Nanostructured Bulk Materials

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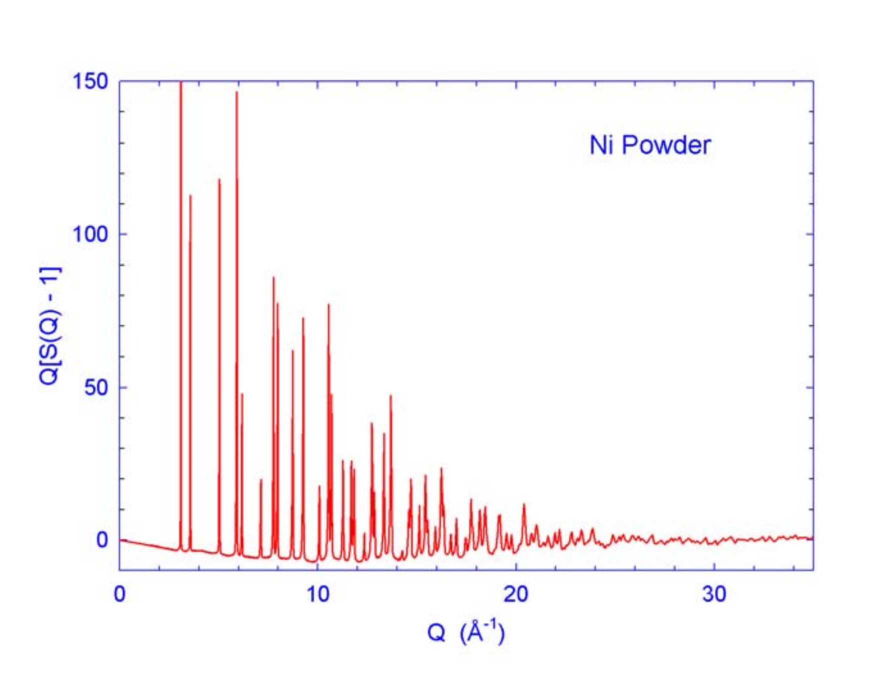
Nanostructured Bulk Materials

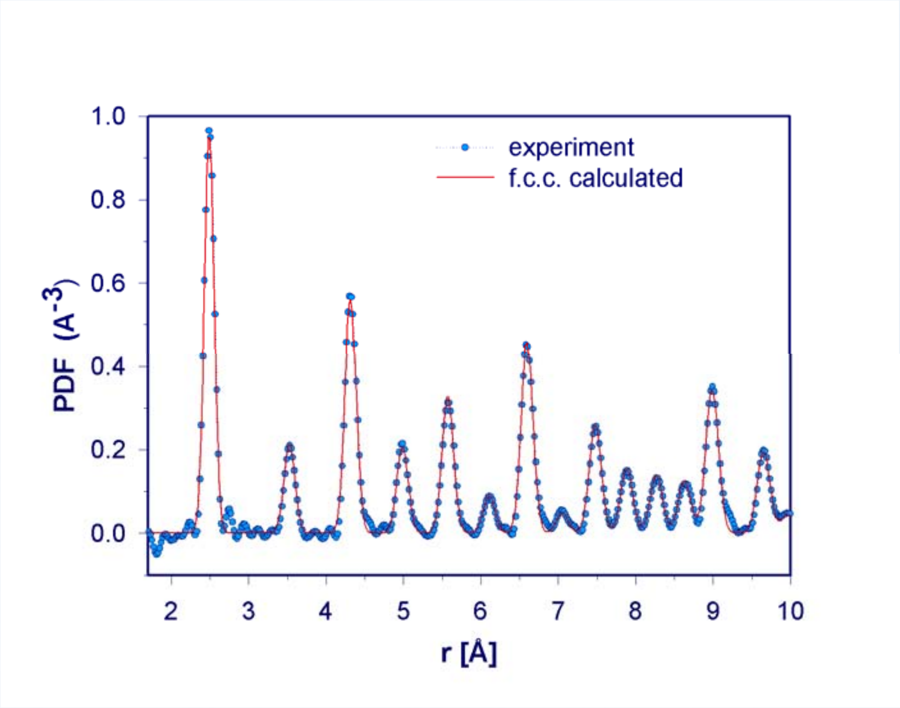
- Possible Research Areas:
  - Nanophase transformations in bulk.
  - Nanoparticles.
  - Structure in fluids, solutions and glasses.

Directly Involved SNS/HFIR Instruments

- NOMAD (high intensity disordered materials diffractometer; PDF)
- ARCS (high intensity wide angle chopper spectrometer; dynamic PDF)
- VULCAN/NRSF2 (in-situ strain measurement)
- POWGEN-3 (powder diffraction)
- SNAP (high pressure diffraction)

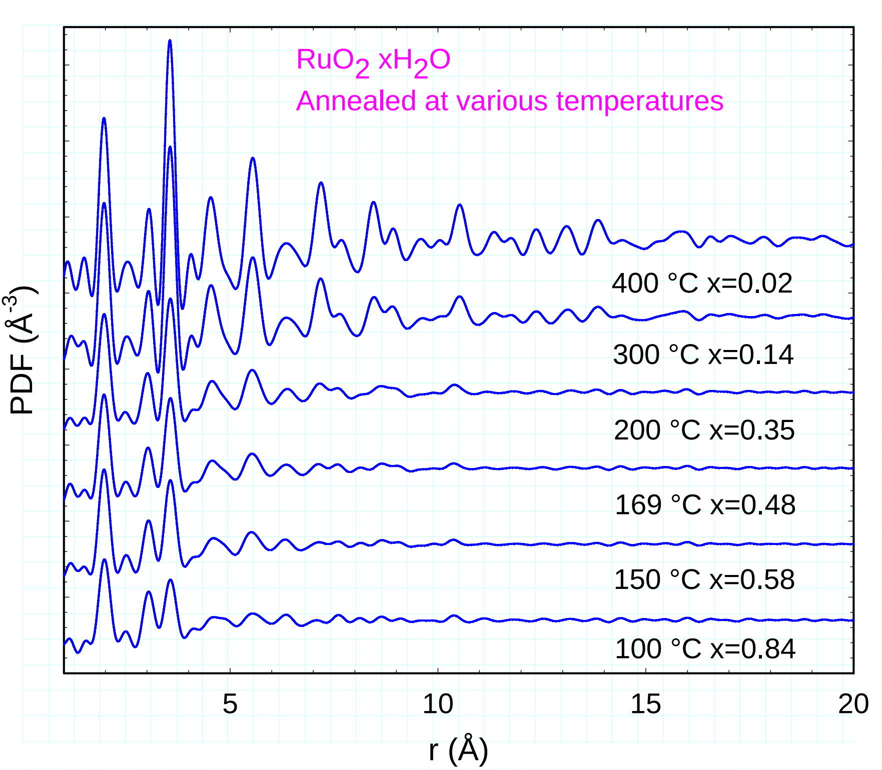
Local Structure by Atomic Pair-Density Function (PDF)

