Structural Refinement of Disordered Zeolites using the PDF Method

María Martínez, Raúl F. Lobo
Department of Chemical Engineering
University of Delaware

Inmaculada Peral
Center for Neutron Research
NIST

Thomas Proffen
Los Alamos Neutron Science Center
LANL

ACNS

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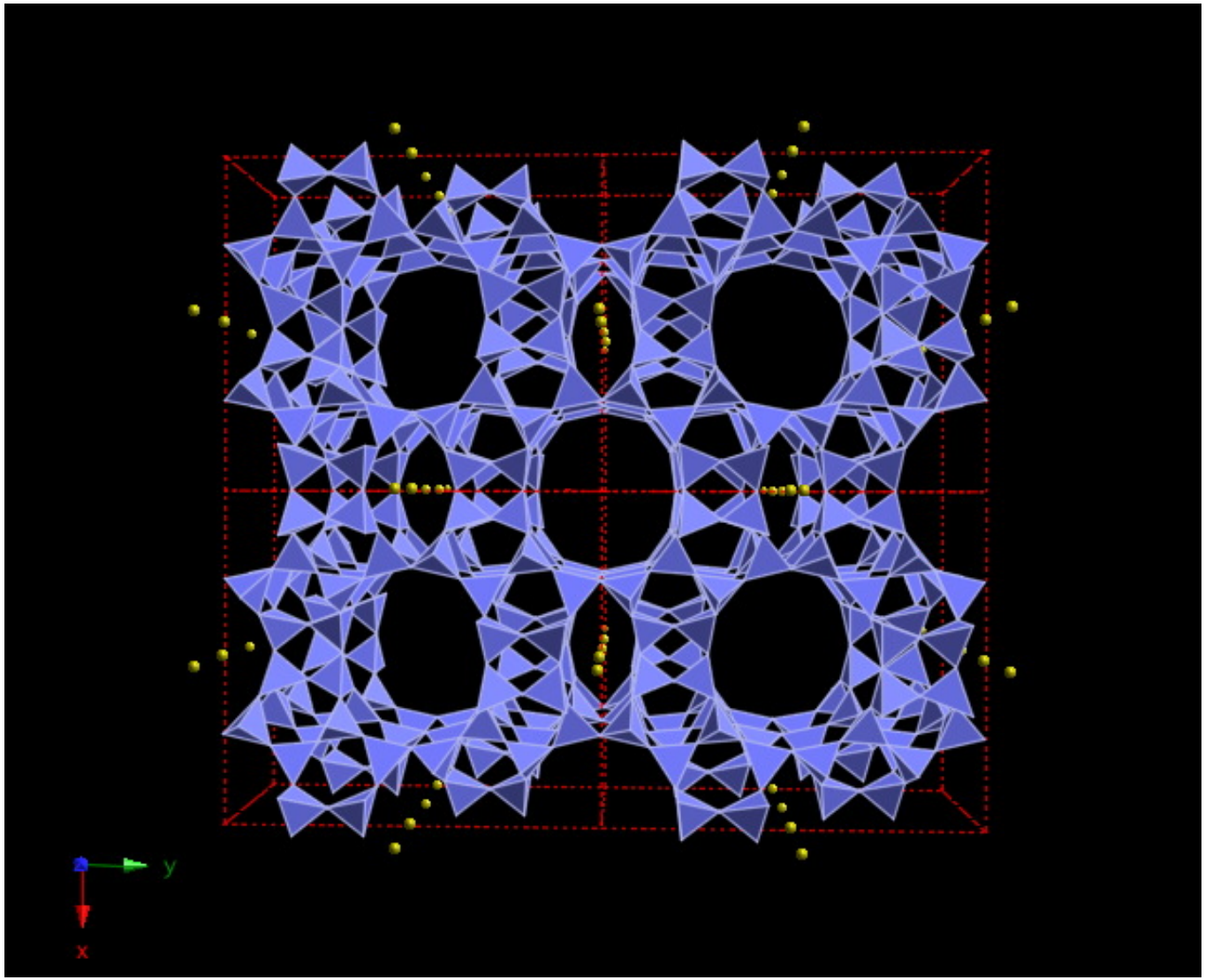
Zeolites

- **Crystalline aluminosilicates** with a 4-connected **tetrahedral framework** structure enclosing **cavities** occupied by **large ions and water** molecules, both of which have considerable freedom of movement, permitting ion exchange and reversible dehydration (Smith, 1988)
- **Most important class of solid acids**
- **Important Environmental Applications**
  - **Catalytic Converters (Diesel and Gasoline)**
  - **DeNOx Catalyst in Power Plants**
  - **VOC Removal**
- **Structure-property relation require detailed atomic information**

Zeolite Mordenite



Why so much interest in Zeolites?

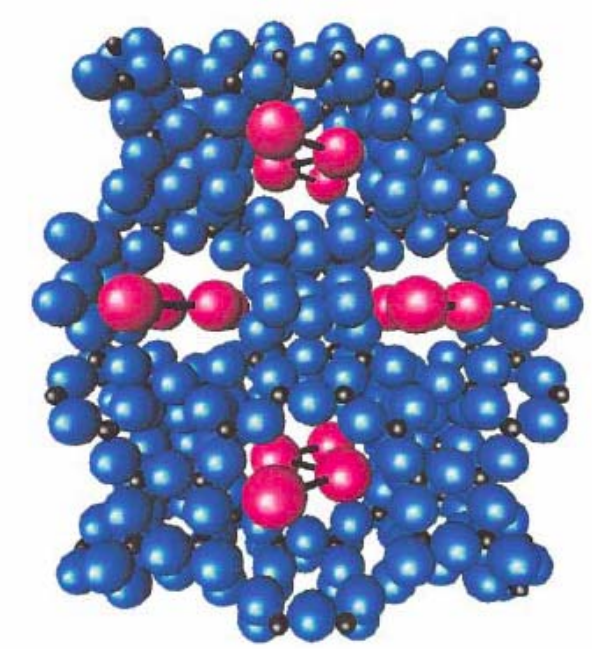
- **Well-defined molecular structure**
  - Establish structure-property relationships
  - Prediction of properties from structure
- **BUT…**
  - *Disorder is an inescapable fact on zeolitic materials*
  - Structure-Property relations are not always simple

Disorder in Zeolites

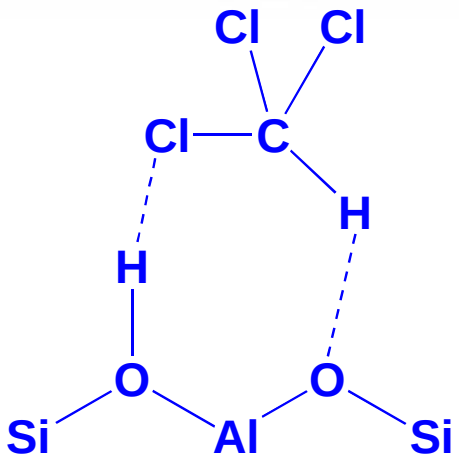
- **Framework Substitution**
  - Other atoms besides Si
- **Extra-Framework Cations**
  - Partial occupancies, multiple cations
- **Adsorbed Species**
  - No translational symmetry
  - Lower symmetry than framework
- **Framework Disorder**
  - Static
  - Dynamic
- **Opportunity for the PDF method**

Previous Application of PDF Method to Zeolites

- Cs atoms in Siliceous Zeolites
  - Petkov, V. et al., PRL, 2002



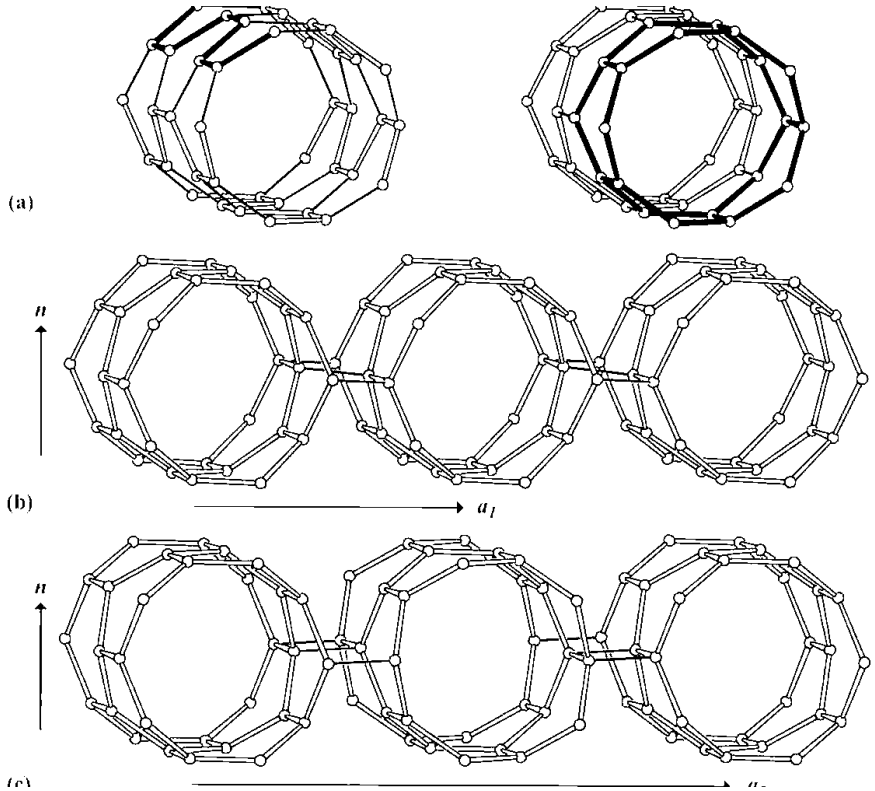
- Coordination of $CHCl_3$ to Acid Sites
  - Eckert, J. et al, JACS, 2002

