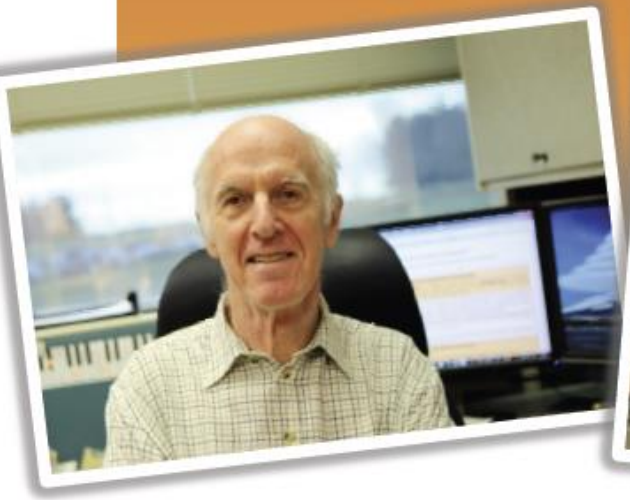
40 years of Neutron Scattering

A Symposium Honoring

John Copley, William Kamitakahara and David Mildner



Solid State Communications, Vol. 41, No. 11, pp. 843–847. 1982.
Printed in Great Britain.

0038–1098/82/110843–05$02.00/0
Pergamon Press Ltd.

DISTRIBUTION OF HYDROGEN VIBRATIONS IN $LaH_{2.28}$ AND $LaH_{2.99}$

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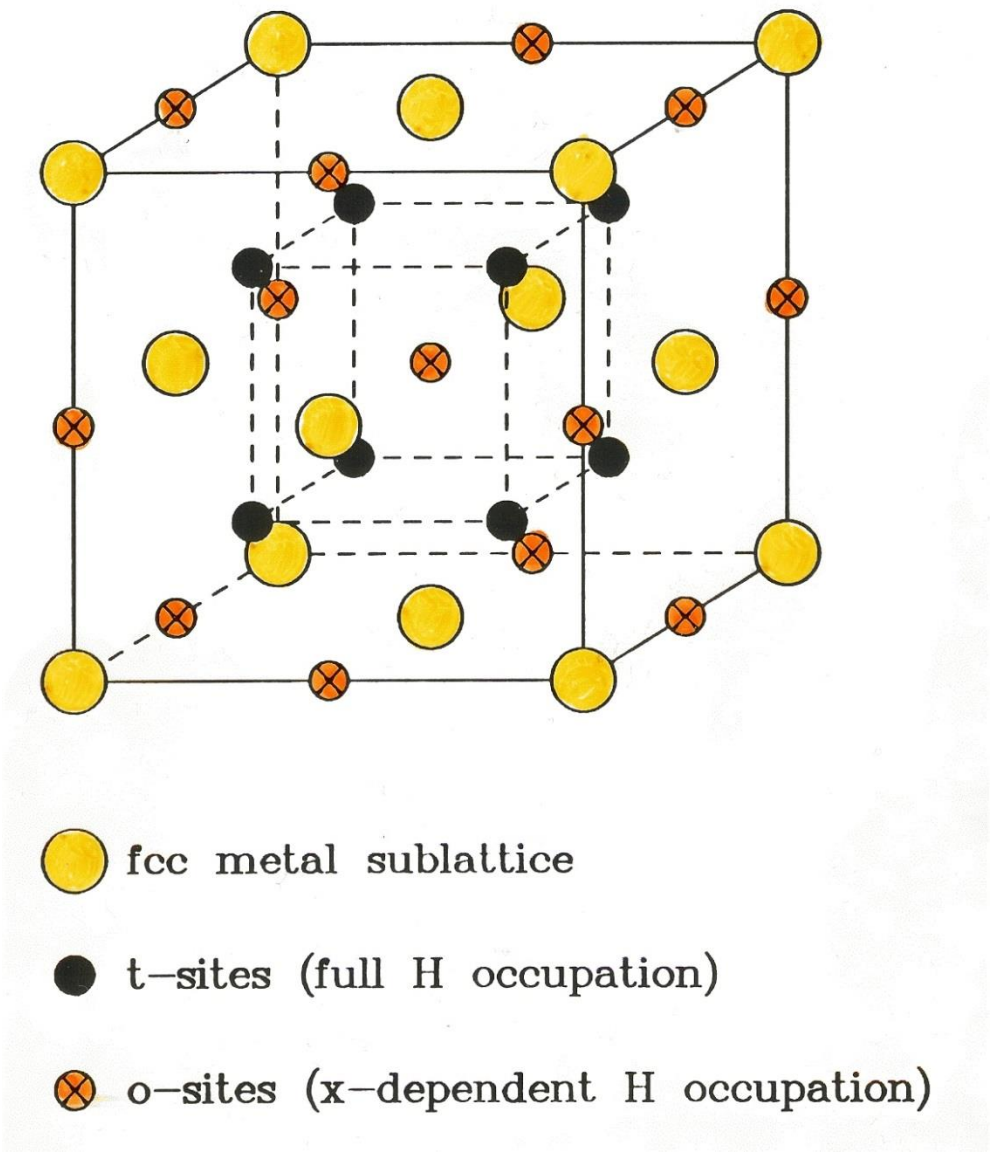
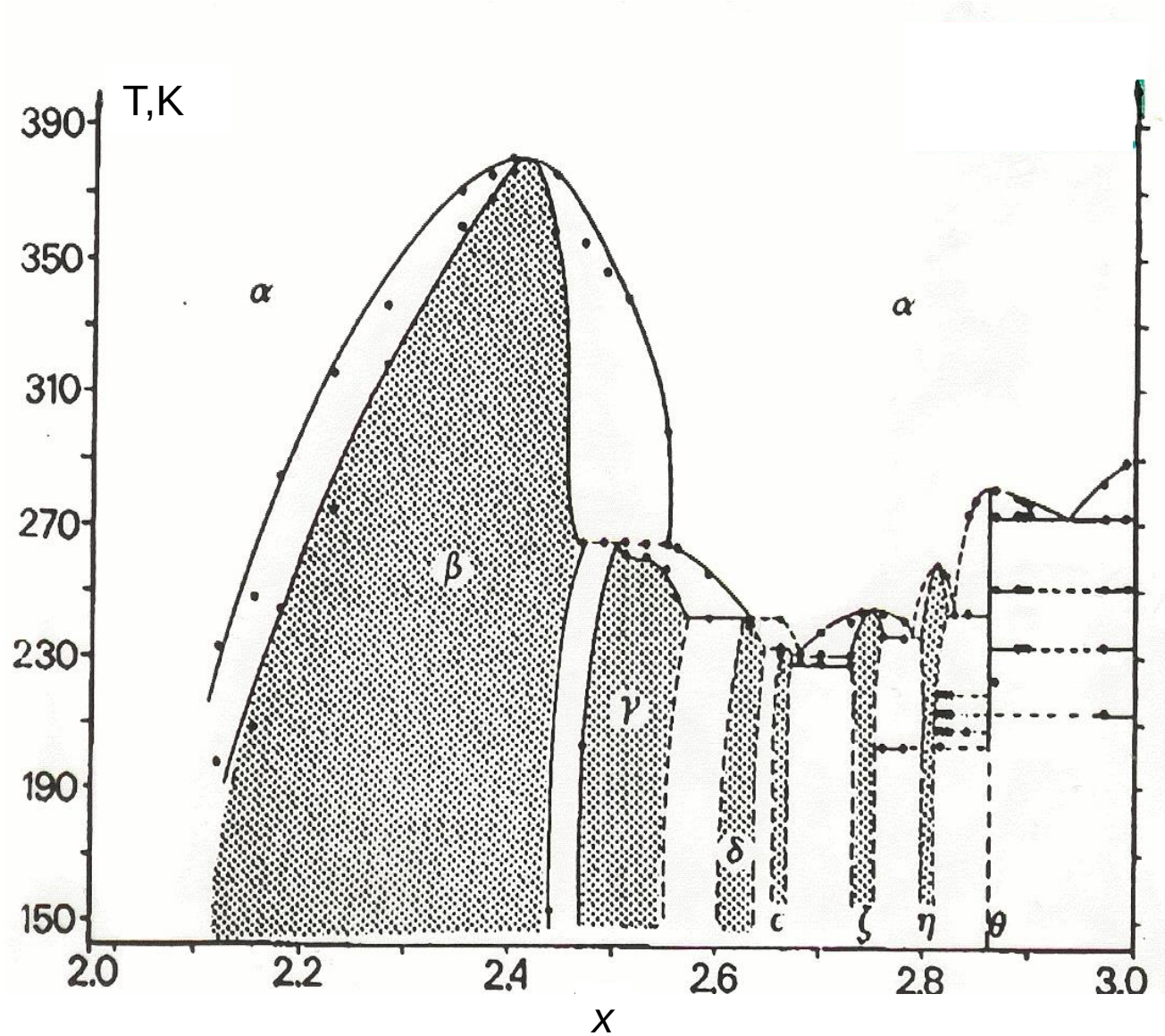
(*Received* 14 *January* 1981; *in revised form* 29 *October* 1981 *by R.H. Silsbee*)