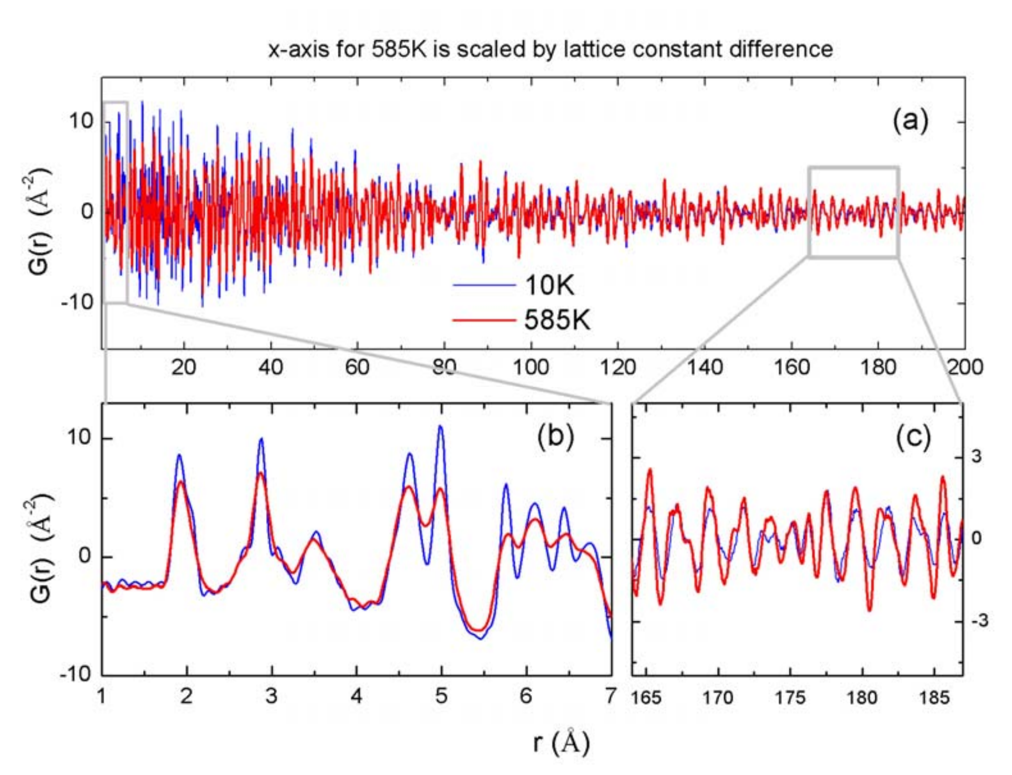




- ***Distribution of distances between atoms, can describe local structural deviations.***
- ***"Underneath the Bragg Peaks", T. Egami and S. J. L. Billinge (Pergamon Press, Oxford, 2003).***

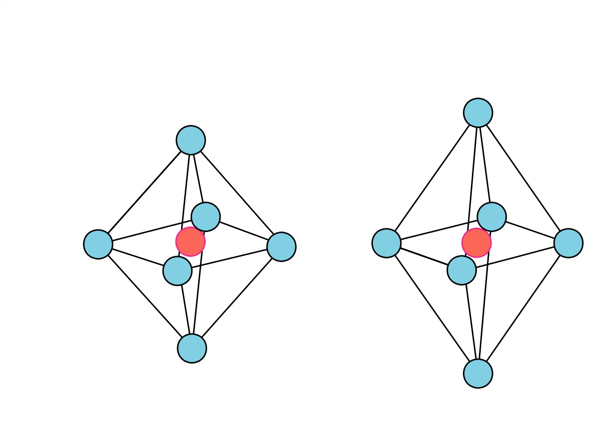
Local Atomic Structure by PDF



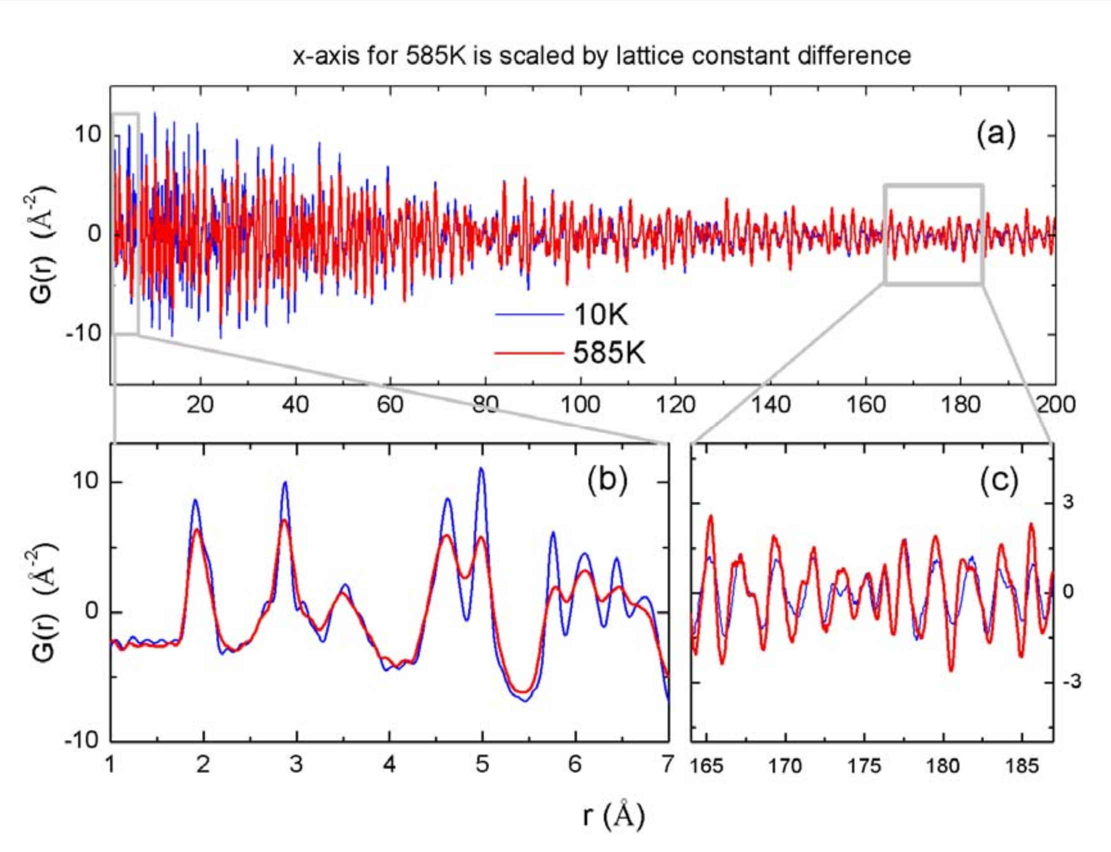


- The pair-density function (PDF) of nano-particle RuO_2-H_2O. It is possible to differentiate nano-particles from the amorphous structure.
- By using a high-resolution pulsed neutron diffractometer it is now possible to determine the PDF up to 200 Å or more.

