Structural Studies of Proton-Conducting Inorganic Electrolytes

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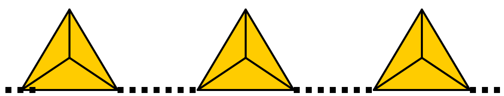
Superprotonic Conductors: Solid Acids

What?

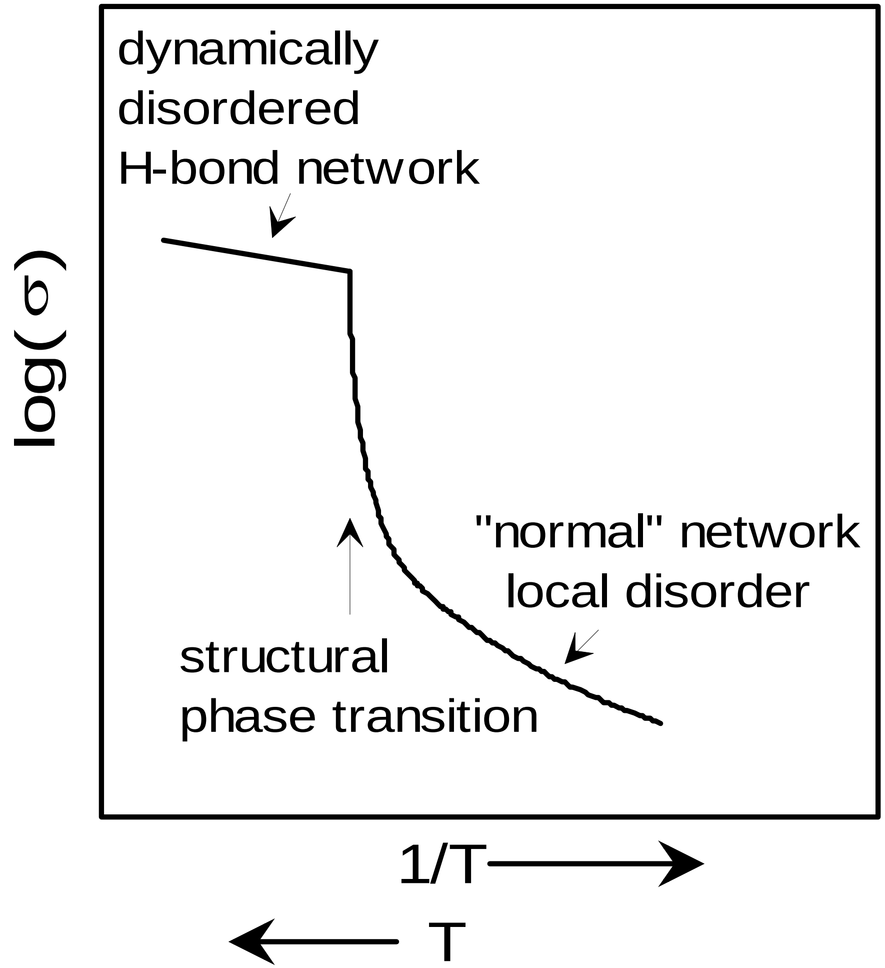
- Chemical intermediates between normal salts and normal acids; “acid salts”

$$\frac{1}{2}(Cs_2SO_4) + \frac{1}{2}(H_2SO_4) \rightarrow CsHSO_4$$



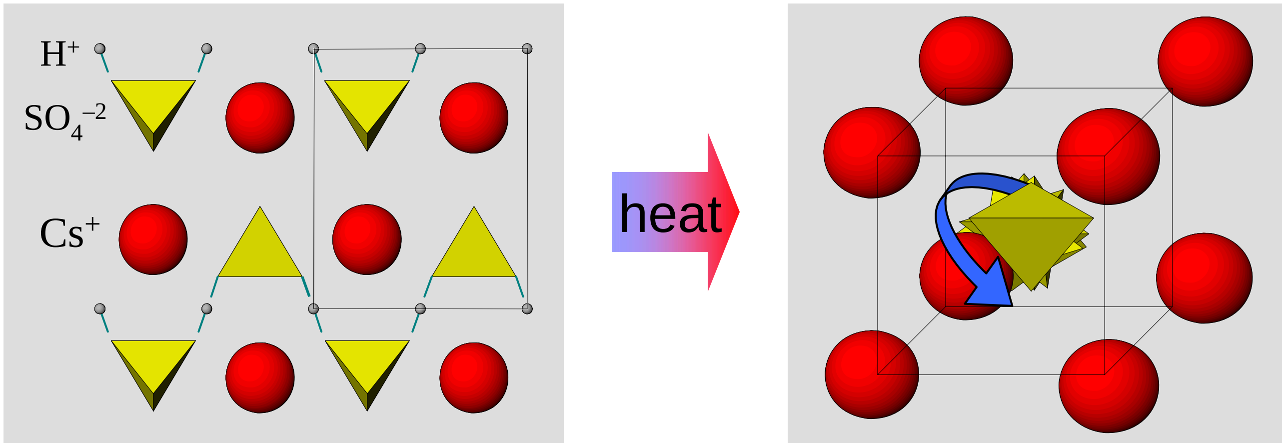
Why?

- Transport properties of liquid acids
- Benefits of the solid state
- Exhibit structural transformations



