

**Challenges in Powder Diffraction:
Coupling Neutrons & Hard X-rays
to Understand 21st Century
Materials**

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Motivation

- As we look to improve properties of materials, their structures become more complex
 - May use defects or local ordering to change properties
 - Crystallite sizes are often small by necessity
- Powder diffraction

Why use both neutrons & x-rays?

- In powder diffraction one never has more than enough data

Why use high energy x-rays?

- So that one can repeat neutron measurements under extreme T, *in situ*, etc. conditions.

Questions?

Why Neutrons?

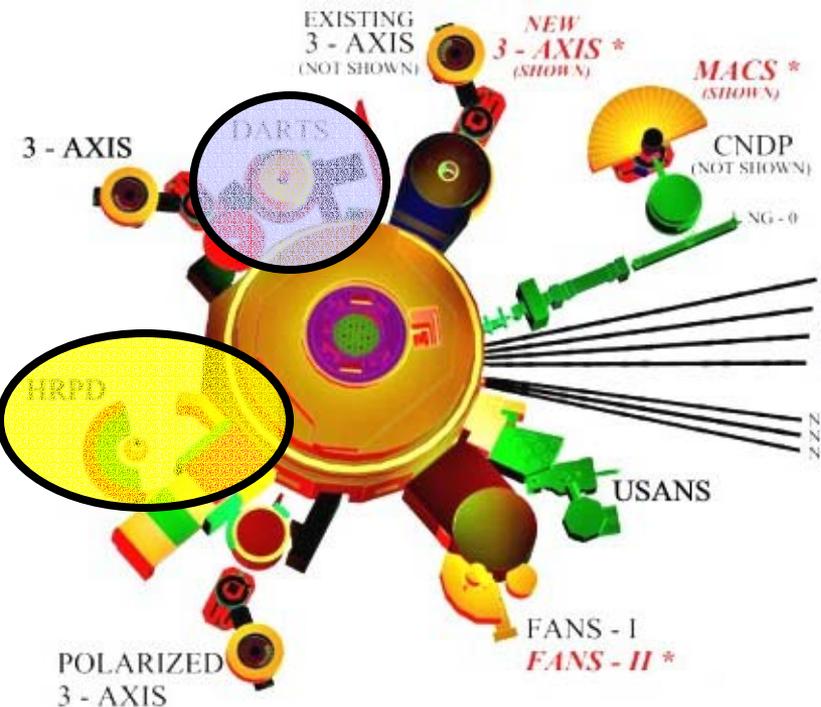
- Diffraction:

- scattering is independent of Z
(*good for light atoms*)
(*isotopic contrast variation*)
- scattering lengths are constant with Q (better *structural precision*)
- neutrons scattered by electron spin (*magnetic structure*)
- many metals are “transparent” (*in situ, high & low T, H field*)
- reflectometry: contrast vs depth (*direct phasing*)

- Spectroscopy:

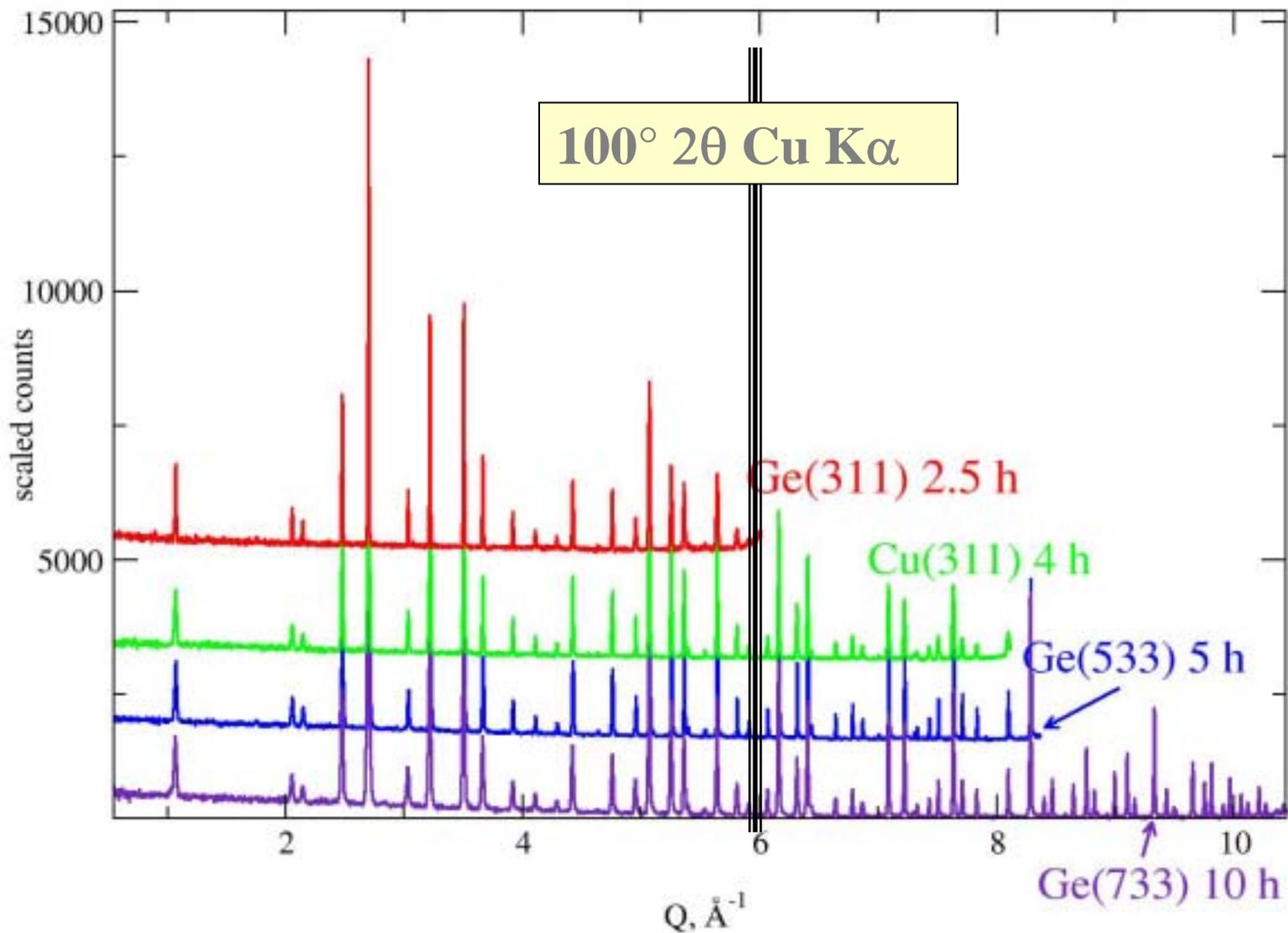
- scattering intensity \propto cross-section (*easy to model*)
- no selection rules
- simultaneously measure ΔQ (momentum) & $\Delta\omega$ (energy)
 \implies *time & distance*
- greatest sensitivity for H
- time scale spans 10^7
- distance scale spans 10^3
(*Unique capability*)
(*Fast measurements or dilute systems*)