Frustrated Orbital Ordering in $LiNiO_2$



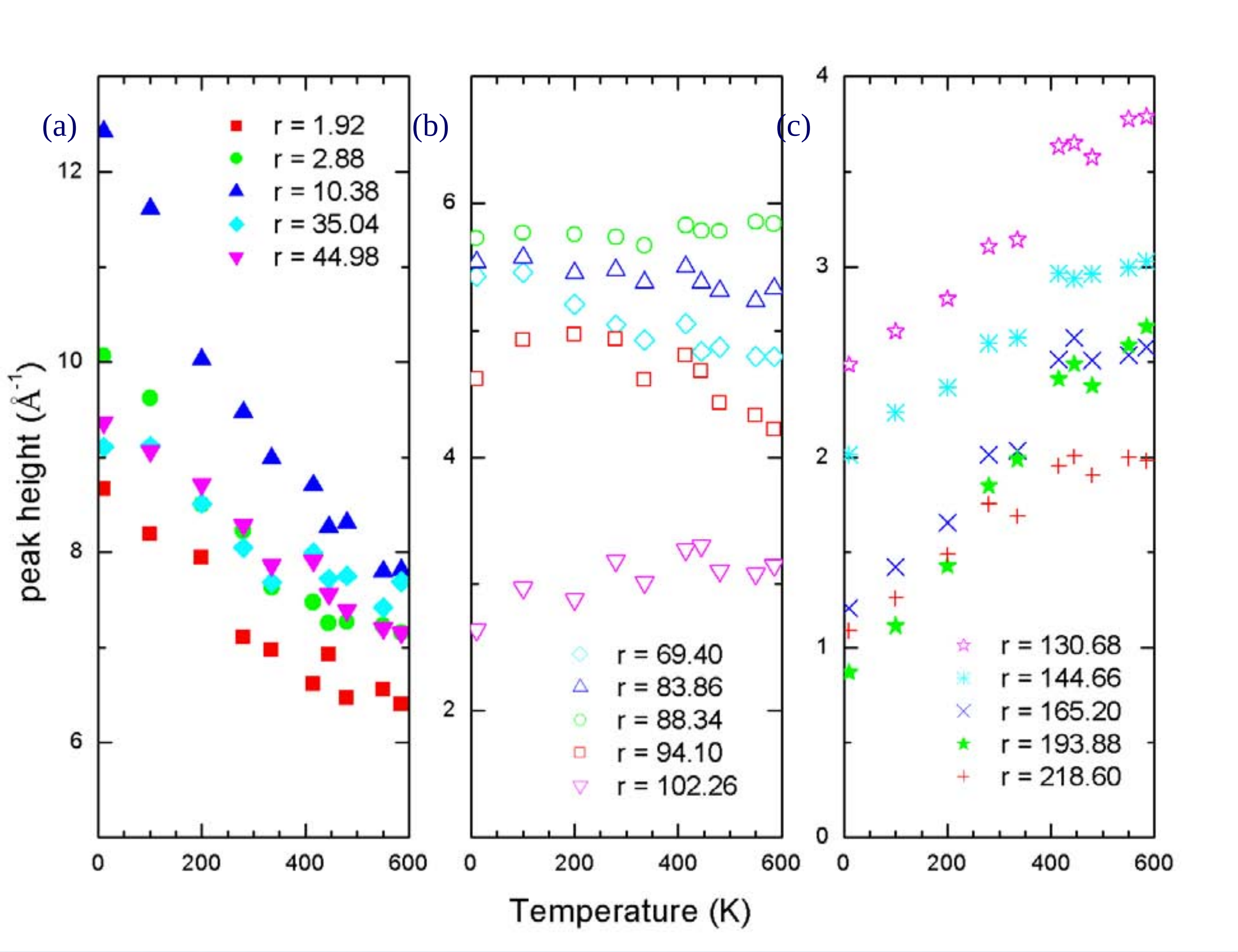
PDF Obtained with the NPDF, LANSCE



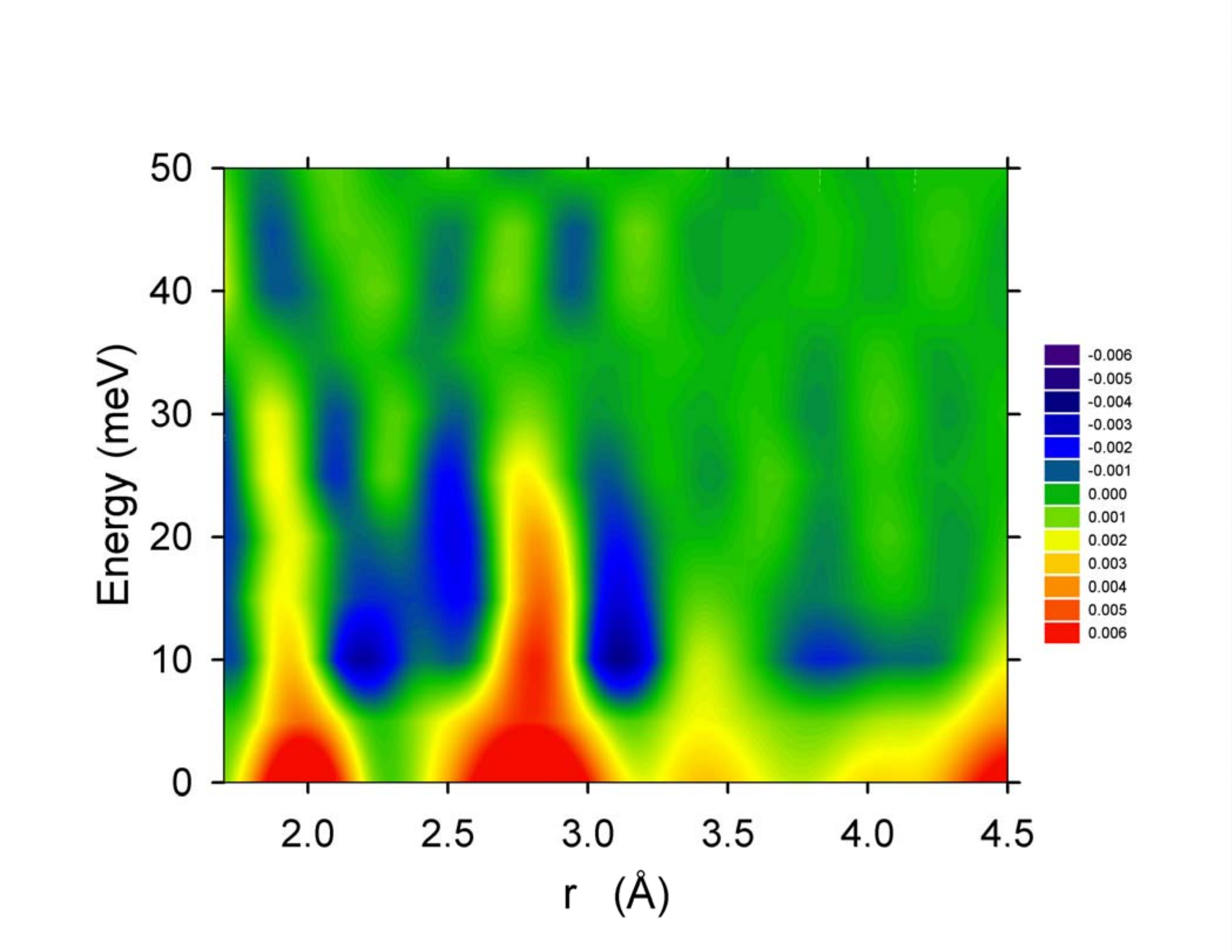
- The first peak of the PDF (Ni-O peak) is consistent with the z^2-type JT orbital state with 4 short, 2 long bonds.
- But there is no long-range JT distortion.

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.