The hydrogen vibrational modes in LaH_x samples have been investigated by pulsed neutron spectroscopy. The results are compared with a simple model emphasizing strong H–H forces and the lack of stoichiometry in $LaH_{2.28}$.

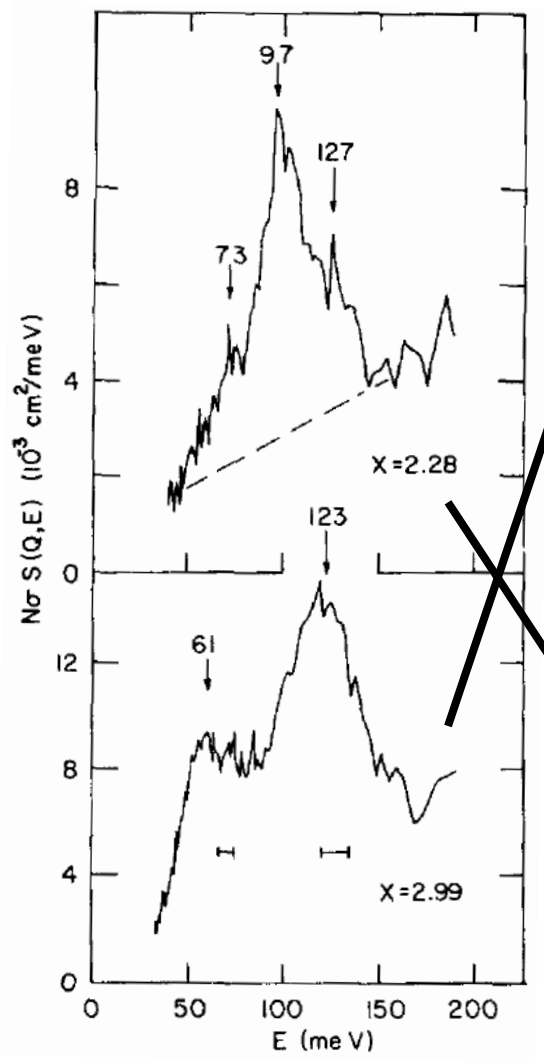
Structure of fcc β-RH_{2+x}

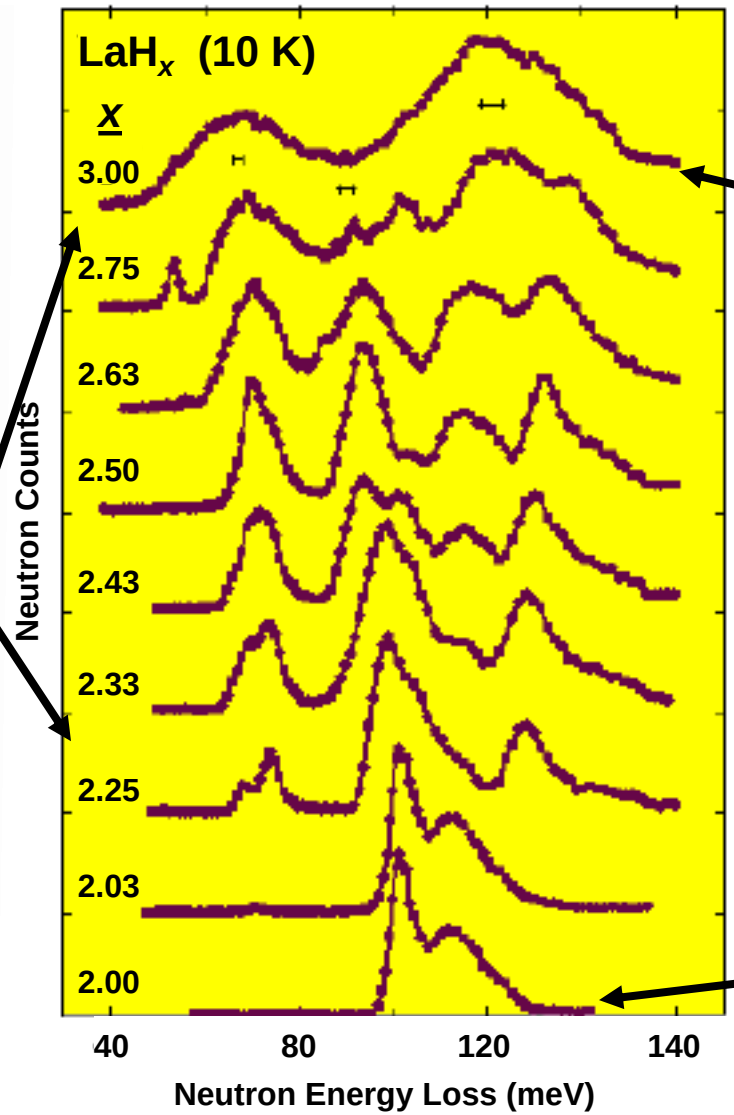