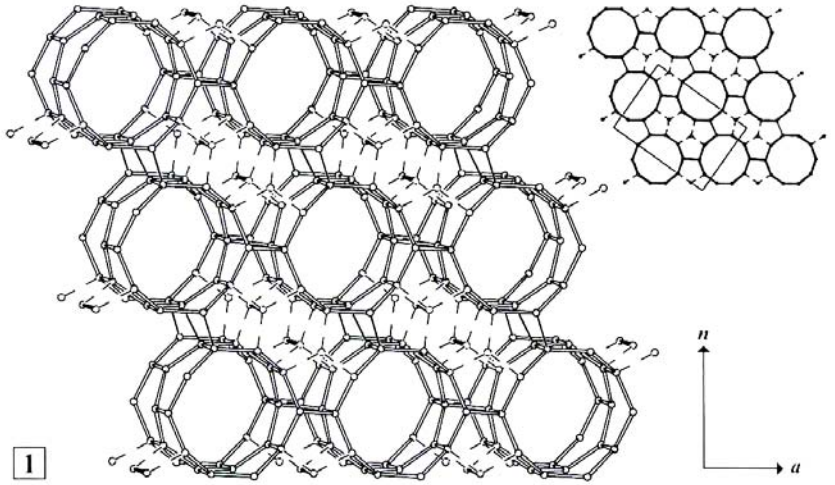


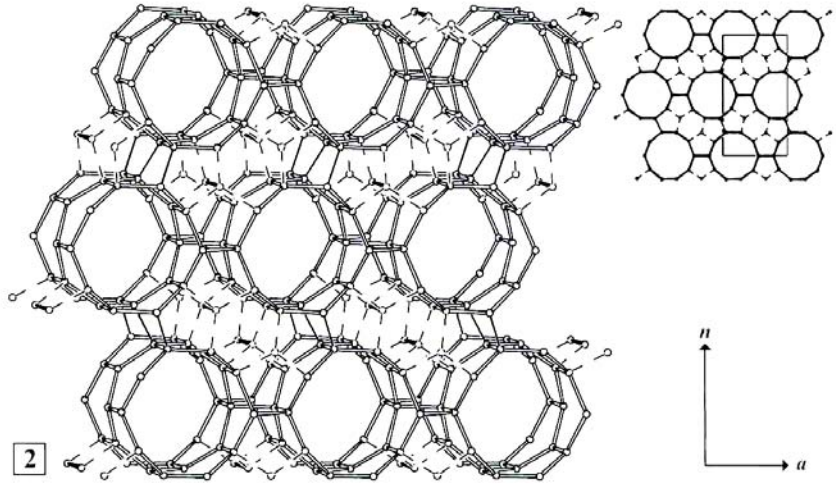
Static Disorder

- **Two-Dimensional Translational Symmetry**
  - Disordered stacking of ordered layers
    - ABC-family of Zeolites
- **One-Dimensional Translational Symmetry**
  - Disordered arrangement of ordered ‘tubes’
    - ZSM-48, SSZ-31 and others
- **Zero-Dimensions**
- ***Description must be Statistical***

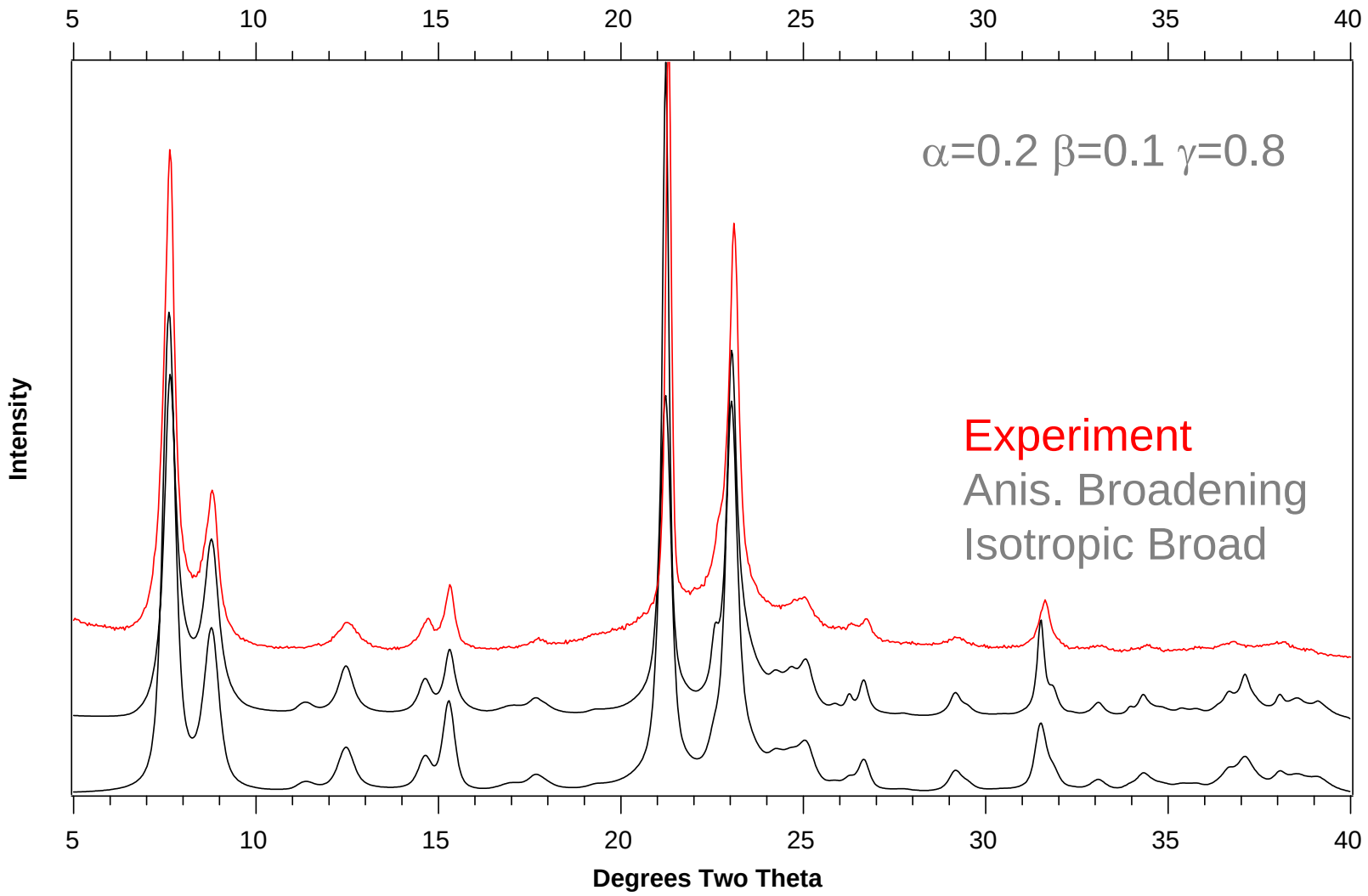
Building ZSM-48 Using 1D Units







ZSM-48: Experiment and Simulation



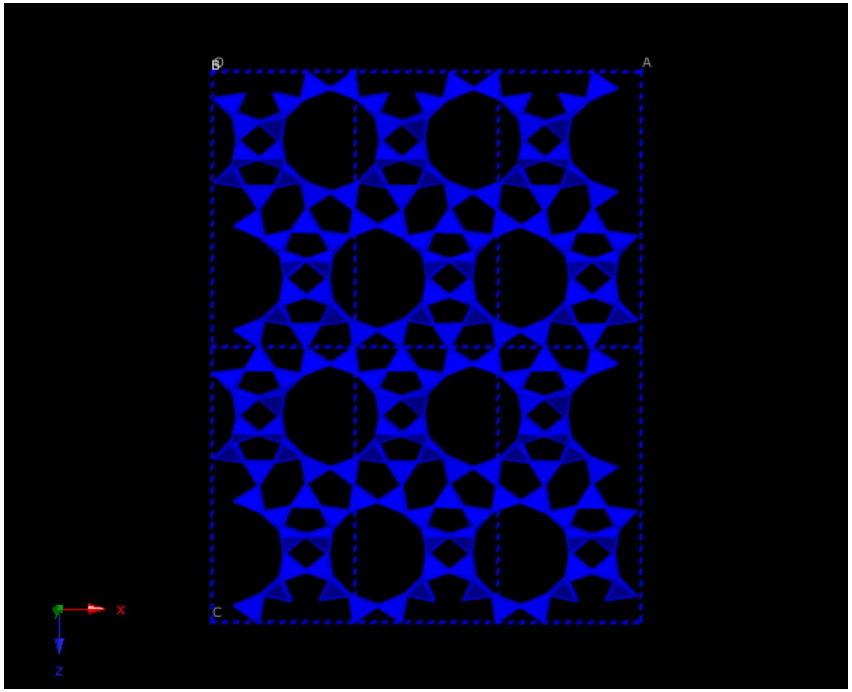
Objectives

- Determine the suitability of the PDF method to investigate the local structure in selected zeolite systems
- Use zeolite beta as a test case
- Zeolite beta:
  - 9 Si and 16 O atoms in asymmetric unit