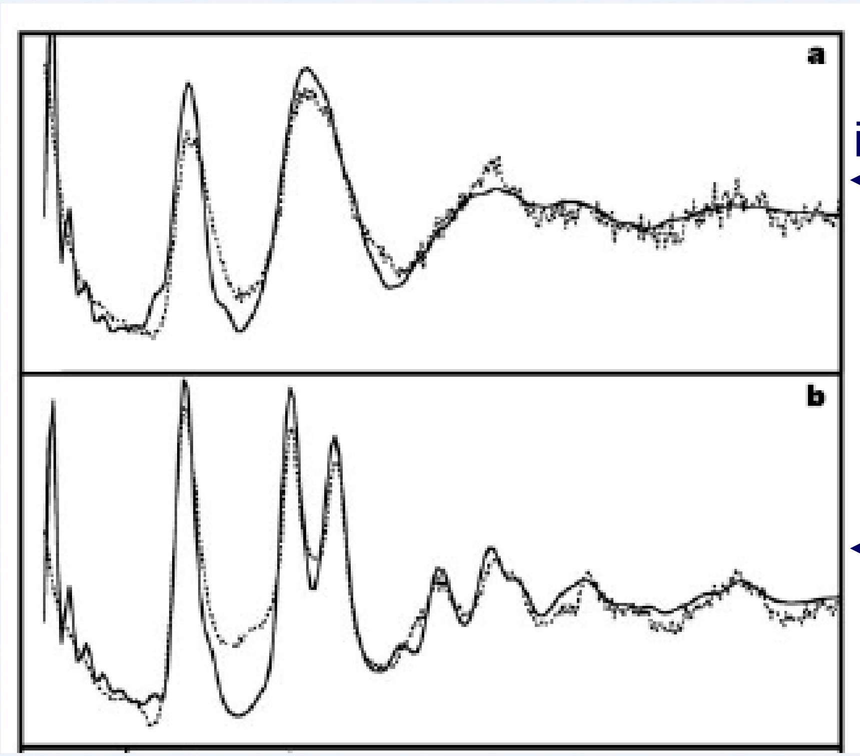


Dynamic PDF of lead magnesium niobate (PMN) at T = 590 K



Solvent-driven structure transformation in nanoparticles

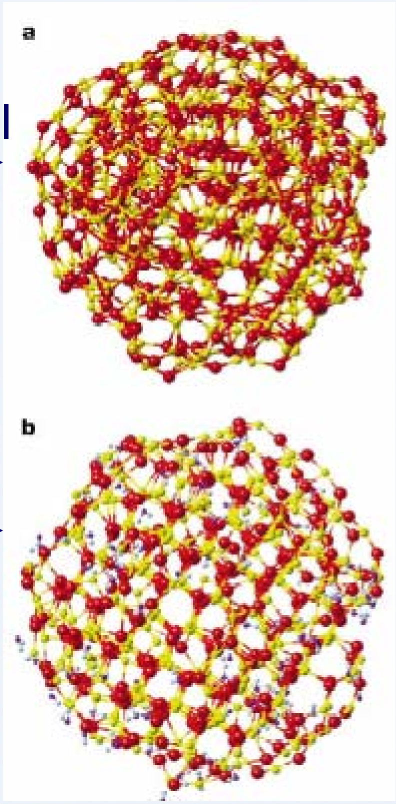
structure function



momentum transfer

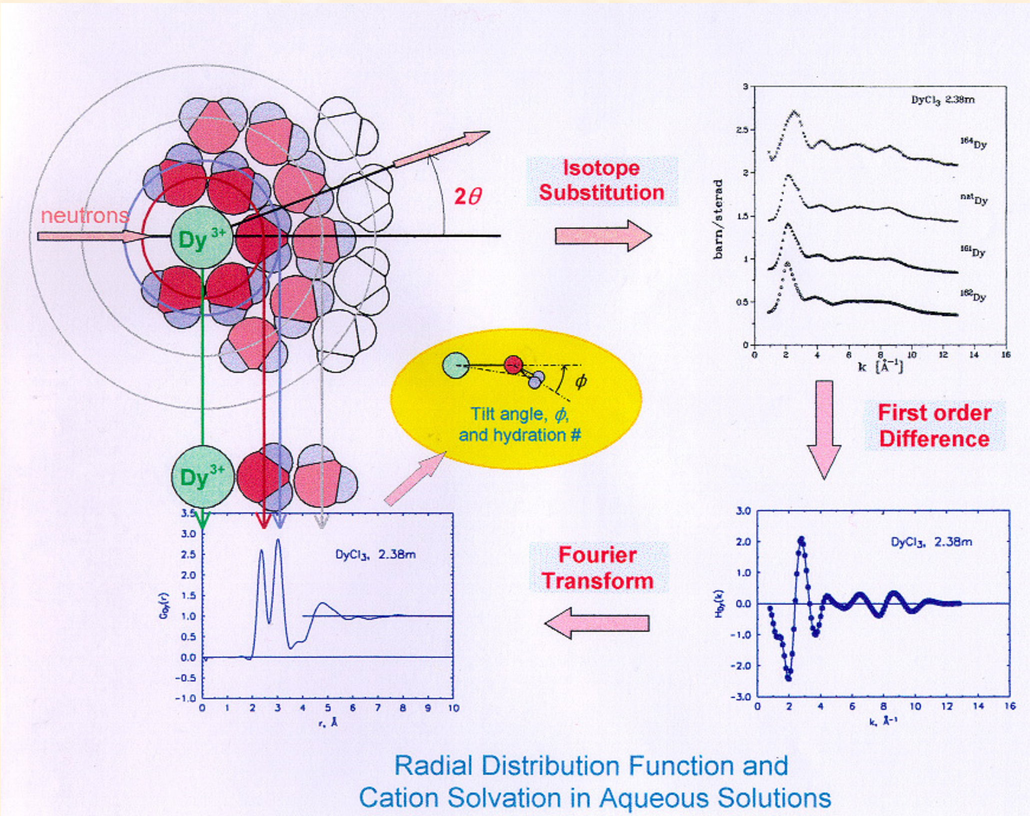
in pure methanol

water present



H. Zhang, B. Gilbert, F. Huang and J. Banfield:
Nature **424** (2003) 1025

Neutron Diffraction with Isotopic Substitution (NDIS) for Determining Hydration/Complexation Structure

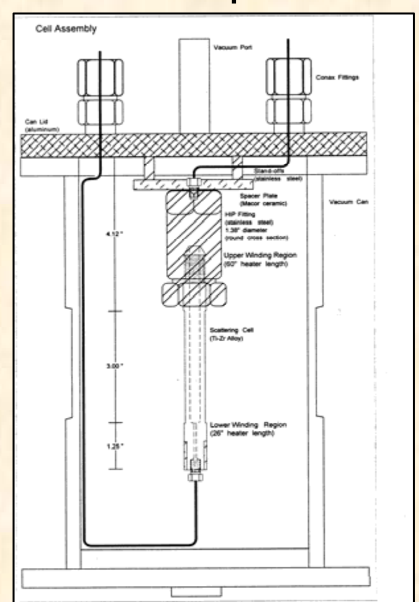


Radial Distribution Function and
Cation Solvation in Aqueous Solutions

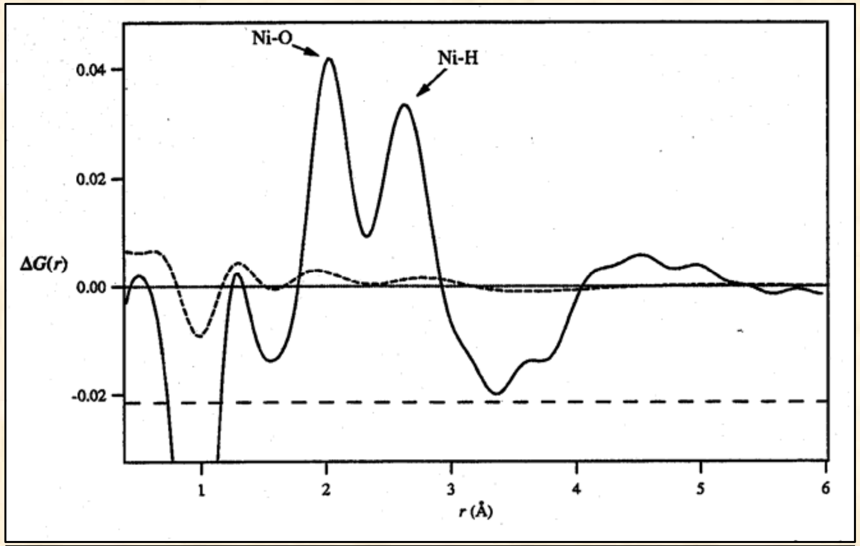
Data from Annis, Hahn, and Narten, J. Chem. Phys. 82, 2086 (1985)

Match T,p,m for two solutions
- D_2O to minimize corrections
- Differ in metal isotope
- Special sample environment needed (null scattering)

Difference gives local environment
- High stability needed
- S/N dependent on system



Structural results from neutron scattering from $NiCl_2$



Results at 298K for $NiCl_2$ at 3.87m.

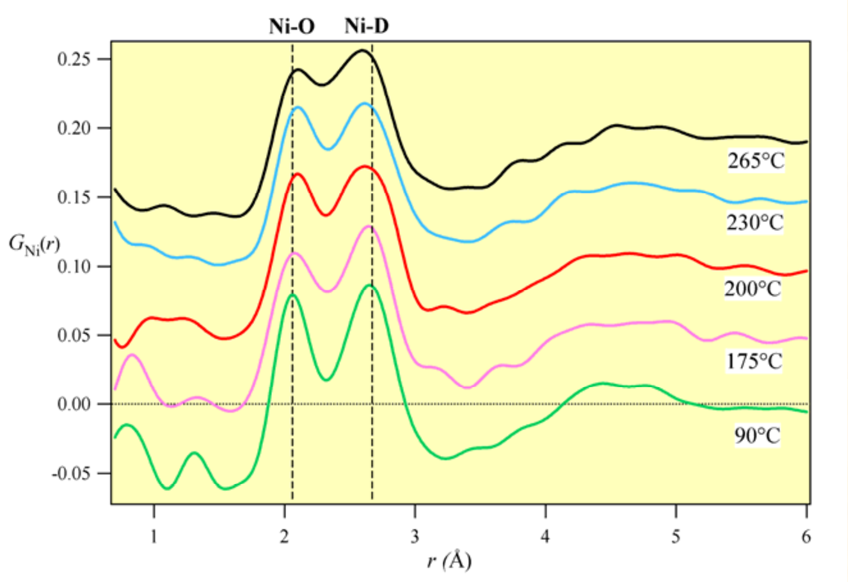
N ≈ 6, $r_{Ni-O} \approx 0.205$ nm, $r_{Ni-H} \approx 0.266$ nm

From Badyal et al., *J. Neutron Res*., 2002.

Results at higher temperatures for $NiCl_2$

Apparent broadening and shifting in hydration peaks; no discernable association.

