Seeing the real atomic correlation in matter: Dynamic and static PDF method

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Many former students, including, **R. J. McQueeney, J.-H. Chung, E. Mamontov, S. Teslic, H. D. Rosenfeld, R. Hu, W. Spronson, Y. Suzuki, S. Aur, and D. J. Srolovitz,** *and postdocs/ visitors,* **B. H. Toby, Y. Waseda, S. Nanao.**

Bragg's Law

$$2d\sin\theta = n\lambda, \quad Q = 4\pi\sin\theta/\lambda = K$$

- **Reduces the positions of 10^{23} atoms to a few numbers!!**
- **But, λ ~ 1 Å. Why can we determine the *d* value with the accuracy much smaller than the wavelength?**
  - **Actually we are measuring the periodicity of the lattice, not the atomic positions.**
  - **$L = N\lambda$, the coherence length, determines the accuracy. Since $N \sim 10^5$, highly accurate measurement is possible.**
- **The assumption of perfect periodicity is the key.**

“Structure” of aperiodic matter

- **Bragg’s law does not work! What shall we do??**
- **Scattering?**

$$\Psi_{scat}(\boldsymbol{Q}) = A\left(\sum_i e^{i\boldsymbol{Q}\cdot\boldsymbol{R}_i}\right)\Psi_{inc}$$

- **By diffraction the phase information is lost.**

$$I(\boldsymbol{Q}) = \left|\Psi_{scat}(\boldsymbol{Q})\right|^2 = \left|A\right|^2 \sum_{i,j} e^{i\boldsymbol{Q}\cdot\left(\boldsymbol{R}_i - \boldsymbol{R}_j\right)}$$

- **But, properties are determined by atom-atom interactions; absolute positions do not matter, correlation does.**

$$\rho(\boldsymbol{r}) = \frac{1}{N}\sum_{i,j}\delta\left(\boldsymbol{r} - \left(\boldsymbol{R}_i - \boldsymbol{R}_j\right)\right)$$

Atomic Pair-Density Function (PDF)

- **Structure function = FT of PDF;**

$$S(\boldsymbol{Q}) = \frac{1}{N}\sum_{i,j} e^{i\boldsymbol{Q}\cdot\left(\boldsymbol{R}_i - \boldsymbol{R}_j\right)} = \int \rho(\boldsymbol{r}) e^{i\boldsymbol{Q}\cdot\boldsymbol{r}}\, d\boldsymbol{r}$$

- **Not only Bragg peaks but diffuse scattering has to be included (total scattering).**
- **3D PDF requires 3D structure function.**
  - **At least 1 GB.**
  - **Time consuming even with a 2D detector.**

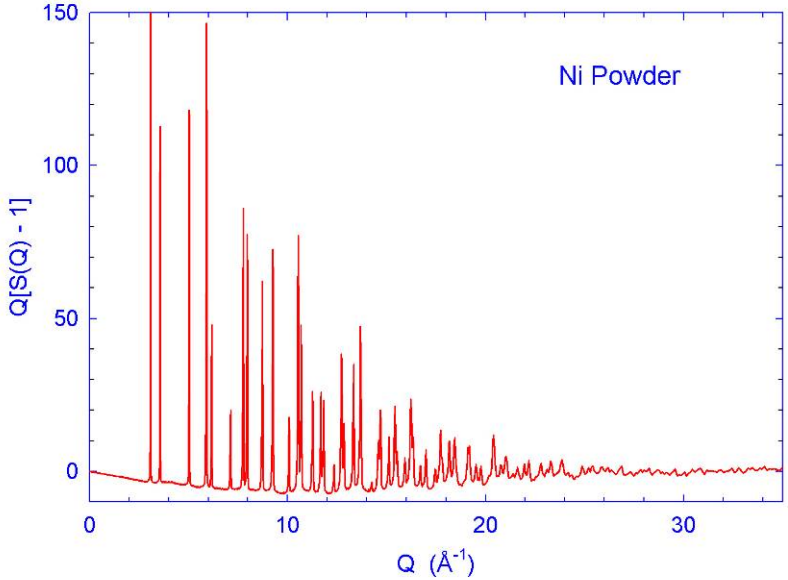
Powder PDF Method

- **Powder averaging**

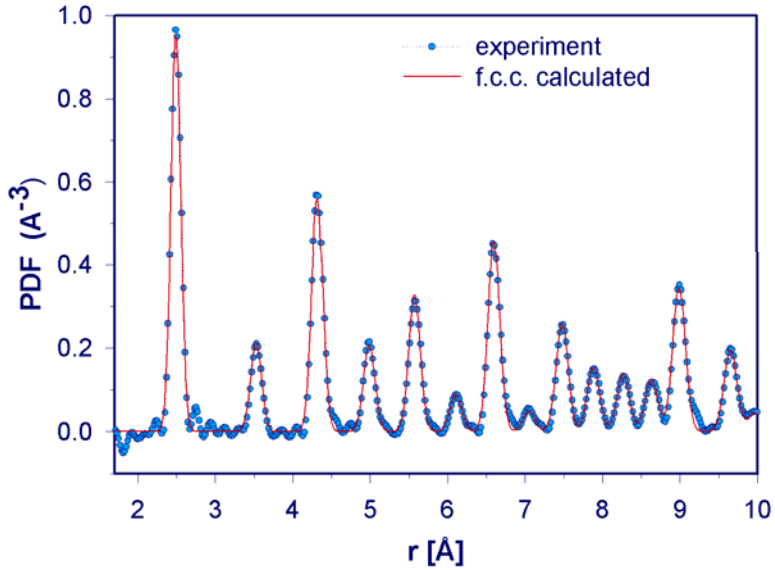
$$\rho(r) = \rho_0 g(r) = \rho_0 + \frac{1}{2\pi^2 r}\int_0^\infty [S(Q)-1]\sin(Qr)Qdq$$

- **Powder averaging is convenient and useful. Orientational information is lost, but all the diffuse scattering intensities are included.**
  - **Good practice to examine 1D PDF before studying diffuse scattering.**
  - **Diffuse scattering tells the periodicity, but not the atomic details (displacements….) unless studied over many Brillouin zones.**
- **Often crystals are not available, or powder samples are better than crystals.**

Local Structure by Atomic Pair-Density Function (PDF)



⇒ ***FT***



- *Distribution of distances between atoms, can describe local structural deviations.*
- *"Underneath the Bragg Peaks: Structural Analysis of Complex Materials", T. Egami and S. J. L. Billinge (Pergamon Press, Oxford, 2003).*

How periodic are the matters in the world?

- **Only bones are crystalline in our body.**
- **Surface of the earth is dominated by ocean.**
- **Inside is mostly molten liquid.**
- **Only silicon chips are perfectly periodic.**
- **Even jewels are not; nitrogen in diamond adds to color.**
- **We now turn to more and more complex functional materials, which are not perfectly periodic.**
- **Materials with *competing interactions*; creates softness out of hard materials.**

Competing forces

Competition is good for you

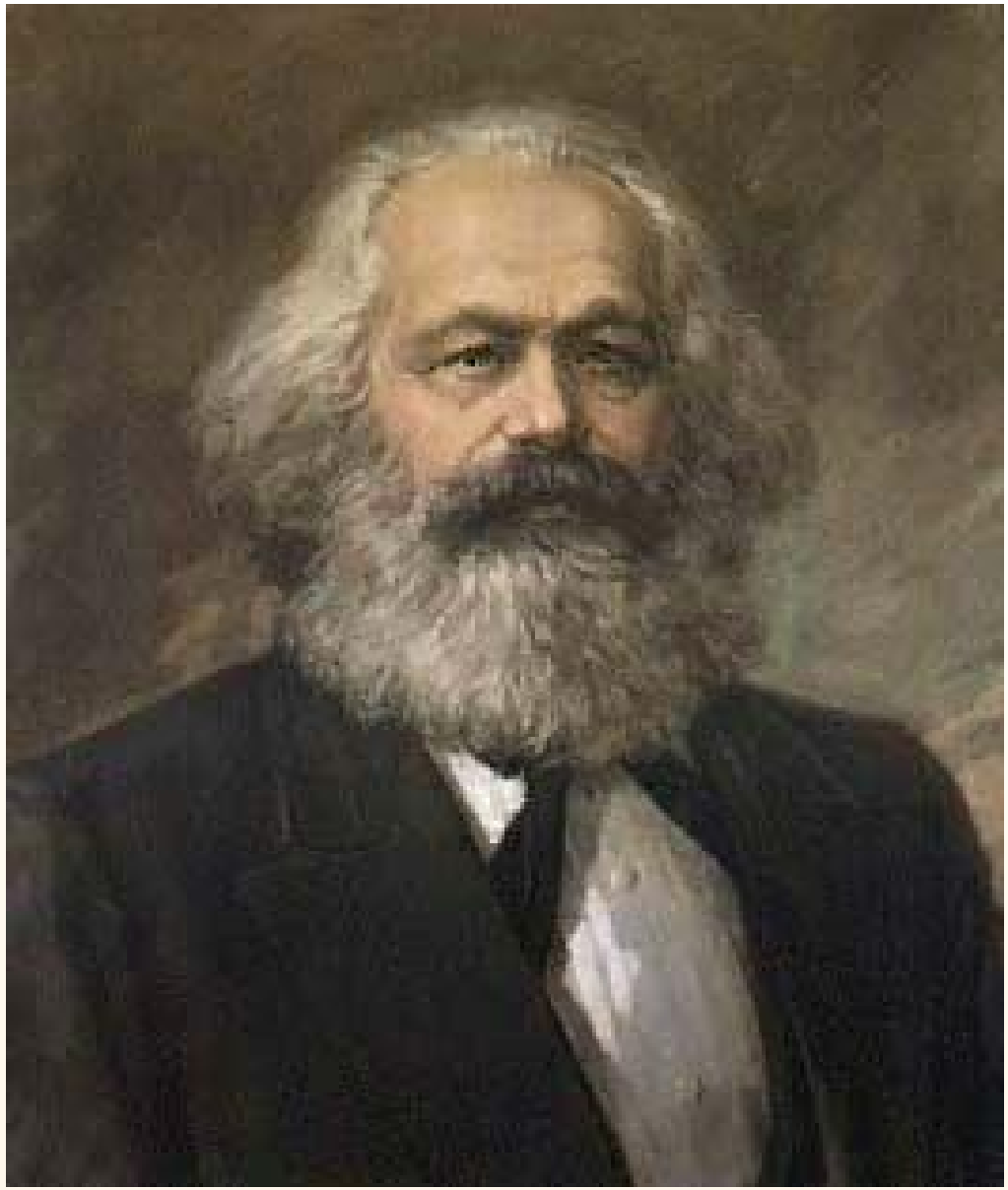
- **Various functional properties are required for modern materials, requiring high-response.**
- **Atomic bonding (~1 eV) is too strong to produce high-response.**
- **Utilizing competing forces (divide and conquer) is the smart way of achieving high-response.**
- **Managing conflict and competition is the key to the smart materials.**
- **Electronic softness in hard materials.**

G. W. F. Hegel

1770-1831

Dialectical method

- **Thesis**
- **Antithesis**
- **Synthesis**



Karl Marx

1818-1883

Failure of Marxism

- **By solving the social conflict by creating the communistic society, *Marx removed dynamic competition, and thus social and economic progress stopped in the former Eastern Europe and Russia*. Consequently the social experiment in the Soviet Union failed.**
- **Marx took a global approach to see the society in two classes, *labor and capitalists*. Such a simple division no longer applies in today's society.**

Marxist Approach in Materials Physics Research

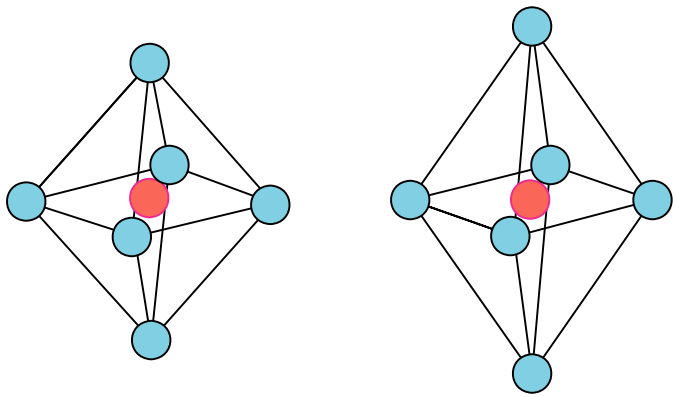
- **Tendency to view the solid as a *homogeneous* material.**
- **Tendency to *avoid conflict or competition* in solids.**
- **In theory, volume average approach, such as the *mean-field approximation*, to reduce the local conflicts to a simplistic global conflict.**