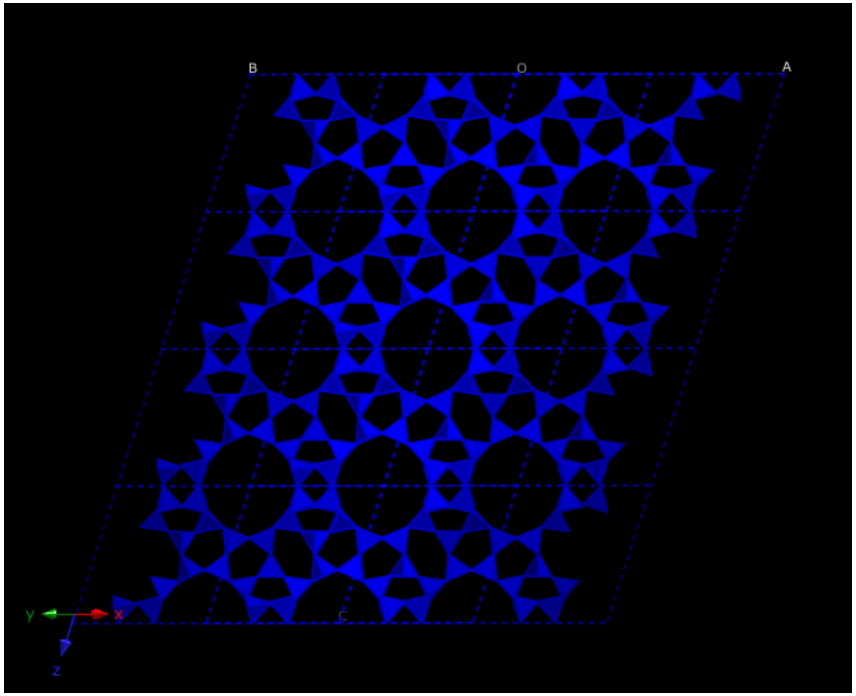
Zeolite Beta

- Important alkylation catalyst
- 12-ring (~7.5 Å) 3-D Pore system
- Intergrowth of two polytypes

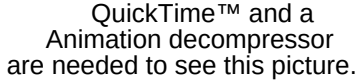
Polytype A



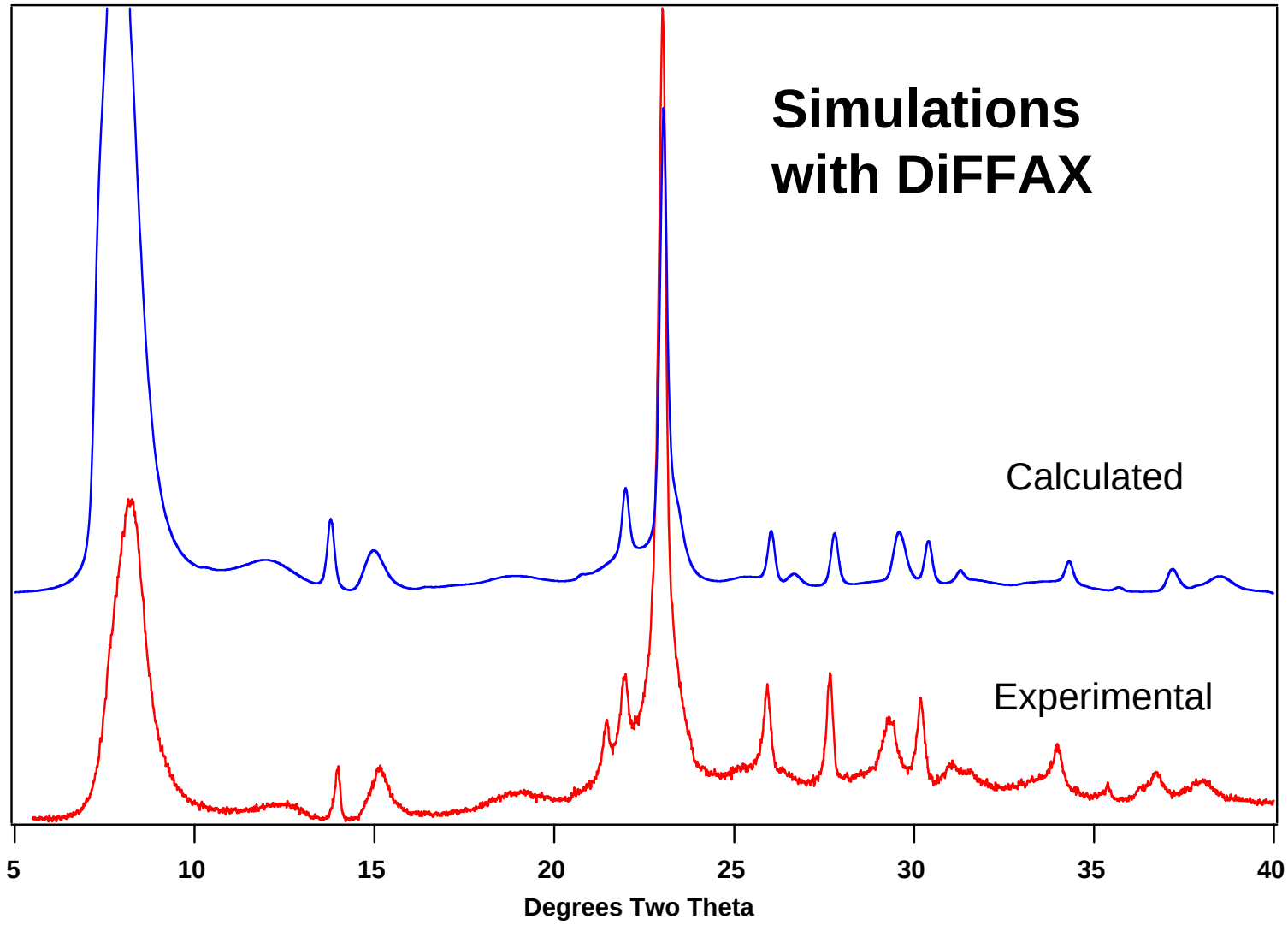
Polytype B



Polytype B


QuickTime™ and a
Animation decompressor
are needed to see this picture.

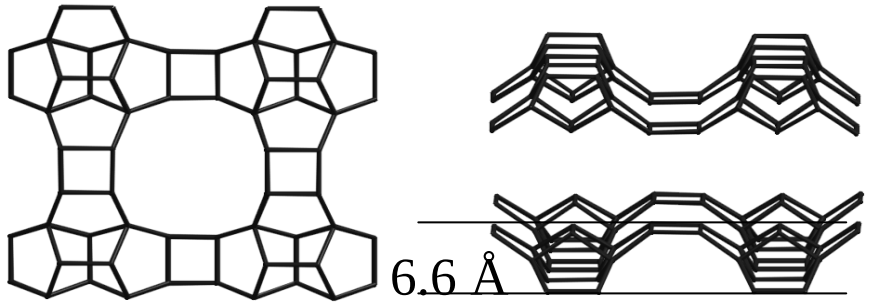
XRD of Beta


Simulations
with DiFFAX
Calculated
Experimental
5
10
15
20
25
30
35
40
Degrees Two Theta