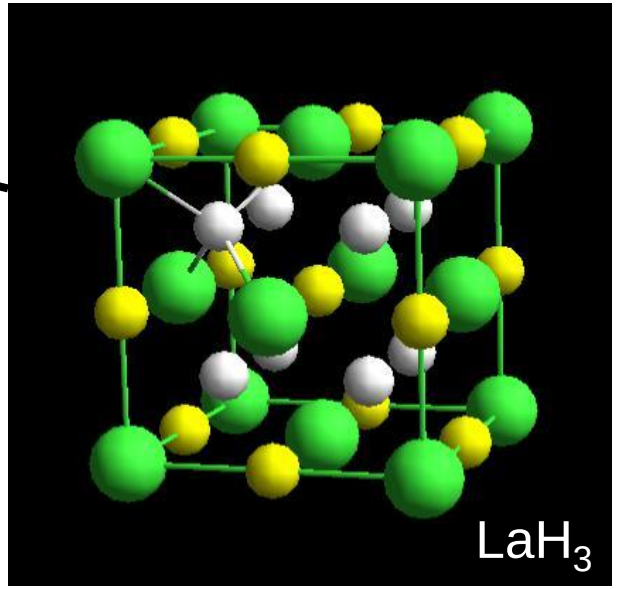
LaH_x Phase Diagram

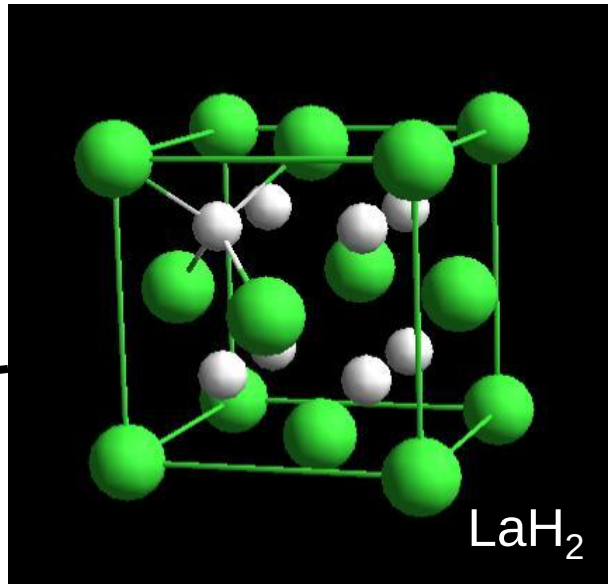


LaH_x Vibrational Densities of States





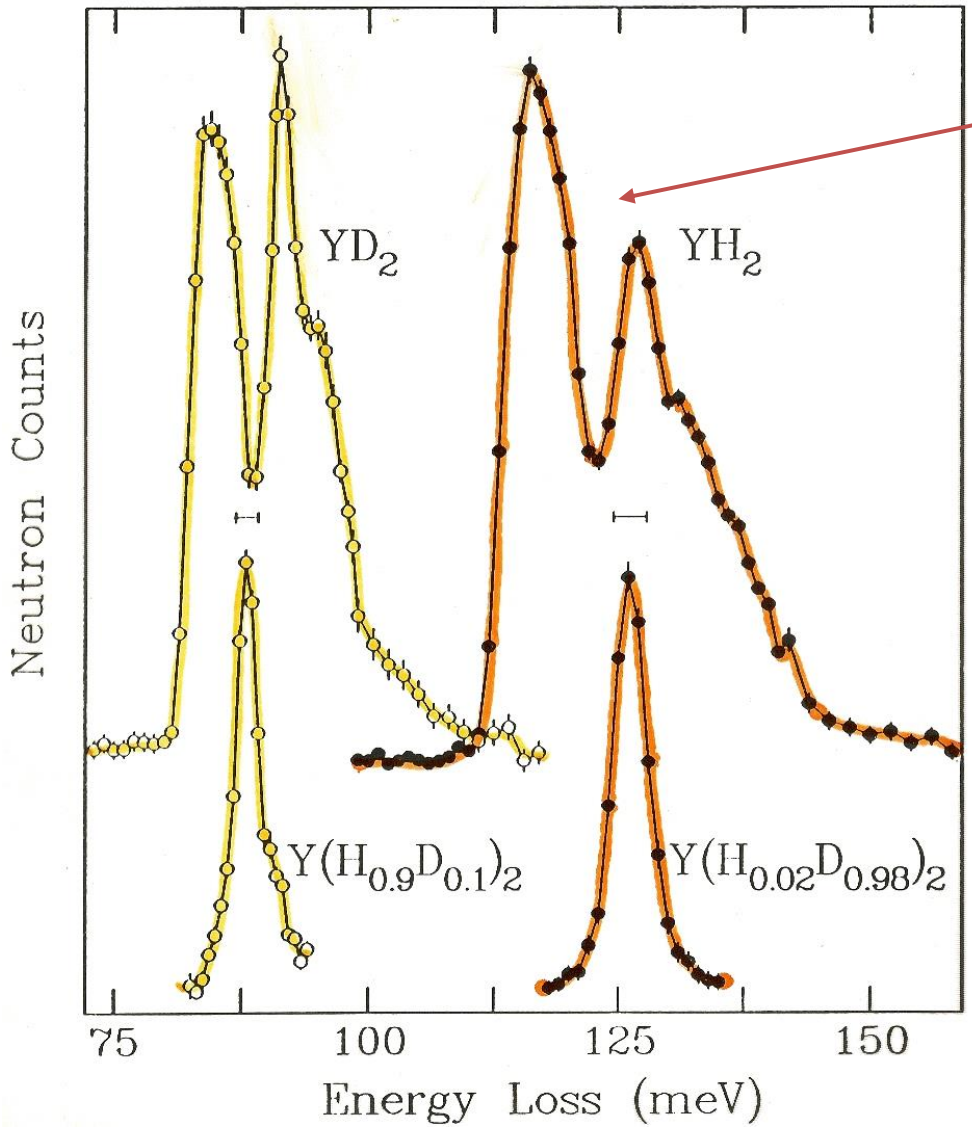




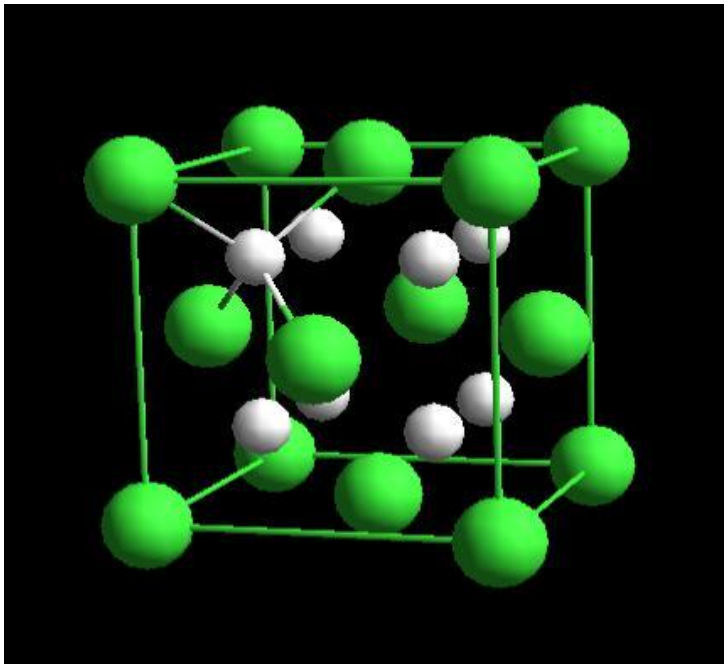
ZING-P' data

FANS data

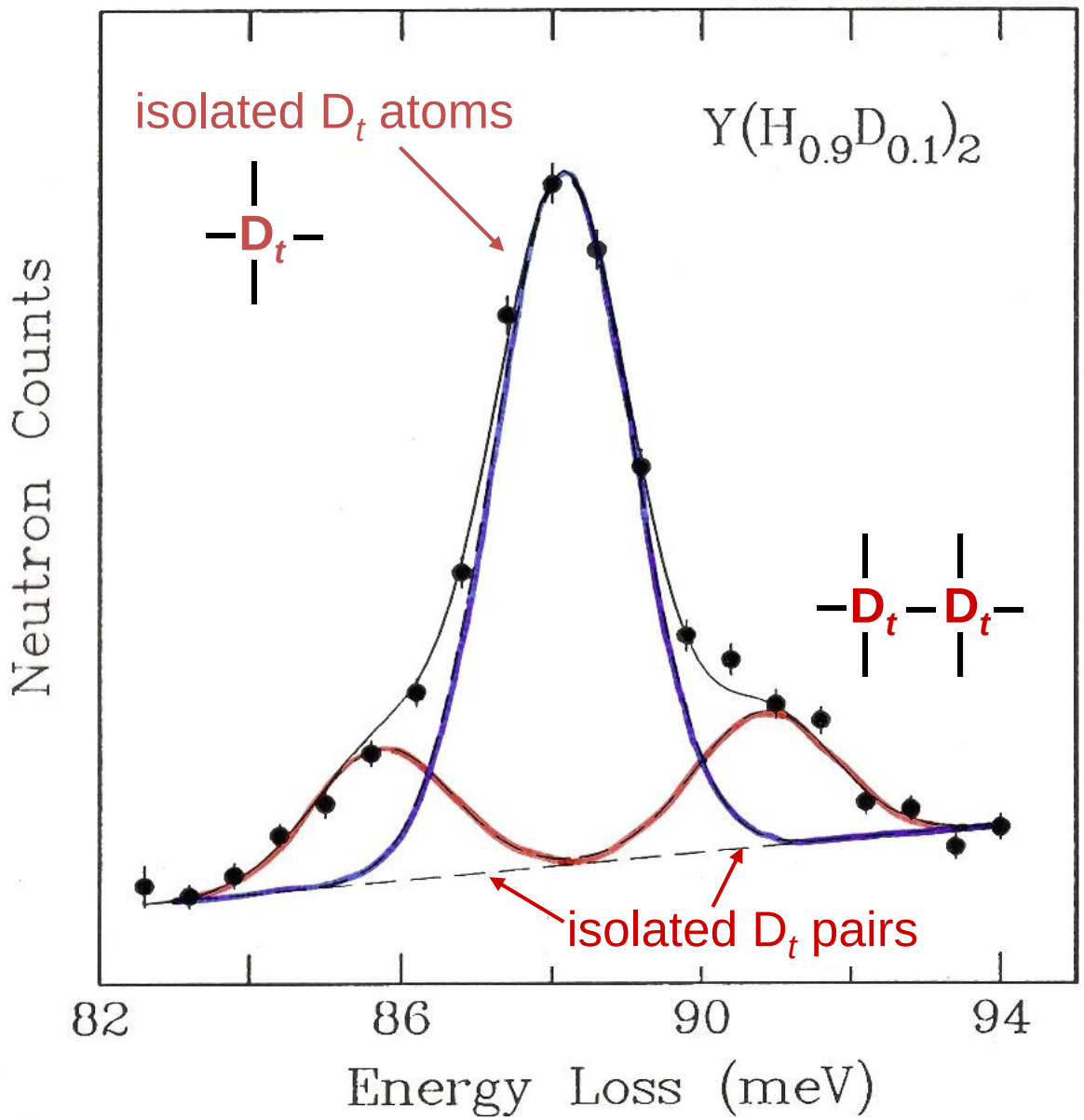