Proton Transport Mechanisms

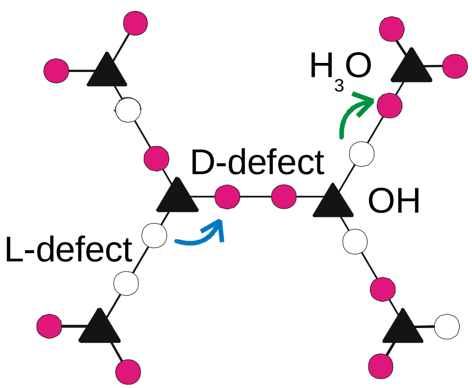
Ordered **Disordered**



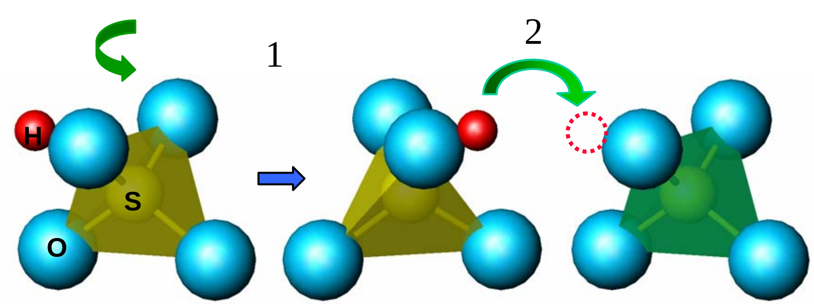
Room Temperature Structure

Superprotonic Structure

Limited defects



Highly defective



(1) Dipole/Tetrahedral group reorientation; (2) Proton transfer

Applications for Solid Acids

- High protonic conductivity, all solid state
  - *Hydrogen gas sensors, water electrolyzers*
  - **FUEL CELLS**
    - **Higher efficiency, cleaner than combustion engines**
- Compared to state-of-the-art polymeric H^+ conductors
  - *Humidification not required => system simplification*
  - *Impermeable to gases => higher power output*
  - *High operating temp*
    - *Higher tolerance to fuel stream impurities => simplication*
    - *Higher catalyst activity => higher power output*
    - *Easier heat rejection => reduction in system size*
  - *Ideal for alcohol (methanol) fuel*
    - $CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$

"Engineering" of Solid Acids

- Understand/control transition behavior
  - $T_{trans} = \Delta H_{trans}/\Delta S_{trans}$
    - *Entropy drives transitions*
    - *Evaluate change in configurational entropy*
- Understand/control magnitude of conductivity
  - *Cond = proton concentration* $(N_a) \times$ *mobility* (μ)
    - N_a *and* μ *determined by both global structure and local environment of protons*
    - *Disorder in structure generally increases* N_a *and* μ
- Both aspects require clear structural elucidation

Neutron Diffraction and Solid Acids

- Scattering lengths erratic with atomic mass
- Sensitive to light elements (e.g. H, D, Li)
  - *H/D (Li, O) positions*
  - *Proper stoichiometry*

I. $Cs_3Li(DSO_4)_4$

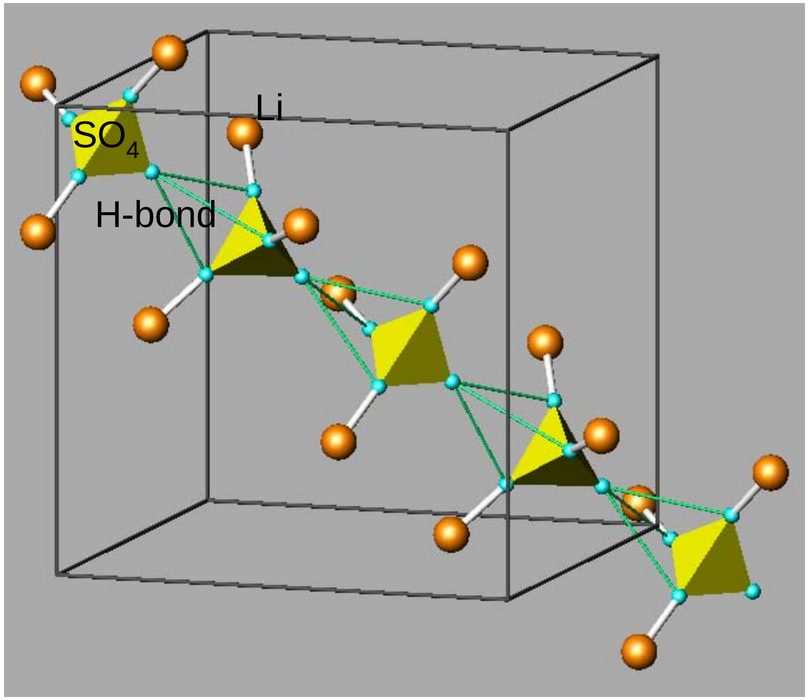
II. $Cs_2Na(HSO_4)_3$

- Able to differentiate between atoms of similar atomic masses (i.e. electron densities)
  - *Distribution of dissimilar species (e.g. S and P)*
    - *Superstructures*
    - *Mixed site occupancies*

III. β-$Cs_3(HSO_4)_2[H_{2-x}(P_{1-x},S_x)O_4]$

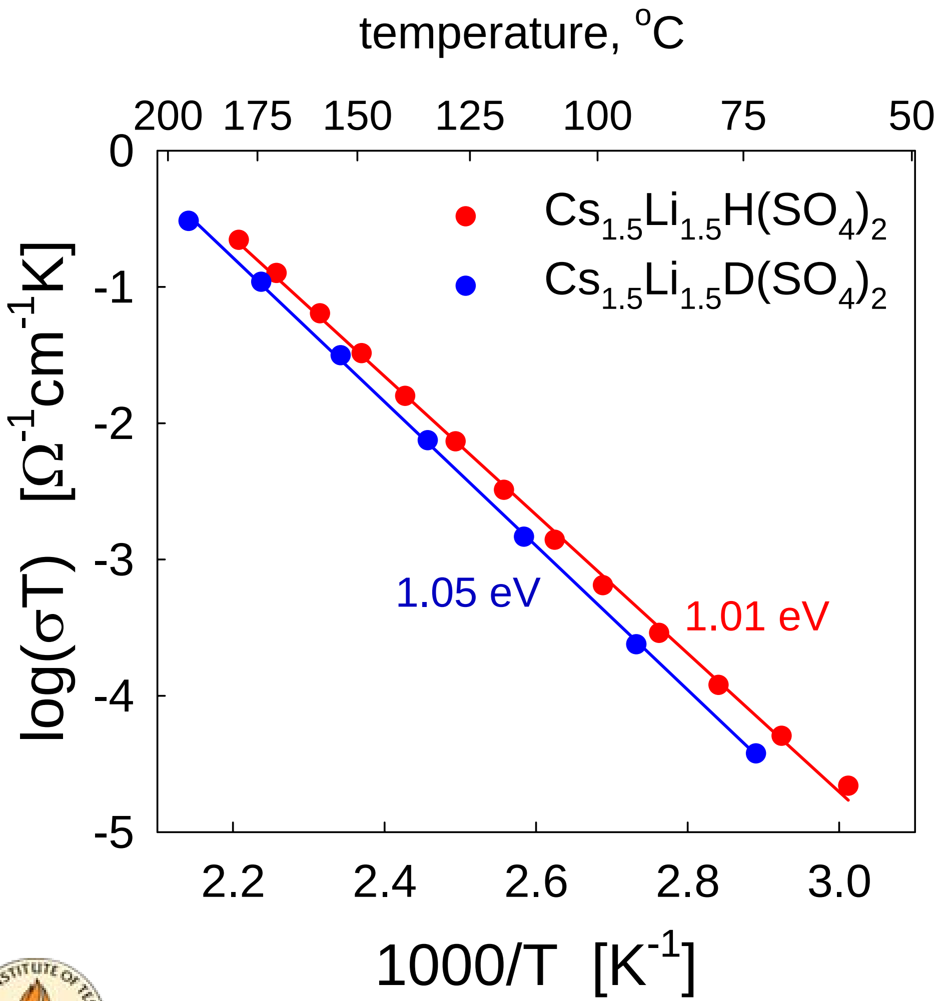
I. $Cs_3Li(DSO_4)_4$: Superprotonic at RT?