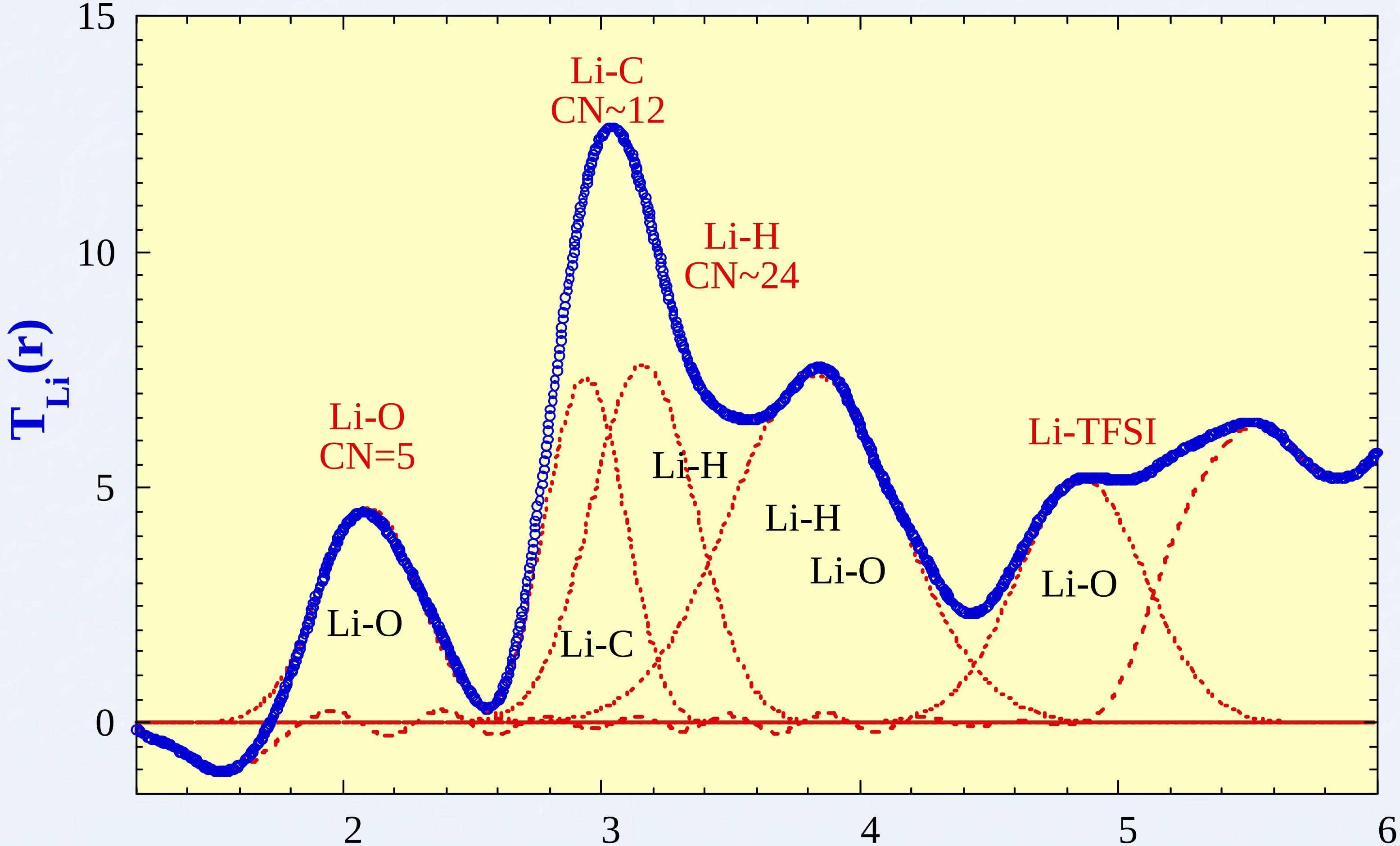
From Badyal and Simonson, *JCP*, 2003



Polymer electrolytes

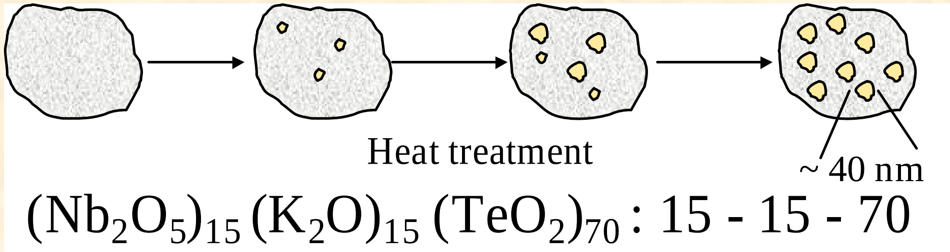
- A leading candidate for vehicle propulsion and secondary batteries in consumer market in coming decade
- Two relaxation processes [Angell 1992]:
  mechanical relaxation (τ_s) and electrical relaxation (τ_σ)
  Decoupling index $R^* = \tau_s(T_g)/ \tau_\sigma(T_g)$
- Optimizing performance involves max. R^*, min. T_g
- Maximizing *R** brings in question of configuration of migrating ions relative to polymer matrix
- Structure: Neutron Diffraction with Isotope Substitution (NDIS):
  H:D, ^{6}Li: ^{7}Li, ^{35}Cl: ^{37}Cl
- Dyamics: quasielastic neutron scattering (QENS)
  neutron spin-echo (NSE)

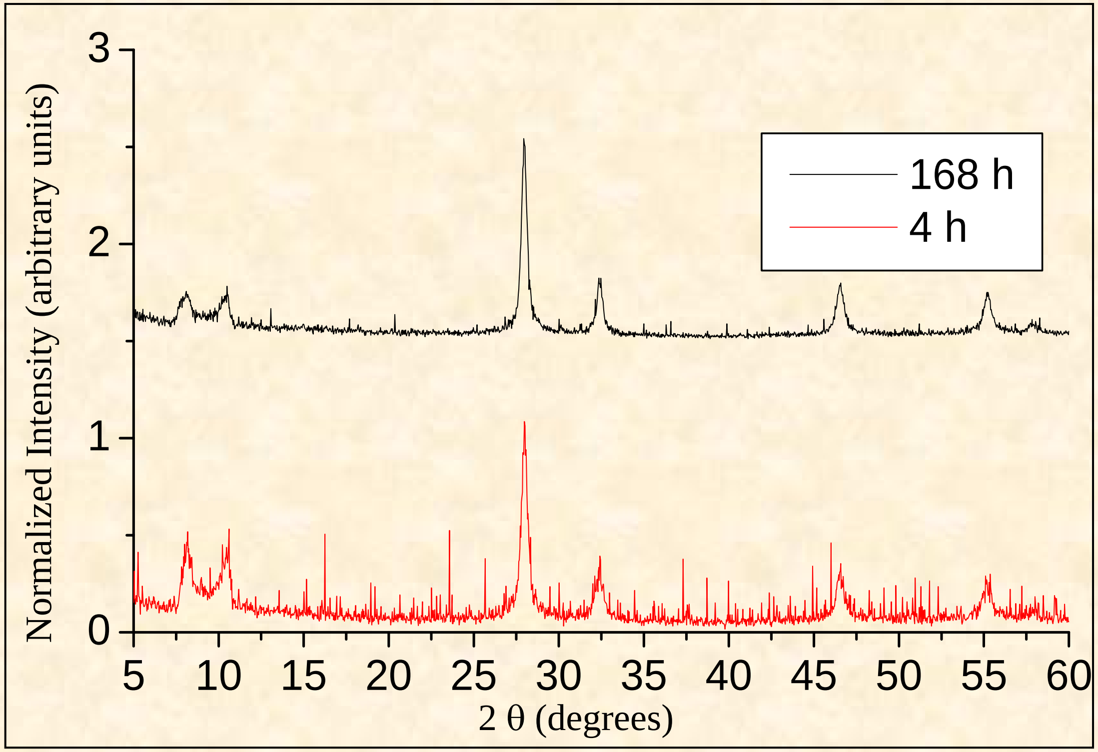
Li difference pair correlation function of $P(EO)_{7.5}LiTFSI$



Application to glass ceramics

Optically transparent glass ceramics can form on heat treatment of quenched glasses.