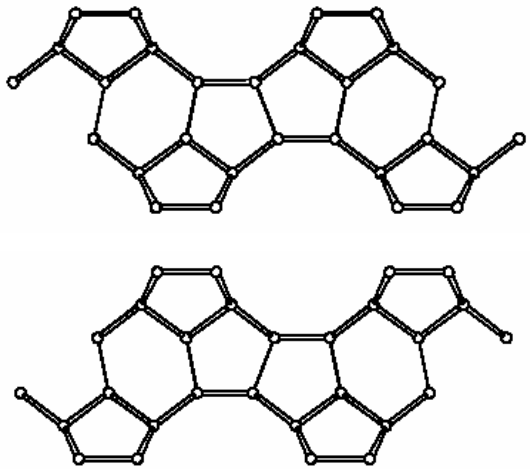
Periodic Building Unit of Beta

- Basic building element is the Periodic Building Unit
  PerBU
- Both polytes A and B can be described from the same PerBU

Views of the Periodic Building Unit (PerBU)



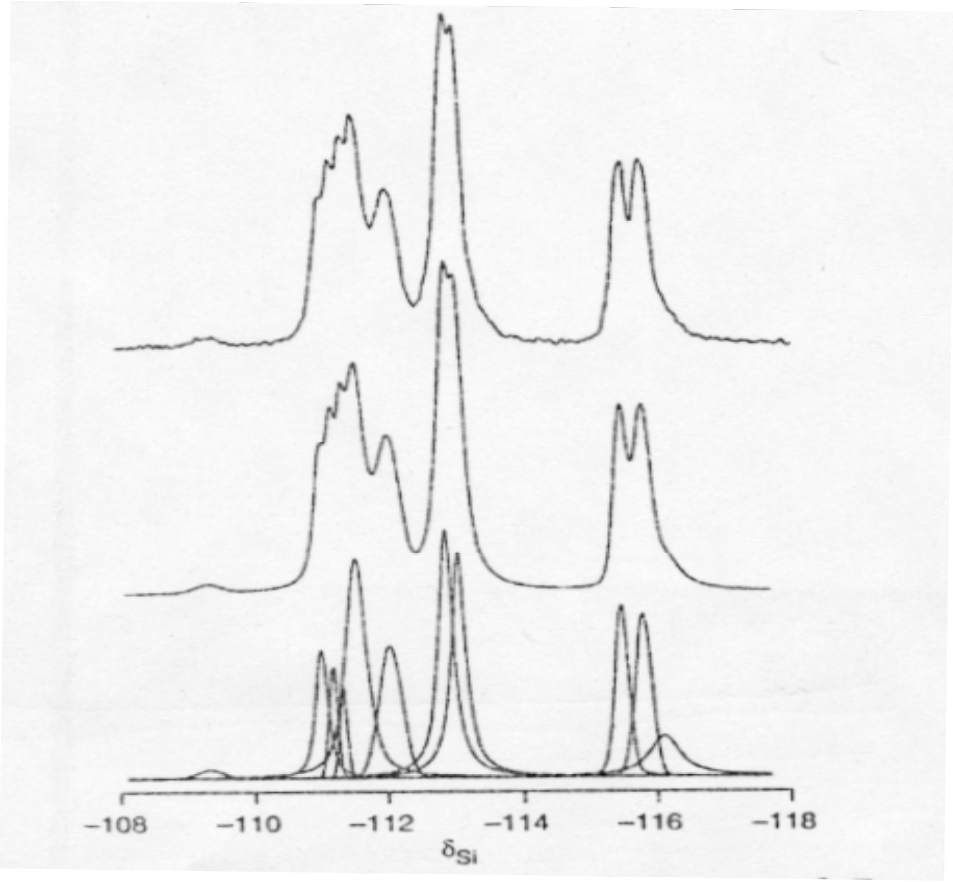
View down *c* axis View down *a* or *b* axis



^{29}Si NMR Spectra of Zeolite Beta

- Highly resolved spectra are obtained
- 9-T sites are distinguished
- PerBU of Polytypes A and B should be the same

Siliceous Beta (Reported)



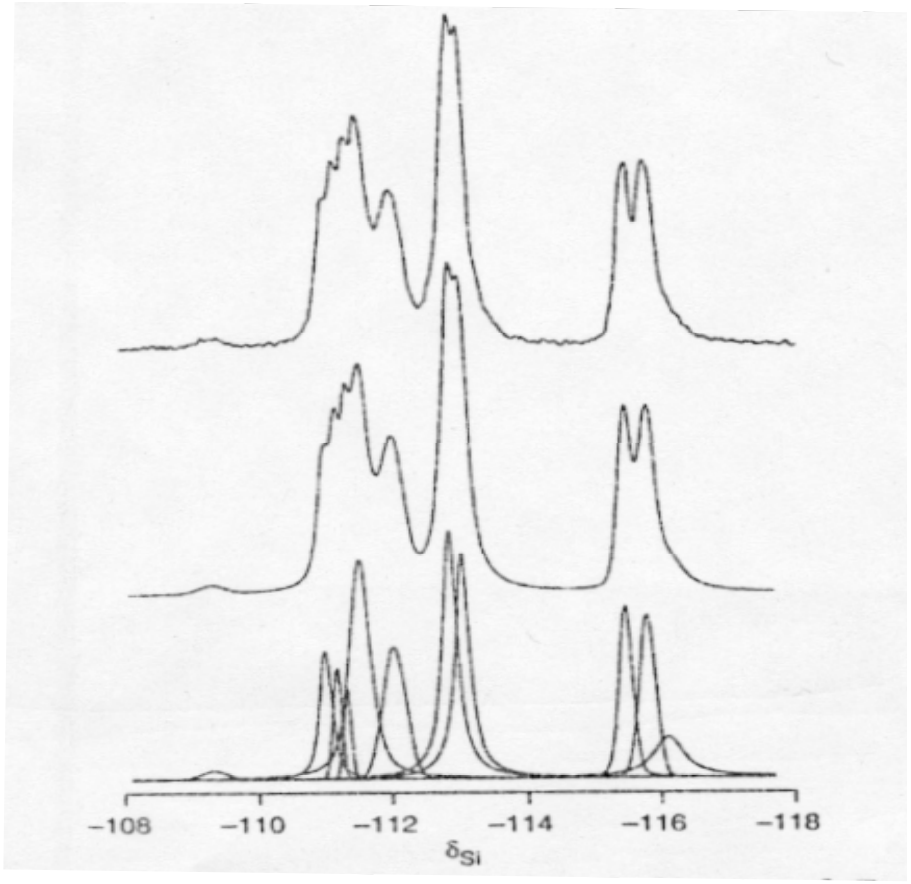
Camblor et al. Chem.Comm. 1996

Sample Preparation

- From B-Beta
  - B removed in acid media
  - T-vacancies are not healed
- From Zn-Beta
  - Highly hydrophobic sample
  - No defects (by NMR)
  - Preferred sample

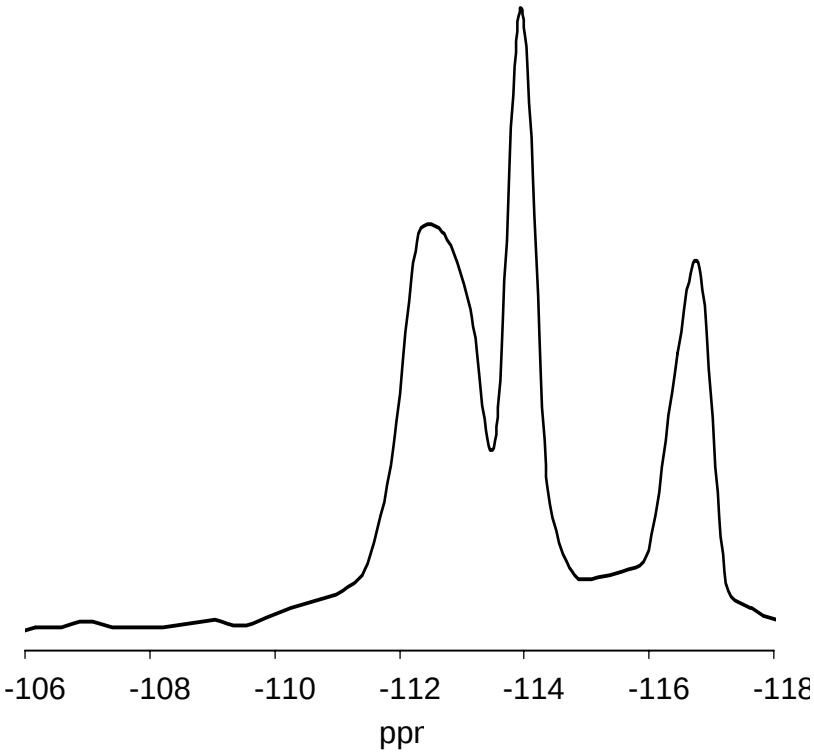
^{29}Si NMR Spectra of Zeolite Beta

Siliceous Beta (Reported)