- Reported compound: $Cs_{1.5}Li_{1.5}H(SO_4)_2$



- $I\bar{4}3d$, a = 11.734 Å
- One Cs, S, Li site; two O sites
- Dynamically disordered H-bonded SO_4 chains
- $d(O_D...O_A)$ = 3.38 Å
- Asymmetric H-bond [O1-O2]
- $d(S-O_D) \sim d(S-O_A)$
- H-bond occupancy = 1/6
- High Li thermal parameters
  - *Merinov, Solid State Ion (1994)*
- Transition at 162K (153K)
  - *Baran, J. Mol. Struct. (1999)*

I. $Cs_3Li(DSO_4)_4$: Conductivity



- Clear isotope effect
- H^+, not Li^+, conductor
- Activation energy is high
- **Conductivity is not high**
- 'Superprotonic'
  - *~ 0.4 eV*
  - *~10^{-3} $\Omega^{-1}cm^{-1}$ just above T_c*

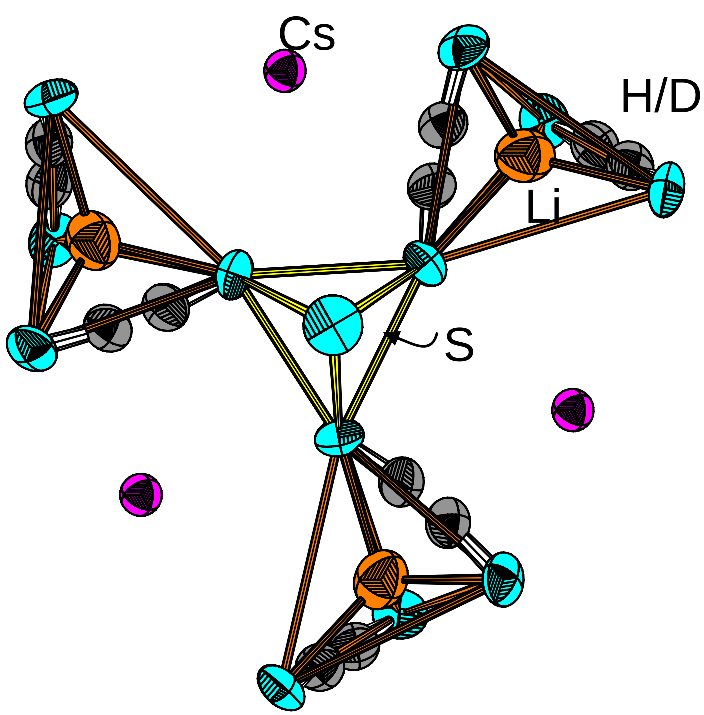
Merinov, Chisholm, Boysen & Haile, Solid State Ionics (2001)

Single Crystal Neutron Diffraction

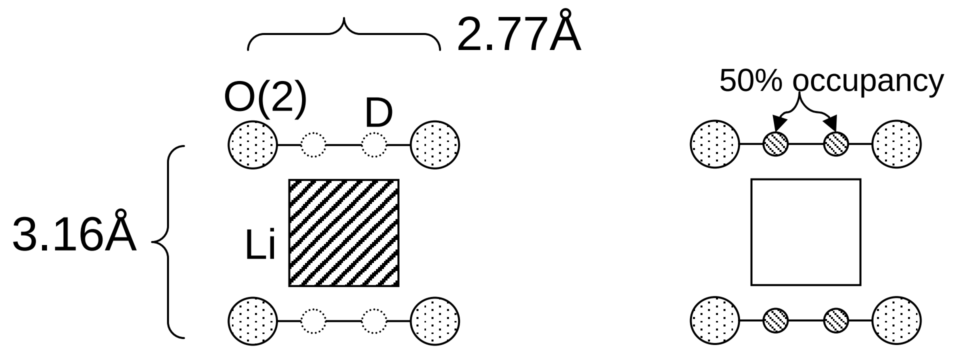
with Wim Klooster

- Experimental
  - *2TanA diffractometer*
  - *High Flux Isotope Reactor*
  - *ANSTO (Australia)*
  - *Deuterated (>50%)*
  - *4.2 × 4.2 × 4.2 mm³*
  - *300K*
- Refinement Statistics
  - $wR(F_o^2) = 0.0495$
  - $S = 1.034$
- Results
  - *Cs, S, O similar to X-ray*
  - *H/D at entirely* ***different*** *location (1-type)*
  - *Symmetric: O(2)-O(2)*
  - *Li occupancy = ⅓*
  - $Cs_3Li(DSO_4)_4$
    - *vs.* $Cs_3Li_3H_2(SO_4)_4$
  - *85% deuteration*
- Chemical analysis
  - *ICP-MS*
  - *Confirms neutron results*

I. $Cs_3Li(DSO_4)_4$: Revised Structure



- Highly distorted LiO_4
- Comprised of O(2) only
- O-O = 2.77, 3.16 Å
- d = 2.77 Å ⇒ H-bond



