{12} and Ψ_{11}/Ψ_{44}; large q: adjustable μ

for the prototype formulae see A. Bosak, D. Chernyshov, Acta Cryst. A **64**, 598 (2008)

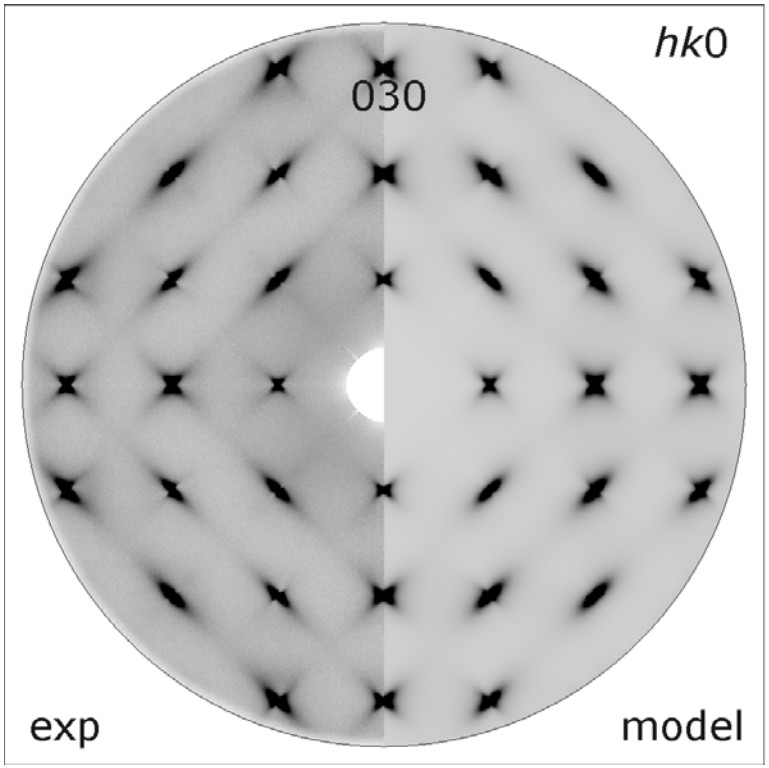
New parametrization: 2D

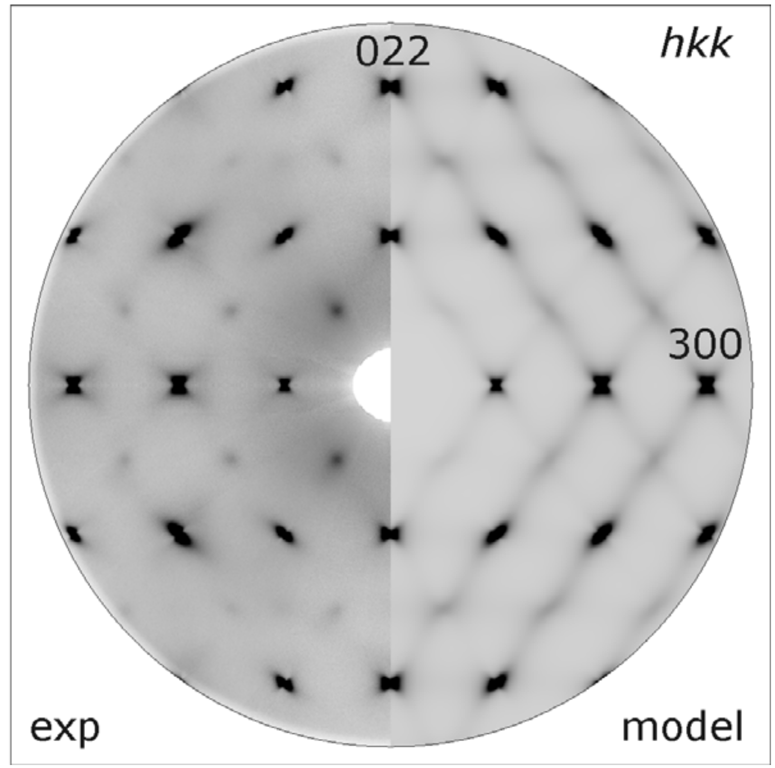


artifacts due
to the fake
FCC structure

shape in the proximity of nodes: **reproduced**
decay: **automatically q^{-2}**
relative intensities of spots: **qualitatively reproduced**