Democratic Approach to Complex Solids

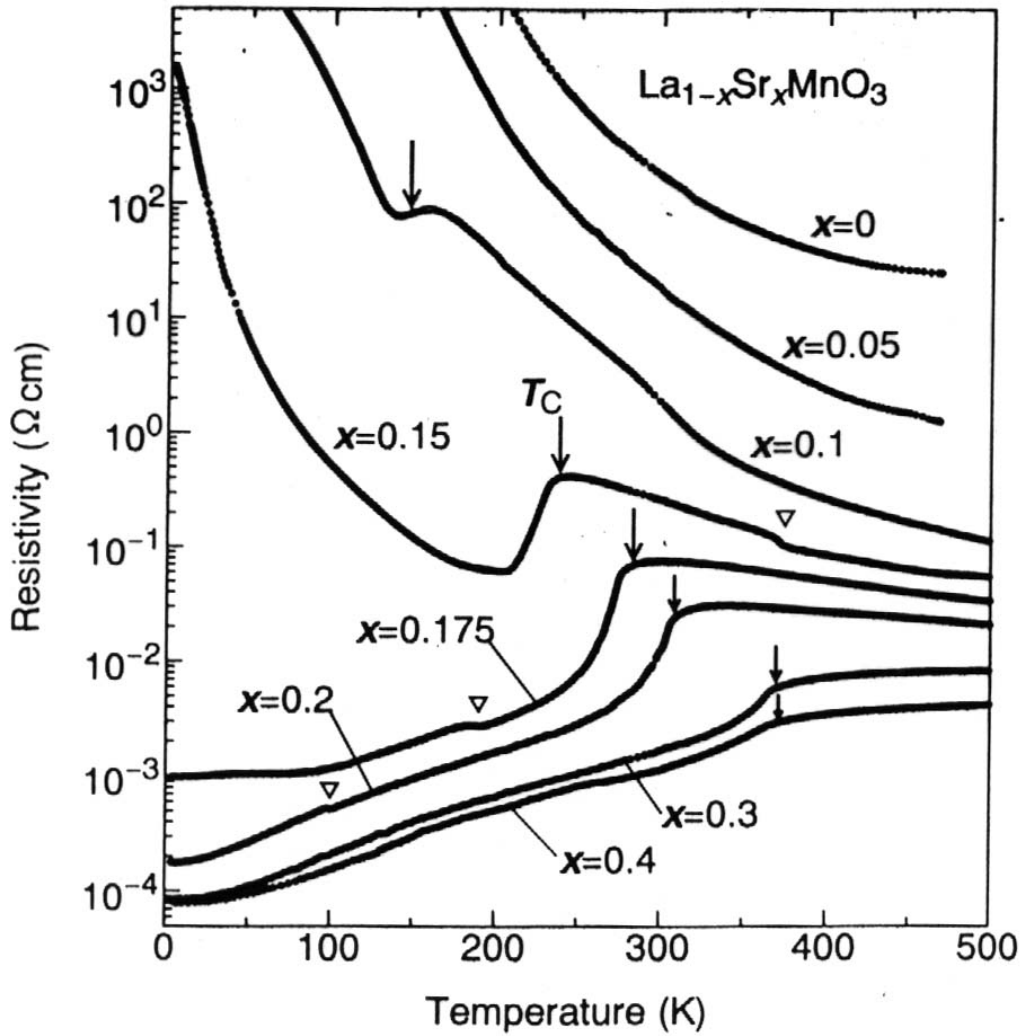
- **Take a *local view*, and evaluate the competition locally.**
- **Build the system as an assembly of the local bodies.**
- **Determine the properties either by majority rule, or by percolation: Thus the phase transition is usually *percolative*.**
- **Focus on the *local structure and dynamics*, rather than the average structure and phonons.**

CMR Phenomenon and Polaron

- **Insulating up to x = 0.16.**
- **Insulating because charges are self-trapped as polarons often forming polaron lattic (charge ordering).**
- **Polaron stability is the key issue.**



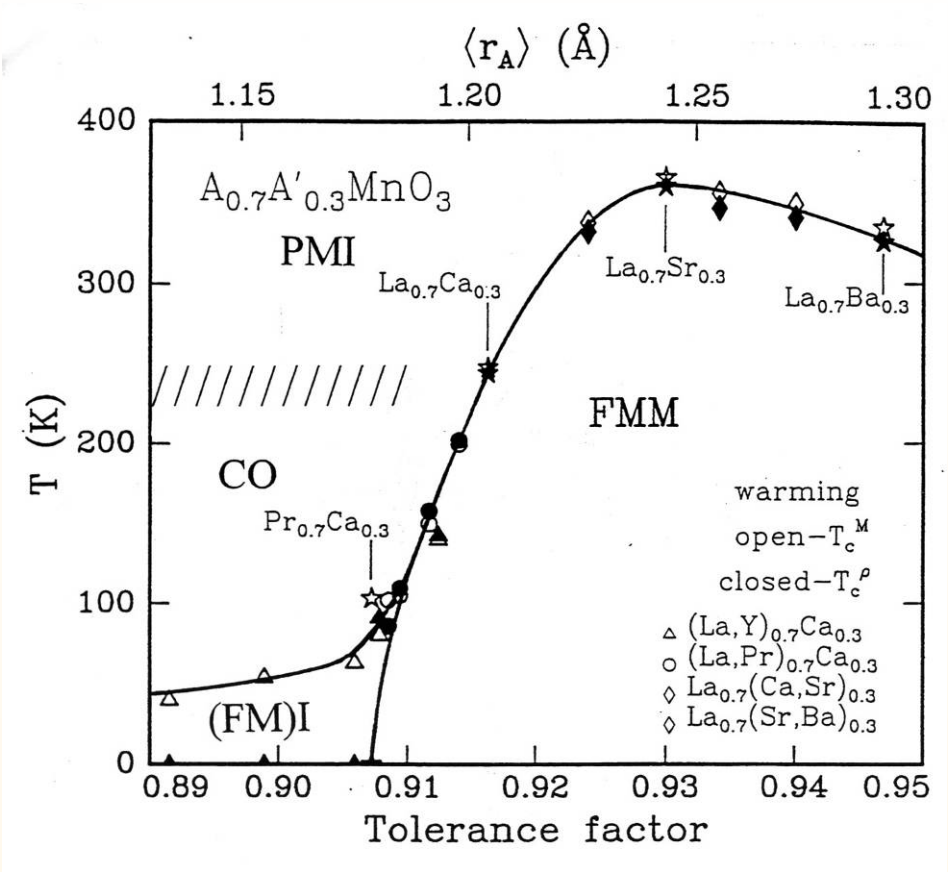
Mn^{4+} **Mn^{3+}**



A. Urushibara *et al.*, Phys. Rev. B **51,** 14103 (1995).

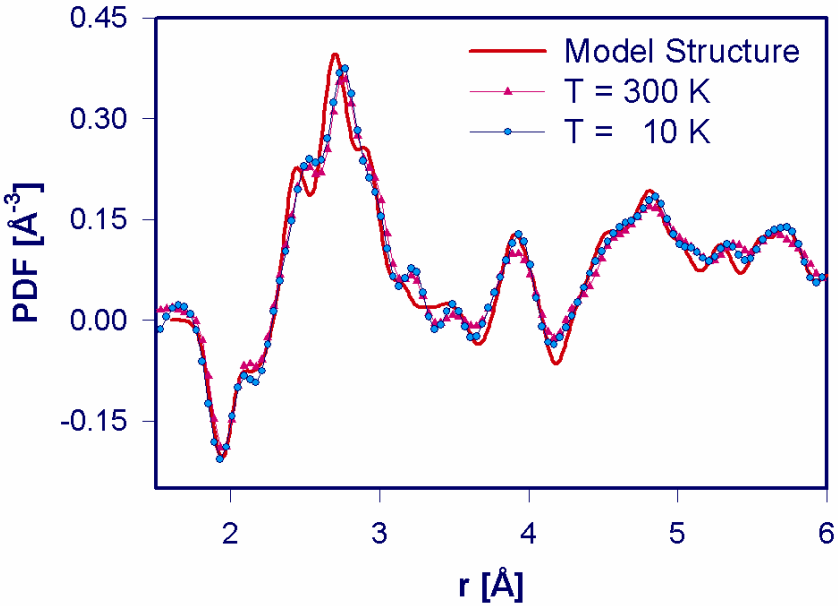
Ionic Size Effect

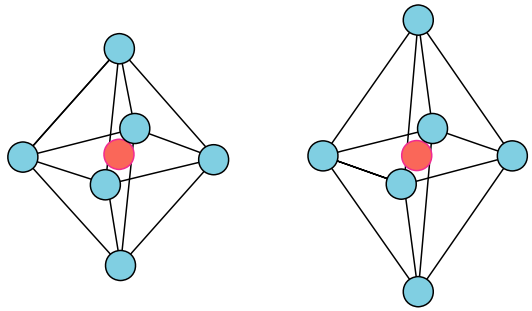
- **Small <r_A>: Insulator with low T_C. Charge localization due to spin/lattice polaron formation.**
- **Large <r_A>: Metal with high T_C. Charge delocalized since polarons are unstable.**

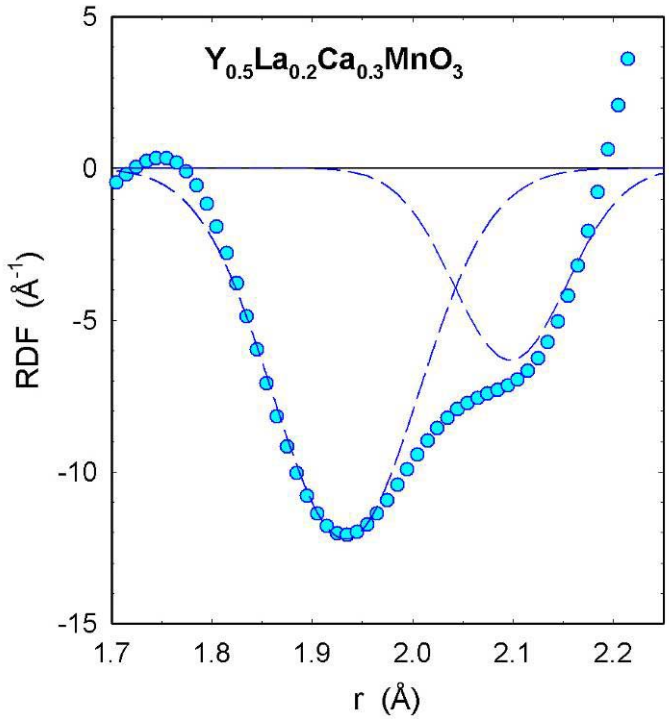


Huang et al. PRL 75, 914 (1995)

Evaluating the density of Mn sites with local JT distortion

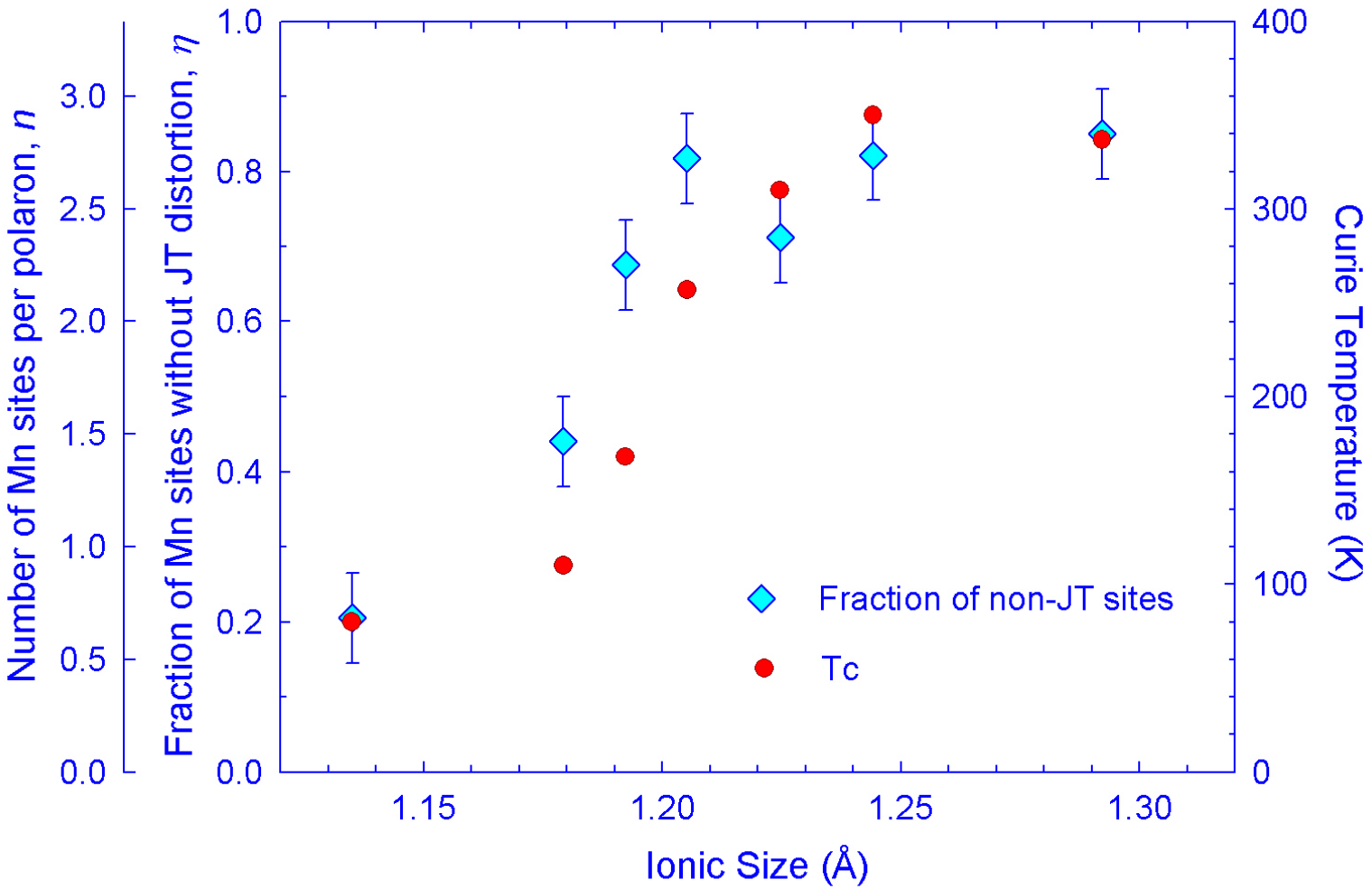






- **PDF of undoped sample (above).**
- **From the intensity ratio of the two subpeaks the density of the Mn sites with local JT distortion can be determined.**