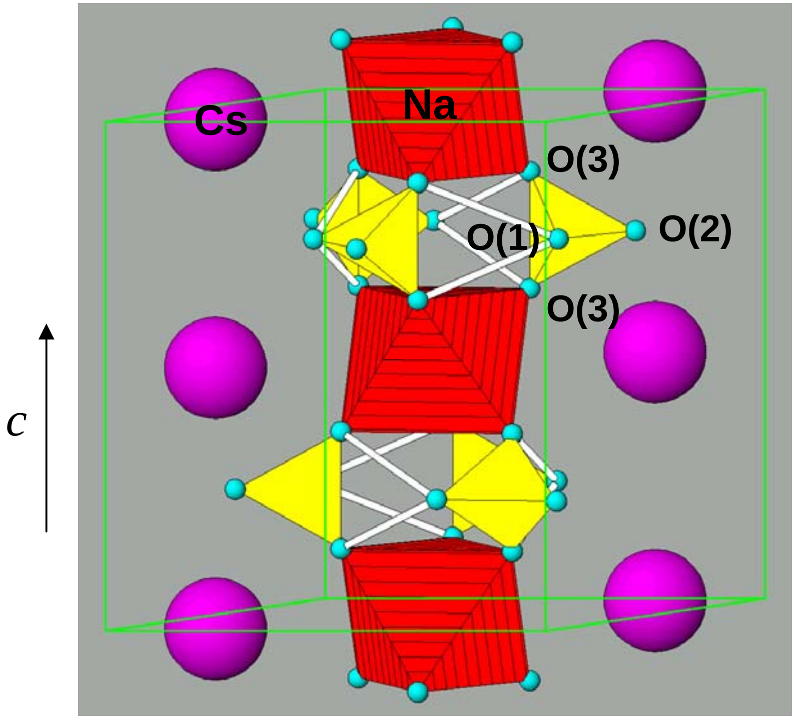
Li site occupied H-bonds not formed	Li site unoccupied H-bonds formed
$^1/_3$ of sites	$^2/_3$ of sites

Klooster, Piltz, Uda & Haile,
J. Solid State Chem. (2004)

'Non-superprotonic' behavior consistent with revised structure

II. $Cs_2Na(HSO_4)_3$: X-ray Diffraction

$Cs_2Na(HSO_4)_3$



hex: a = 8.571(2), c = 9.980(2) Å

Unusual 3-membered (HSO_4) rings

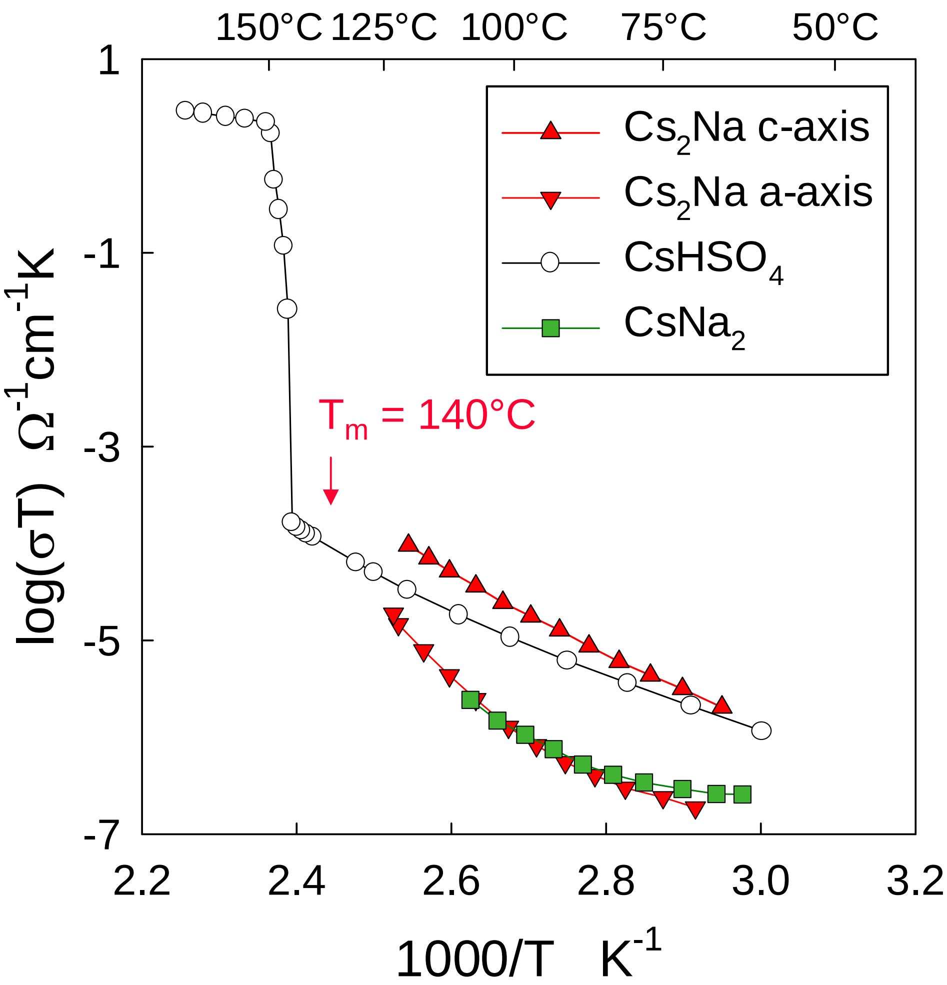
- Hexagonal structure
  - *One Cs, Na, S site; 3 O sites*
  - *Diffraction symbol 6/m $P6_3$--*
- X-ray diffraction unable to identify space group
  - *$P6_3$ or $P6_3/m$?*
- O—O distances suggest two sites with O(1) as donor
  - *O(1)—O(2) = 2.96 Å*
  - *O(1)—O(3) = 3.02 Å*
- NMR data ⇒ only one proton position
- H position unknown

Chisholm, Cowan, Haile & Klooster, Chem. Mater. (2001)

II. $Cs_2Na(HSO_4)_3$: Conductivity

Observations:

- $\sigma_{33} > \sigma_{11}$
- But H-bonds in a-b plane?
- σ_{11} exhibits curvature
- No transition before melt