Crystallography & Materials Characterization



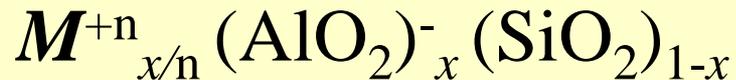
- High Resolution Powder Diffractometer, BT-1
 - Crystallographic studies
 - 0.3 - 1800 K
 - 25 % of time for users (internally funded)
 - “Rapid” proposal system
- Residual Stress/Texture Diffractometer, BT-8
 - Most versatile in world
 - Engineering studies (collaborative use)

Routine neutron powder diffraction @ NIST



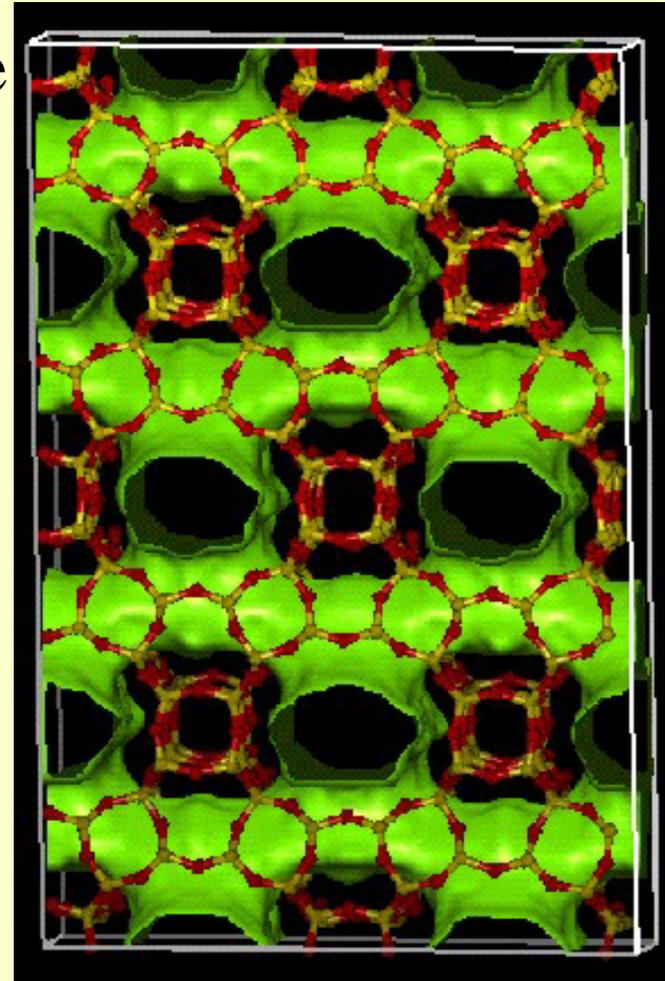
Zeolitic Materials

- Zeolites are **porous** aluminosilicate minerals [*naturally occurring*]
- ...built from tetrahedral SiO_4 and AlO_4 units
- Charge balance requires extra-framework cations:



Many other framework atoms can be used to create *zeolitic* materials

Used for catalysis, selective adsorption, ion exchange...



Research Goals

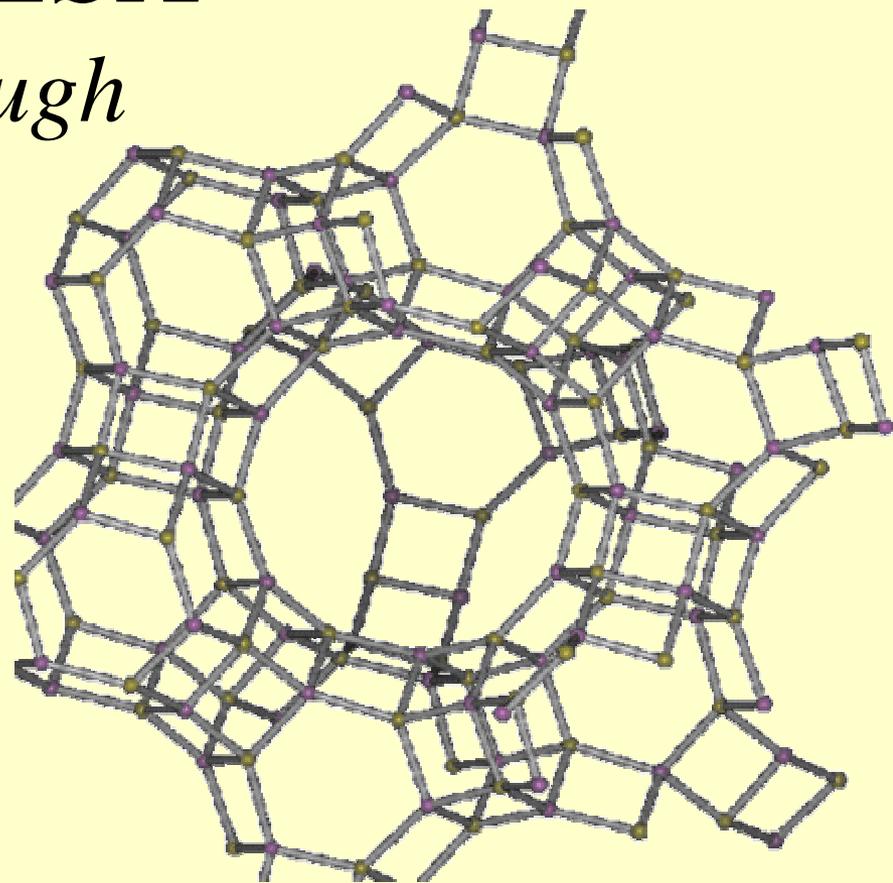
- Determine framework topologies
- Find factors that affect cation siting
- Locations of adsorbed species

Single crystals are rarely available and even when available may not represent the bulk material