Isotope Dilution Spectroscopy of β-$Y(H_xD_{1-x})_2$



H_t-H_t dynamic coupling interactions



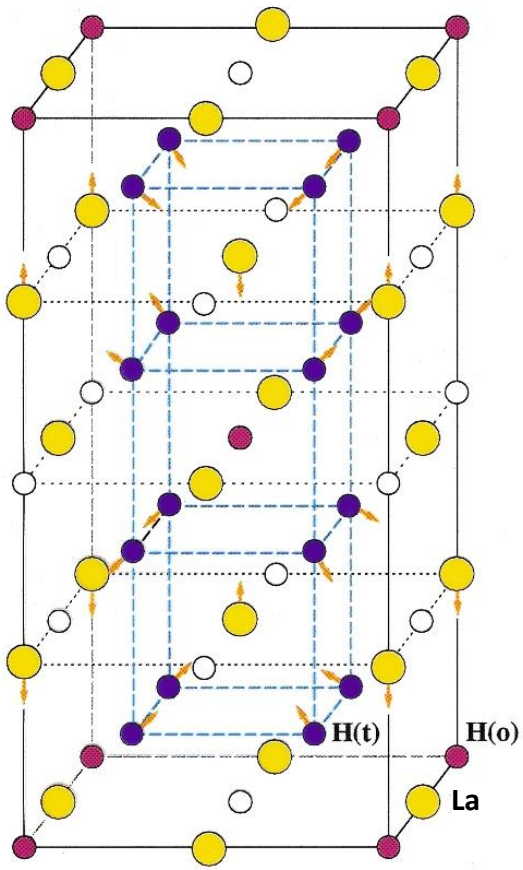
Isotope Dilution Spectroscopy of β-$Y(H_xD_{1-x})_2$

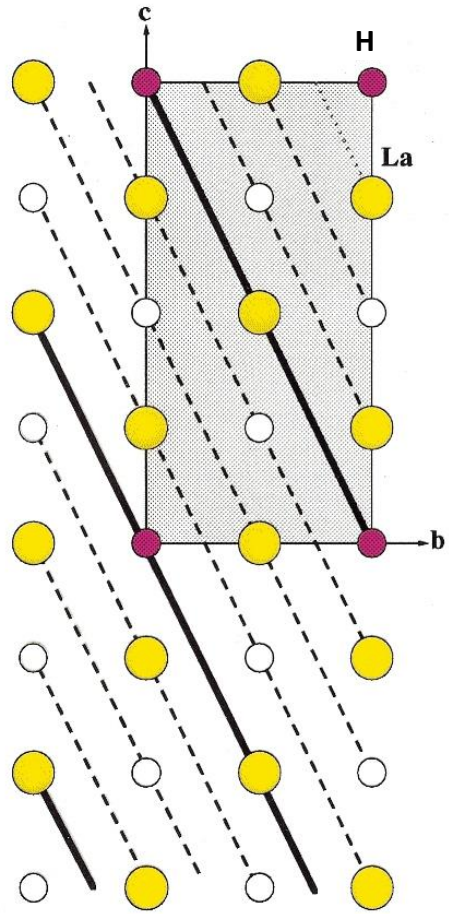


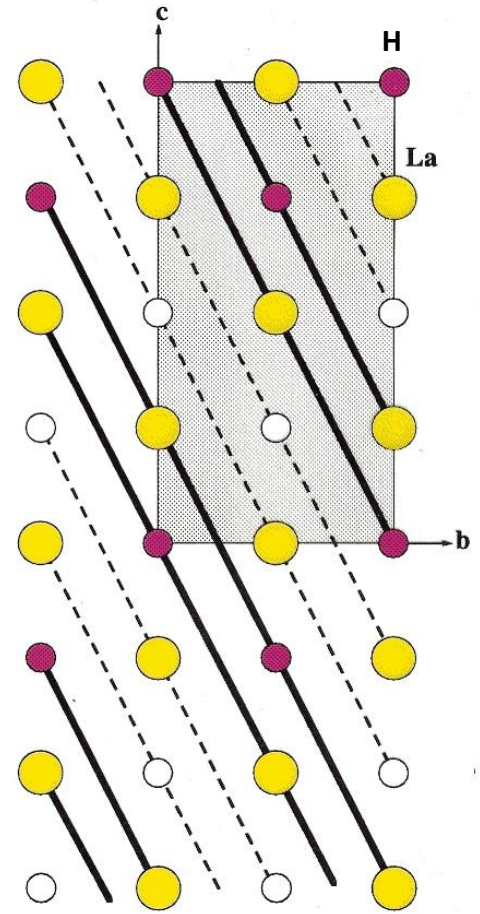
$$\frac{F_{D\text{-}D}}{F_{Y\text{-}D}} \approx 6\%$$