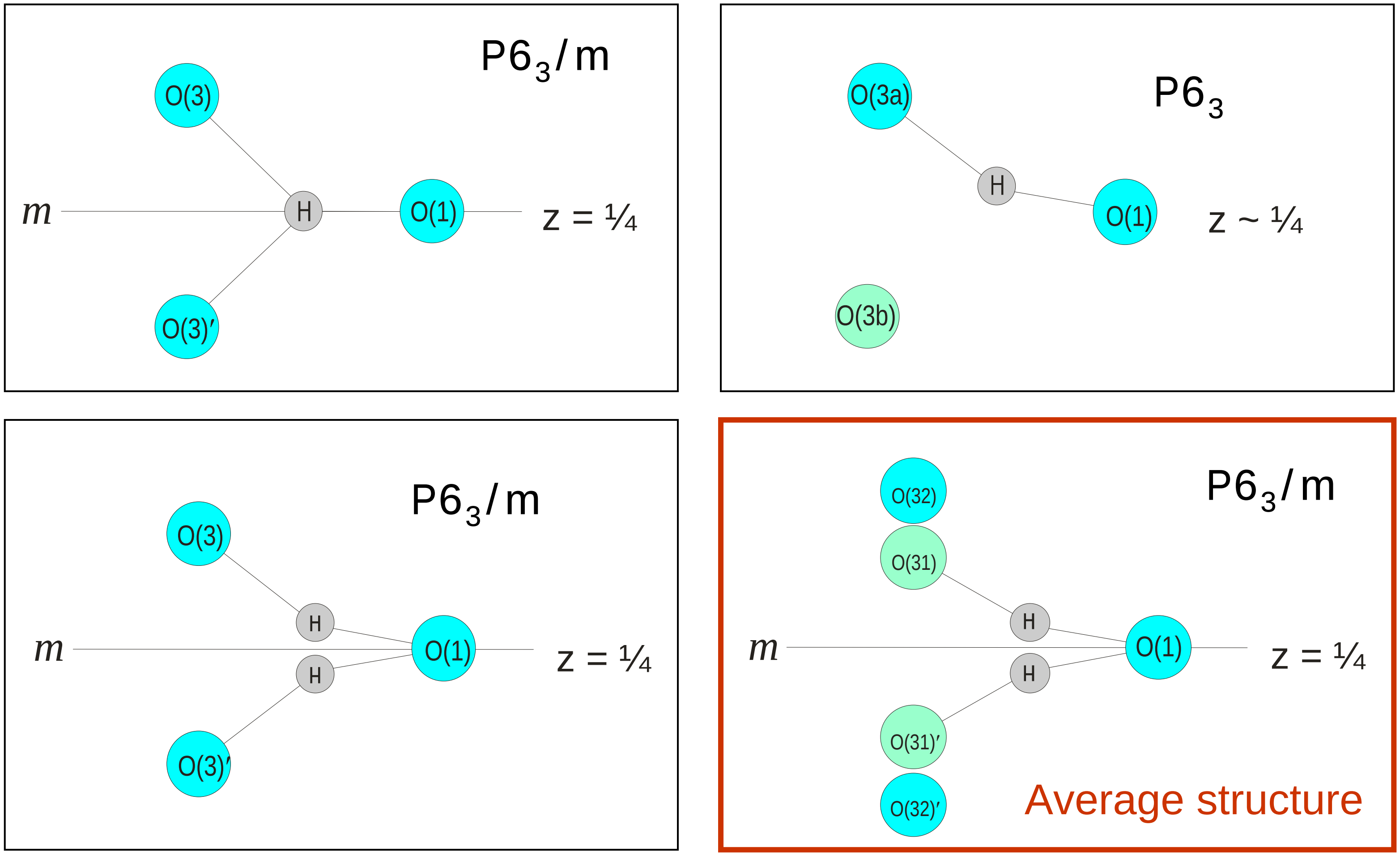
Single Crystal Neutron Diffraction

with Wim Klooster

- Experimental
  - *HB2A beam port, 4-circle diffractometer*
  - *HIFR, ORNL*
  - *Protonated*
  - $5.5 \times 2.5 \times 2.5\ mm^3$
  - *300 K*
- Refinement Statistics
  - $wR(F_o^2) = 0.1715$
  - $S = 1.385$

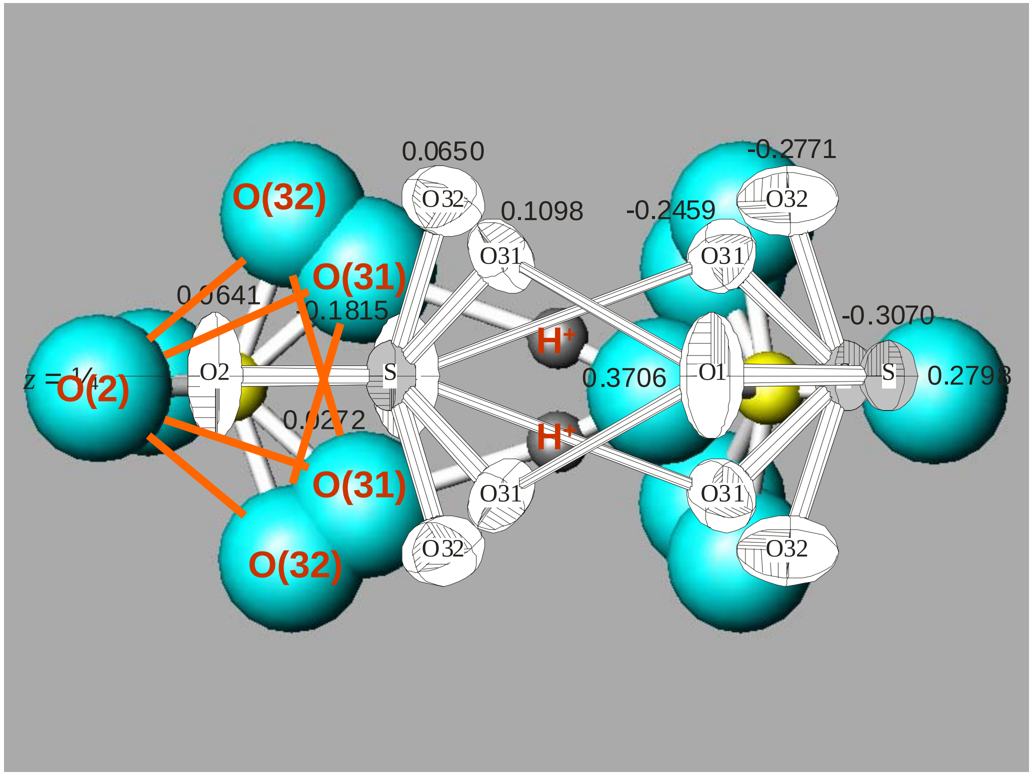
II. $Cs_2Na(HSO_4)_3$: Neutron Diffraction