Crossover



D. Louca et al., PRB **64**, R180403 (2001)

Competing Forces and Polaron stability

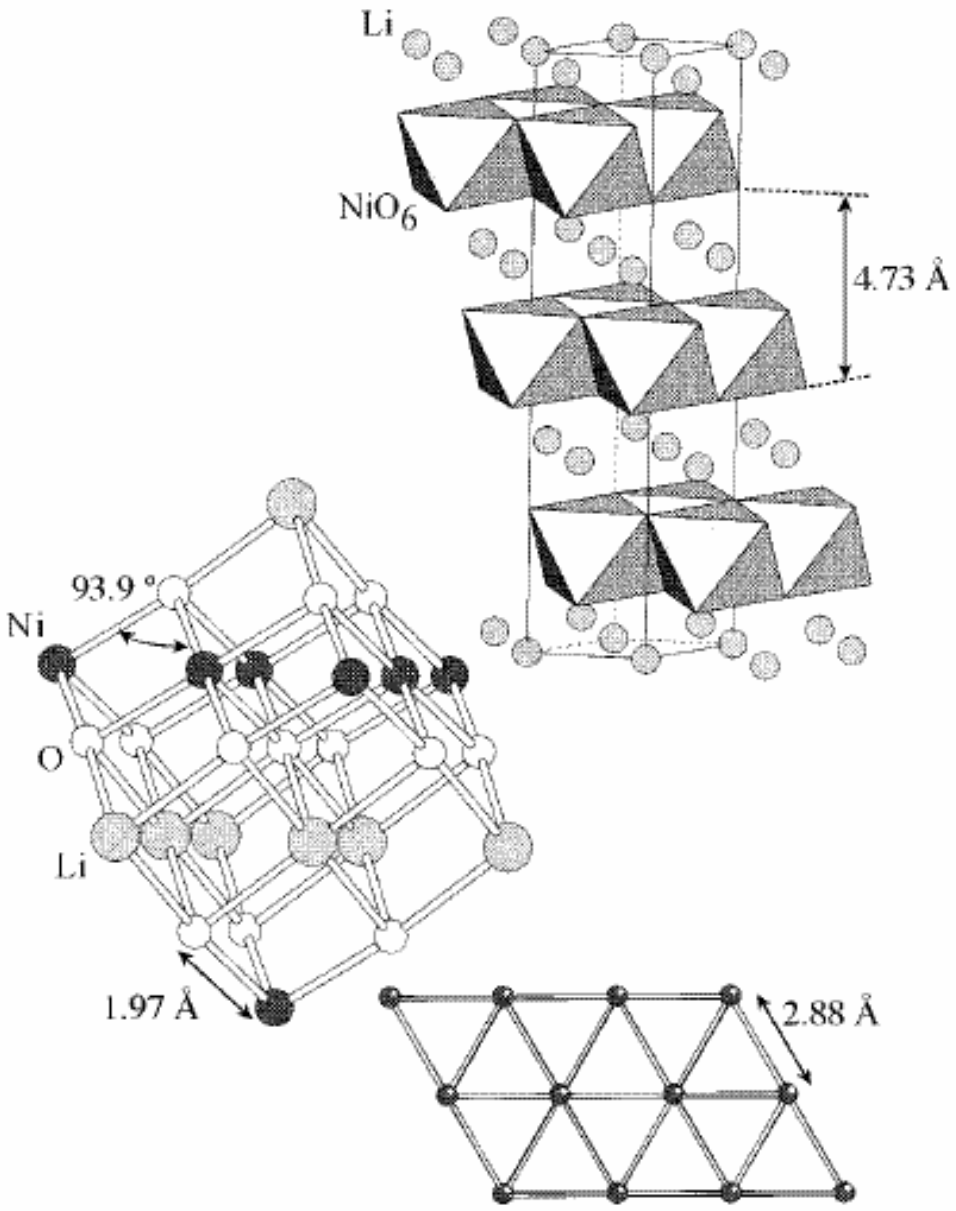
- **The critical parameter**

$$\lambda = \frac{g^2}{tK\langle \cos\theta \rangle}$$

- **Localizing force**
  - ***g*** **: Electron-phonon coupling**
- **Delocalizing force**
  - ***t*** **: Electron hopping**
  - ***K*** **: Elastic constant**
  - **<*cos*θ>: Magnetic correlation**
- **Structure sensitivity through long-range stress field. [T. Egami and D. Louca, *Phys. Rev. B* 65, 094422 (2002)]**

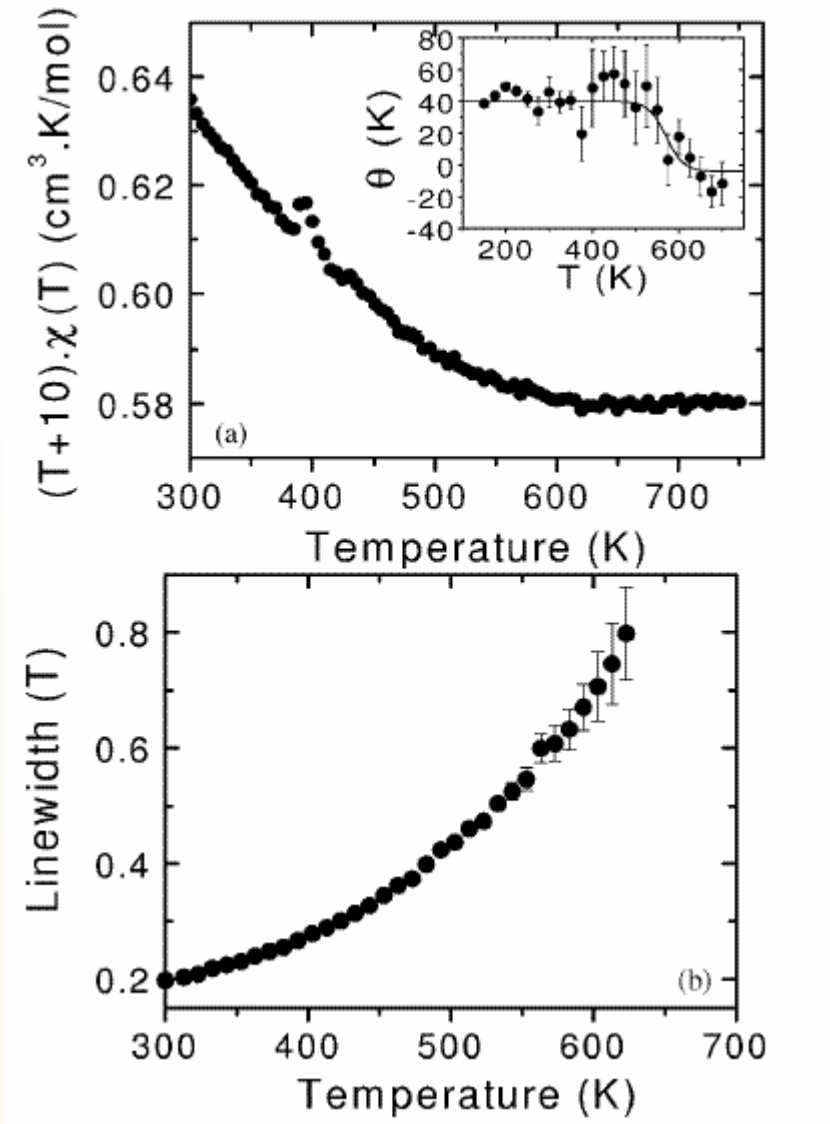
$Li^{+}Ni^{3+}O^{2-}_{2}$

- **Ni^{3+}: d^7 (low spin state: S = ½)**
- **NiO_6 edge-sharing to form a 2-d layer of** triangular **lattice**
- **NiO_2^- layer separated by Li^+**
- **Ni spins frustrated in 2D triangular lattice.**