H_o-Ordered $LaH_{2.25}$ $LaH_{2.50}$ and Structures

Low-*T* ordered arrangement of **(042)** planes containing the *o*-site H atoms



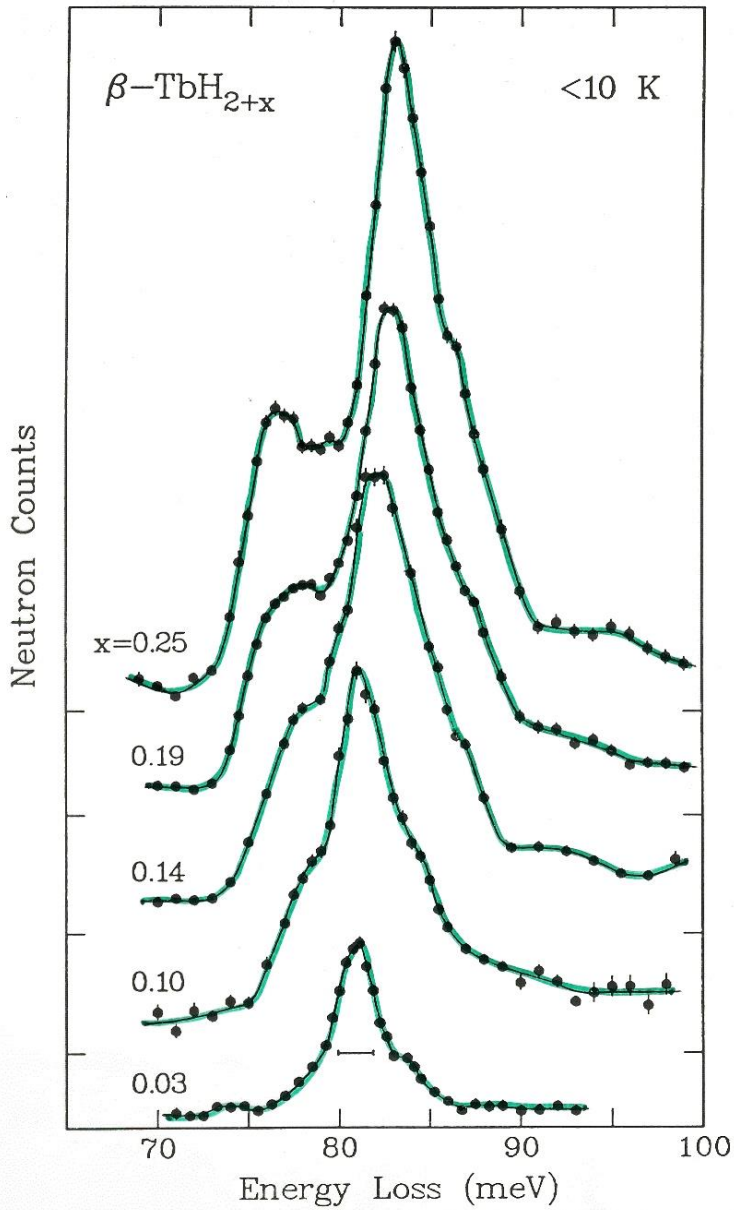


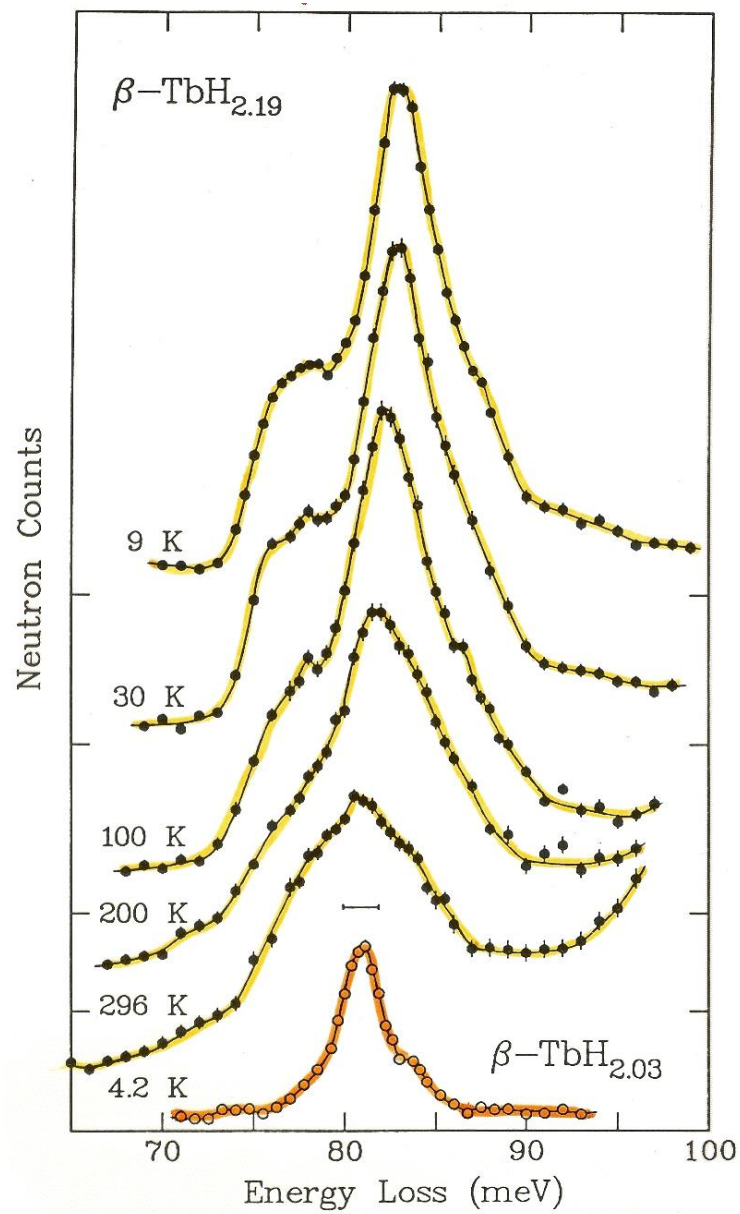