- Fourier difference maps: O(1)—O(3) occupied; O(1)—O(2) empty



II. $Cs_2Na(HSO_4)_3$: Orientational Disorder

- Locally
  - *Two orientations of SO_4 groups possible*
- Globally
  - *Neither preferred*
  - *Disorder may be*
    - *Static, or*
    - *Dynamic*
- Configurational entropy
  - *Rln(2)=5.8 J/mol*K*



II. $Cs_2Na(HSO_4)_3$: Conductivity

Observations:

- $\sigma_{33} > \sigma_{11}$
- But H-bonds in a-b plane?
- σ_{11} exhibits curvature
- No transition before melt

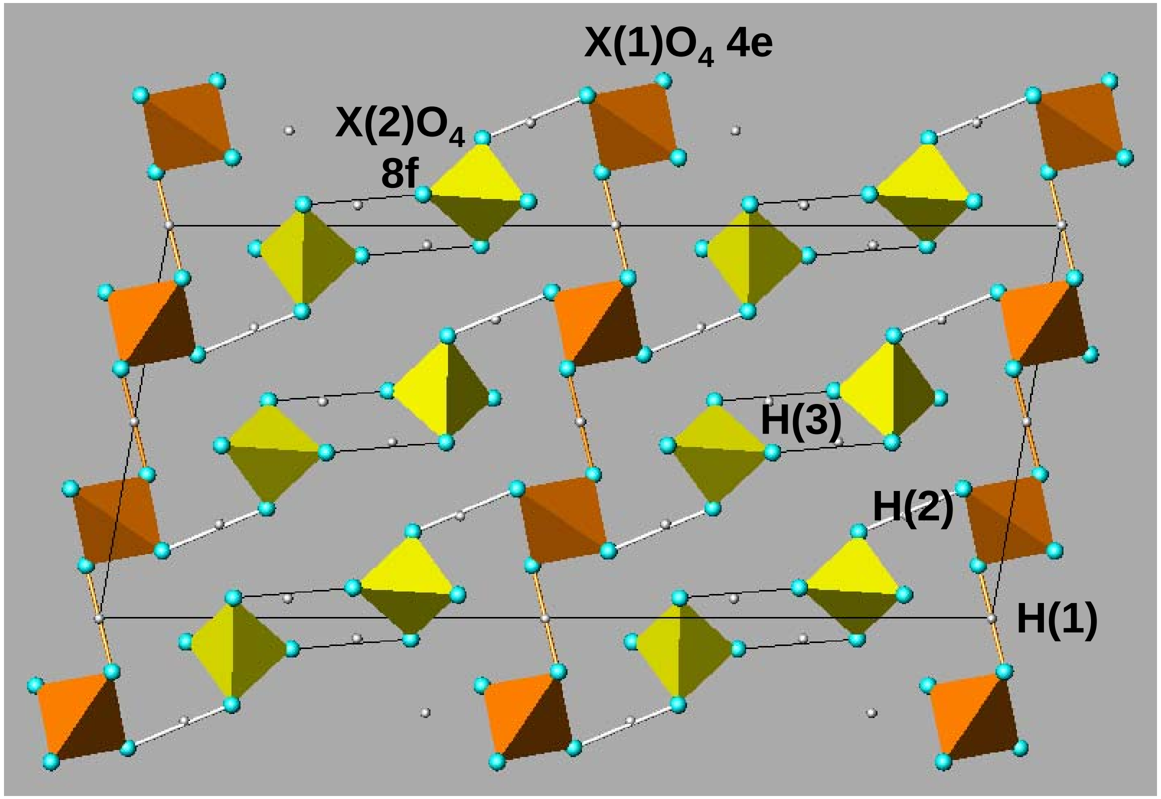
Interpretation:

- O(32)-O(32) = 3.1 Å
- Interstitial sites along c
- Temperature sensitive disorder
- Configurational entropy stabilizes structure relative to a superprotonic phase
- More likely due to small size of Na^+ cation