Camblor et al. Chem.Comm. 1996

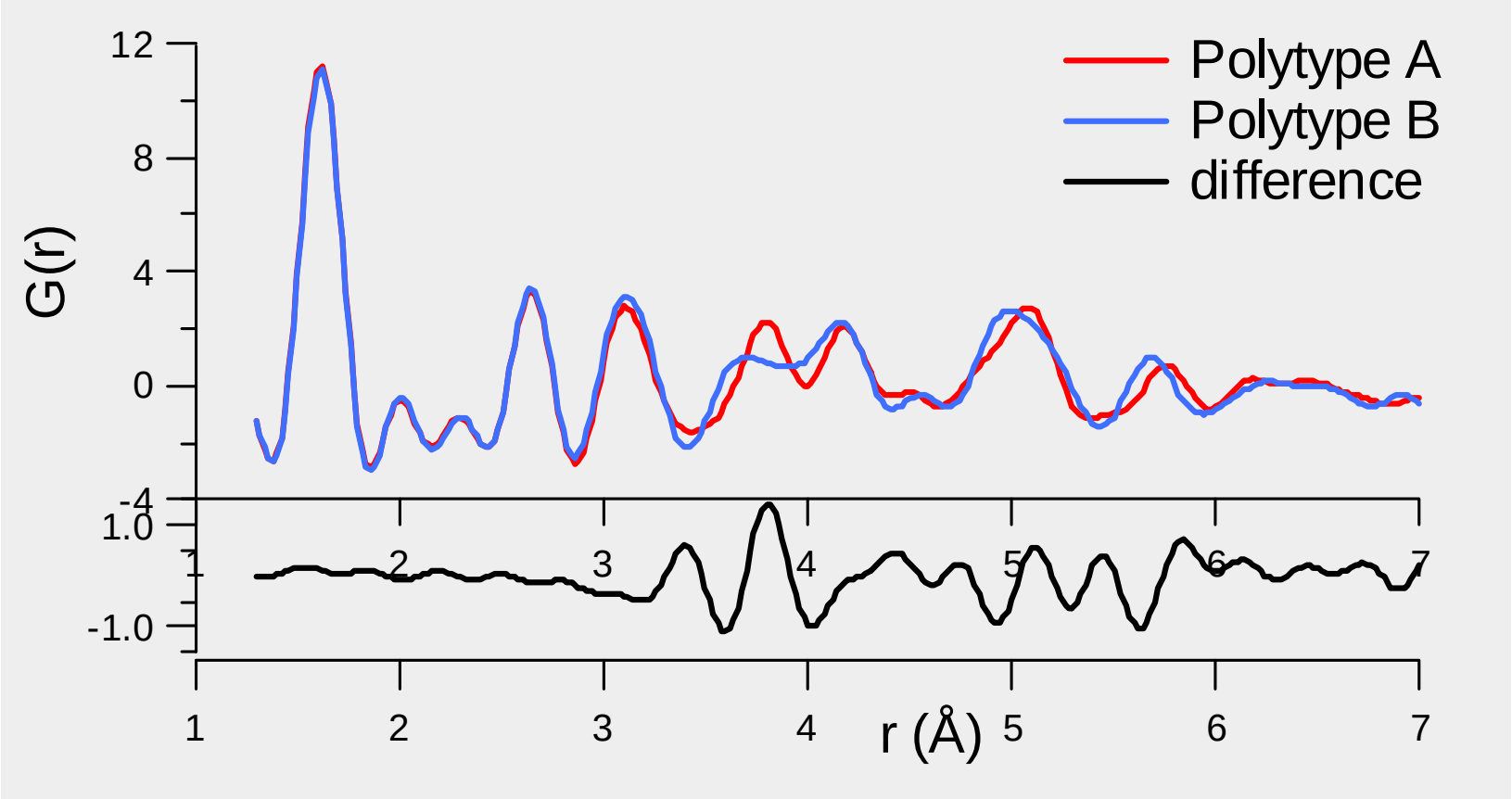
Our Sample



Scattering Measurements

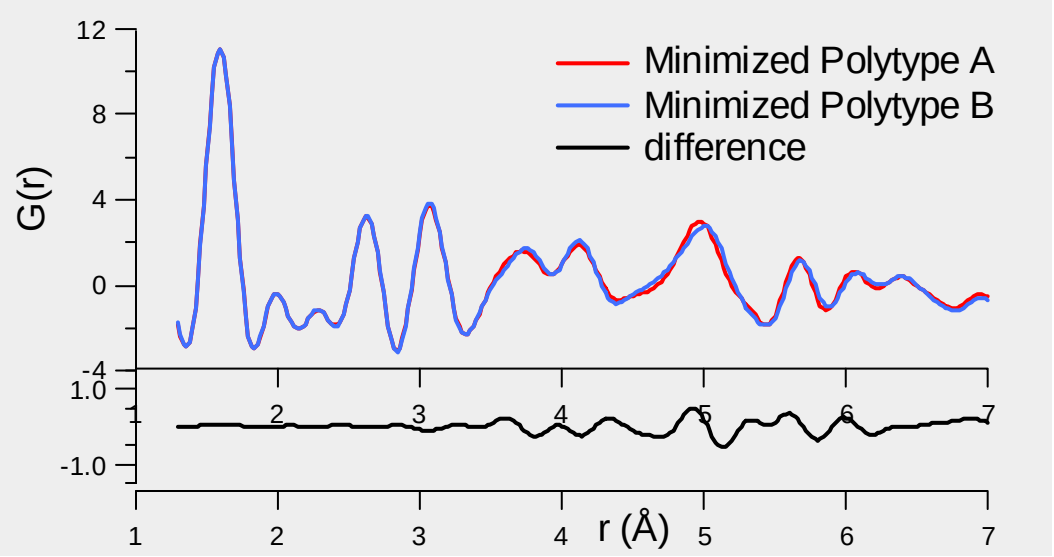
- Neutron PDF
  - GLAD, IPNS (good statistics 20 $Å^{-1}$)
  - NPD, LANL (good statistics up to 30 $Å^{-1}$)
- X-ray PDF
  - APS, λ=0.1573 Å
- Data treatment with ATLAS, PDFGetX and PDFGetN
- Refinement with PDFFit

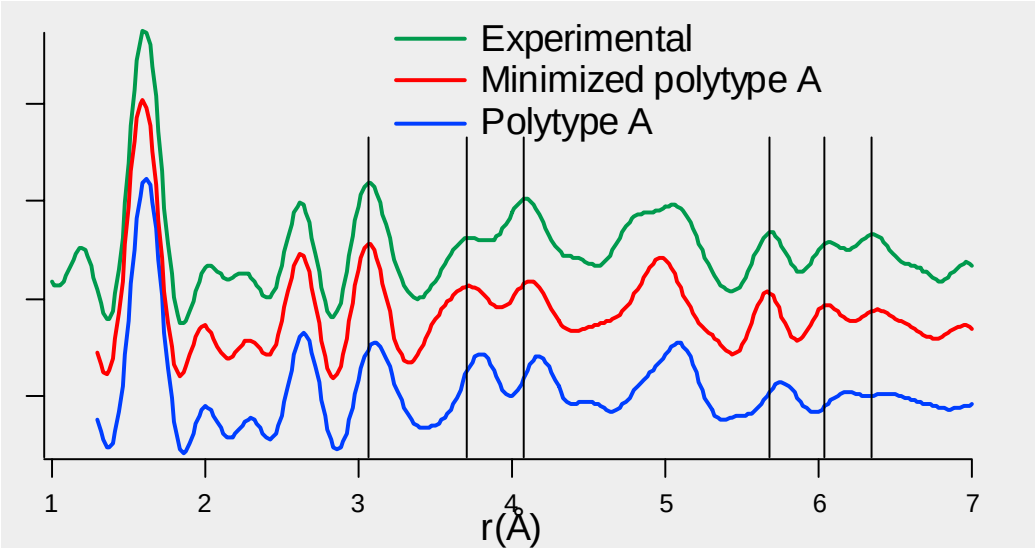
Simulated PDF of polytypes of Zeolite Beta (as reported)