~250% increase in S/N ratio for 168h heat treatment compared to 4h heat treatment.

Limiting crystallite size ~80nm.

Growth faster than nucleation.

Data needed to evaluate models of kinetic behavior.

Courtesy of Prof. Josef Zwanziger, Dalhousie University

Partially Crystallized Bulk Metallic Glass Contains High-density Nanometer Sized Crystallites

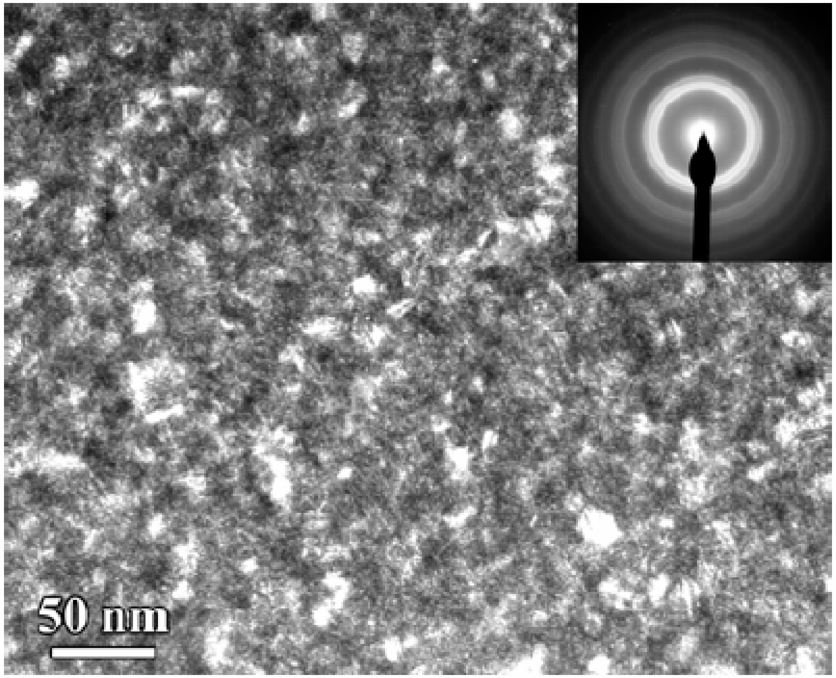
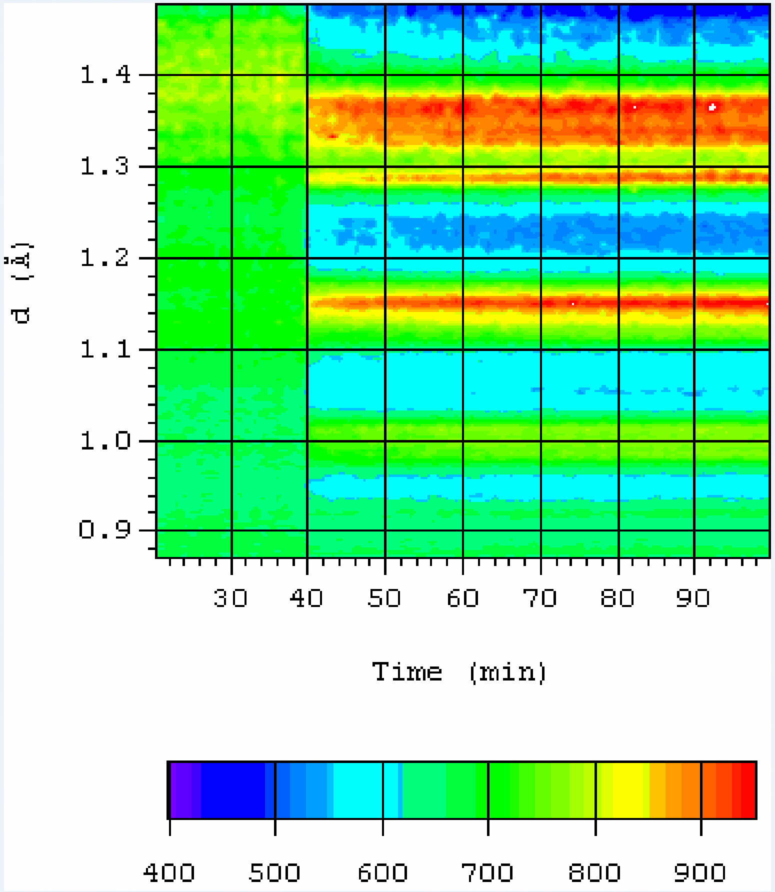
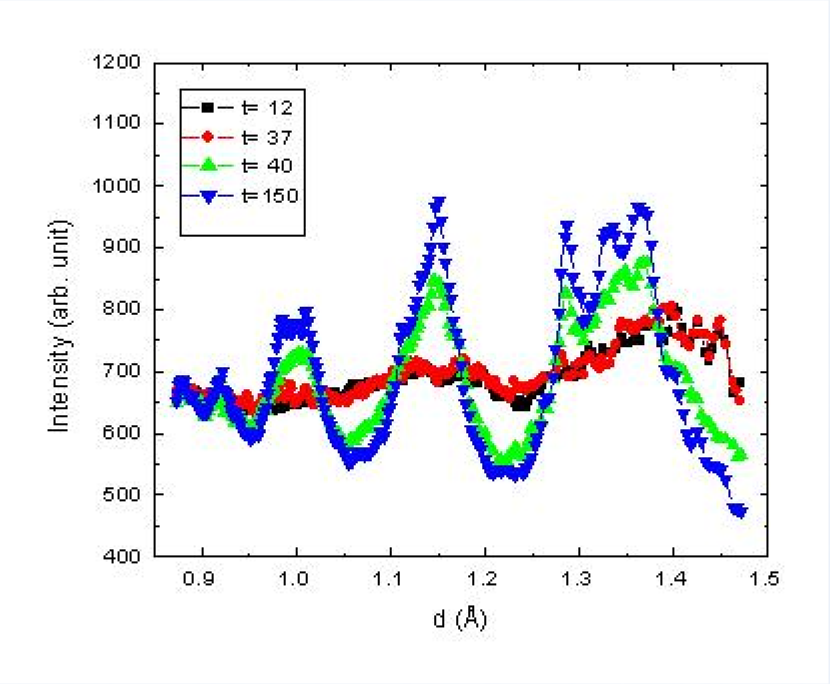


Figure 4
Dark-field transmission electron microscopy image with diffraction pattern (inset) of Vit105, annealed for 15 h at 673 K (Pekarskaya *et al.* 2003).

- e.g., upon isothermal annealing
- Density 10^{23}-10^{24} m^{-3}
- Crystallite size ~10 nm
- Even for temperatures close to T_g