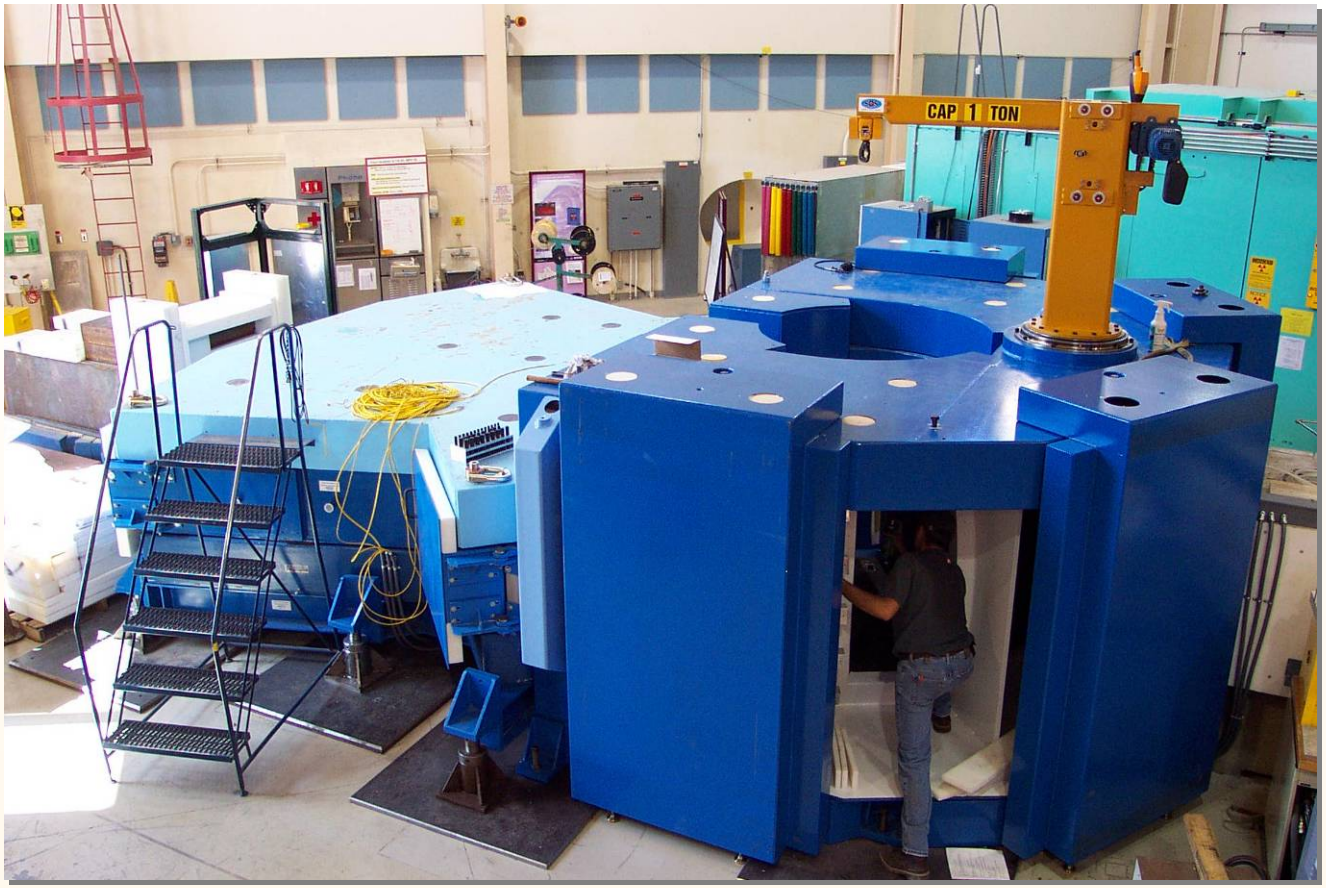


Orbital Moment

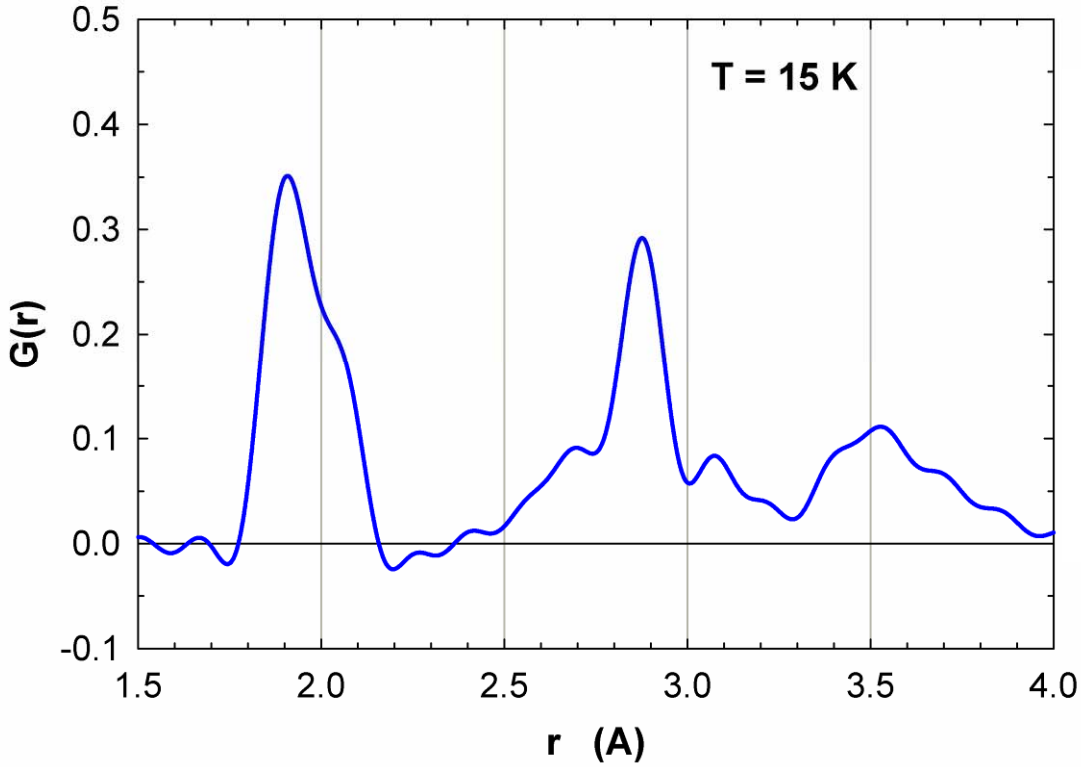
- **Ni^{3+}, (t_{2g}^6, e_g^1), is a Jahn-Teller ion.**
- **$NaNiO_2$ is Jahn-Teller distorted.**
- **But $LiNiO_2$ shows no collective Jahn-Teller distortion. *What is the role of the orbital ordering?***
- **Reynaud, *et al*. [PRL 86, 3638 (2001)] observed a change in the magnetic properties around 550 K, and related it to orbital short-range ordering.**

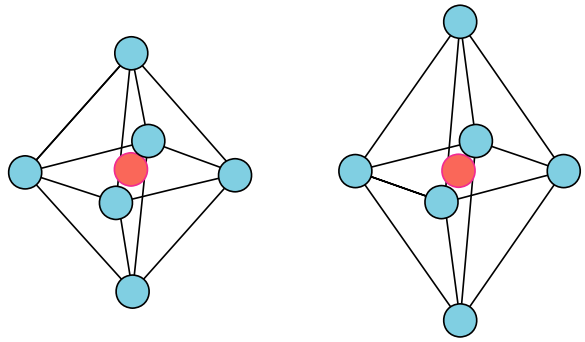


High-resolution pulsed neutron scattering with NPDF, LANSCE, LANL (Th. Proffen)

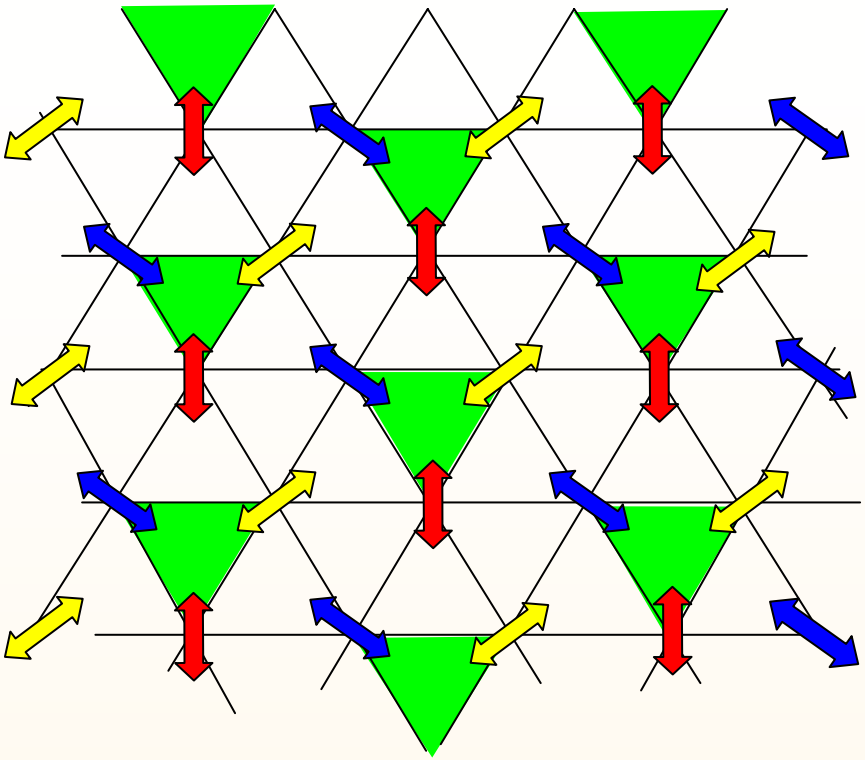


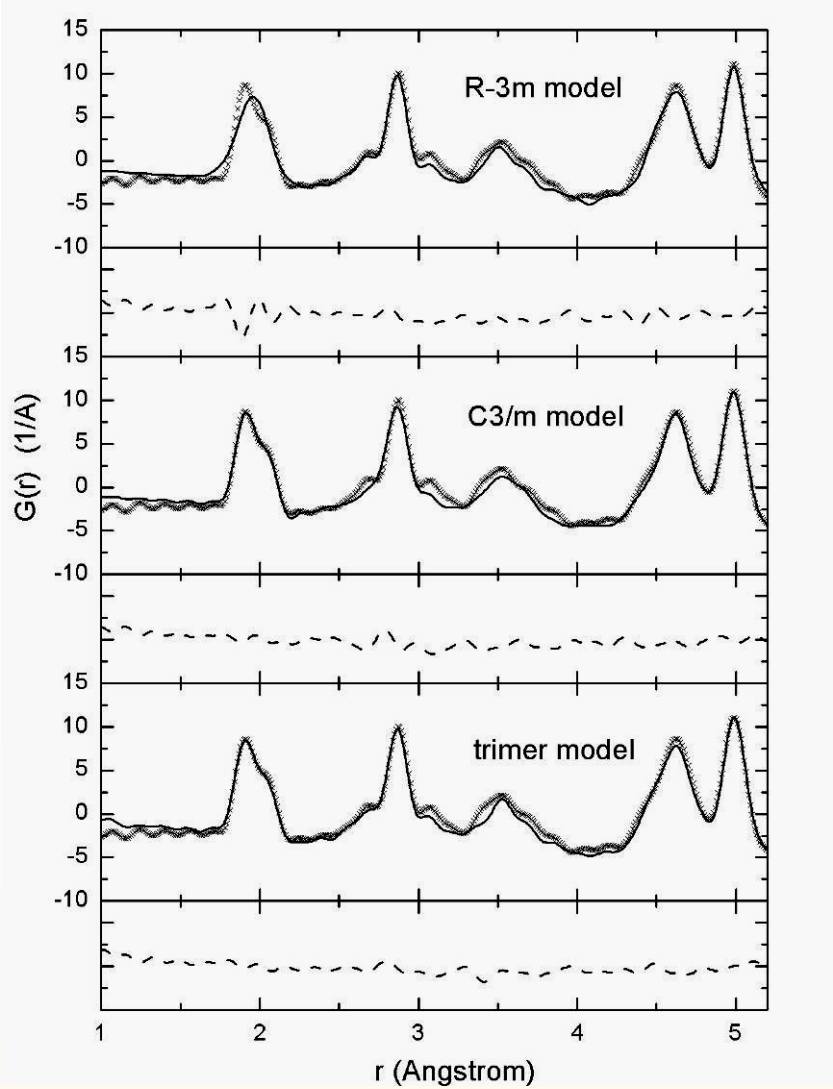
- **High Q resolution ΔQ/Q = 0.0015, high real space resolution for PDF.**





- **The first peak of the PDF (Ni-O peak) is consistent with the z^2 orbital state with 4 short, 2 long bonds. For $x^2 - y^2$ state, 2 short, 4 long bonds.**





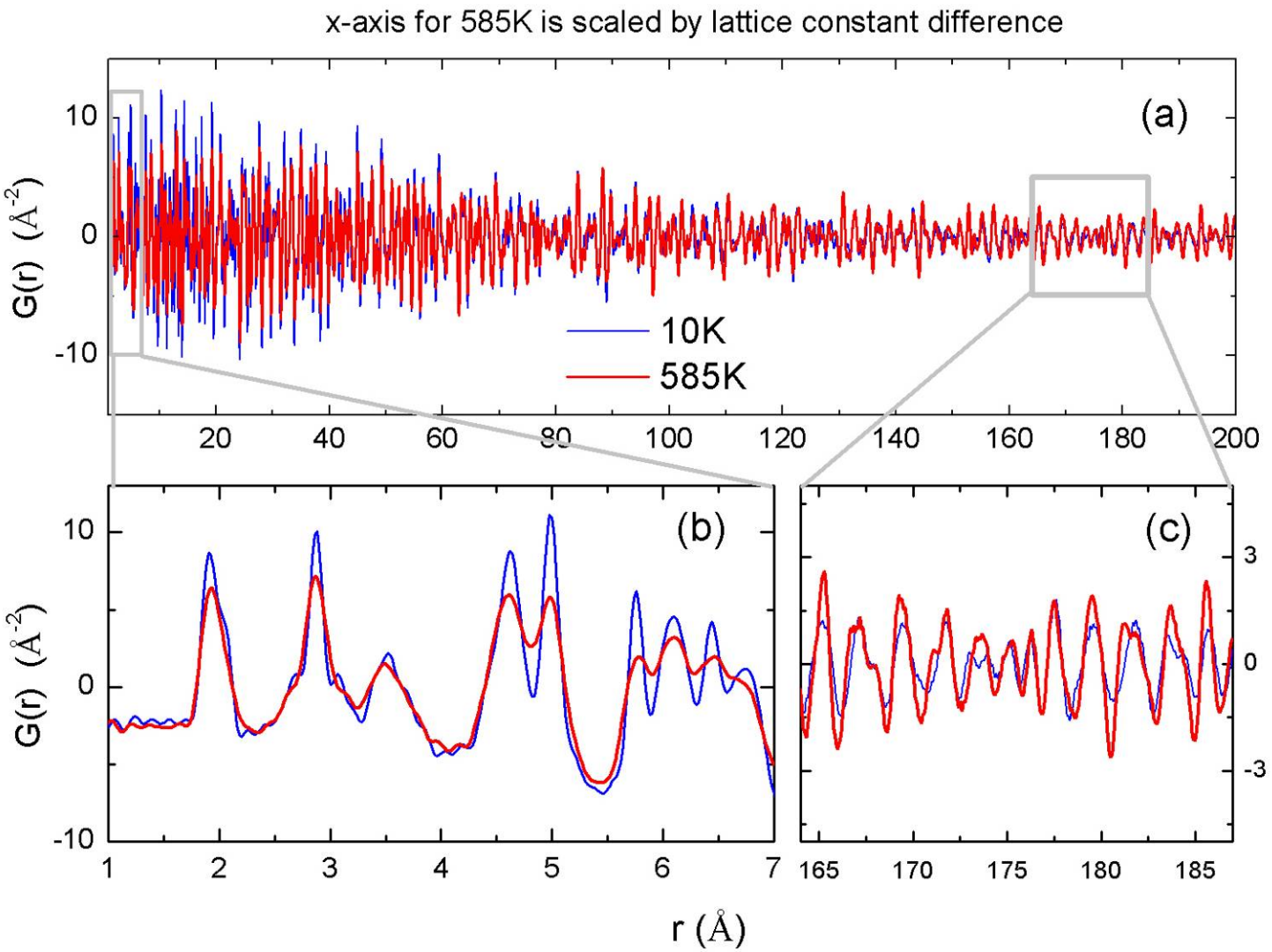
- **3 sublattice (trimer) model.**
- **No macroscopic structural distortion.**

J.-H. Chung et al. PRB **71**, 064410 (2005)