NPDF Beta: Energy Minimization

- After energy minimization (GULP) the PDF of both polytypes is nearly identical

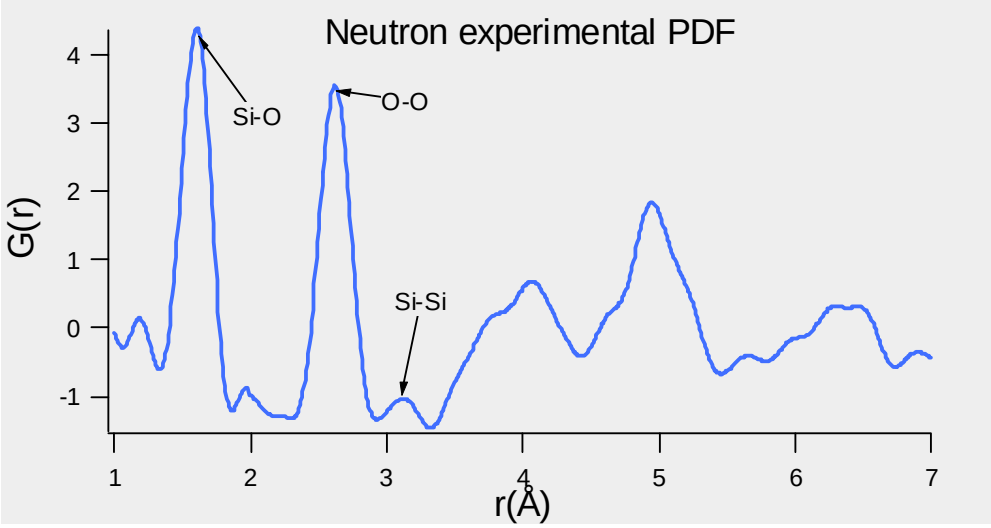


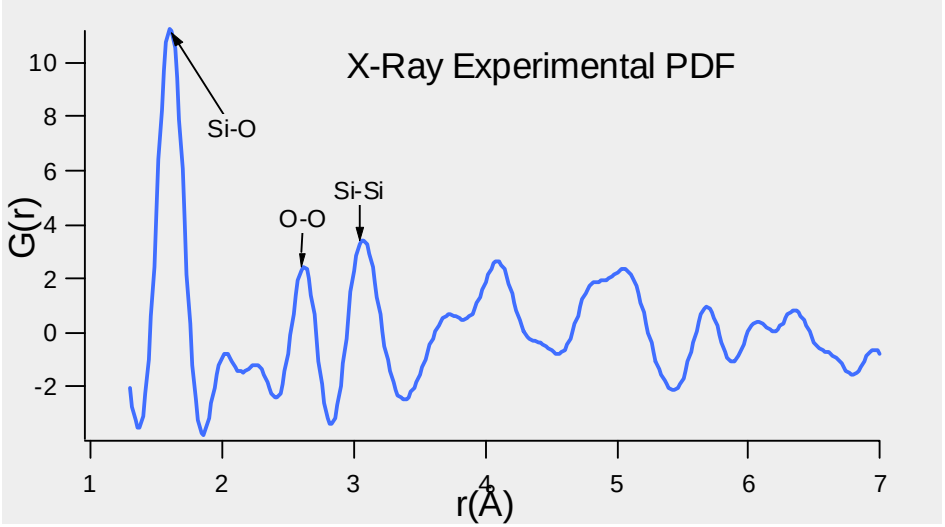


- Comparison of experimental measurement and minimized structure match well

NPDF vs. XPDF

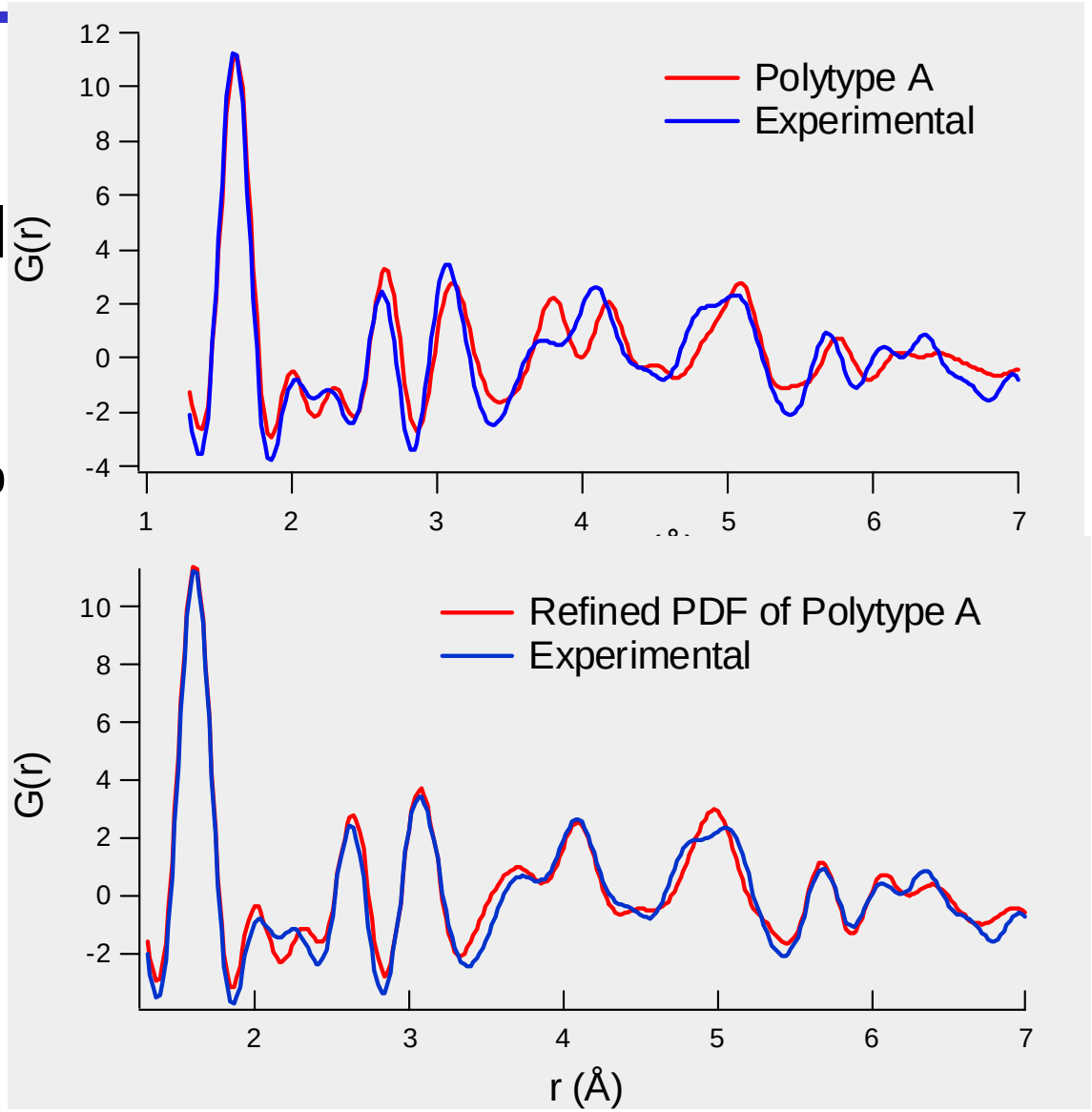
- NPDF was not sufficient
- XPDF is better but gives distorted tetrahedra
  - Need to use scattering length ratios at Q=4.4 Å^{-1} f_{Si}/f_O=2.2 gives good fit of first two peaks