An Abrupt Amorphous-to-Crystalline Transformation Was Observed at t=40 min

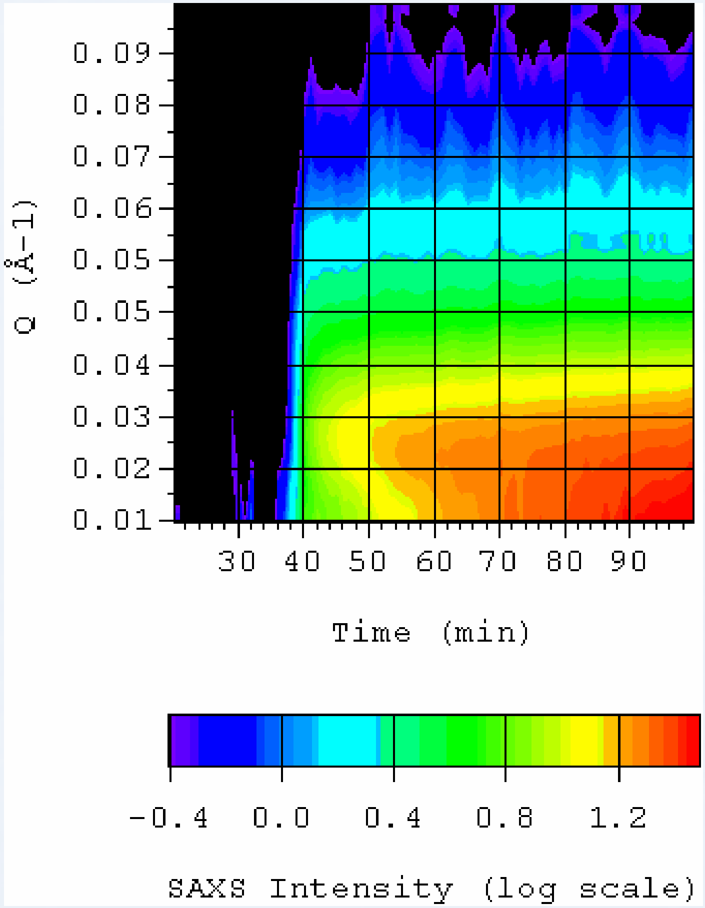


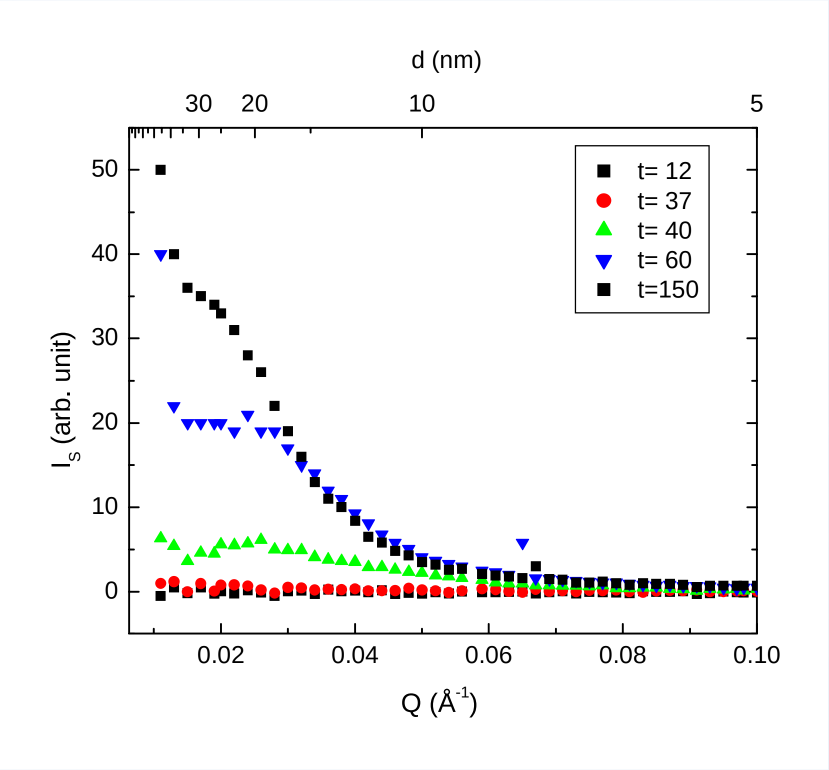


Crystalline phase is primarily Zr_2Ni

Our Sample Is BAM-11, $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$

Small Angle Scattering Data Show Phase Separation Prior to Crystallization

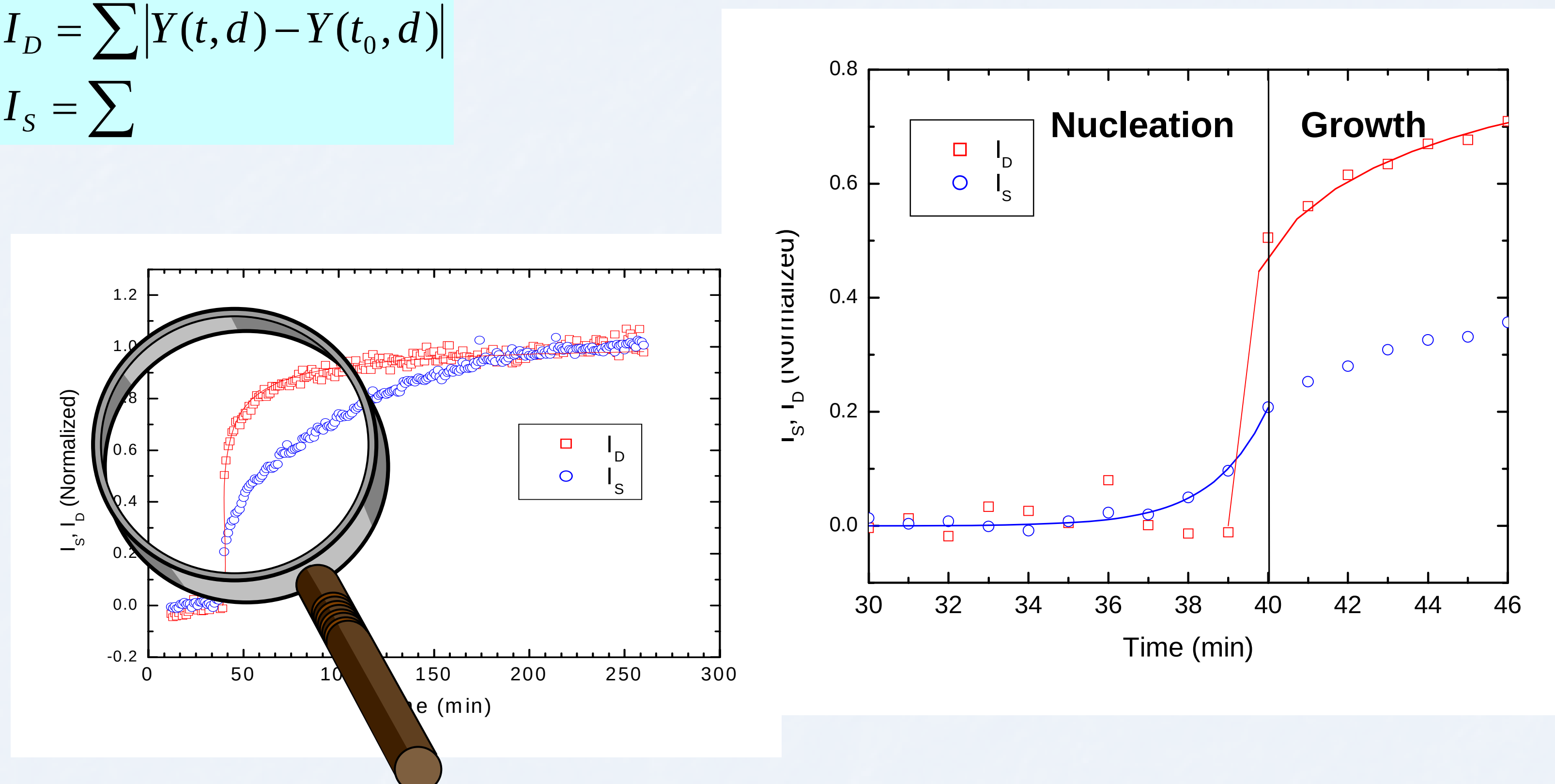




Small angle scattering profile exhibits characteristic interference peak

Combined Data Show Phase Separation Before Crystallization

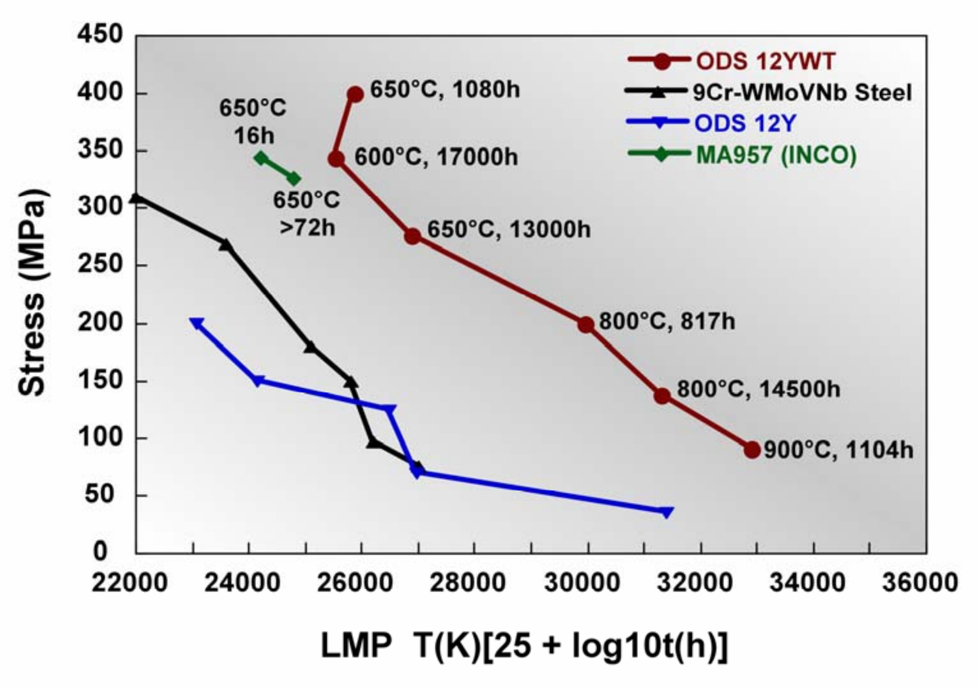
$$I_D = \sum \left| Y(t,d) - Y(t_0,d) \right|$$
$$I_S = \sum$$