- **3 sublattice (trimer) model gives the best fit.**

Temperature dependence

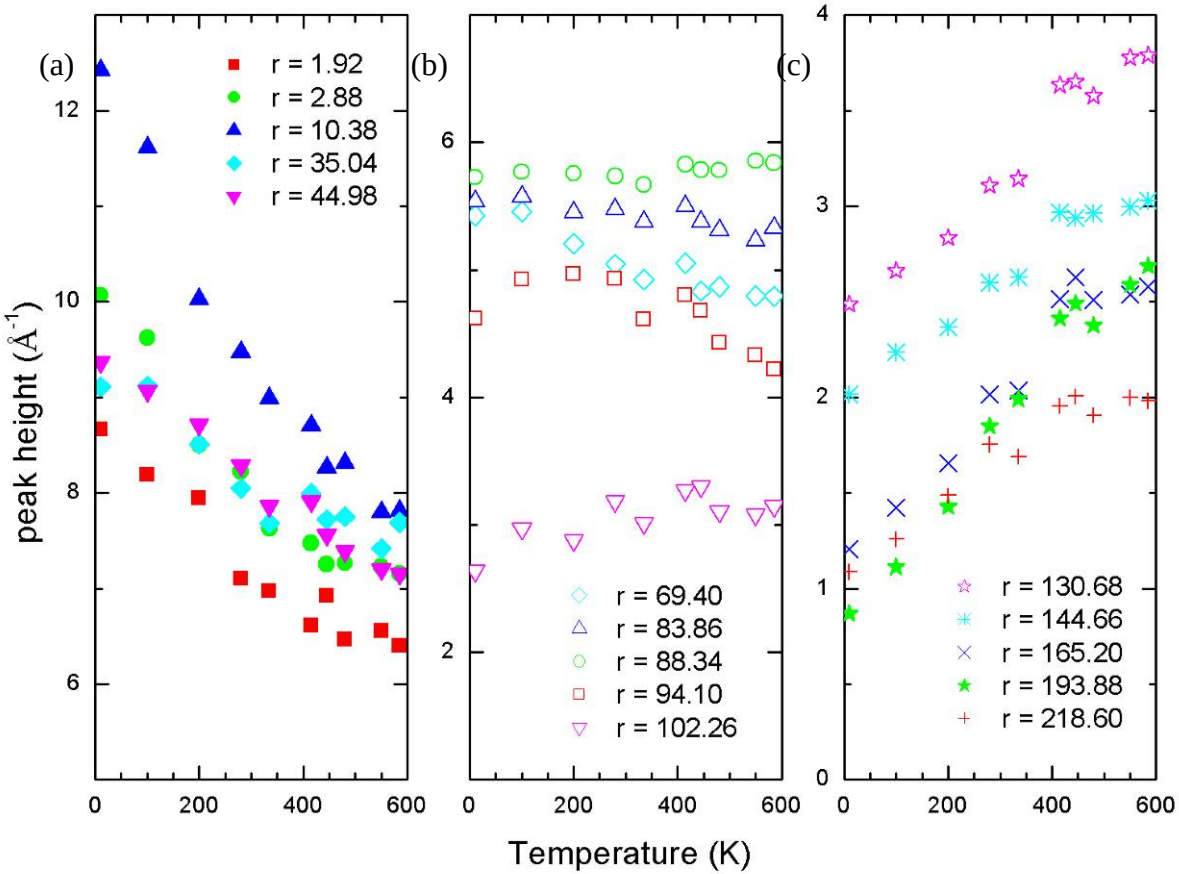
PDF Obtained with the NPDF, LANSCE

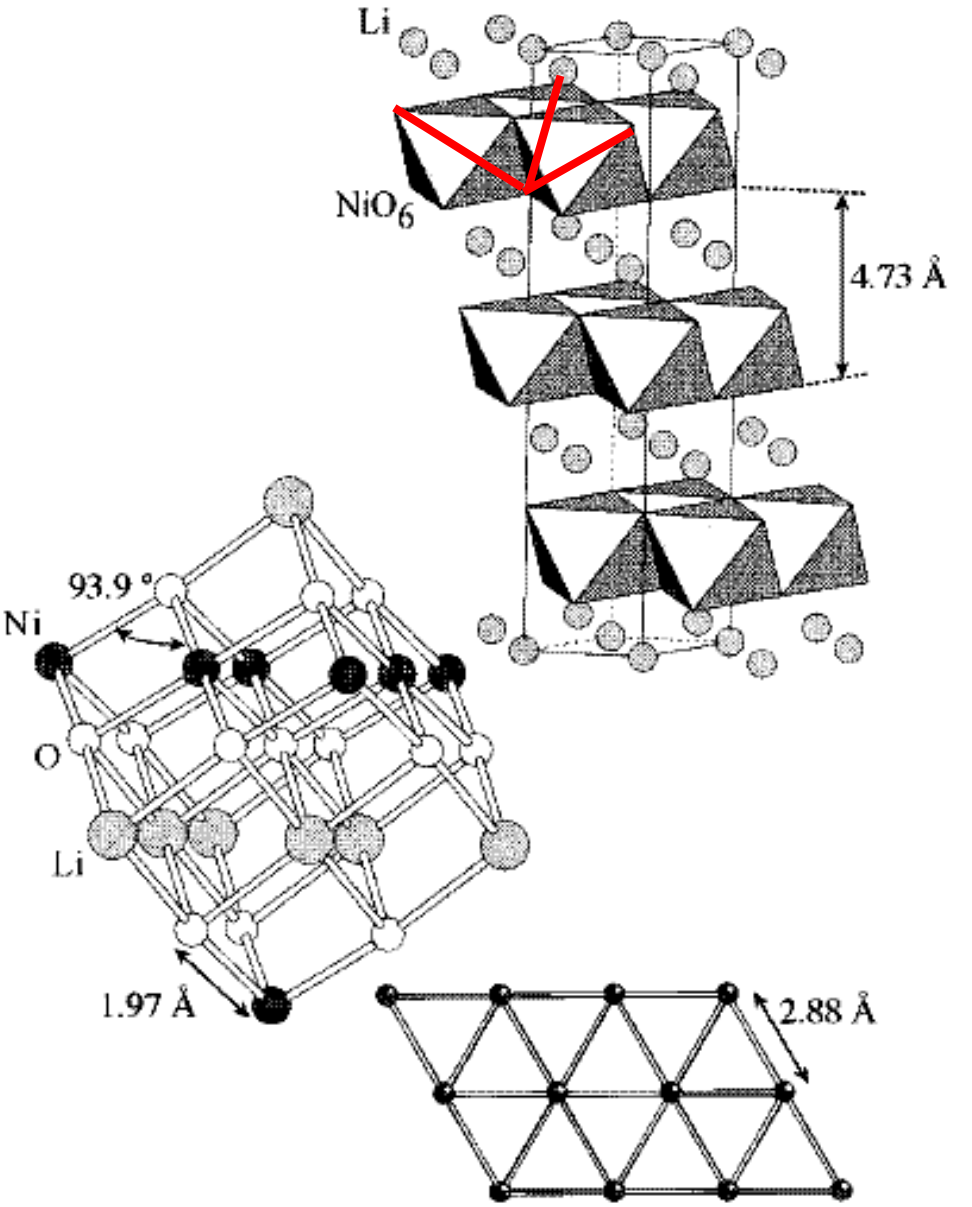


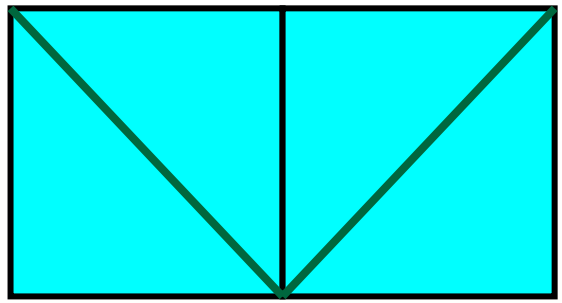
- **The PDF height depends upon temperature differently at short and long distances.**

Temperature Dependence

- **For r < 60 Å peak height decreases with T.**
- **For r > 100 Å peak height increases with T.**
- **Local ordering vs. domain formation.**







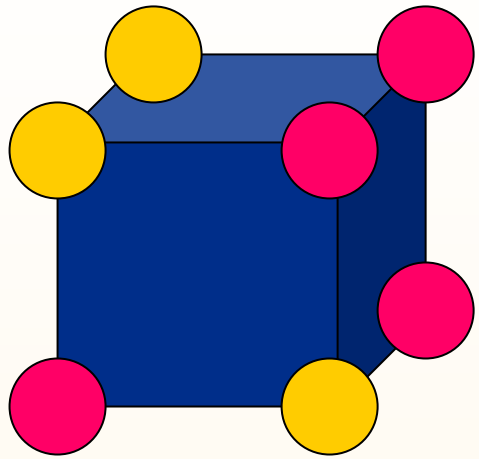
- **JT axis not in the plane.**
- **Neighboring JT axes at right angle.**
- **Tri-sublattice ordering produces curvature in the plane.**
- **Local ordering competes against the total lattice.**
- **This conflict produces domains.**

Relaxor Ferroelectrics and Dynamic PDF

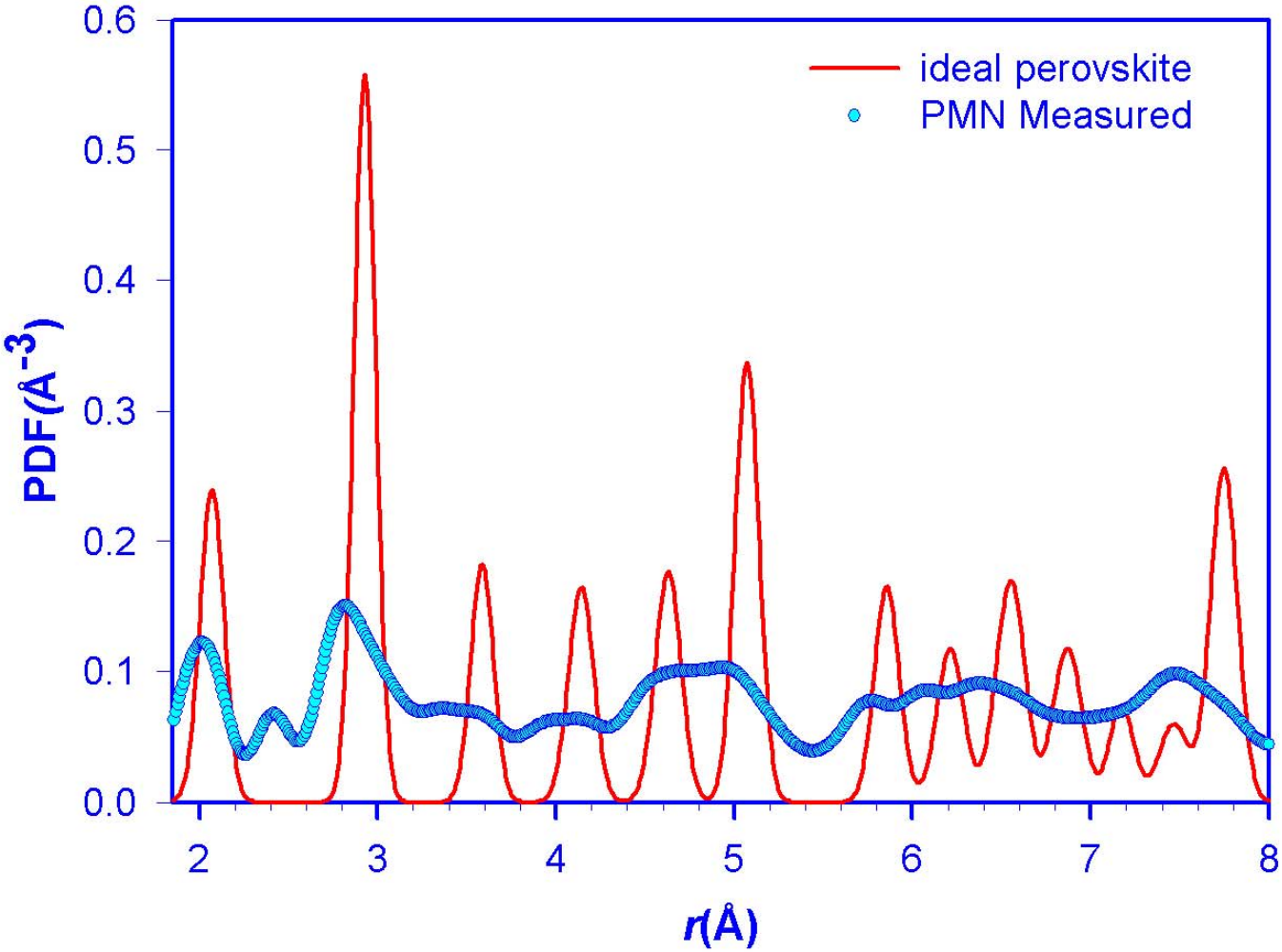
- **Relaxor ferroelectrics: Ferroelectrics with diffuse transition.**
- **Dielectric relaxation observed below T_{max}.**
- **Dielectric permittivity smoothly depends upon temperature and frequency; Widely used because of temperature stability.**
- **Seen only in disordered mixed-ion systems, such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN).**
  - **Mixed valences; Mg^{2+}, Nb^{5+} in PMN, Zn^{2+}, Nb^{5+} in PZN, Pb^{2+}, La^{3+} in $(Pb,La)(Zr,Ti)O_3$ (PLZT).**
  - **Dilute impurities in high dielectric solid, such as $SrTiO_3$.**

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

- **Average structure is a simple perovskite, with polarization along (111) resulting in rhombohedral distortion.**
- **Pb polarization is locally along (100).**
- **Random Nb^{5+}/Mg^{2+} site occupation.**
- **Chemical ordering leaves one sublattice randomly occupied (Davies).**
- **Competition between local chemical disorder and ferroelectricity.**