New parametrization: 2D

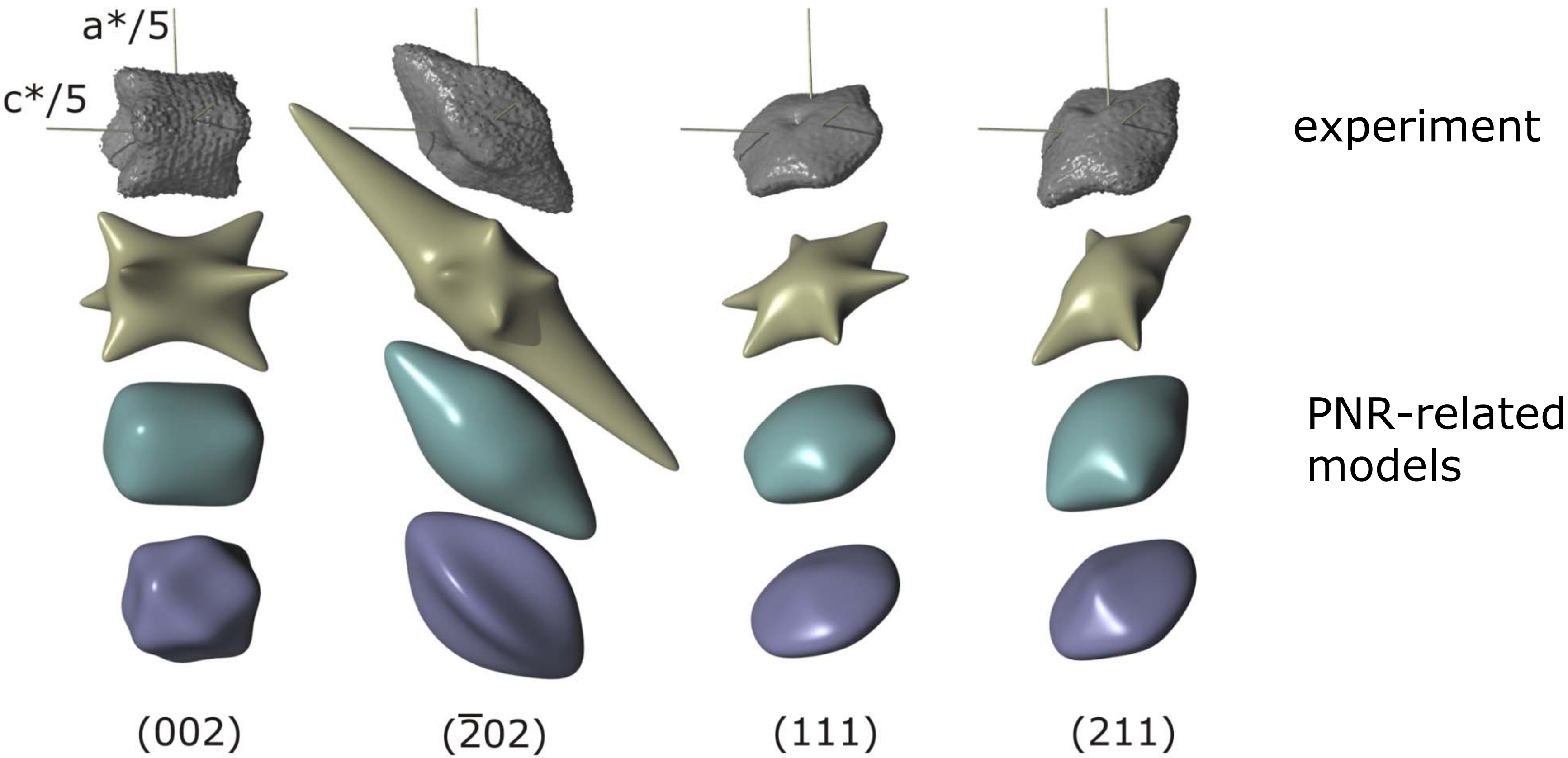




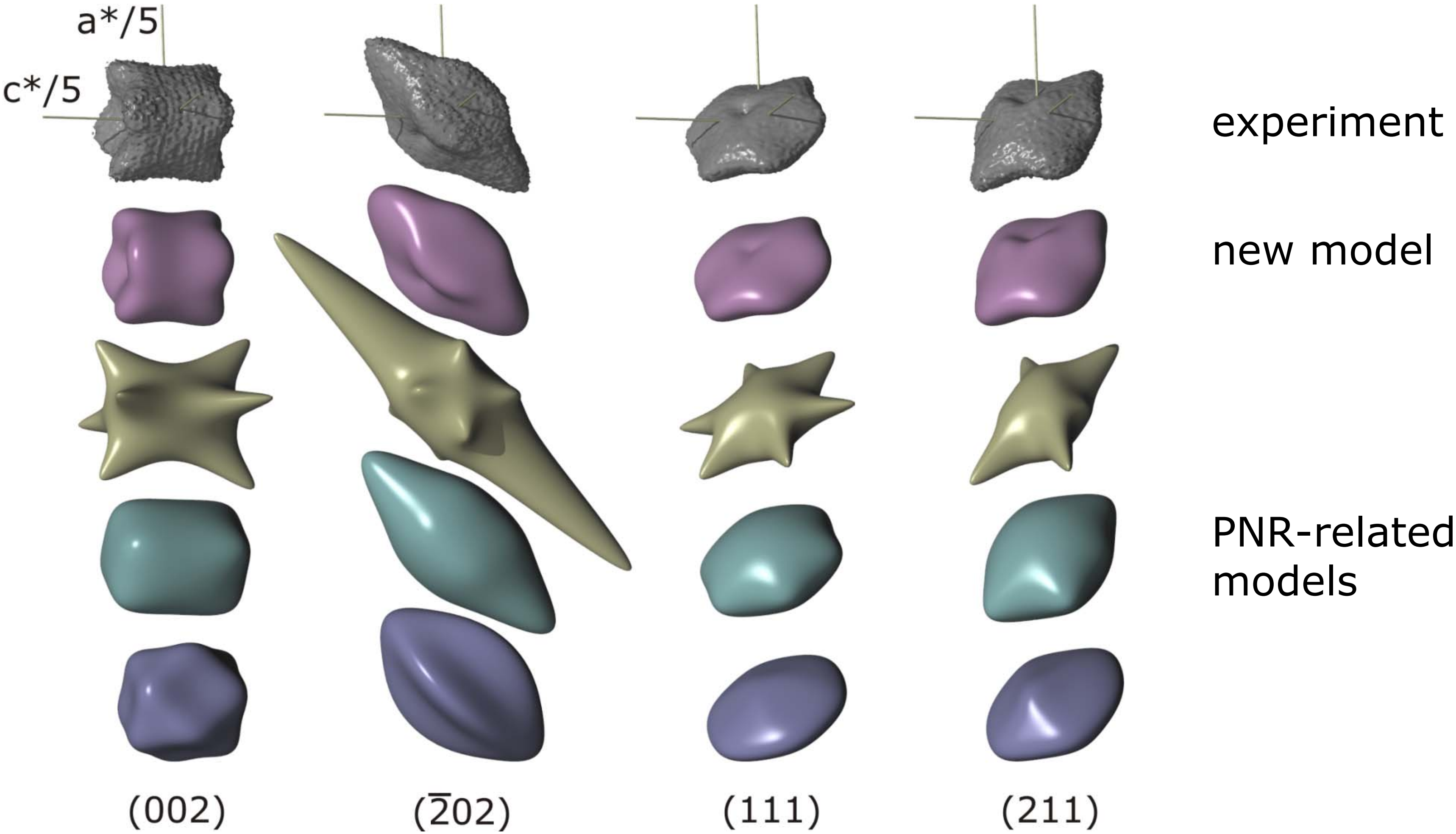
μ = **0.95**

shape in the proximity of nodes: **reproduced**
decay: **automatically q^{-2}**
relative intensities of spots: **qualitatively reproduced**