Simple case: Ca LSX

X-rays are not enough

- LSX => 1:1 Si:Al X
(Faujasite)
- Cubic, $Fd\bar{3}$
- small, constrained,
asymmetric unit
- ideal specimen: diffracts
beautifully

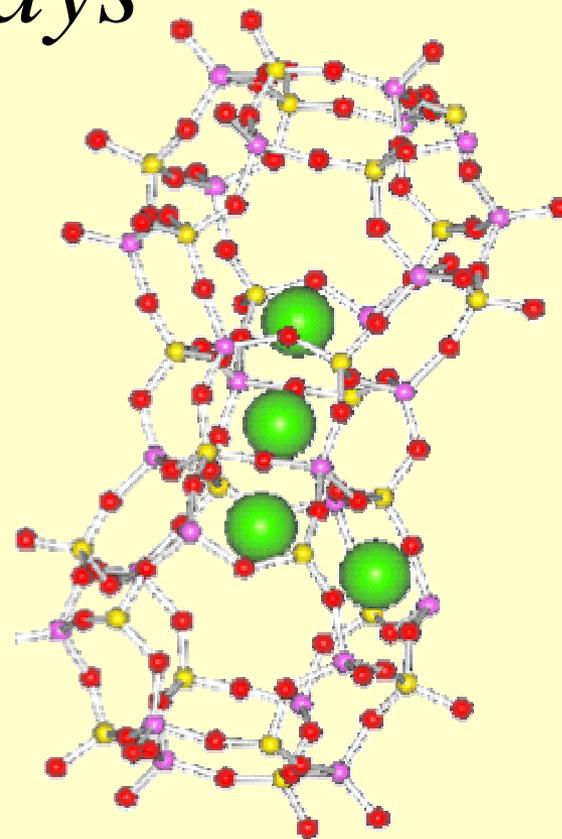


Vitale, G., Bull, L. M., Morris, R. E., Cheetham, A. K., Toby, B. H., Coe, C. G., and MacDougall, J. E., "Combined Neutron and X-Ray-Powder Diffraction Study of Zeolite Ca LSX and A ^2H NMR Study of Its Complex with Benzene", *Journal of Physical Chemistry* **99**, 16087 (1995).

CaLSX:

Neutrons vs. X-rays

- Neutrons alone:
 - detailed & precise framework geometry
 - inaccurate Ca positions
 - wrong Ca occupancies!
- Synchrotron X-rays alone:
 - insensitive to framework



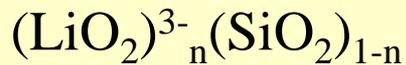
Excellent fit with Neutron & X-ray combined

Even with a single xtal: RUB-29

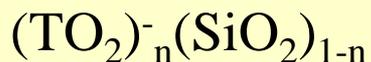
1st lithosilicate to be fully characterized

LiO₄ is more flexible than other zeolitic building blocks

Lithosilicates have potential for highest framework charge



vs



– High densities of cations

RUB-29 is stable to >450 C

RUB-29 is has unusual stability

- heating to >450 C
- multiple dehydration cycles
 - Most 1:1 Aluminosilicates degrade easily

Ion exchange applications?

RUB-29 is a ionic conductor

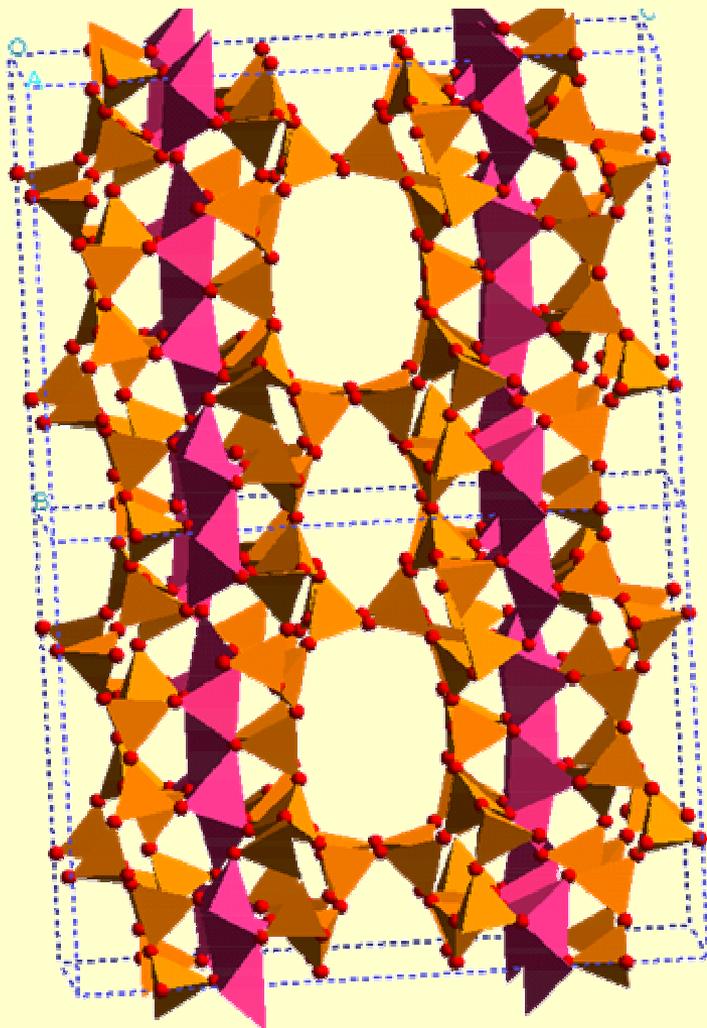
NMR: All Li are mobile <250 C

– battery/fuel cell applications?