$LaH_{2.25}$ $I4/mmm$

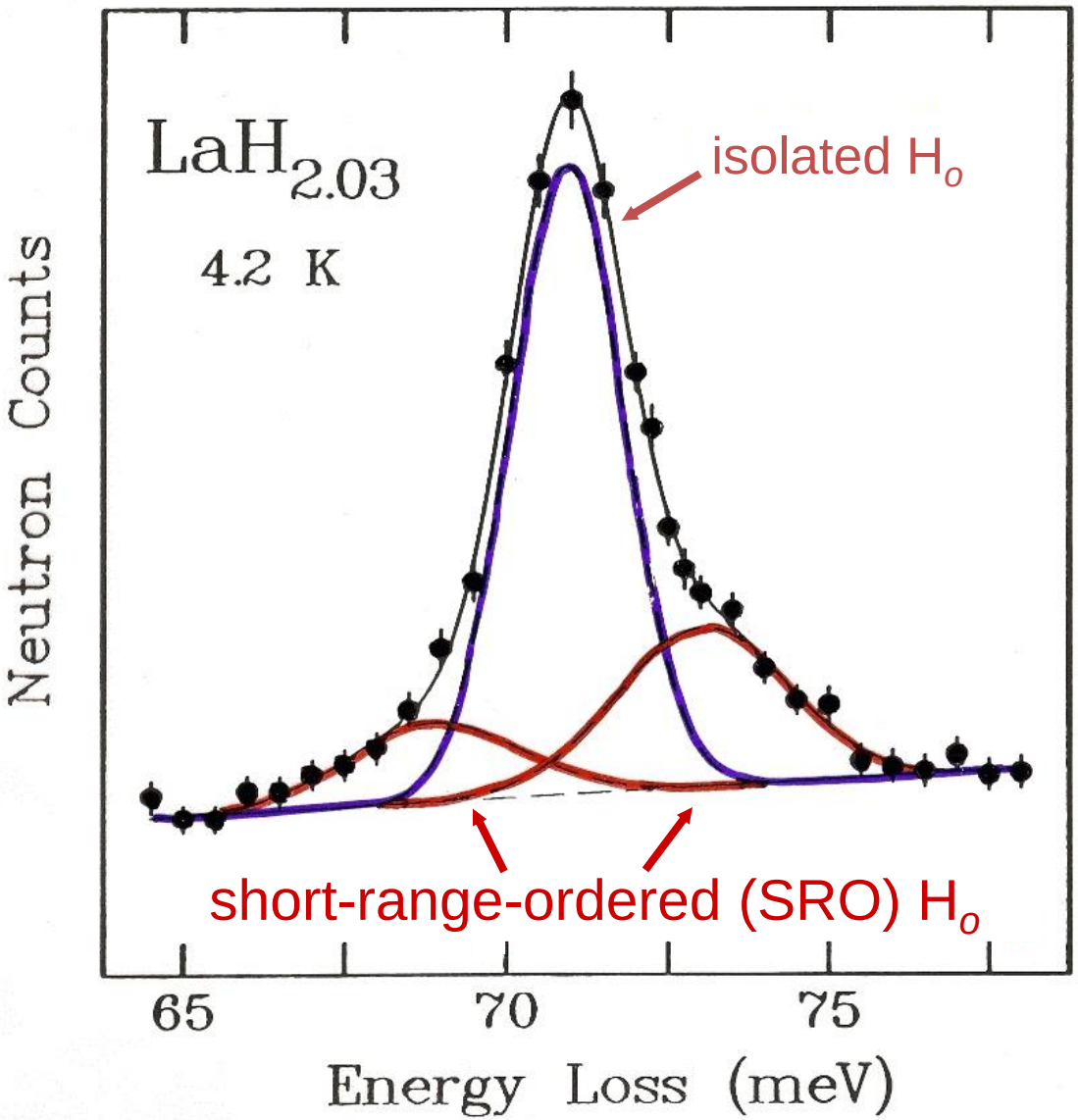
$LaH_{2.50}$ $I4_1/amd$

H_o Ordering in β-TbH_{2+x}

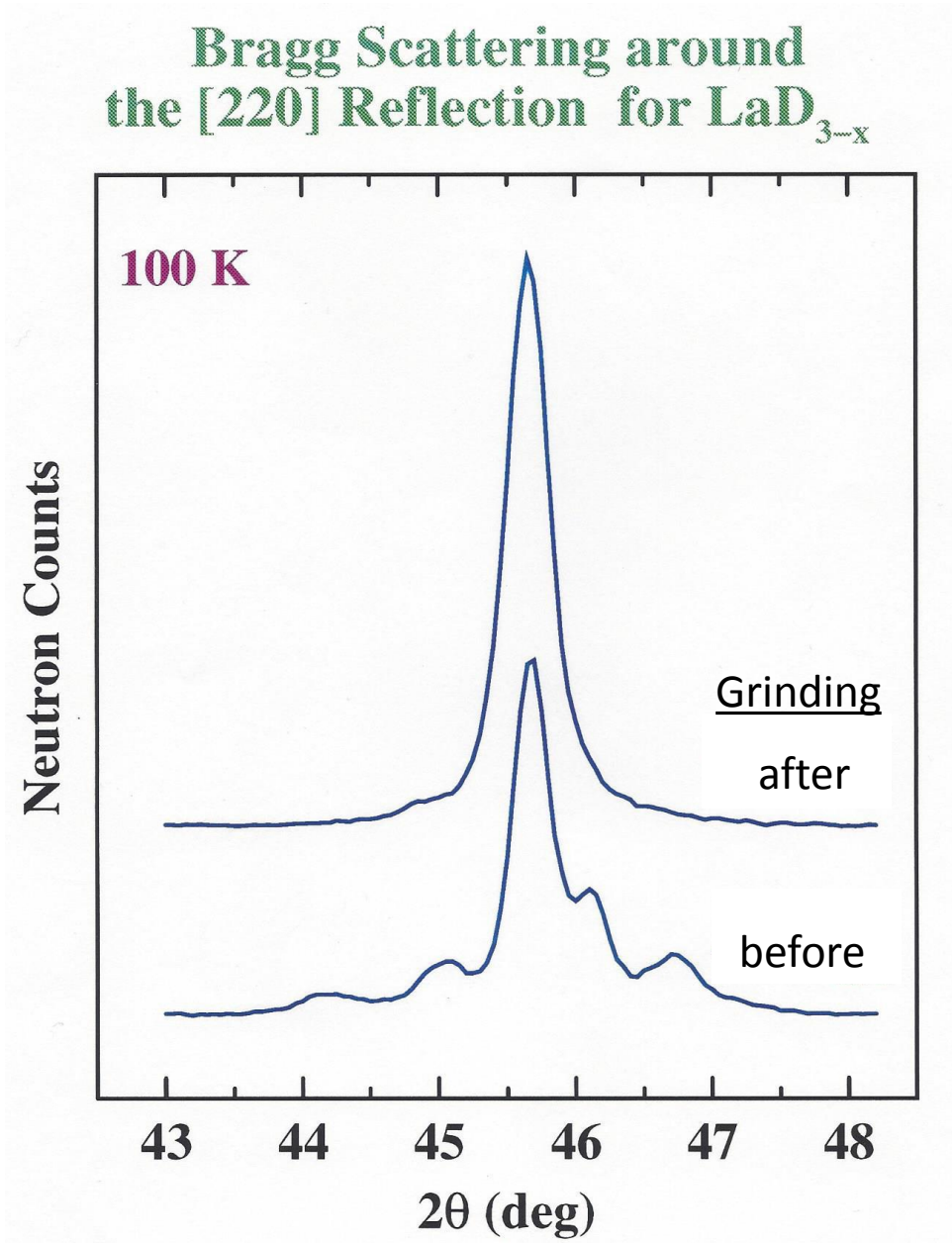


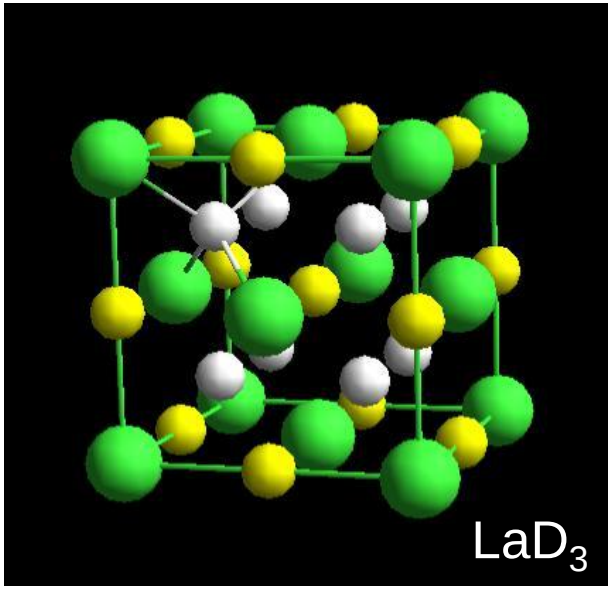


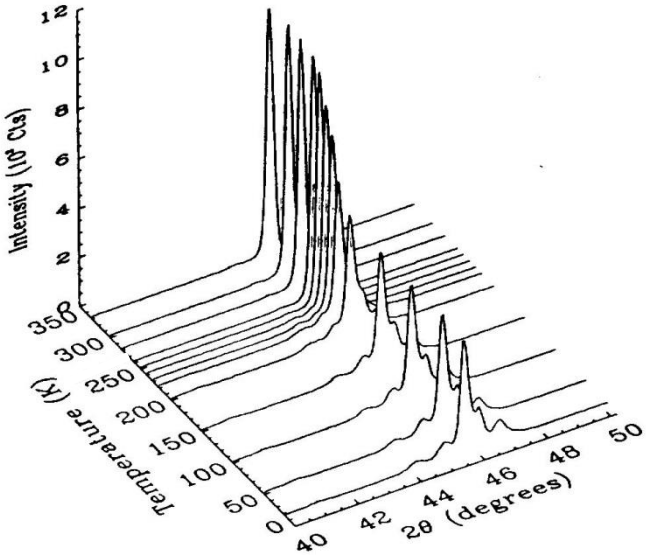