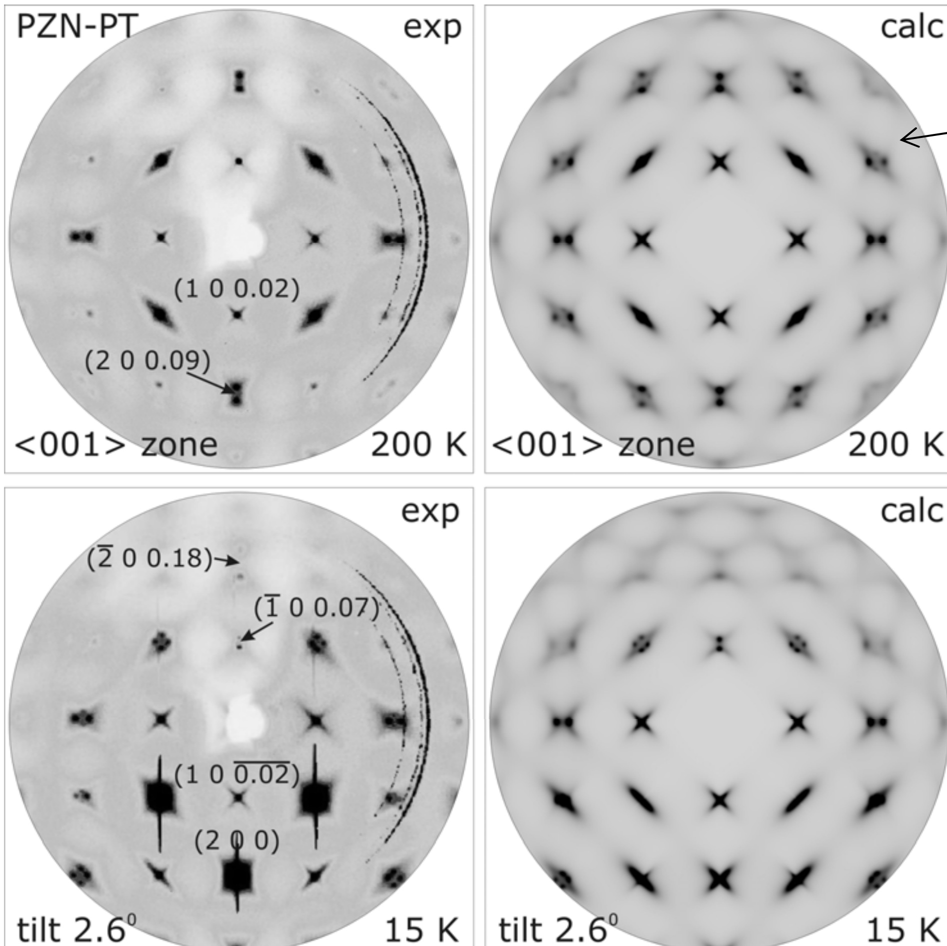
New parametrization: 3D



New parametrization: 3D



Reconciling with the old data



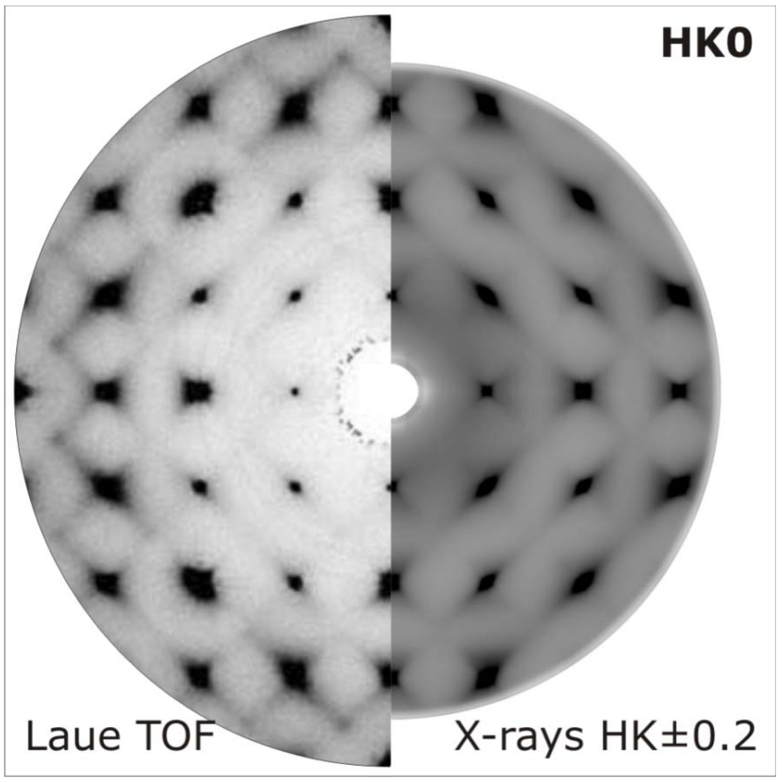
Ψ_{12} increased by 20% *vs.* PMN-PT

no artificial low-symmetry entities are introduced

cubic symmetry **only**

experimental data for PZN-PT:
G.Xu, Z. Zhong, H. Hiraka, G. Shirane, Phys. Rev. B **70**, 174109 (2004)