RUB-29: A new zeolitic family (lithosilicates)

Dr. So-Hyun Park

SUNY Stony Brook/Ruhr-U-Bochum/NCNR



Exceedingly complex zeolitic material:

35 framework atoms (4 Li)

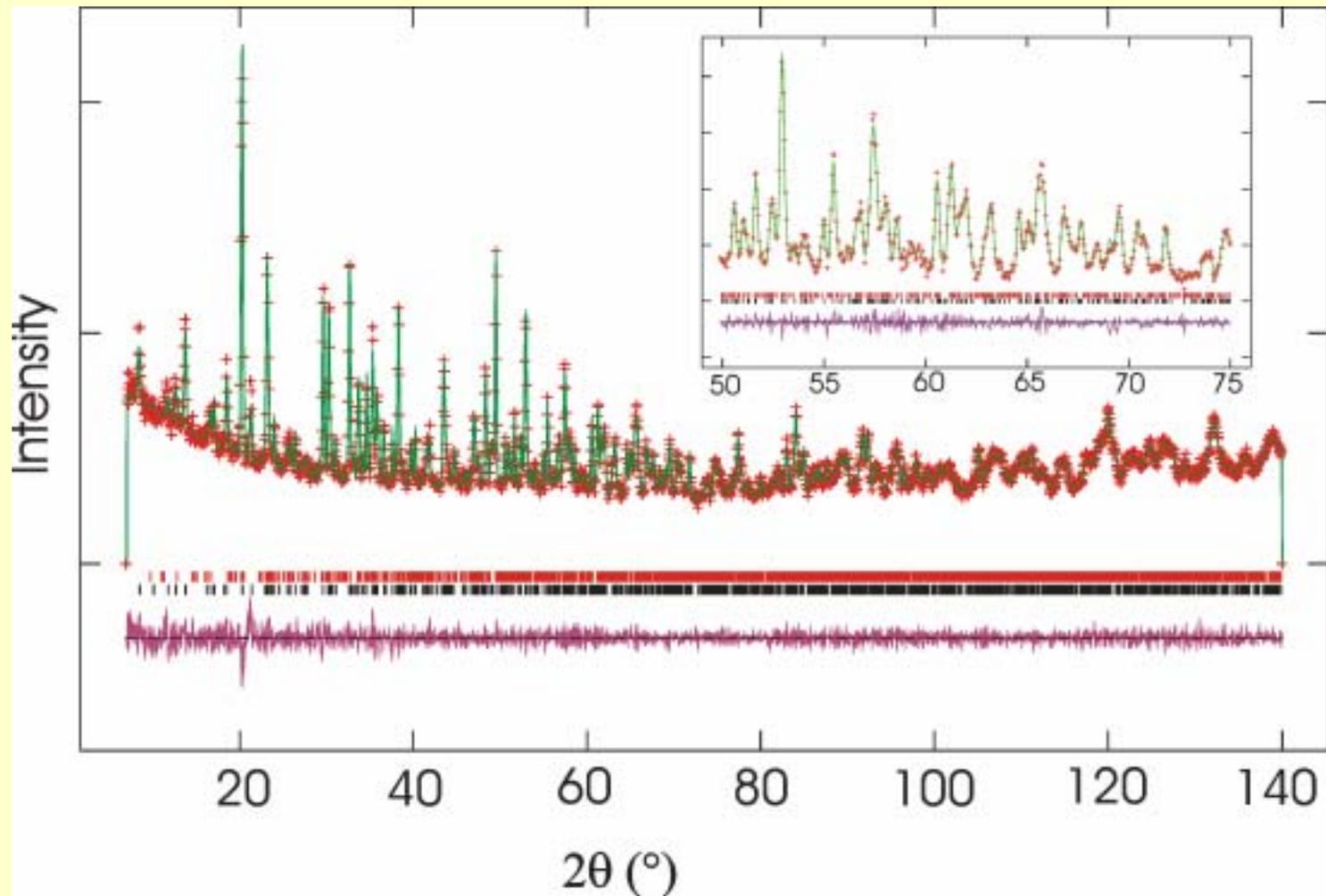
11 extra-framework (4 Li)

~ Framework structure determined from
10x10x2 μm single crystal (hair $>50\mu\text{m}$)

- Neutron data needed to find Li
- Layered silicate “glued” by LiO_4 layers
- First observation of two building units (stable only with Li)

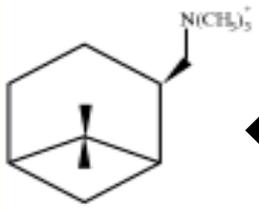
Park, S.-H., Parise, J. B., Gies, H., Liu, H., Grey, C. P., and Toby, B. H., *Journal of the American Chemical Society*, (2000).

RUB-29: Superb Fit



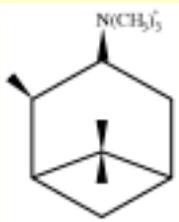
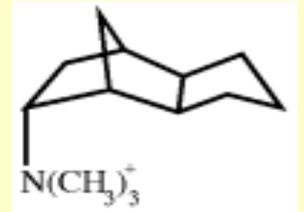
CIT-1: Unraveling how zeolites form

Many zeolitic materials are synthesized using organic “structure directing agent” (SDA) cations
CIT-1 illustrates interesting zeolite-SDA interactions



◀ 1 Makes CIT-1 (~1% stacking faults)

2 Makes SSZ-33 (similar to CIT-1, but with >30% stacking faults) ▶



◀ 3 Cannot be used to make either CIT-1 or SSZ-33

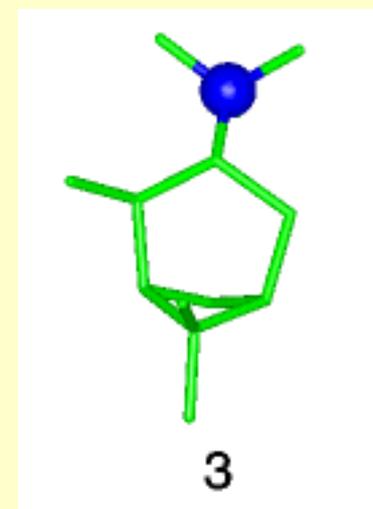
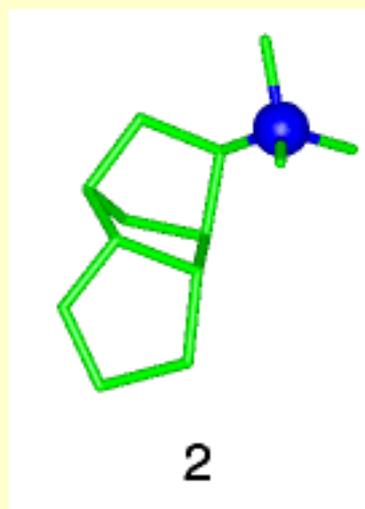
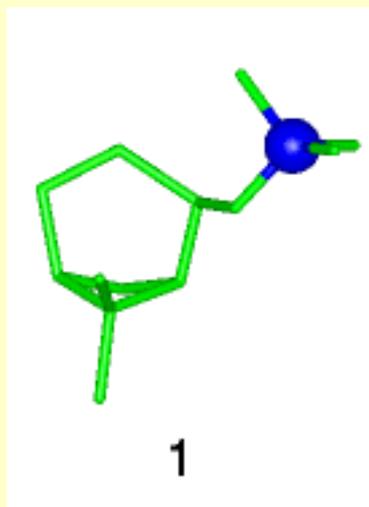
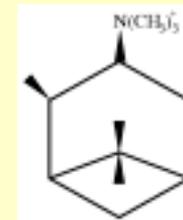
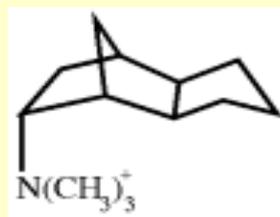
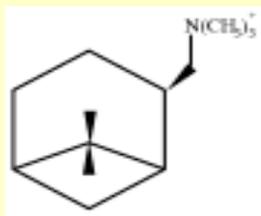
Why?