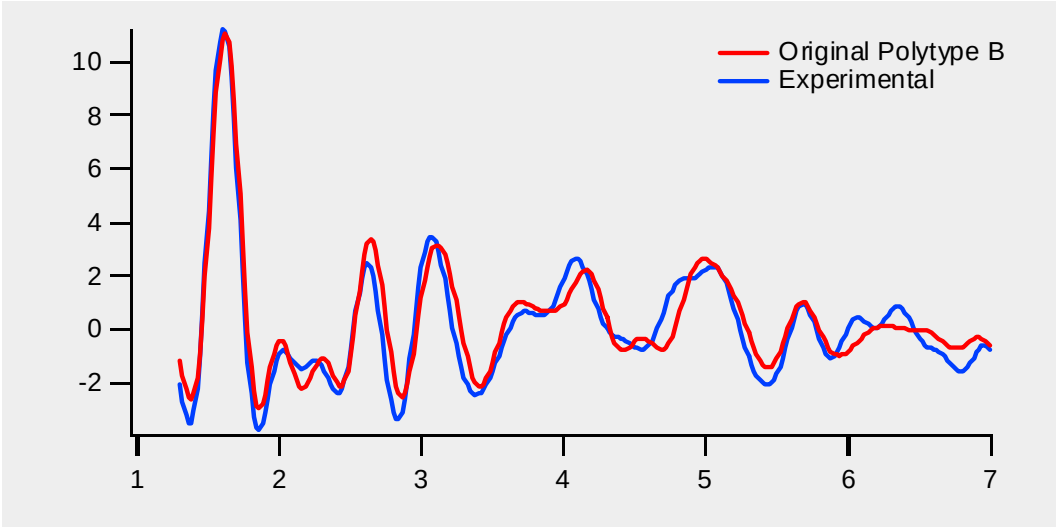
Progress of Refinement Polytype A

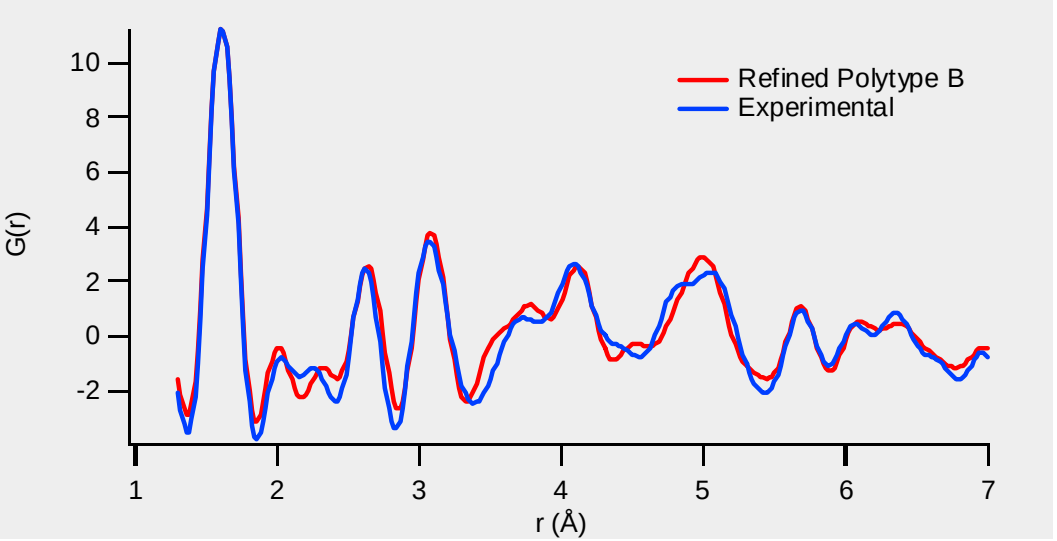
- Comparison of starting and final models after refinement
  - Initial R_w=33.7%
  - Final R_w=20.3%



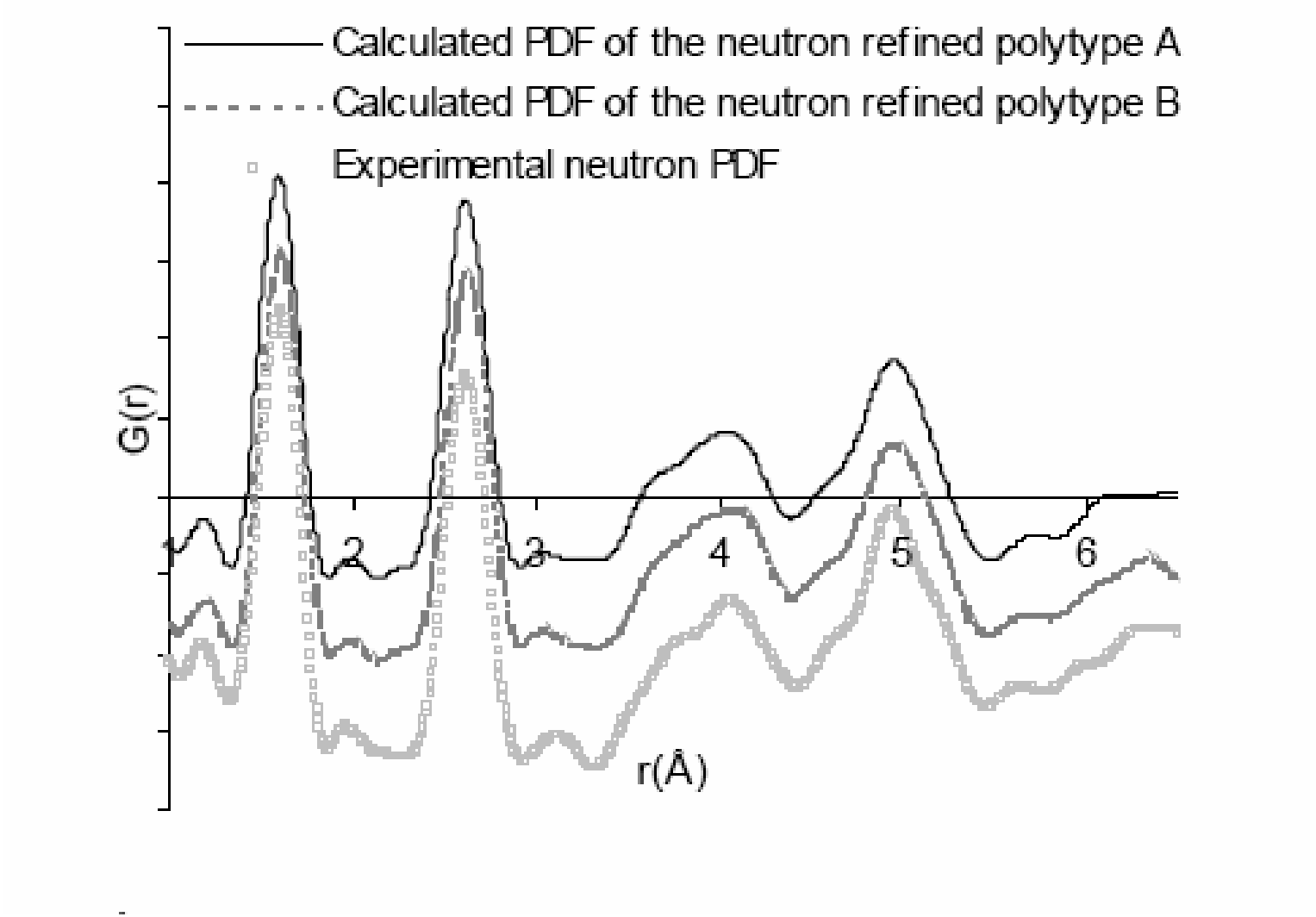
Refinement of Polytype B

- Comparison of starting and final models after refinement
- Initial R_w=30% (XPDF)
- Final R_w=20.0 %
- Final R_w=20.8% (NPDF)





Refinement of the NPDF



Refined bond distances

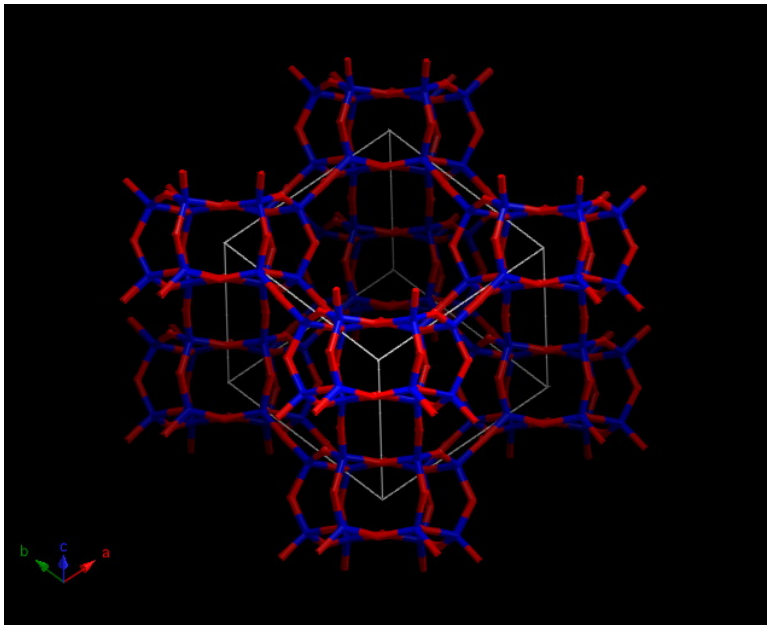
		<Si-O> (Å)	σ (Å)	<O-Si-O>(º)	σ (º)
Polytype A	Original	1.616	0.0001	109.47	0.01
	Refined	1.609	0.0164	109.43	3.91
Polytype B	Original	1.616	0.0015	109.47	0.08
	Refined	1.609	0.0240	109.41	3.82

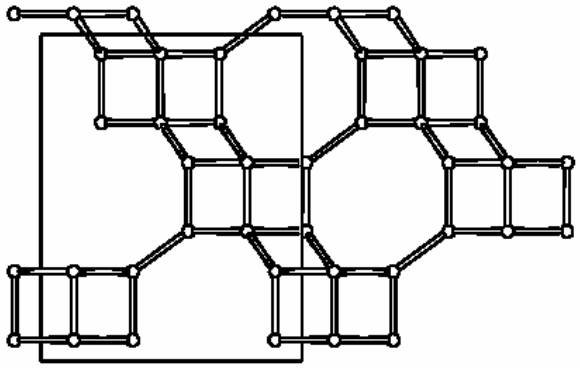
Conclusions

- The PDF method can be used for the refinement of the PerBUs of zeolite structures provided:
  - Sample is compositionally simple
  - Both Neutron and X-ray data sets are refined sequentially (or simultaneously)
  - Complexity of the PerBU is about 9-T atoms or less