Laue TOF *vs.* X-ray scattering



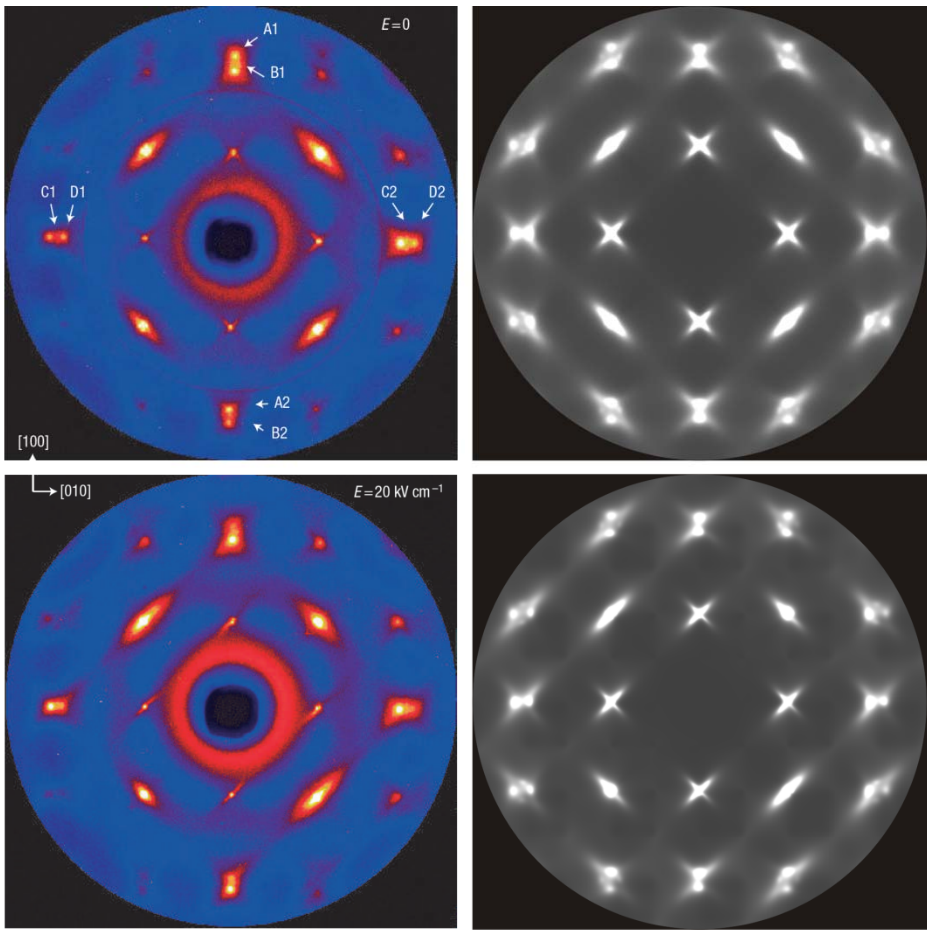
main features of Laue TOF pattern are reproduced when the integration layer thickness of ±0.15-0.2 r.l.u. is taken

T.R. Welberry, Metallurgical and Materials Transactions A, 39A, 3170 (2008)

More than description…

- 2 parameter TDS-like formalism reproduces experimental 1D, 2D, and 3D data better than any PNR models
- Parametric model could be used for structure-property correlations
- It also has a *predictive power* – what would be under electric field?

Electric field effect



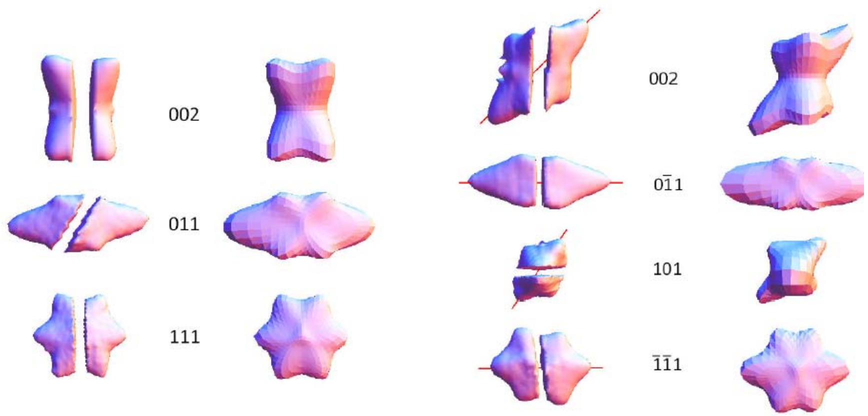
exp model

experimental data for PZN-PT:
G. Xu, Z. Zhong, Y. Bing,
Z.-G. Ye, G. Shirane,
Nature Materials **5**, 134 (2006)

field applied along <111>
intensity redistribution and pattern symmetry lowering is reproduced by replacing the uniform distribution of Pb displacements over sphere by ellipsoid-like distribution with <u>1 parameter</u>

Pleasant surprise

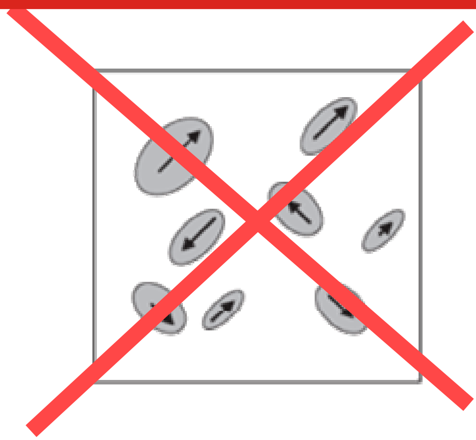
MS30.P08(C417) | B.A. Frandsen: Quantitative modeling of diffuse scattering from a relaxor ferroelectric



No field applied With field applied

- 3D reconstructions from CCD images
- similar low-q formalism, based on purely cubic symmetry

If no polar domains – than what?



?