There is no obvious difference
between the organic species

no faults

faults

neither



CIT-1: Structural Analysis

Synchrotron & neutron powder data with partially deuterated “as synthesized” sample

- symmetry of SDA much lower than CIT-1

Visually fit SDA to difference Fourier

- two superimposed SDA orientations needed

- Reasonable fit to x-ray & neutron data

- ***Problem***: occupancy ~4 SDA cations/unit cell

- literature value, from TGA is 3!

- Is this structure right? (uniqueness problem)

CIT-1: Molecular Modeling

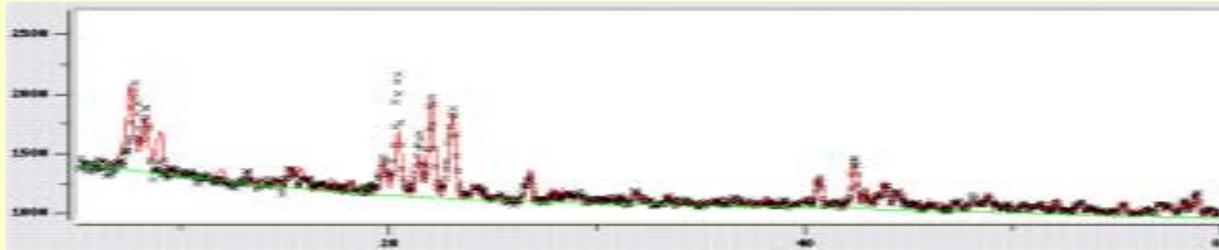
- Commercial Monte Carlo rigid body insertion (MSI Solids Docking)
 - no stable models with 4 SDA per cell
 - numerous models with 3 SDA per cell
- Analysis of lower energy models:
 - SDA cations populate only three orientations (labeled as A, B & C)

How do these models fit the data?

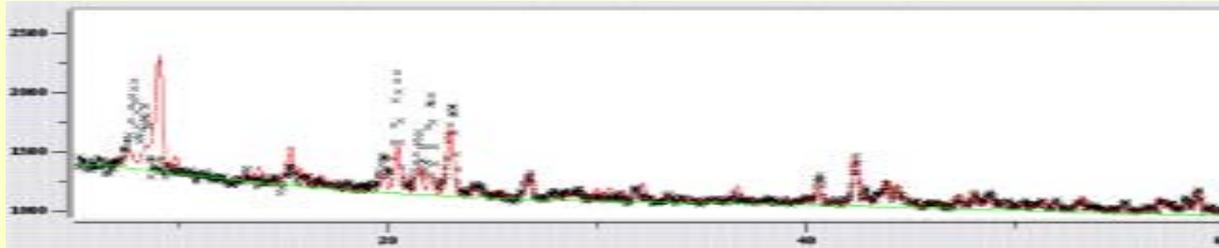
Which of the three fits the data?



A



B



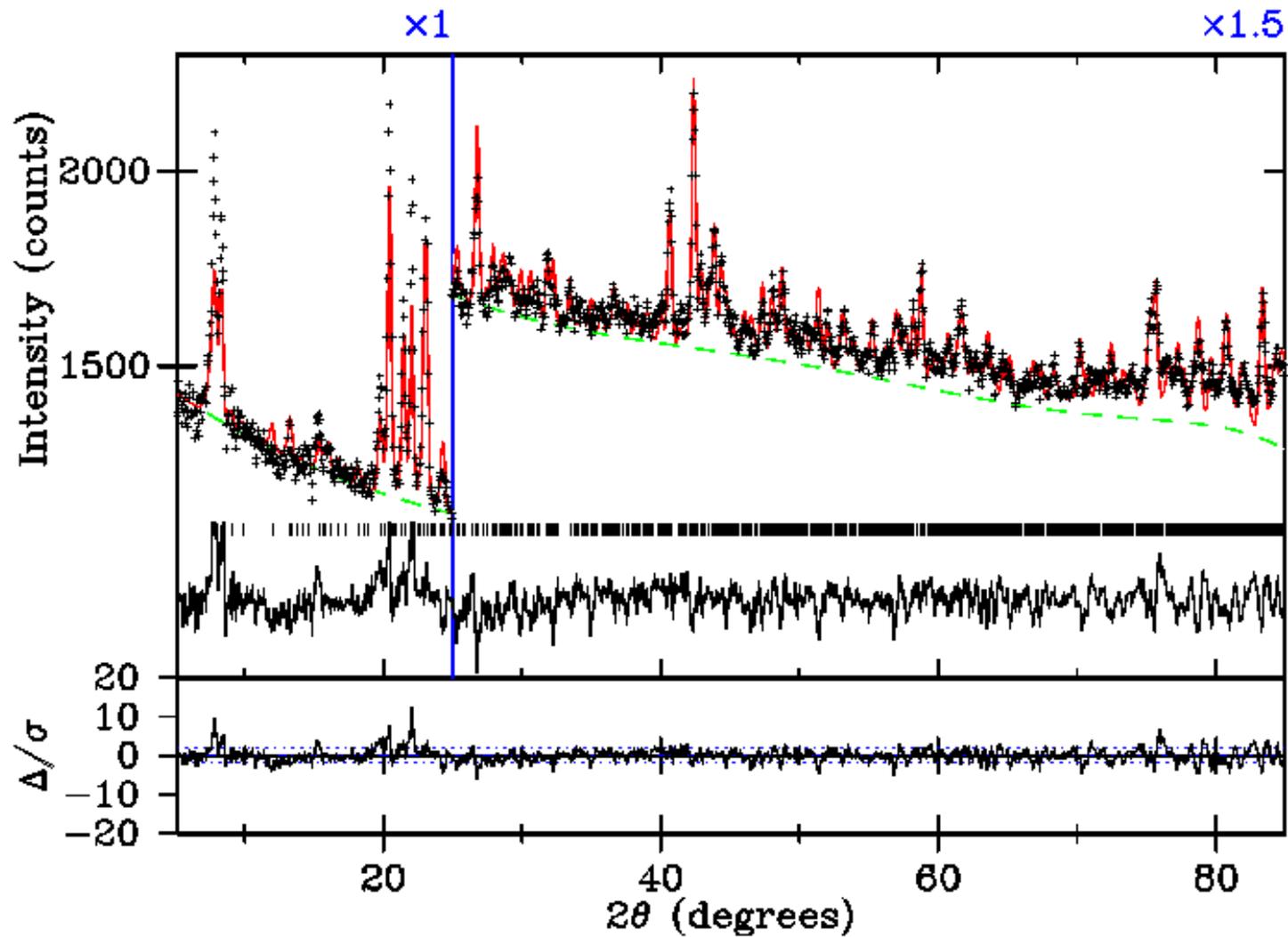
C

None of the above!