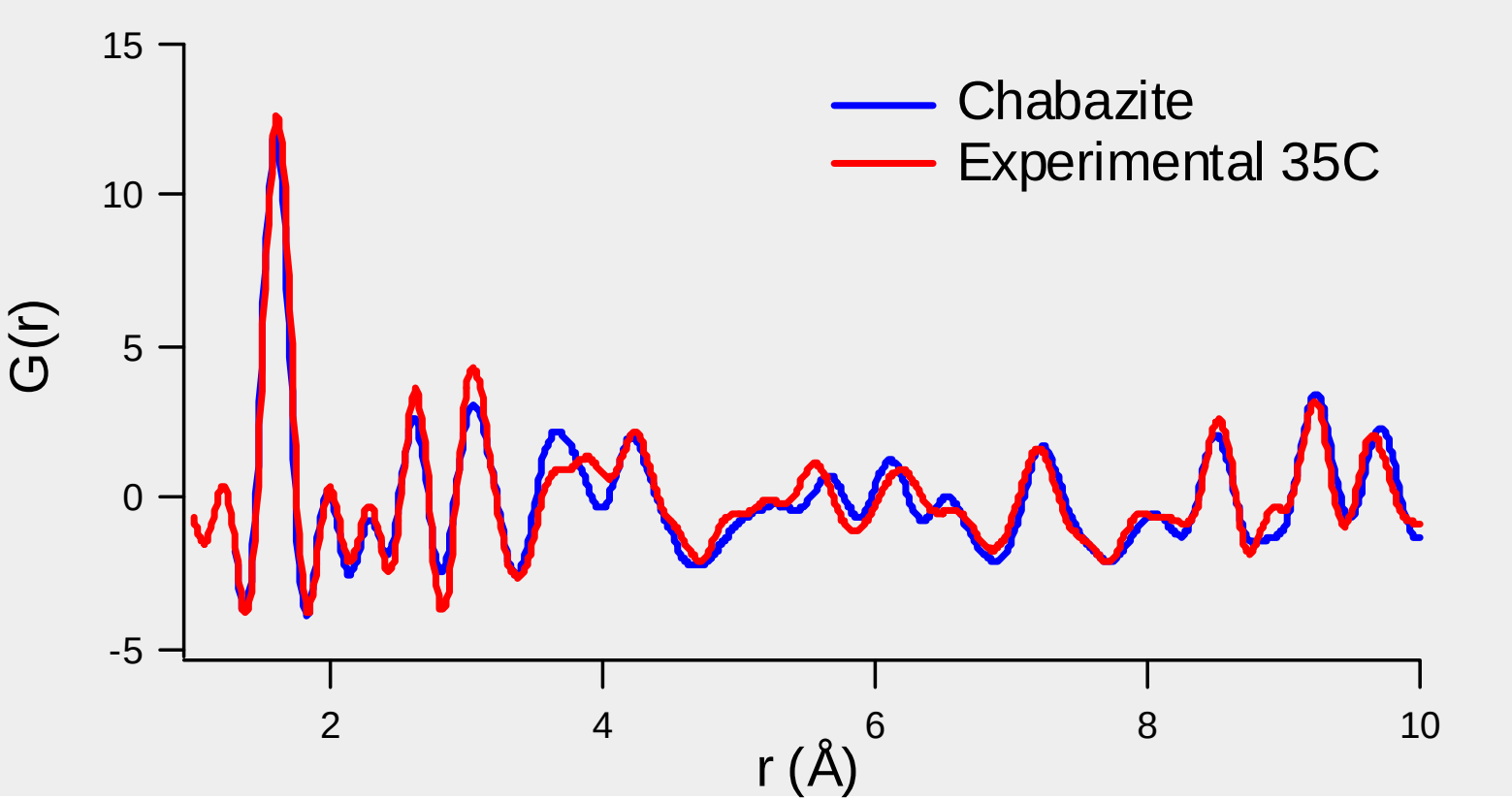
Application of PDF to Dynamic Disorder

- Zeolite Chabazite
- Large negative thermal expansion coefficient
- Diffraction suggests Si-O-Si linkages are contracting
- Others suggest rocking of rigid tetraherda

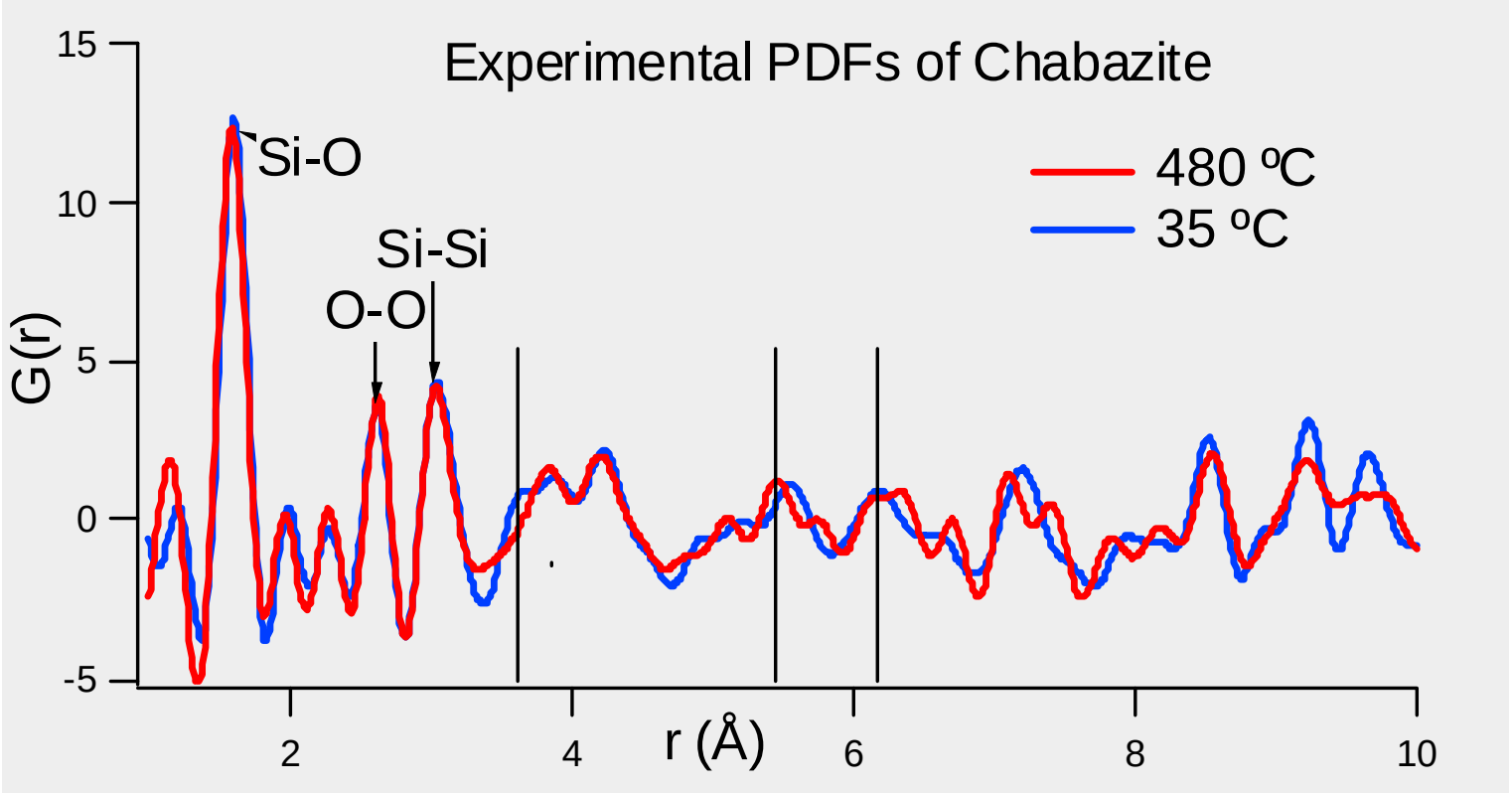




Chabazite: RT Experiment and Model



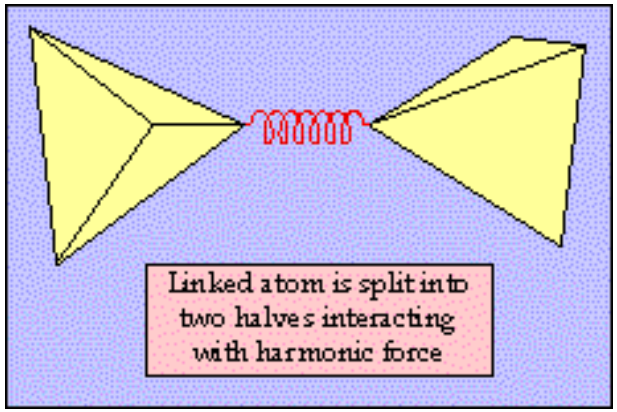
PDF of Chabazite



- Data consistent with rocking of rigid tetrahedra in sample
- Mechanim of contraction still unknown

On going studies…

- Use Rigid-Unid-Modes (RUMs) to analyze the motion of tetrahedra in the zeolite



- Based on the RUMs, predict most stable configurations and determine if these are consistent with PDF data

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  - Sarvjit Shastri
  - Chris Benmore
  - Valeri Petkov
  - Thomas Proffen
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