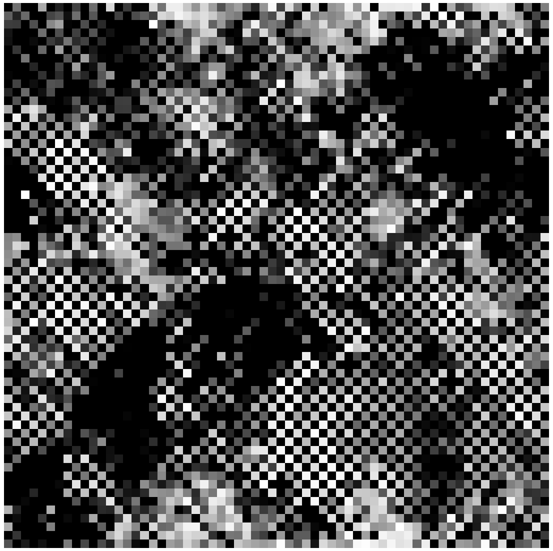
Parameterization can be used to generate real space structure with required correlation properties

Ψ_{11}/Ψ_{12} and Ψ_{11}/Ψ_{44} $\to \Re(\mathbf{Q}) \to \mathbf{U}(\mathbf{Q}) \to \mathbf{P}_i$

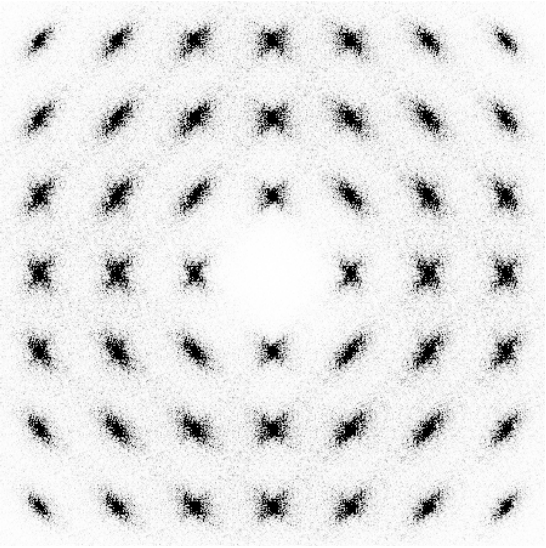
(as before we consider only lead subattice)

Real space model: concept at work

- cluster 64^3 was populated by $3*64^3$ waves with random phases and appropriate amplitudes
- all local displacements were normalized to the radius of Pb sphere (e.g. 0.08*a*)



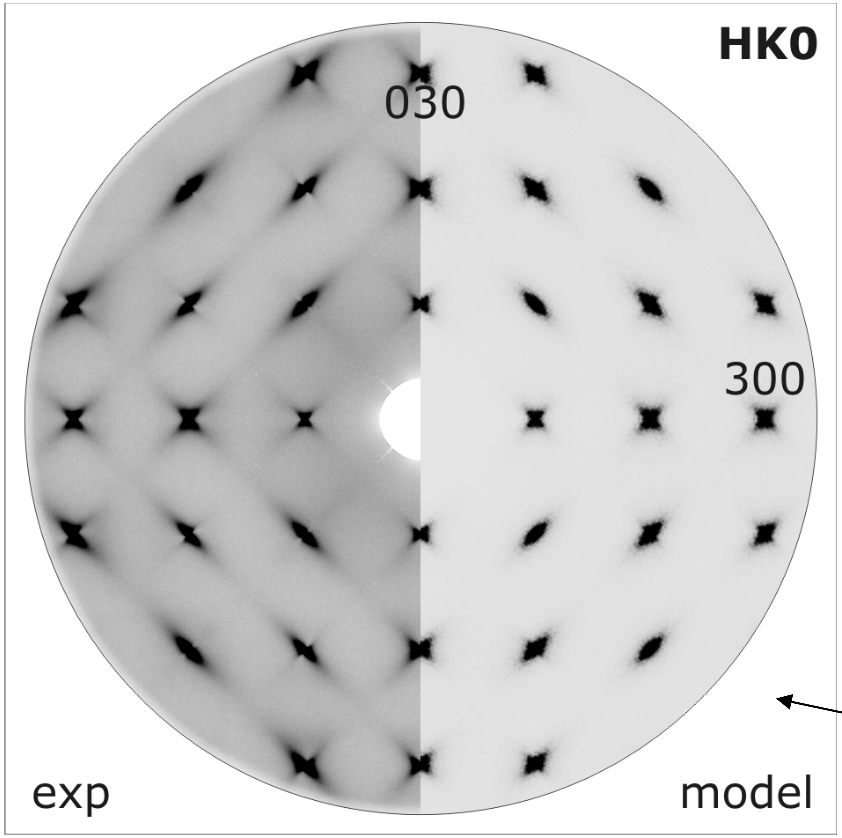
cut of real space cluster
x component



HK0 scattering from cluster
decay as q^{-2}

Real space model: concept does work

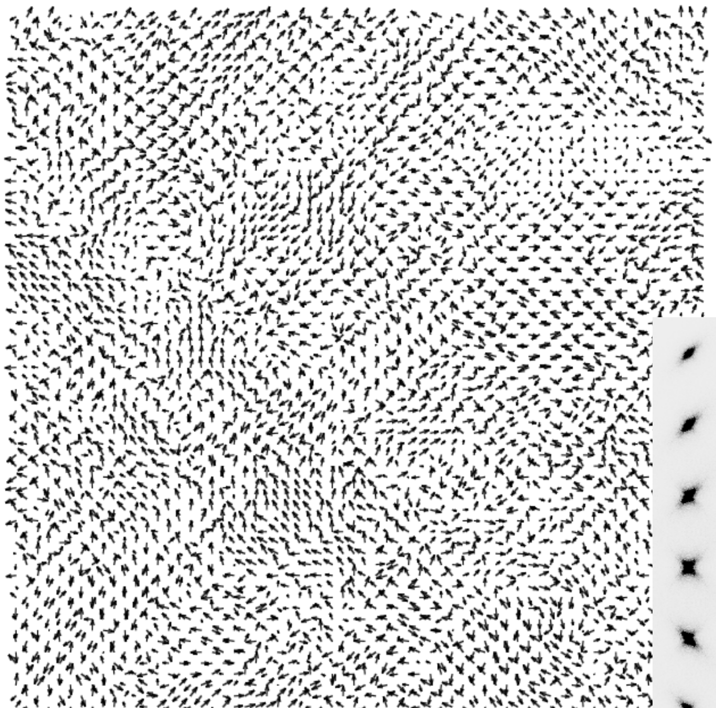
- 4 clusters generated + Laue averaging (x48)