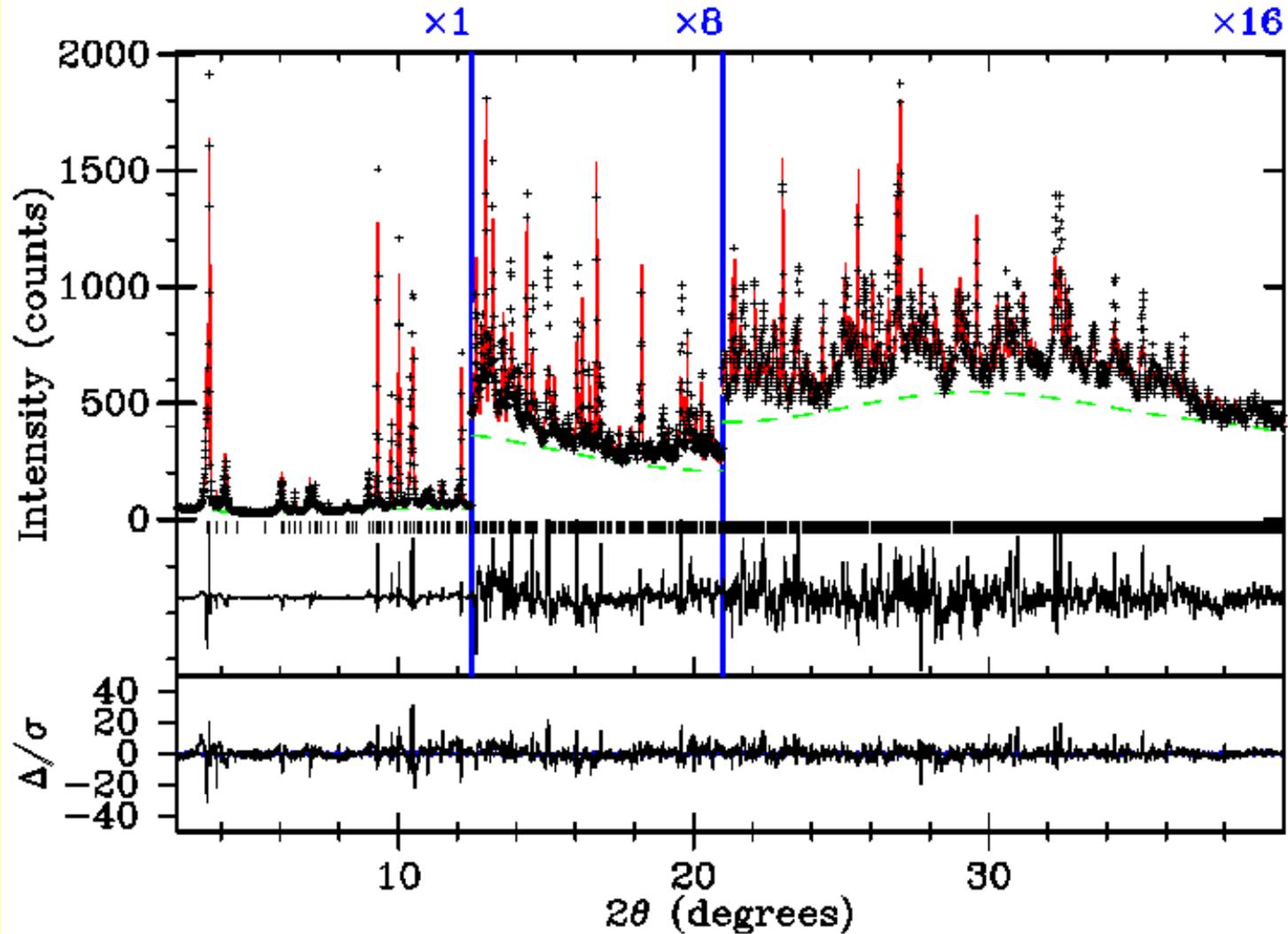
Right answer: $3/4A+1/4B!$

- Using all three orientations and refining occupancies yields an adequate fit:
 - ~ 3 molecules/cell in orientation A
 - ~ 1 molecule/cell in orientation B
 - ~ 0 molecules/cell in orientation C
- A & B cannot be distinguished by x-rays
- Refined positions ~same as initial approach

Neutron Fit



X-ray Fit



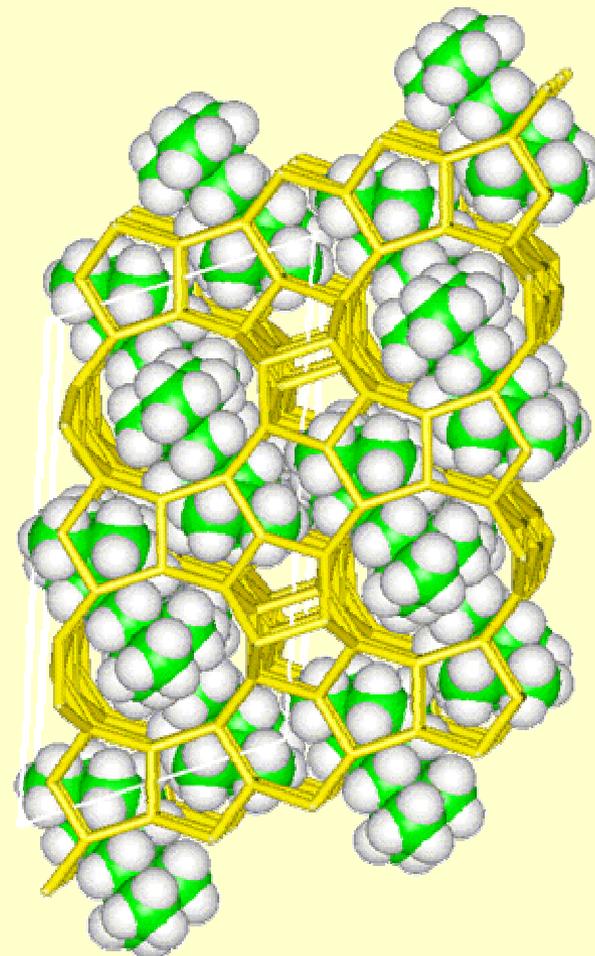
But, can four molecules fit?