H_o Sublattice Ordering in β-LaH_{2+x}



Low-*T* Incommensurate Structure in β-LaD_{3-x}



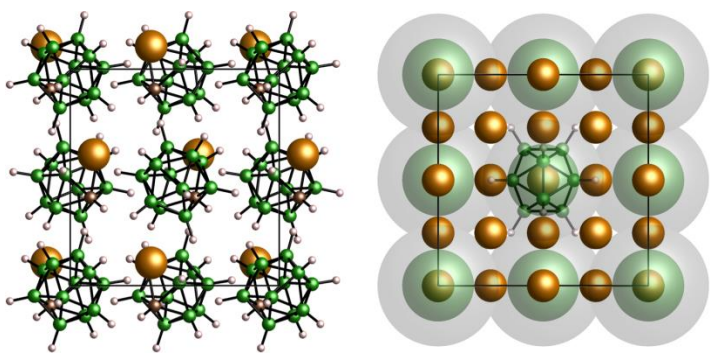




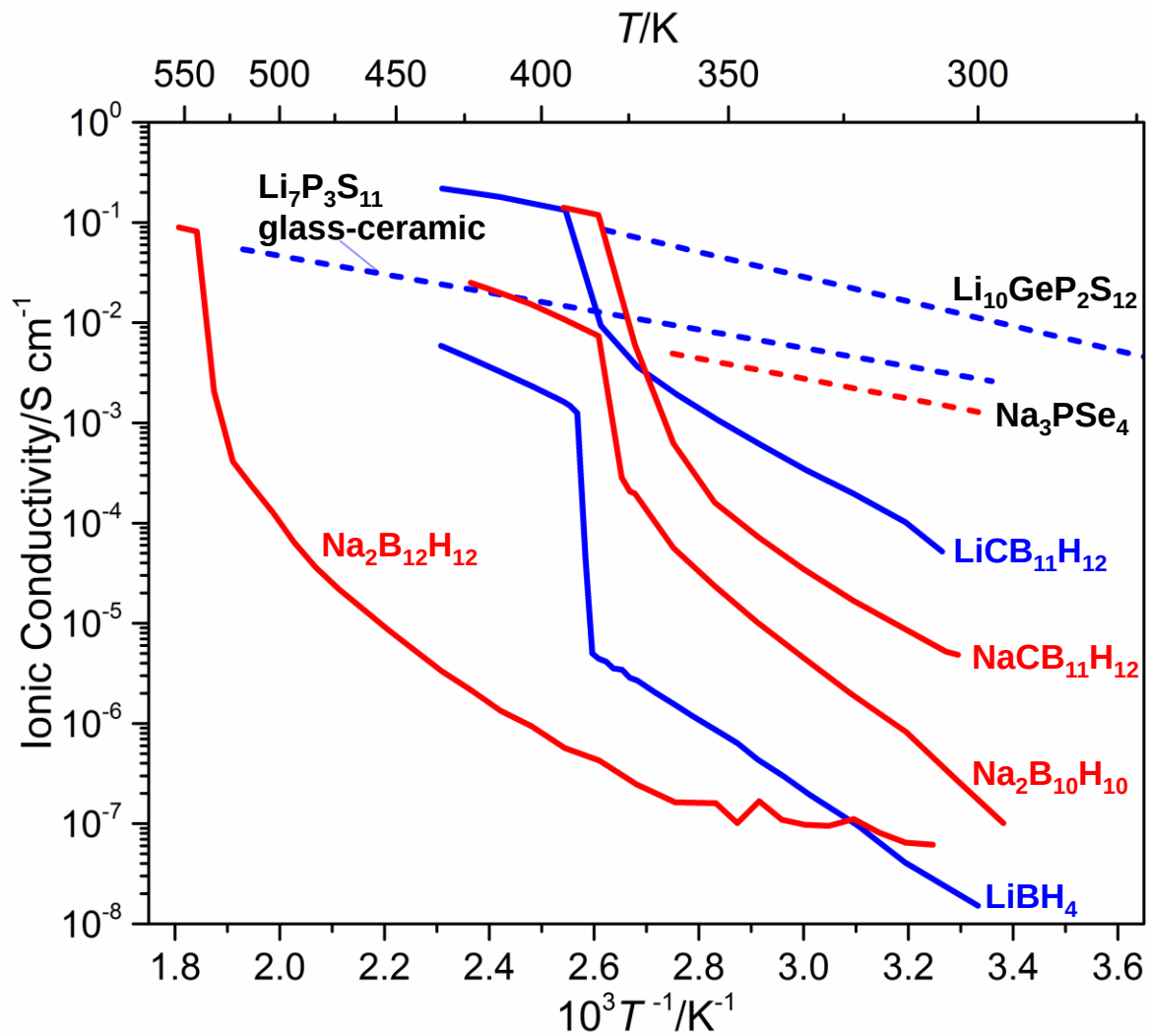
Ionic Conduction in Li and Na Hydroborates