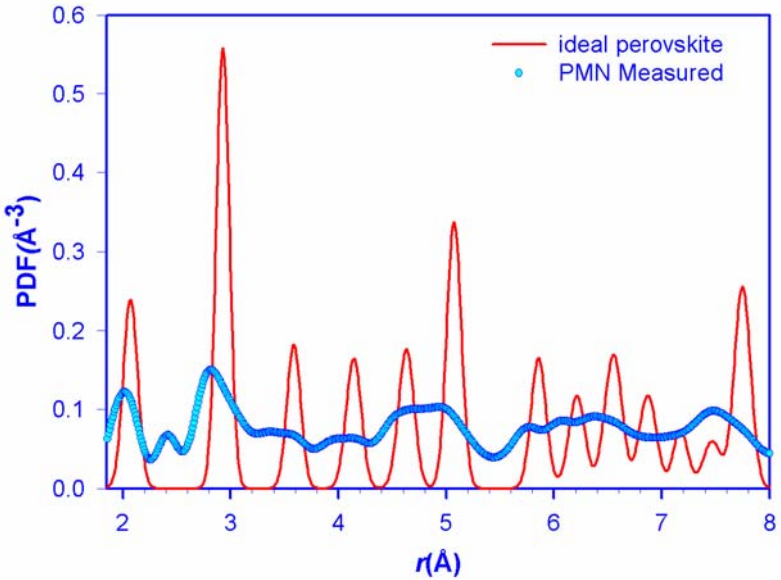


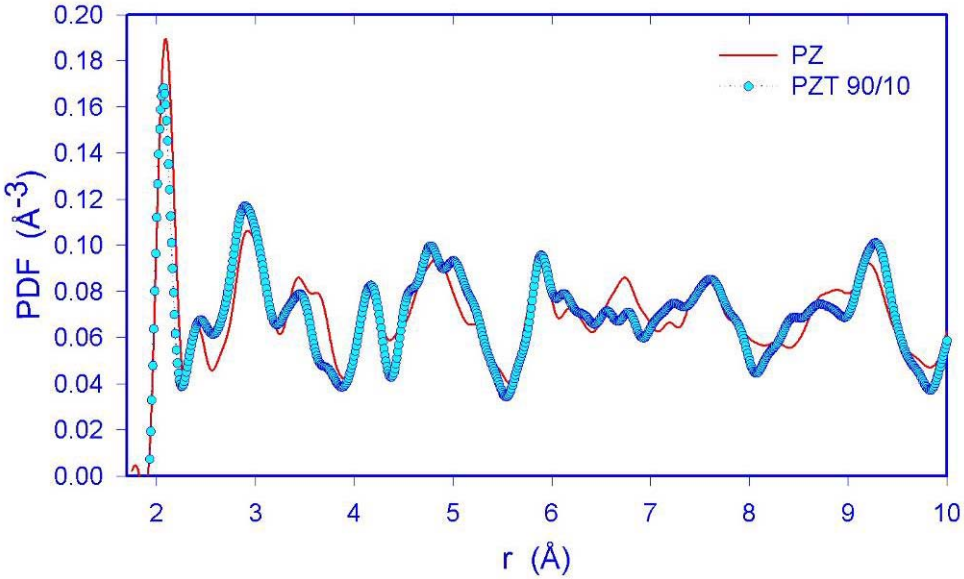
B site occupied by Nb^{5+} and Mg^{2+}.

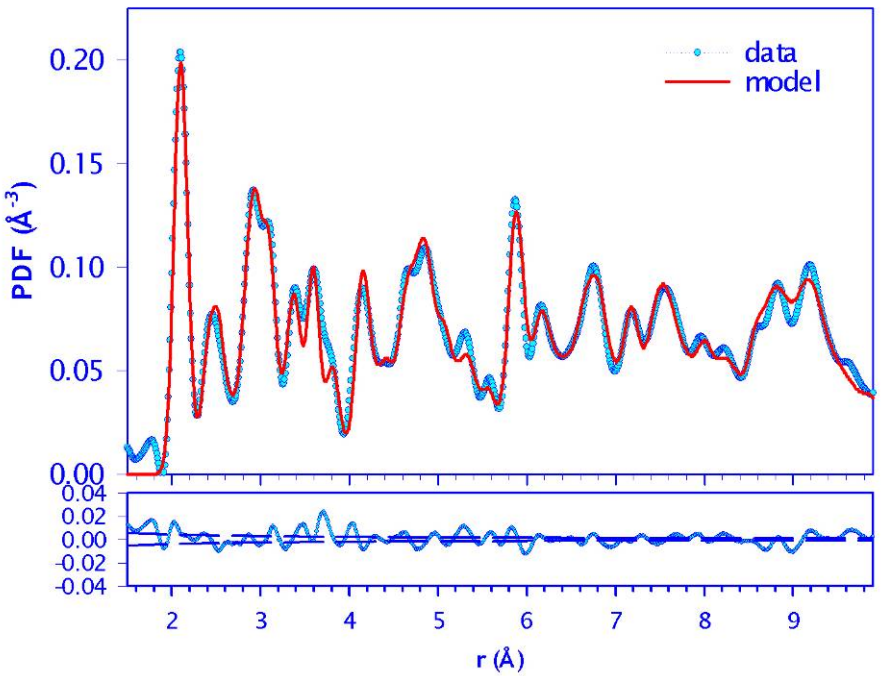

ideal perovskite
PMN Measured
PDF(Å-3)
r(Å)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
2
3
4
5
6
7
8

PDF of PMN

Pb polarization





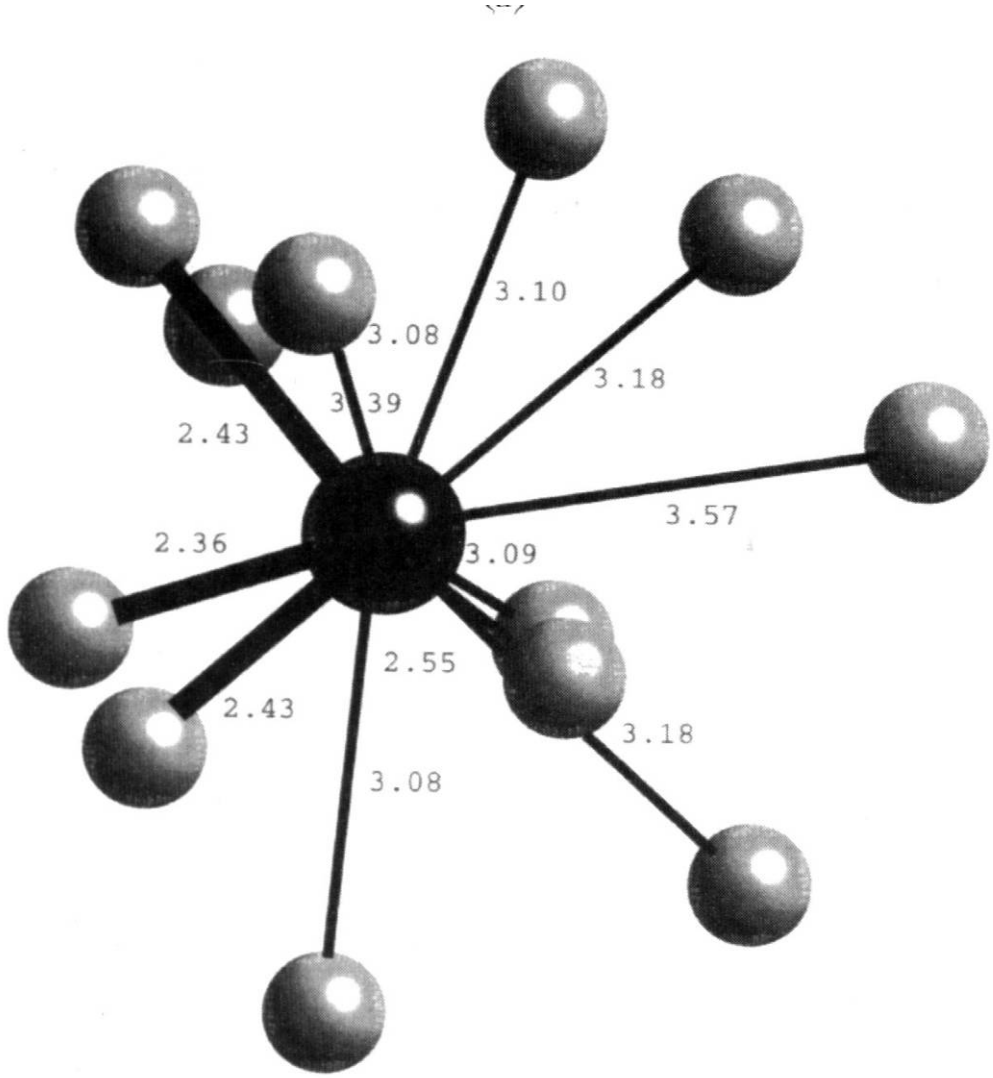


- PDF of PMN

Pb^{2+} in $PbZrO_3$

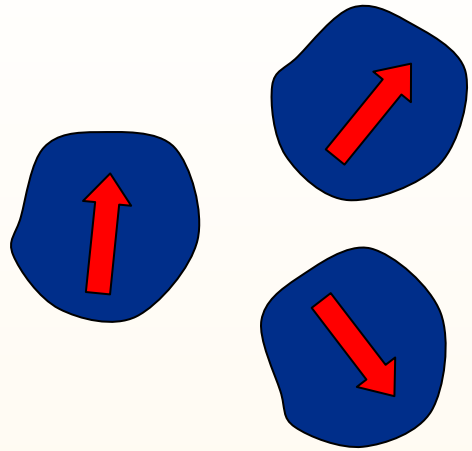
Pb is off-centered by 0.5 Å in the O_{12} cage

Lone-pair *s*-*p* electrons of Pb



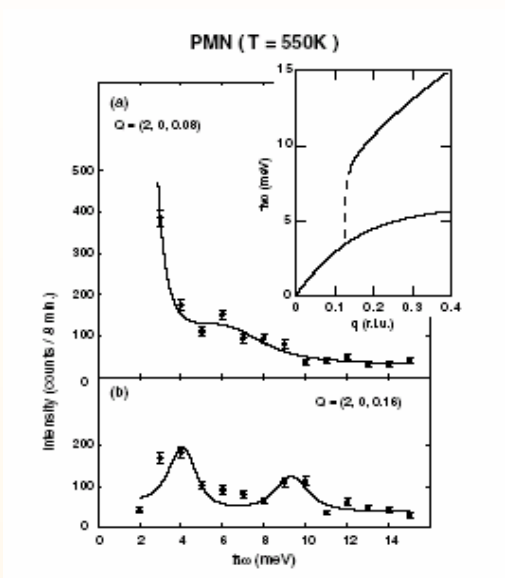
Origin of the Relaxor Behavior

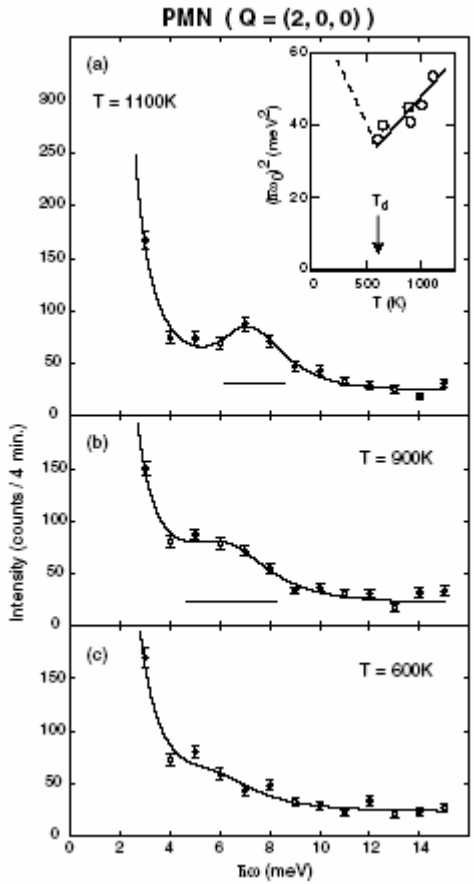
- **Spin-glass behavior: Freezing temperature is ~230K for PMN.**
- **Formation of polar nano-regions (PNRs).**
- **Low-frequency relaxation behavior understood in terms of random interactions among the PNR, by spin-glass models (Kleemann, Glintchuk, Blinc…..).**



Phonon Water Fall

- **LO phonons disappear at low Q below T_d.**
- **Water-fall between T_f anf T_d.**
- **Consistent with polar nano-regions (PNR).**