Optimize with molecular modeling

- Very compact structure
- No unfavorable interactions
- ~ same as crystallographic model

Yes!

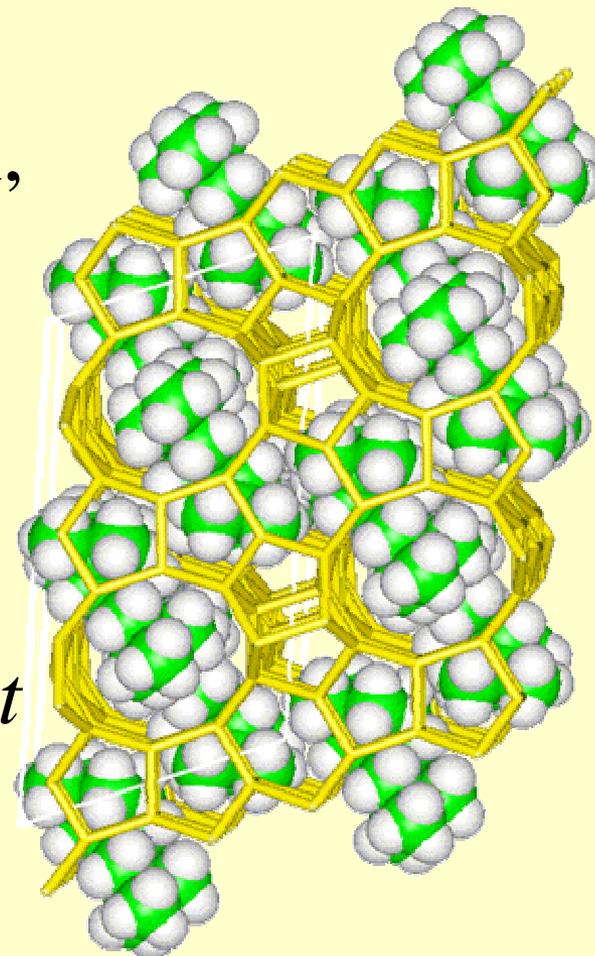
- More experiments:
 - prompt- γ also gives 4 SDA/Cell
 - repeat TGA: 3.4 SDA/Cell



How do SDA 1, 2 & 3 Compare?

- Optimize packing of each SDA, 4 cations per cell with MM
 - SDA 1 & 2 agree within 4.5 kcal
 - SDA 3 is 55 kcal less stable

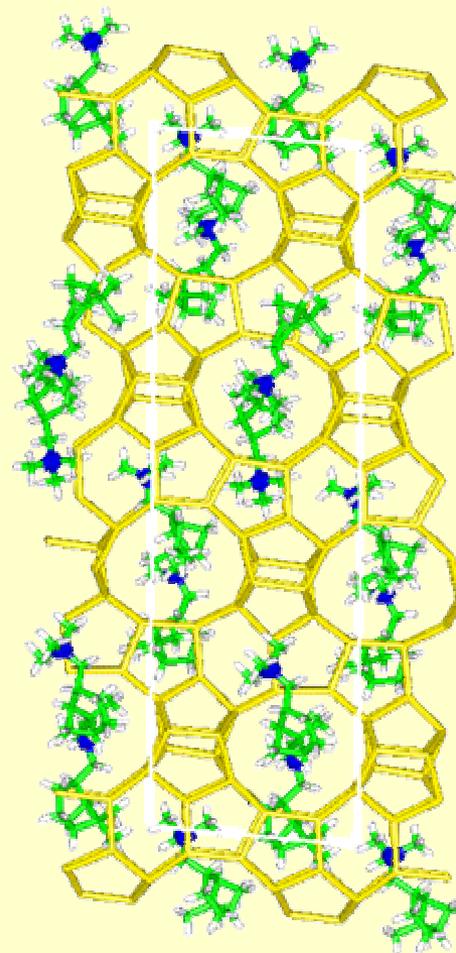
This explains why SDA 3 does not make CIT-1 while 1 & 2 do



Why no stacking faults with SDA 1?

- Repeat packing simulations in a “faulted” cell
 - 1 & faults: -41 kcal/mol
 - 2 & faults: +5 kcal

Opposite of expected result!



CIT-1: Conclusions

- Use caution interpreting Monte-Carlo results for “key in lock” problems
- Crystallography and Molecular Modeling are complementary & are in agreement
- Explained why SDA 3 does not make CIT-1
- Stacking faults likely a kinetic phenomenon

Toby, Brian H., Khosrovani, Nazy, Dartt, Christopher B., Davis, Mark E., and Parise, John B., "Structure-directing Agents and Stacking Faults in the CON System: A Combined Crystallographic and Computer Simulation Study.", *Microporous and Mesoporous Materials* 39, 77 (2000).

Understanding the M1/M2 Propane Ammoxidation Catalyst

Why: world use of acrylonitrile is 10^{10} lbs/year

- made from propene
- propane much cheaper

Propane catalyst is a multi-phase mixture of two very complex layered (Mo,V,Te,Nb) oxides

How:

- Combinatorial synthesis: enhanced concentration of each phase.
- TEM: framework topology
- X-ray: approximate structure
- Neutrons: oxygen-metal distances