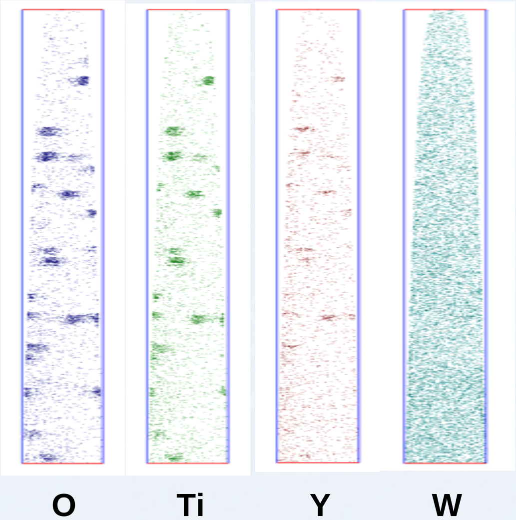
- Phase separation occurred first, setting stage for crystallization
- Rapid rise of small angle scattering intensity for t < 40 min
- Slow growth of diffraction intensity for t > 40 min.

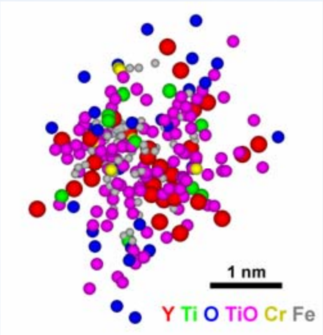
Wang et al., PRL 2003

Oxide-Dispersion-Strengthened Steel Containing Y-Ti-O Nanoclusters Exhibits Outstanding Mechanical Properties at High Temperature



Atom probe showed that Y-Ti-O form nanoscale clusters that are highly stable even at high temperatures

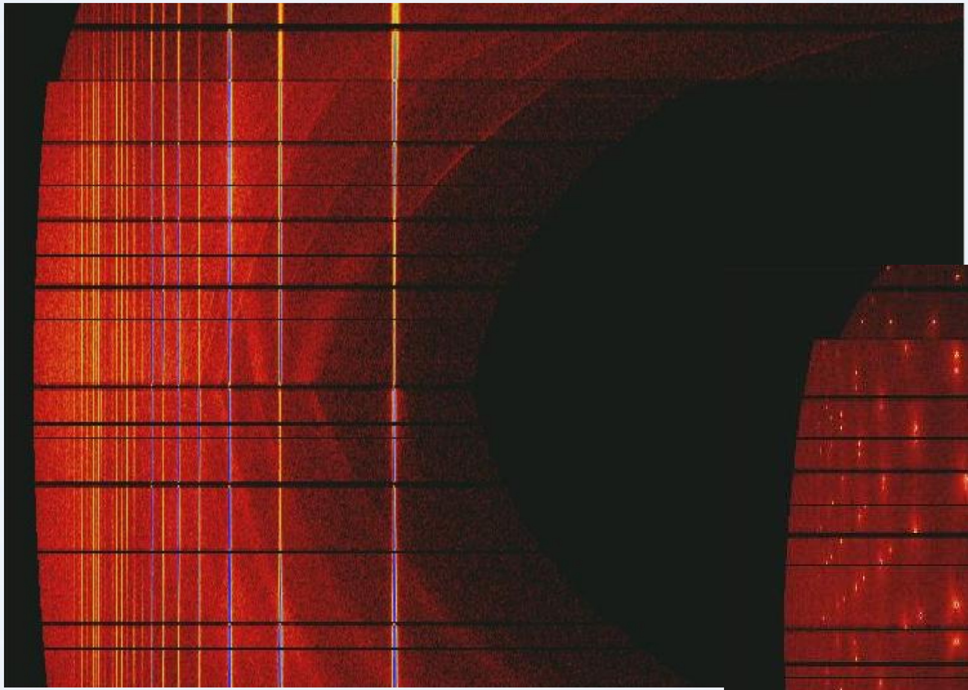




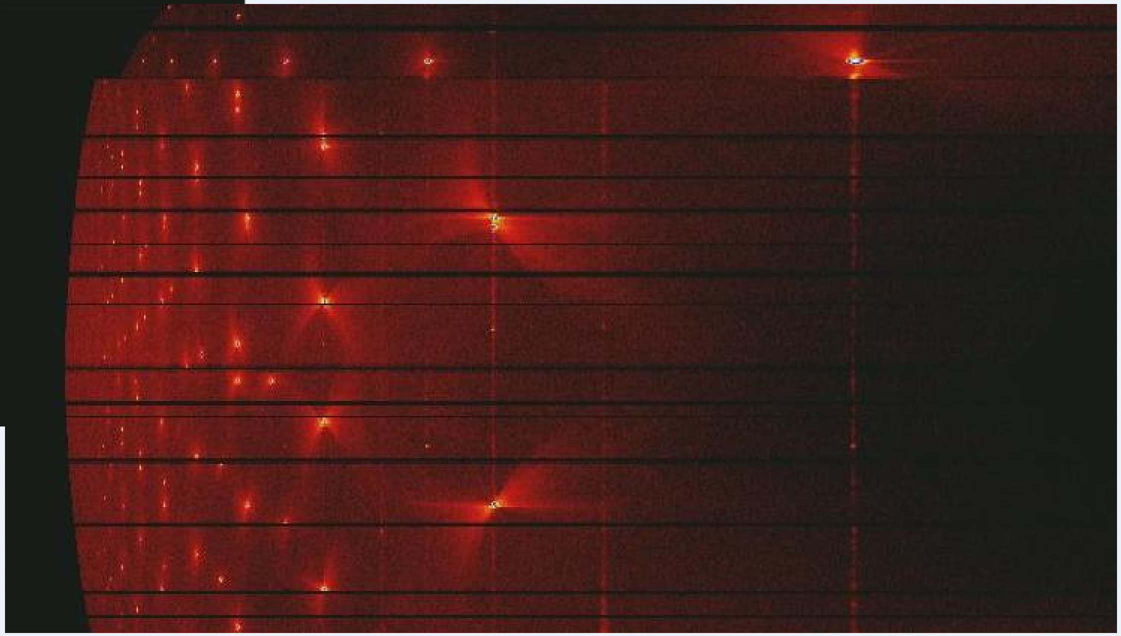
Creep rate is reduced by six orders of magnitude in ODS steel containing Y-Ti-O. This degree of improvement represents a major breakthrough in the use of ferritic alloys for high temperature structural applications, which could tremendously benefit energy-generation systems

In-situ Neutron Diffraction Studies to 1300°C Demonstrated the Thermal Stability of Mechanically-Alloyed ODS Steel

Room temperature diffraction patterns after heating to 1300°C



Cast ODS steel recrystallized and grew into single crystals



Mechanically alloyed ODS steel are stable after heating to 1300°C

Nanoscale control of materials structure via phase transformation

CNMS Contribution to "Bulk Nanoscience"

Sample preparation and characterization
- Nanostructured and nanoparticle materials
- Processing/treatment approaches
- Specialized sample labeling
  - H/D substitution in hydrogenous systems
  - Isotopes beyond H/D for enhanced contrast
- Enhanced access to additional ORNL capabilities

Cooperation and collaboration
- Expertise in synthesis and characterization
- Nanomaterials Theory Institute