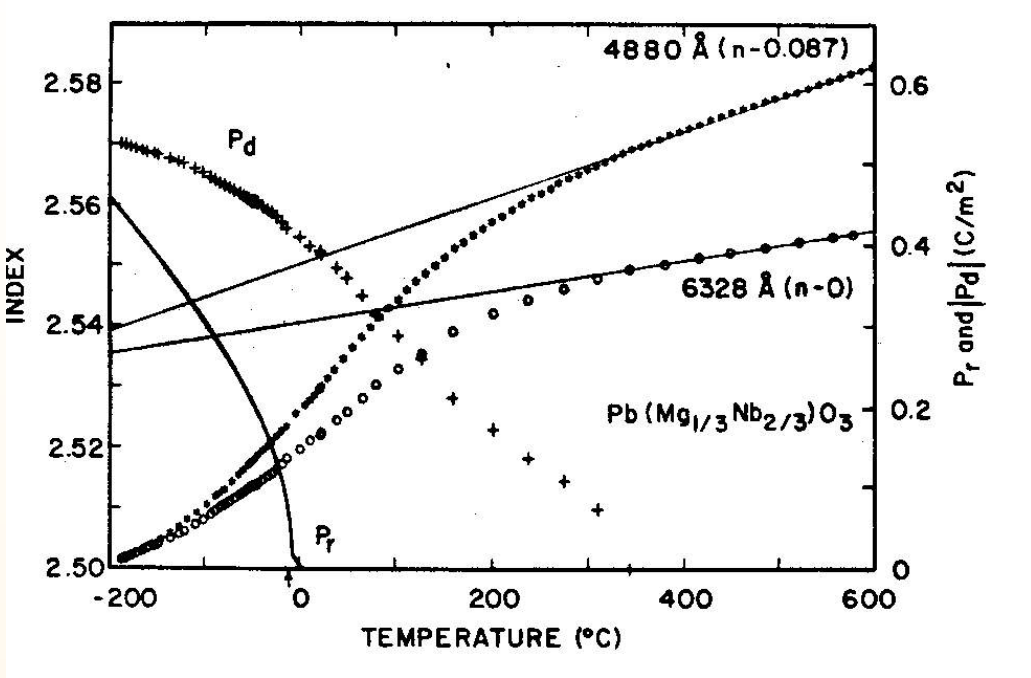




P. Gehring et al., *PRL* **87**, 277601 (2000).

Burns Temperature

- **At high-frequency (optical frequency) changes are observed at Burns temperature, Td ~ 600 K for PMN.**
- **PNR formed only below Td?**



G. Burns and F.H. Dacol, Solid State Communications, 48 (1983) 853-856

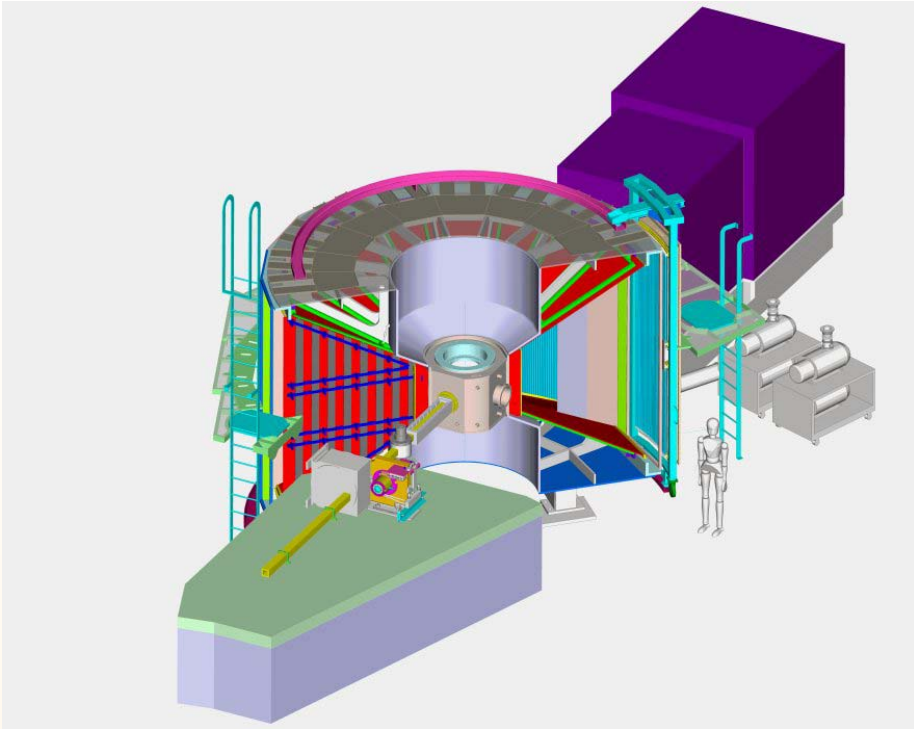
Origin of PNR

- **How to observe dynamics of NPR?**
- **How does it depend on T?**
- **Role of atomic level disorder?**
- **Interplay of dynamics and disorder?**

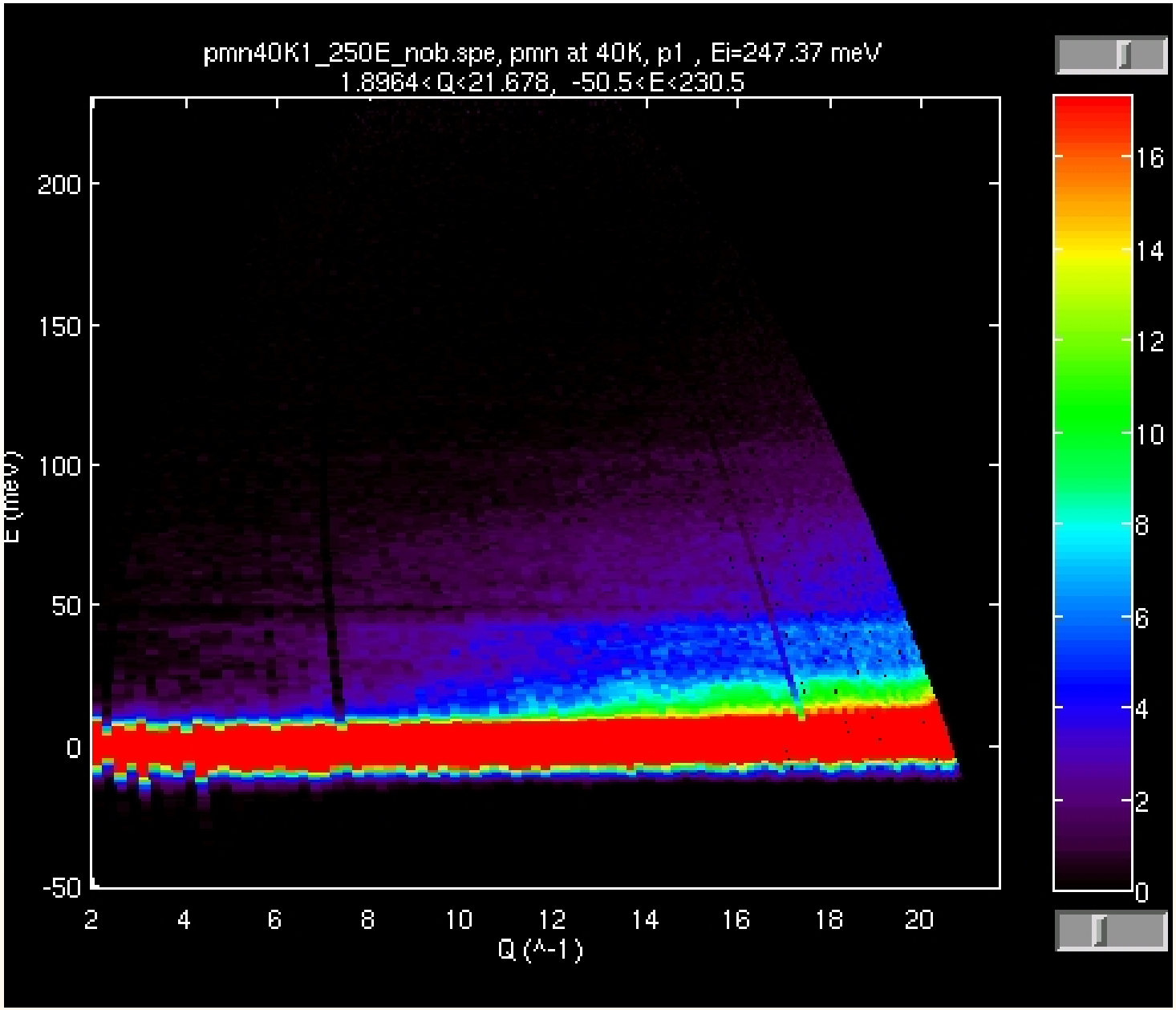
- **Neutron scattering experiment:**
  - Static PDF (instantaneous up to ~ 50 meV)
  - Dynamic structure factor
  - Dynamic PDF **– Dynamics of local structure.**

Dynamic PDF by Inelastic Neutron Scattering

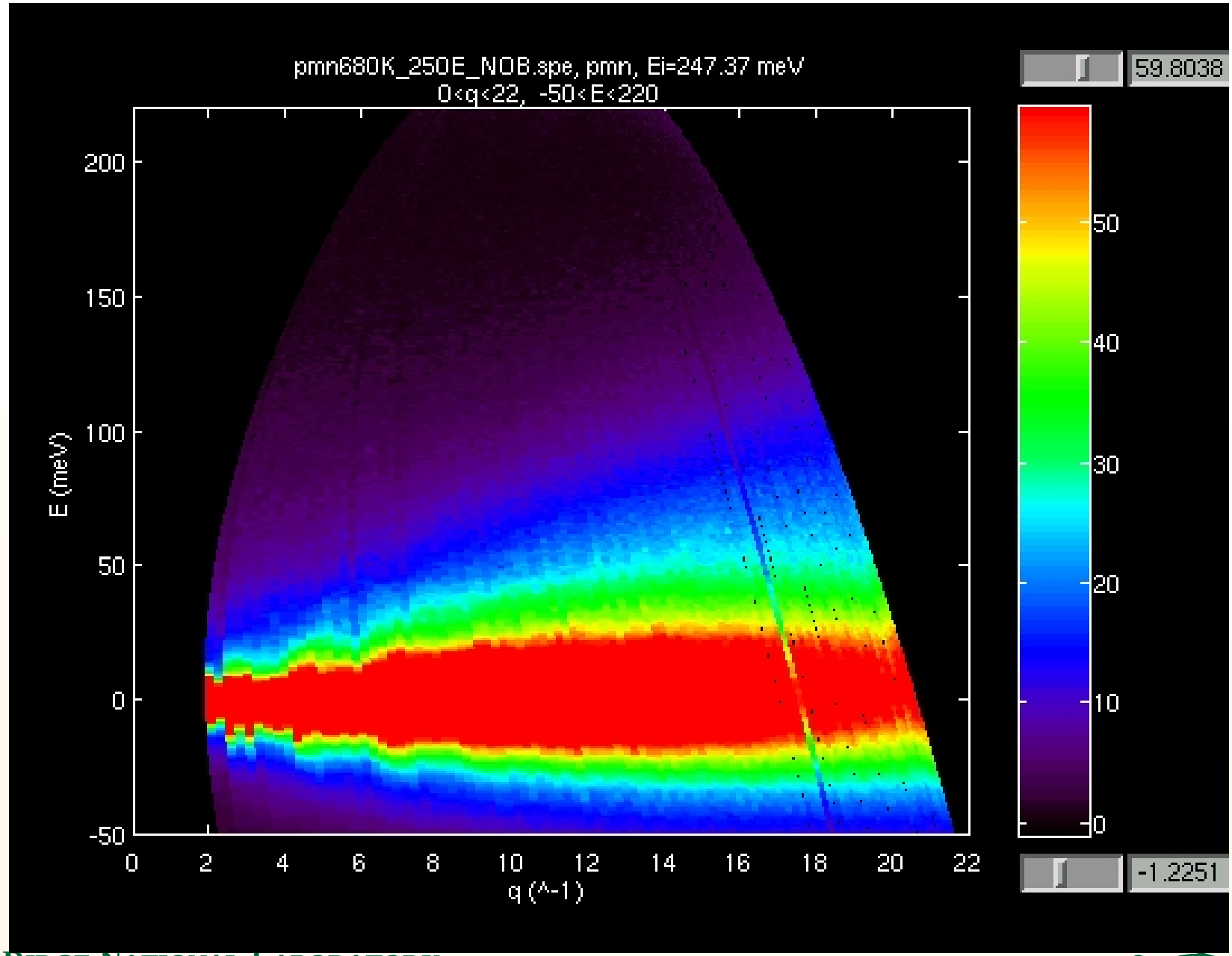
- **Fourier-transform of $S(Q,\omega)$ is the** dynamic PDF**.**
- **$S(Q,\omega)$ has to be determined over large ranges of *Q and* ω.**
- **Measurement with** PHAROS **(inelastic chopper spectrometer) of LANSCE, Los Alamos NL.**
- **Powder sample 100 grams.**
- **Incident energy 250 meV, covering up to 20 $Å^{-1}$.**
- **Intensity corrected for absorption, background, multiple scattering and multi-phonon intensity.**



MERLIN, ISIS


pmn40K1_250E_nob.spe, pmn at 40K, p1 , Ei=247.37 meV
1.8964<Q<21.678, -50.5<E<230.5
E (meV)
200
150
100
50
0
-50
2
4
6
8
10
12
14
16
18
20
Q (^-1)
16
14
12
10
8
6
4
2
0

T = 40 K


pmn680K_250E_NOB.spe, pmn, Ei=247.37 meV
0<g<22, -50<E<220
E (meV)
q (^-1)
59.8038
-1.2251