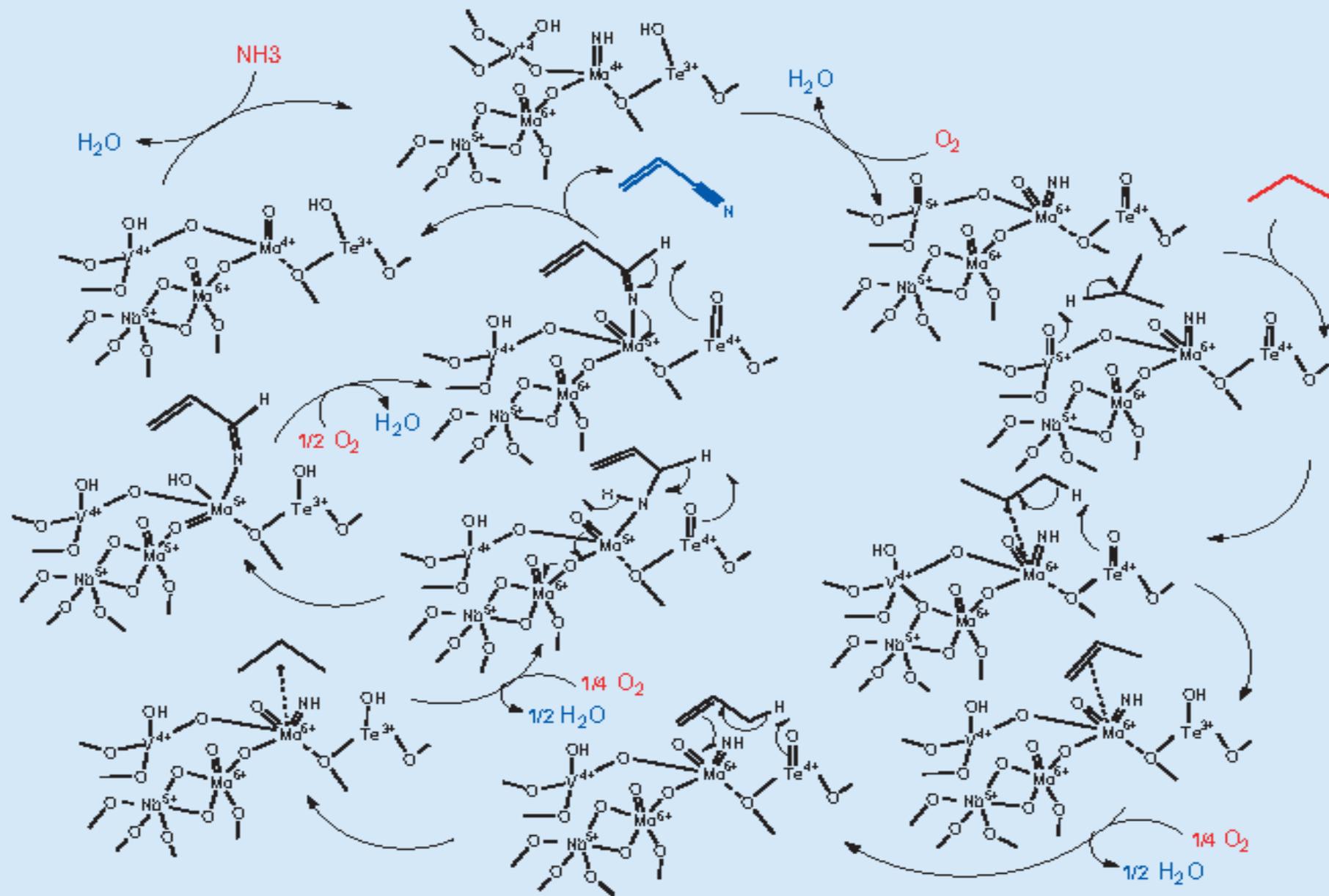


Fig. 2. A schematic mechanism for propane ammoxidation by the M1 catalyst that details the cation centers believed to be responsible for reactive process [3].

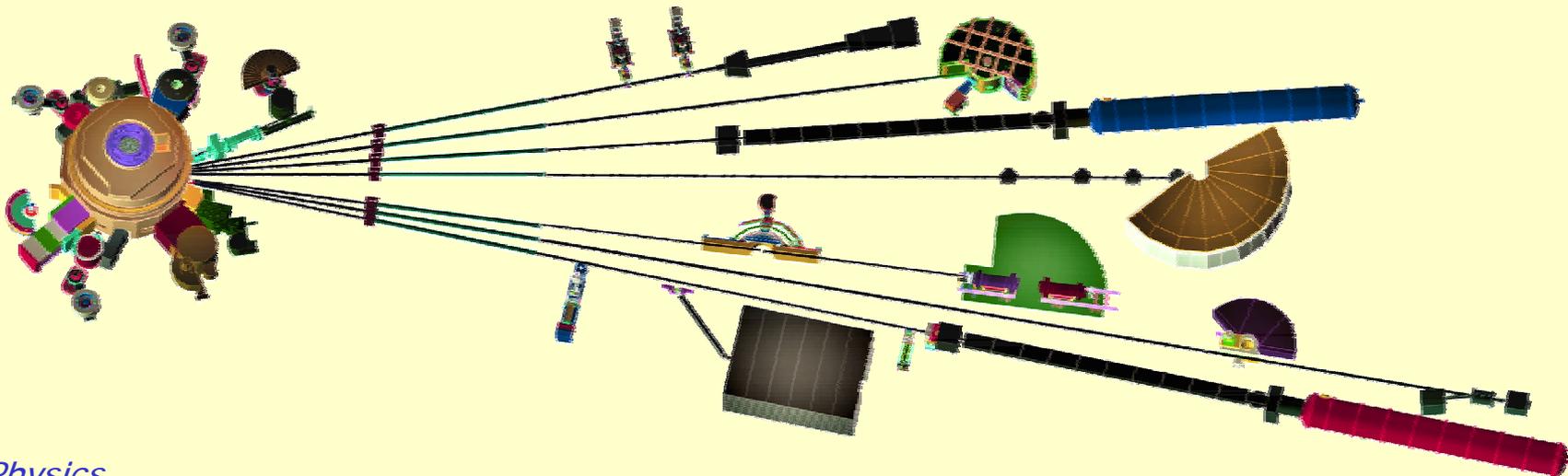
Conclusions

- When characterizing complex powder samples, x-ray diffraction is often not enough
- Even x-rays and neutrons together may leave important questions unanswered (need TEM, computation,...)
- Future: need to study functional materials in something approximating working conditions

POSTDOCTORAL OPPORTUNITIES FOR U.S. CITIZENS

NI ST Center for Neutron Research

www.ncnr.nist.gov



*Physics
Chemistry
Biology
Materials science
and engineering*

National Research Council/NI ST Postdoctoral Research Associateships

www4.nationalacademies.org/pga/rap.nsf

Starting salary: ~\$56K

*Inquiries:
dan@nist.gov
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*Applications due mid-January
Decisions mid-March
Starting dates July-September
Eligibility limited to U.S. Citizens*