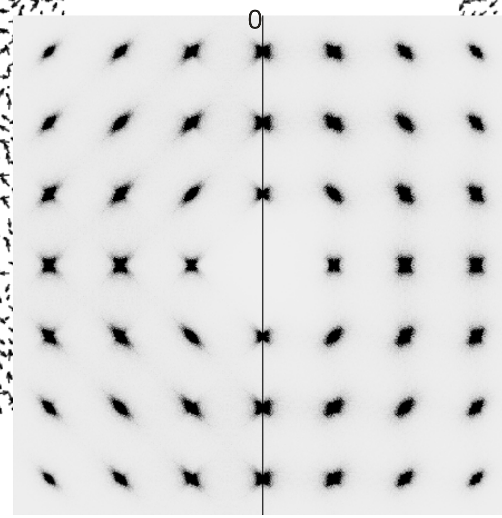
experimental scattering can be reproduced by Pb displacement pattern **without introducing PNRs**

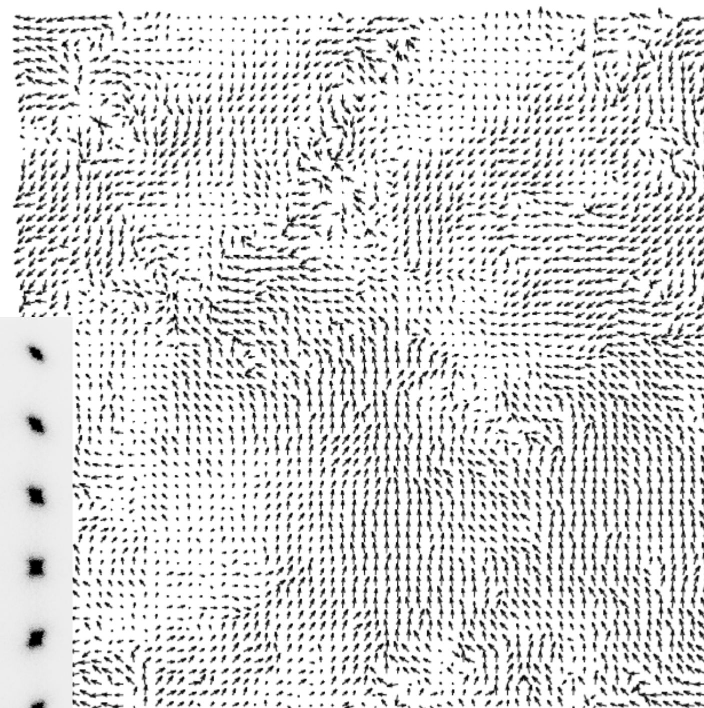
microscopic model!