III. β-$Cs_3(HSO_4)_2[H_{2-x}(P_{1-x},S_x)O_4]$

X-ray diffraction study

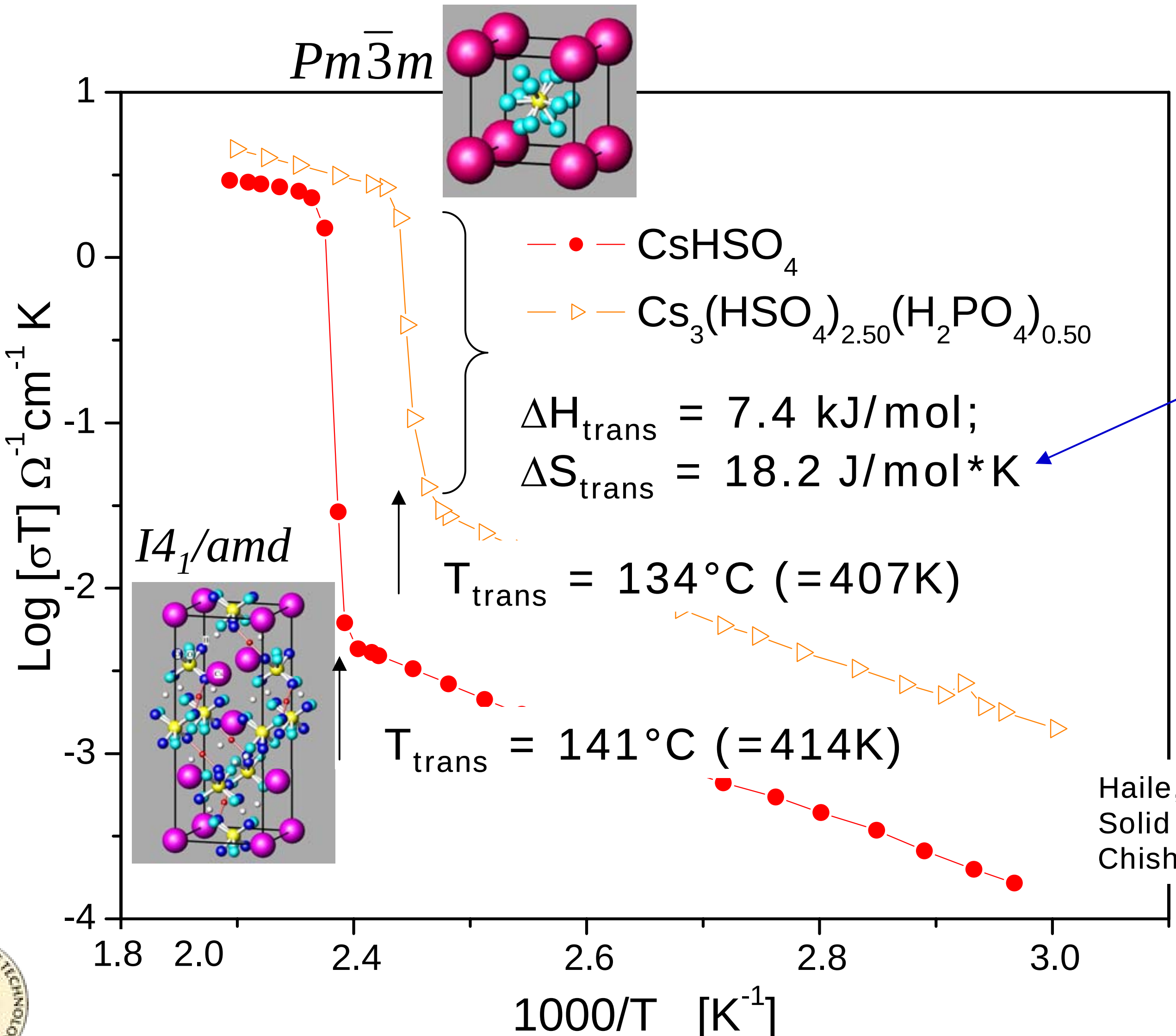
C 2/c
x ~ 0.5
X(1) ~ S,P
X(2) ~ S



P,S distribution, H positions obtained only indirectly

Haile, Calkins & Boysen, J. Solid State Chem. (1998)

III. β-Cs_3... Conductivity



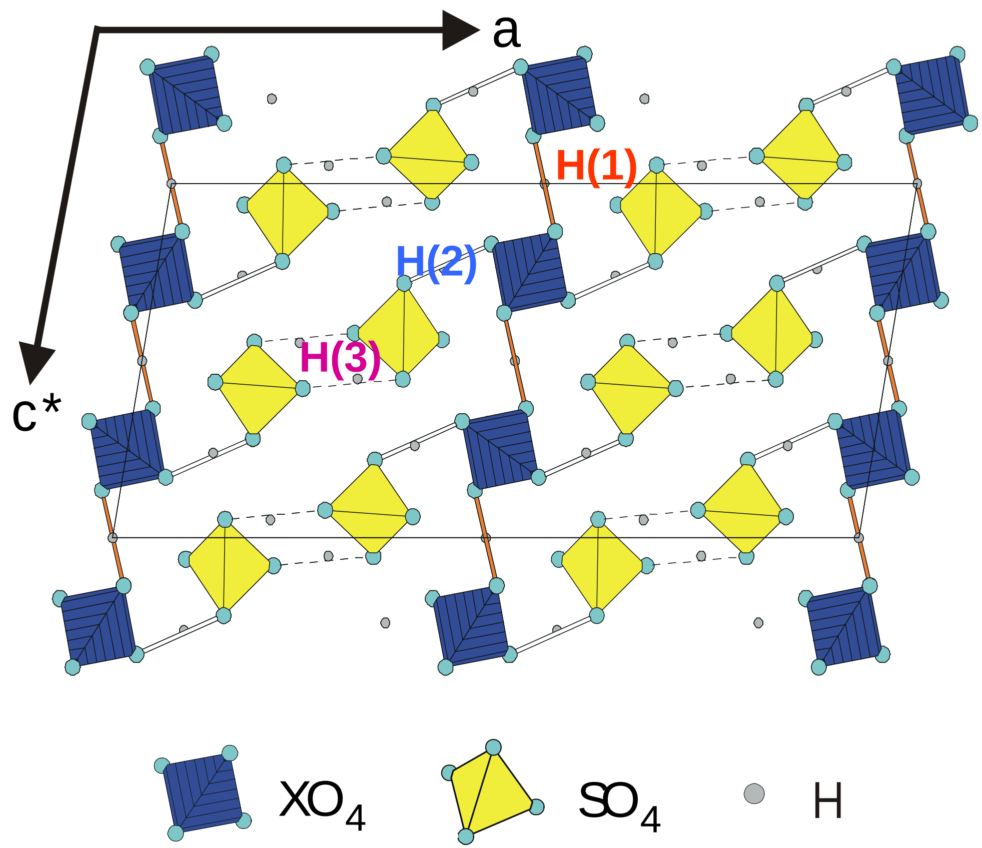
Evaluate based on structure?

Haile, Calkins and Boysen, Solid State Ion (1997)
Chisholm, PhD Thesis (2003)

III. β-Cs_3... Neutron Diffraction

with Wim Klooster

- Basic structure confirmed
- XO_4 anions
  - $X(1)O_4 = (P_{½}S_{½})O_4$
  - $X(2)O_4 = SO_4$
  - $x = 0.500(6)$
- Proton positions
  - ***H(1)***: *symm, centered bond:full; site:full occ*
  - ***H(2)***: *asymm, acentered bond:full, site:~ ¼, ¾*
  - ***H(3)***: *asymm, distributed bond:½; site:¼ occupancy*
- Global disorder/local order



Haile and Klooster, Acta Cryst. (1999)