T = 680 K

Static PDF

- **Dynamic structure factor:**

$$S(\mathbf{Q},\omega)=\frac{1}{N\langle b\rangle^2}\sum_{\nu,\mu}b_\nu b_\mu\int\left\langle\left\langle e^{i\mathbf{Q}\cdot\left(\mathbf{R}_\nu(0)-\mathbf{R}_\mu(t)\right)}\right\rangle\right\rangle e^{-i\omega t}dt$$

- **Elastic structure factor describes the average structure:**

$$S(\mathbf{Q},0)=\frac{1}{N\langle b\rangle^2}\sum_{\nu,\mu}b_\nu b_\mu e^{i\mathbf{Q}\cdot\left(\langle\langle\mathbf{R}_\nu\rangle\rangle-\langle\langle\mathbf{R}_\mu\rangle\rangle\right)}$$

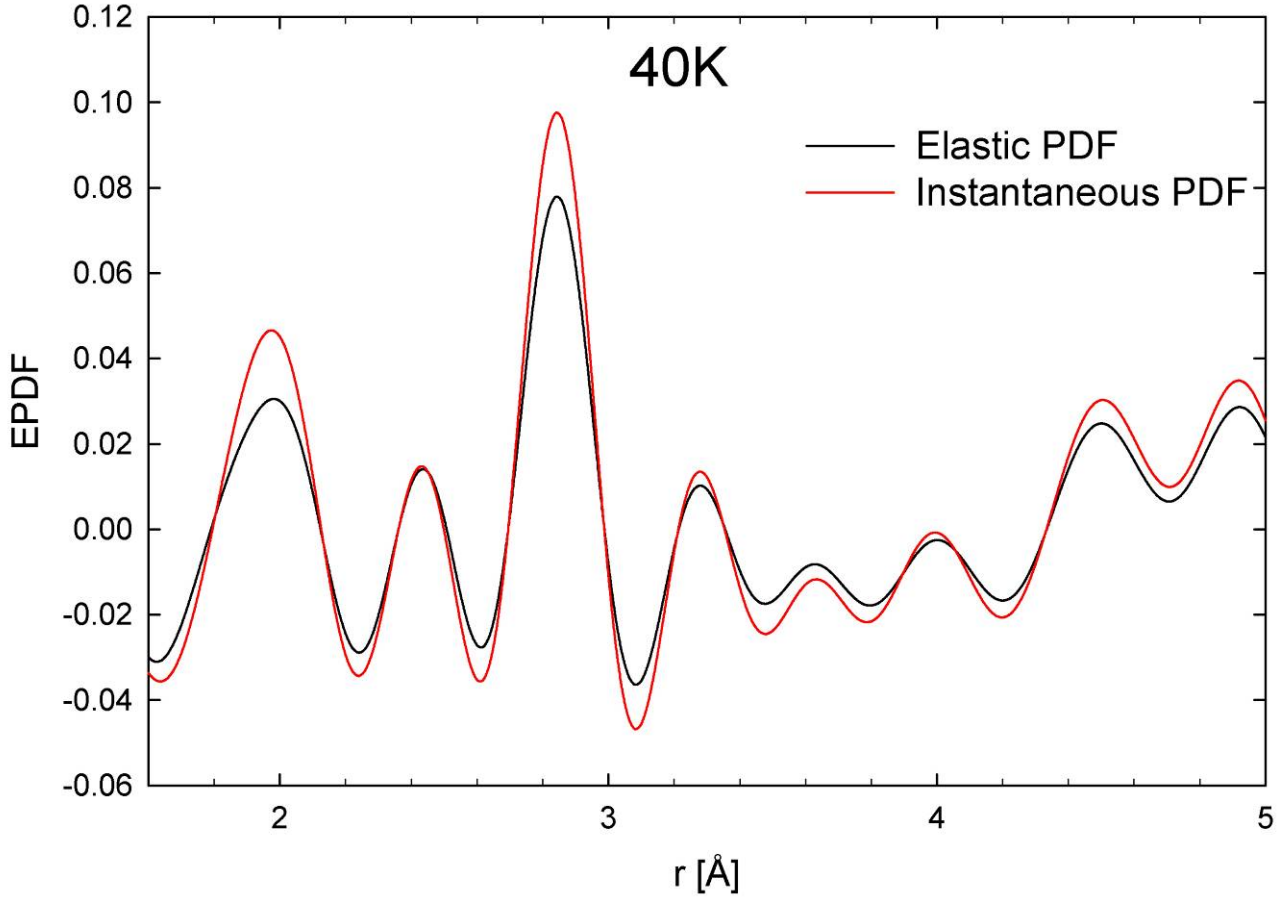
Instantaneous PDF

- **Energy integrated structure factor describes the instantaneous (snap-shot) structure:**

$$S_{total}(\boldsymbol{Q}) = \int_{-\infty}^{\infty} S(\boldsymbol{Q},\omega)\,d\omega$$

$$= \frac{1}{N\langle b\rangle^2}\sum_{\nu,\mu} b_\nu b_\mu \int\int \left\langle\left\langle e^{i\boldsymbol{Q}\cdot\left(\boldsymbol{R}_\nu(0)-\boldsymbol{R}_\mu(t)\right)}\right\rangle\right\rangle e^{-i\omega t}\,dt\,d\omega$$

$$= \frac{1}{N\langle b\rangle^2}\sum_{\nu,\mu} b_\nu b_\mu \left\langle\left\langle e^{i\boldsymbol{Q}\cdot\left(\boldsymbol{R}_\nu(0)-\boldsymbol{R}_\mu(0)\right)}\right\rangle\right\rangle$$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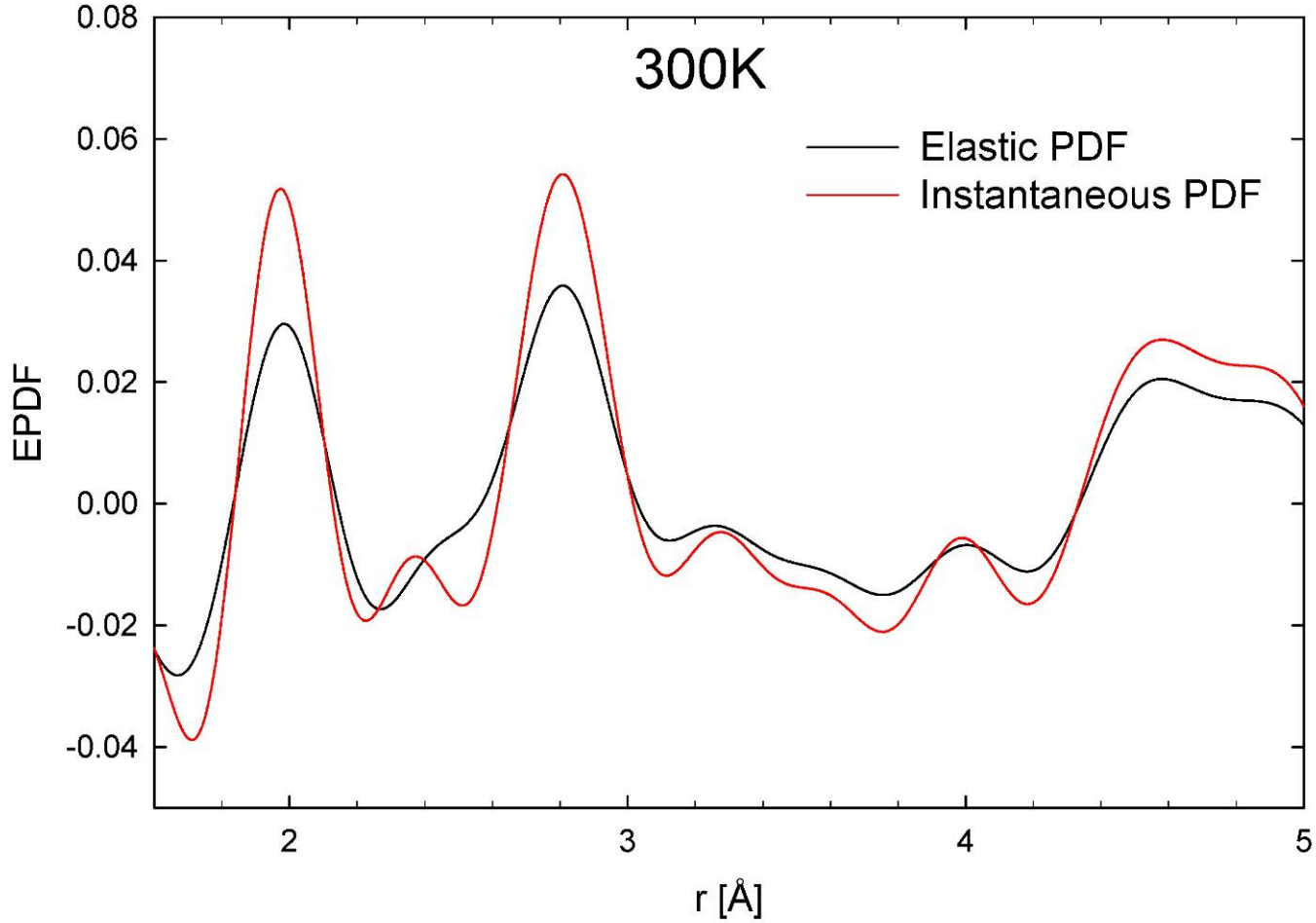
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Case In-Betwen

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Correlations in Space and Time and Born Approximation Scattering in Systems of Interacting Particles

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(Received March 16, 1954)

A natural time-dependent generalization is given for the well-known pair distribution function $g(\mathbf{r})$ of systems of interacting particles. The pair distribution in space and time thus defined, denoted by $G(\mathbf{r},t)$, gives rise to a very simple and entirely general expression for the angular and energy distribution of Born approximation scattering by the system. This expression is the natural extension of the familiar Zernike-Prins formula to scattering in which the energy transfers are not negligible compared to the energy of the scattered particle. It is therefore of particular interest for scattering of slow neutrons by general systems of interacting particles: G is then the proper function in terms of which to analyze the scattering data.

After defining the G function and expressing the Born approximation scattering formula in terms of it, the paper studies its general properties and indicates its role for neutron scattering. The qualitative behavior of G for liquids and dense gases is then described and the long-range part exhibited by the function near the critical point is calculated. The explicit expression of G for crystals and for ideal quantum gases is briefly derived and discussed.

$$\rho(\mathbf{r},t)=\int S(\mathbf{Q},\omega)e^{-i[\mathbf{Q}\cdot\mathbf{r}-\omega t]}d\mathbf{Q}dt=\frac{1}{N\langle b\rangle^2}\sum_{\nu,\mu}b_\nu b_\mu\delta\left(r-\left[\boldsymbol{R}_\nu(0)-\boldsymbol{R}_\mu(t)\right]\right)$$

$$S(\mathbf{Q},t)=\frac{1}{N\langle b\rangle^2}\sum_{\nu,\mu}b_\nu b_\mu\left\langle\left\langle e^{i\mathbf{Q}\cdot\left(\boldsymbol{R}_\nu(0)-\boldsymbol{R}_\mu(t)\right)}\right\rangle\right\rangle$$

Dynamic PDF

$$\rho(\mathbf{r},\omega) = \int \rho(\mathbf{r},t) e^{i\omega t} dt$$

$$= \frac{1}{N\langle b\rangle^2} \sum_{\nu,\mu} b_\nu b_\mu \int \delta\left(r - \left[\boldsymbol{R}_\nu(0) - \boldsymbol{R}_\mu(t)\right]\right) e^{i\omega t} dt$$

$$\boldsymbol{R}_\nu(t) = \langle\langle \boldsymbol{R}_\nu \rangle\rangle + \boldsymbol{u}_\nu(t),$$

$$\boldsymbol{u}_\nu(t) = \int \boldsymbol{u}_\nu(\omega) e^{-i\omega t} d\omega$$

$$\rho(\mathbf{r},\omega) = \frac{1}{N\langle b\rangle^2} \sum_{\nu,\mu} b_\nu b_\mu \delta\left(r - \left[\langle\langle \boldsymbol{R}_\nu \rangle\rangle - \langle\langle \boldsymbol{R}_\mu \rangle\rangle\right] + \left\langle\left\langle \boldsymbol{u}_\nu(\omega) - \boldsymbol{u}_\mu(\omega) e^{i\theta} \right\rangle\right\rangle\right)$$

$$+ O(2\omega) + O(3\omega) + \ldots\ldots\ldots$$

Dynamic PDF Method

- **Describes local dynamics (lattice or spin).**
- **Local dynamics of atoms in liquids and glasses, certain types of chemical reaction, atomic transport in fast ionic conductors.**
- **Powerful tool for ARCS (SNS) and MERLIN (ISIS).**
- **Potential for wide use.**

Slide not available

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Conclusions

- **Bragg's law saved us from hard work, but in the absence of periodicity we are forced to do hard work.**
- **Even for crystalline solids finding the lattice structure often is not enough to understand their properties, particularly for complex solids.**
- **Competing forces can create deviations from periodicity.**
- **Seeing atomic correlation is the best way to understand the structure of aperiodic systems.**
- **Static as well dynamic PDF determined by pulsed neutron or high-energy x-ray scattering are the powerful methods to investigate these complex materials.**