Real space model: displacement pattern



100 nm

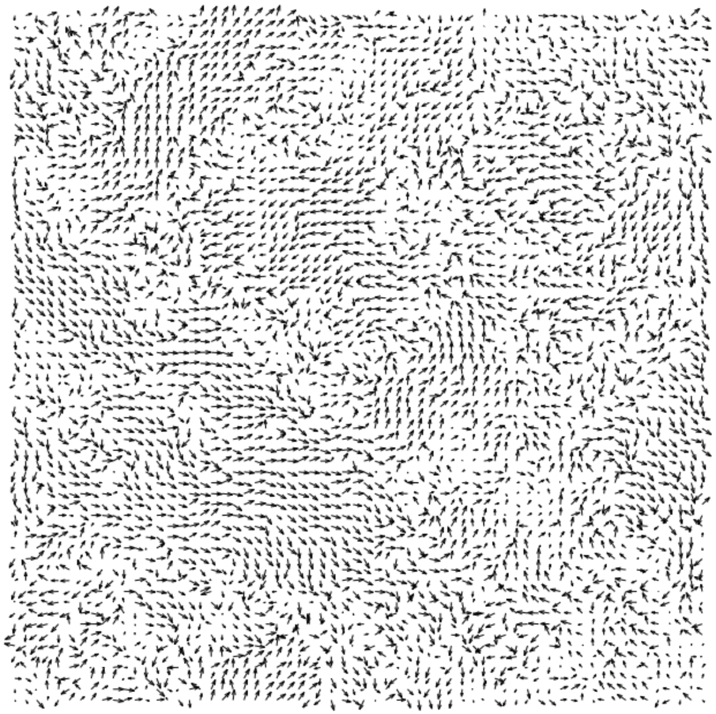




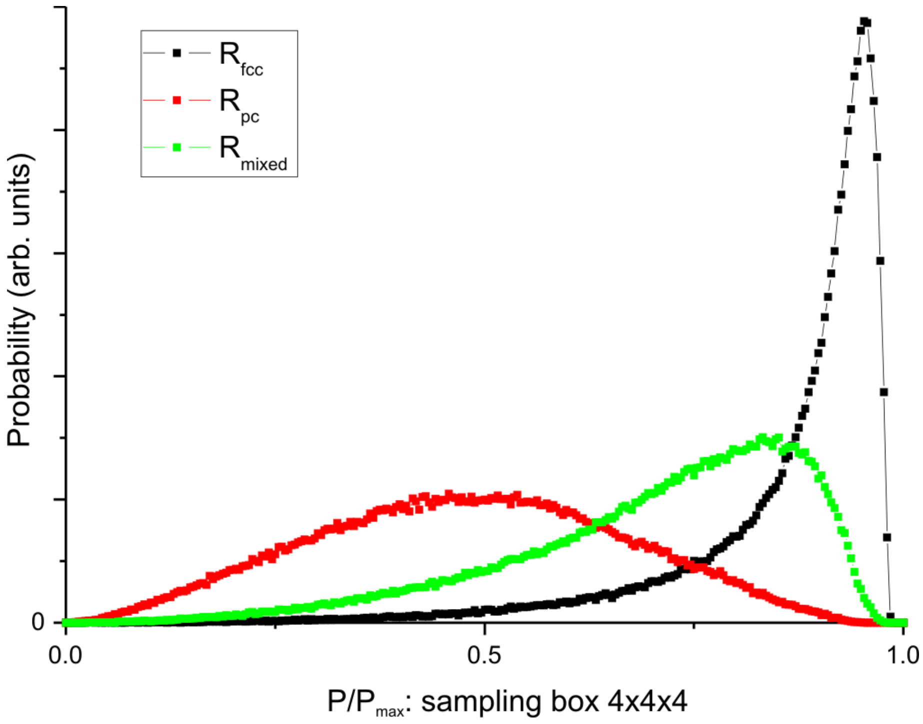
fcc-like model

primitive cubic model

Real space model: displacement pattern

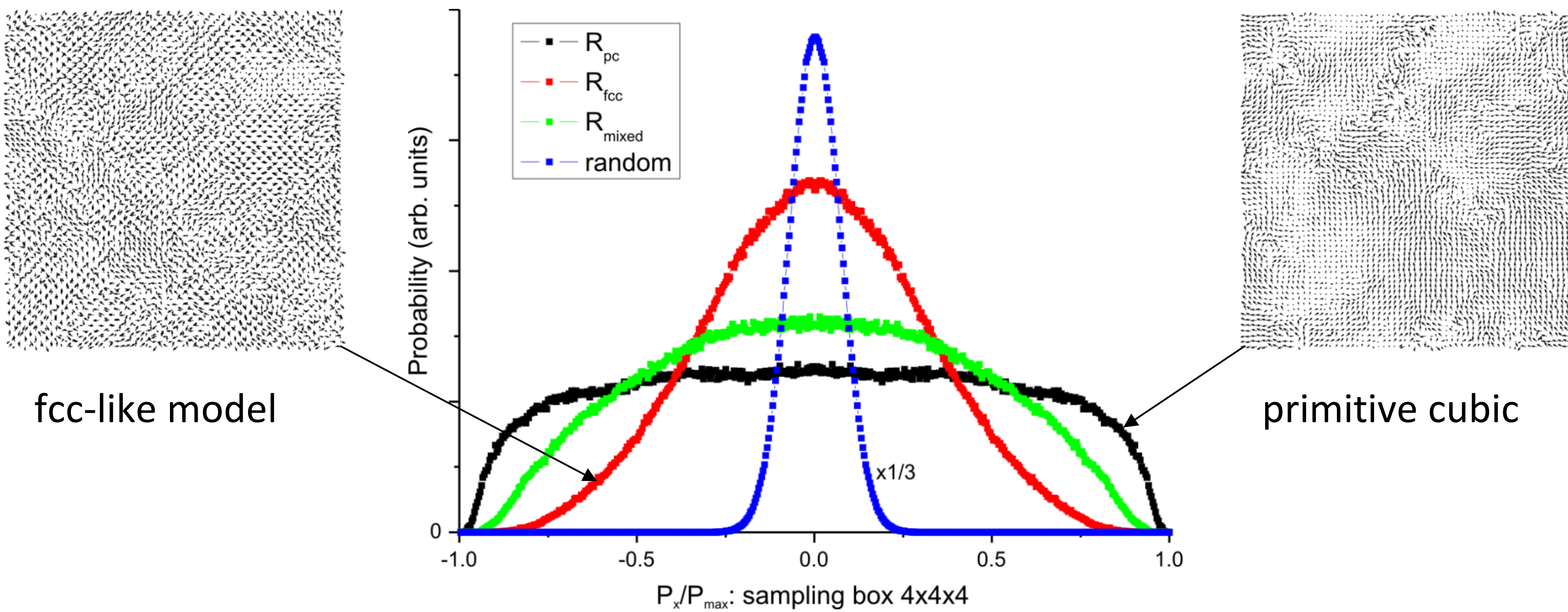


mixed model



$$\Re_{mixed}(\mathbf{Q}) = \mu\Re_{fcc}(\mathbf{Q}) + (1-\mu)\Re_{pc}(\mathbf{Q})$$

Local polarisation

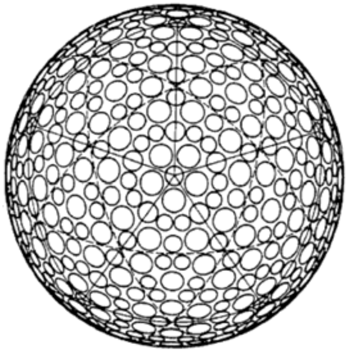


Using 2D ^{93}Nb NMR, the probability distribution of local polarization in PMN is found to be Gaussian

[R. Blinc, J. Dolinšek, A. Gregorovič, B. Zalar, C. Filipič, Z. Kutnjak, A. Levstik, and R. Pirc, Phys. Rev. Lett. 83, 424 (1999)]

Microscopic model behind

- The set of possible positions of Pb is very large and can be approximated by a spherical shell
- Pb ions interact essentially *via* the BO_3 octahedral framework; they can be aligned by a dynamical local distortion - phonon with sufficient amplitude and proper polarization
- The probability of switching is therefore inversely proportional to the frequency of the wave ($\sim\omega^{-2}$ for $\hbar\omega << k_B T$), and the Pb displacement pattern remains frozen, unless it is affected by another wave/phonon. The quasielastic diffuse scattering mimics the thermal diffuse scattering pattern from acoustic phonons



golf ball
U.S. Patent 4,560,168

- Relaxor-specific component of diffuse scattering (RSDS) should disappear at high temperature as Pb displacements will become a free uncorrelated movement over the spherical shell
- RSDS should disappear under high pressure as Pb ions will be immobilised in the emerging local minima on the sphere
- RSDS should deform in an applied electric field as Pb ions as additional anisotropy will be created over the displacement shell; features perpendicular to the field direction should shrink
- The naturally created hierarchy of displacement patterns in space and their respective lifetimes should result in the large spread of relaxation times
- The uniform slow fading of polarization in switched domain without wall movement is also in line with our concept.

- X Relaxor-specific component of diffuse scattering (RSDS) should disappear at high temperature as Pb displacements will become a free uncorrelated movement over the spherical shell
- RSDS should disappear under high pressure as Pb ions will be immobilised in the emerging local minima on the sphere
- RSDS should deform in an applied electric field as Pb ions as additional anisotropy will be created over the displacement shell; features perpendicular to the field direction should shrink
- The naturally created hierarchy of displacement patterns in space and their respective lifetimes should result in the large spread of relaxation times
- The uniform slow fading of polarization in switched domain without wall movement is also in line with our concept.