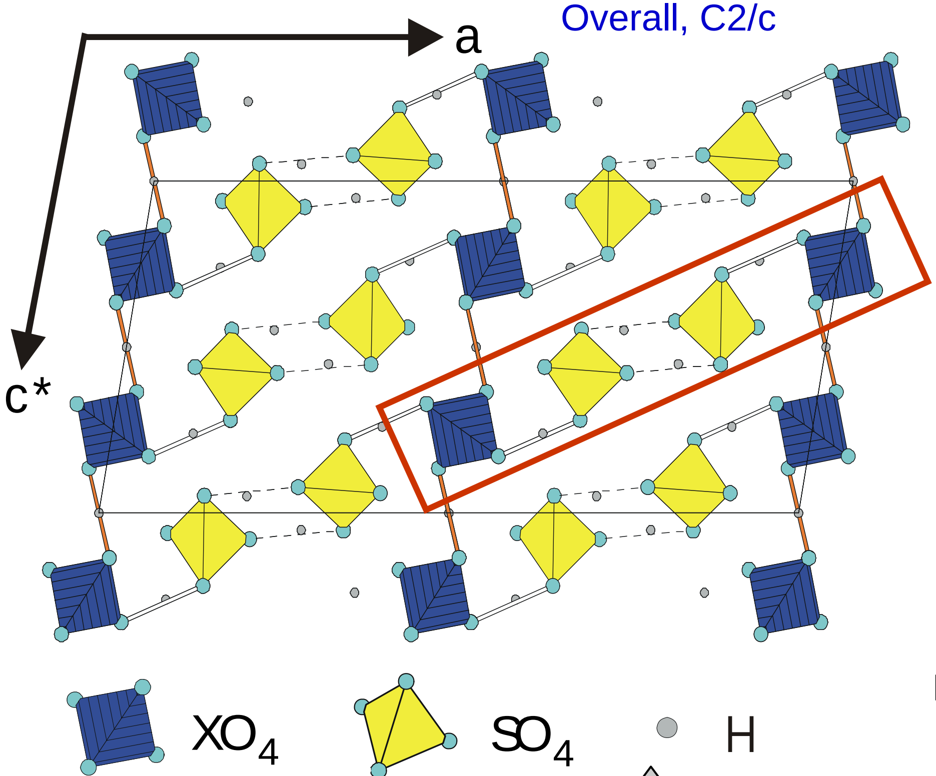
Single Crystal Neutron Diffraction

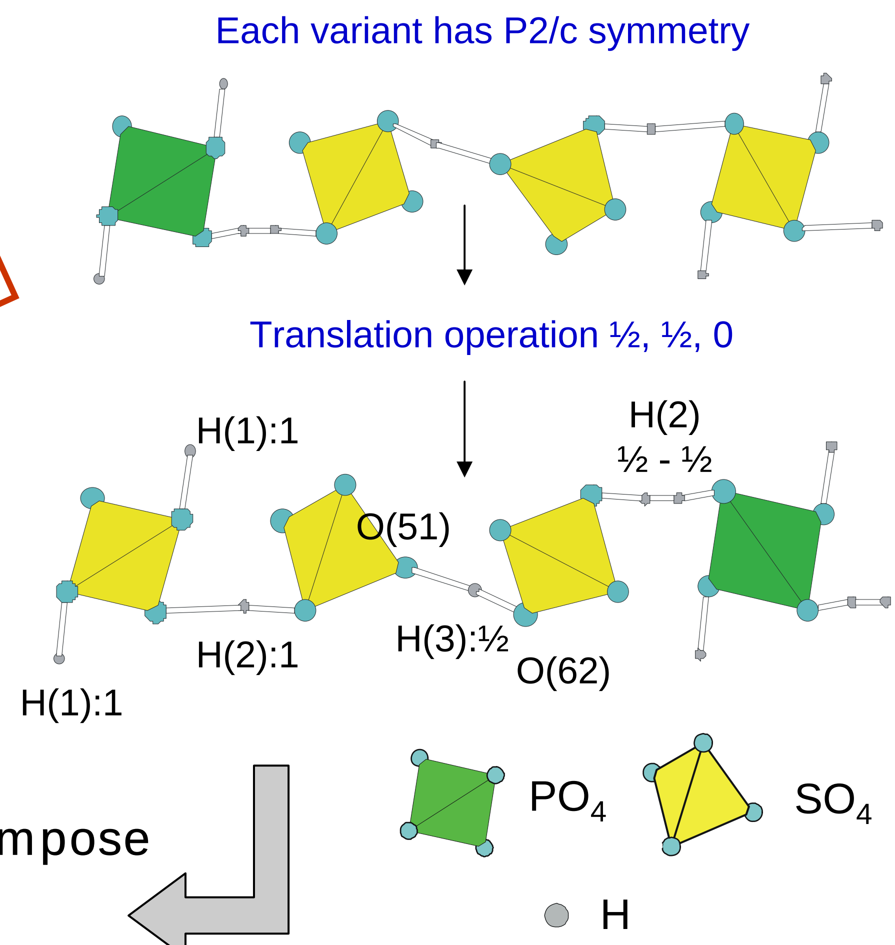
with Wim Klooster

- Experimental
  - *H6M beam port, 4-circle diffractometer*
  - *High Flux Reactor at Brookhaven National Labs*
  - *Protonated*
  - $1.4 \times 3.2 \times 2.2\ mm^3$
  - *15.0 (5)K, DISPLEX CS-202 closed cycle refridgerator*
- Refinement Statistics
  - $wR(F_o^2) = 0.081$
  - $S = 1.25$

III. β-Cs_3... Neutron Diffraction

- XO_4 chains in one of two arrangements





superimpose

Summary

- $Cs_3Li(DSO_4)_4$
  - *Structure, stoichiometry revised on the basis of SCND*
  - *Rationalize 'non-superprotonic' behavior*
- $Cs_2Na(HSO_4)_3$
  - *Space group determined by SCND*
  - *Proton/SO4-orientation disorder revealed*
    - *Insight into proton conduction, lack of phase transition*
- β-$Cs_3(HSO_4)_2[H_{2-x}(P_{1-x},S_x)O_4]$
  - *Presumed structure confirmed by SCND*
  - *Multiple sources of entropy detailed*
    - *Quantitative analysis of entropy of RT phase*
    - *Confirmation of entropy model developed for SP phases*

Acknowledgements

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  - *Calum Chisholm, Dane Boysen, Lisa Cowan*
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