H. Hiraka, S.-H. Lee, P.M. Gehring, G. Xu, G. Shirane, Phys. Rev. B **70**, 184105 (2004)

- X Relaxor-specific component of diffuse scattering (RSDS) should disappear at high temperature as Pb displacements will become a free uncorrelated movement over the spherical shell
- X RSDS should disappear under high pressure as Pb ions will be immobilised in the emerging local minima on the sphere
- RSDS should deform in an applied electric field as Pb ions as additional anisotropy will be created over the displacement shell; features perpendicular to the field direction should shrink
- The naturally created hierarchy of displacement patterns in space and their respective lifetimes should result in the large spread of relaxation times
- The uniform slow fading of polarization in switched domain without wall movement is also in line with our concept.

J. Kreisel, P. Bouvier, B. Dkhil, B. Chaabane, A. Glazer, P. Thomas, T. Welberry, Ferroelectrics **302**, 293 (2004)

- ☒ Relaxor-specific component of diffuse scattering (RSDS) should disappear at high temperature as Pb displacements will become a free uncorrelated movement over the spherical shell
- ☒ RSDS should disappear under high pressure as Pb ions will be immobilised in the emerging local minima on the sphere
- ☒ RSDS should deform in an applied electric field as Pb ions as additional anisotropy will be created over the displacement shell; features perpendicular to the field direction should shrink
- ☐ The naturally created hierarchy of displacement patterns in space and their respective lifetimes should result in the large spread of relaxation times
- ☐ The uniform slow fading of polarization in switched domain without wall movement is also in line with our concept.

G. Xu, Z. Zhong, Y. Bing, , Z.-G. Ye, G. Shirane, Nature Materials **5**, 134 (2006)
S.B. Vakhrushev, A.A. Naberezhnov, N.M. Okuneva, B.N. Savenko, Phys. Solid State **40**, 1728 (1998)

- X Relaxor-specific component of diffuse scattering (RSDS) should disappear at high temperature as Pb displacements will become a free uncorrelated movement over the spherical shell
- X RSDS should disappear under high pressure as Pb ions will be immobilised in the emerging local minima on the sphere
- X RSDS should deform in an applied electric field as Pb ions as additional anisotropy will be created over the displacement shell; features perpendicular to the field direction should shrink
- X The naturally created hierarchy of displacement patterns in space and their respective lifetimes should result in the large spread of relaxation times
- The uniform slow fading of polarization in switched domain without wall movement is also in line with our concept.

D. Viehland, S.J. Jang, L.E. Cross, M. Wutting, J. Appl. Phys. **68**, 2916 (1990)

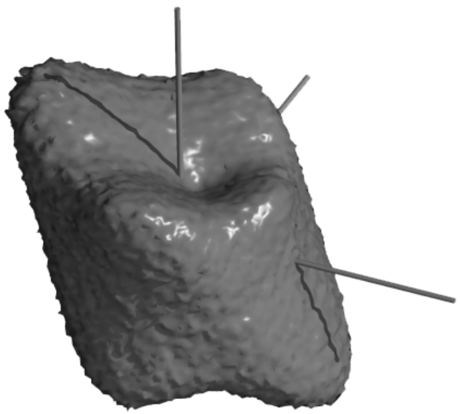
- Relaxor-specific component of diffuse scattering (RSDS) should disappear at high temperature as Pb displacements will become a free uncorrelated movement over the spherical shell
- RSDS should disappear under high pressure as Pb ions will be immobilised in the emerging local minima on the sphere
- RSDS should deform in an applied electric field as an additional anisotropy will be created over the displacement shell; features perpendicular to the field direction should shrink
- The naturally created hierarchy of displacement patterns in space and their respective lifetimes should result in the large spread of relaxation times
- The uniform slow fading of polarization in switched domain without wall movement is also in line with our concept.

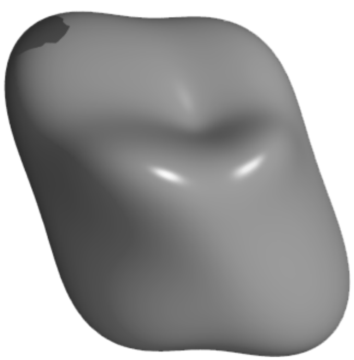
A. Kholkin, A. Morozovska, D. Kiselev, I. Bdikin, B. Rodriguez, P. Wu, A. Bokov, Z.-G. Ye, B. Dkhil, L.-Q. Chen, M. Kosec, S.V. Kalinin, Adv. Functional Materials **21**, 1977 (2011)

Conclusions I

- The characteristic diffuse scattering in Pb-containing relaxors is incompatible with any proposed static PNR models ($\xi_\alpha \sim 10$ nm)
- We suggest a phenomenological pseudo-TDS model with a minimal number of adjustable parameters (2 to 3) and keeping average cubic symmetry
- Proposed model even in the current very simple form fits much better available experimental data
- Corresponding real space realization is a superposition of displacements - at variance with a distribution of polar domains.

Conclusions II





- Diffuse clouds of complex 3D shape require 3D real-space models

- Special care has to be taken about effects distorting 2D images (geometrical correction, orientation matrix, thickness of reciprocal layers …)

- Often there is a volume of good old data on 1D q-dependences – should not be ignored.

- If a disordered structure affects the properties – the model has to be compatible with physical properties.

Where to move

- More realistic modeling - with all atoms in the unit cell.
- From statistical properties of real space realizations to physical properties.

- Why the decay is sometimes a bit faster than q^{-2}? Is it related to the attraction/repulsion poles on the Pb-locus sphere?
- Does Pb pattern results from normal phonon population, or it resembles the mechanism of “rogue waves” creation? Or non-linear discrete breathers? Or critical fluctuations?
- And what happens in lead-free relaxors?

Acknowledgments

- Efim Kats
  Institut Laue-Langevin, Grenoble, France
- Björn Winkler
  Goethe-Universität, Frankfurt a.M., Germany

Thank you for your attention!

http://lanl.arxiv.org/abs/1101.0490

Acta Crystallographica A, 2011 в печати