Solid-State Ionic Conductivity

Order-Disorder Phase Transition

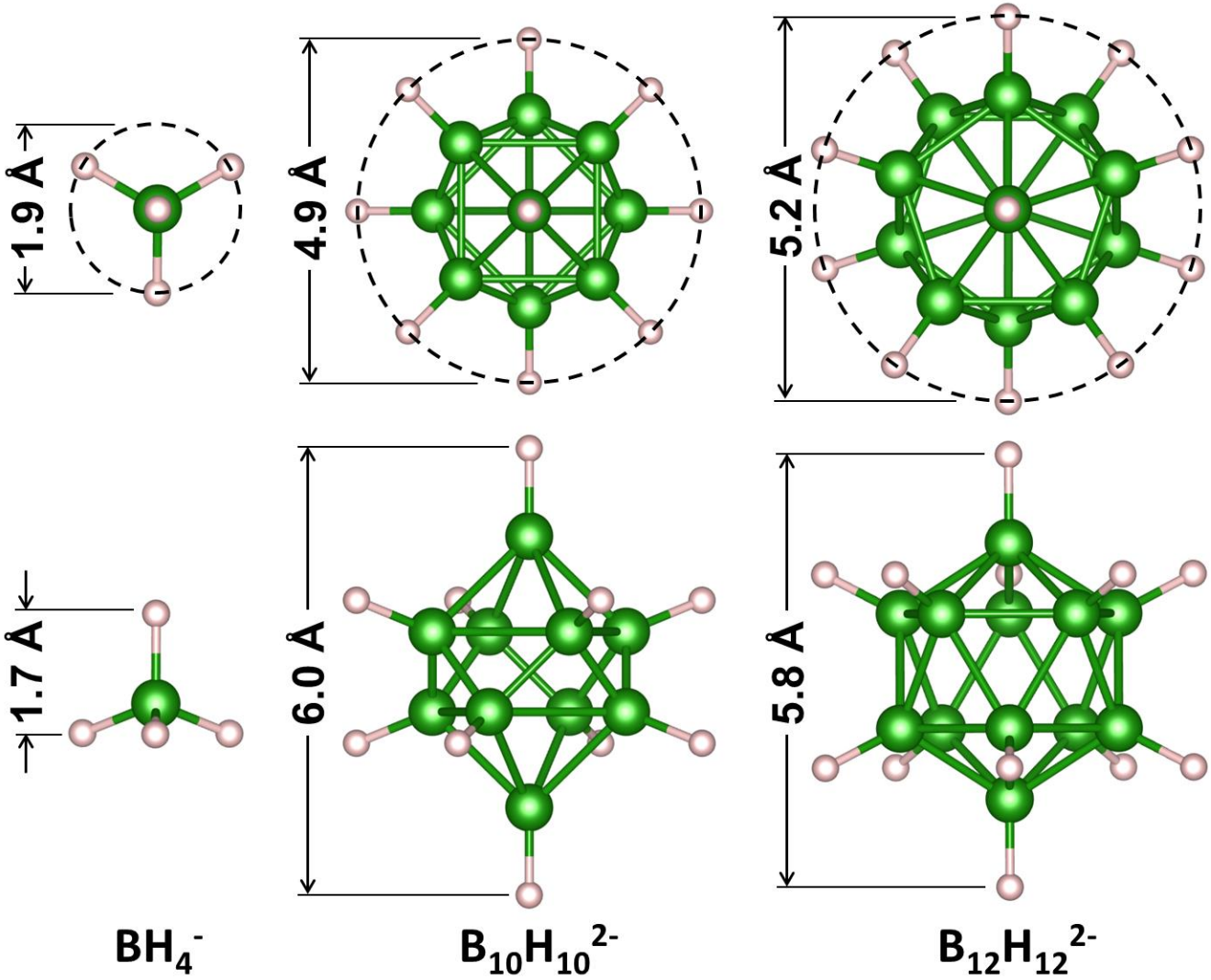


$MCB_{11}H_{12}$



Tang et al. , Energy Environ. Sci. **8**, 3637 (**2015**).

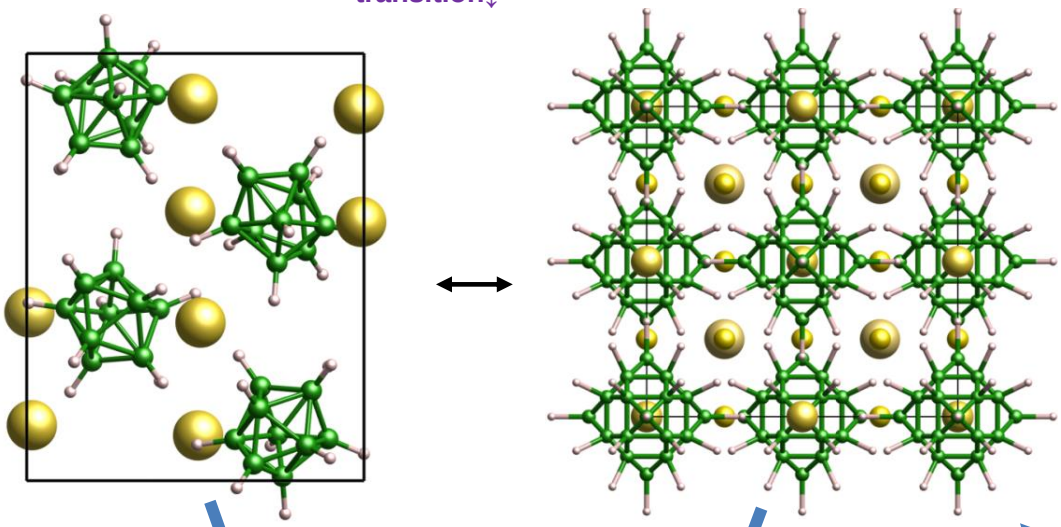
Relative Anion Sizes of Hydroborate Anions

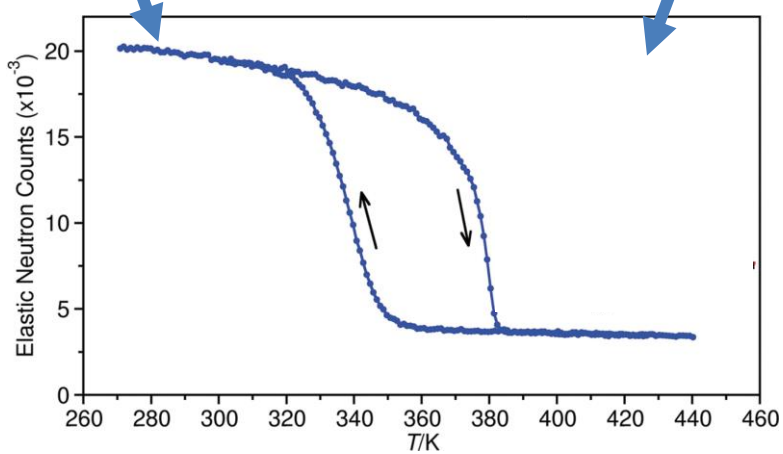


Order-Disorder Phase Transition in $Na_2B_{10}H_{10}$

LT monoclinic ($P2_1/c$) ↔ HT cubic ($Fm\bar{3}m$)

$T_{transition\downarrow} \approx 360$ K





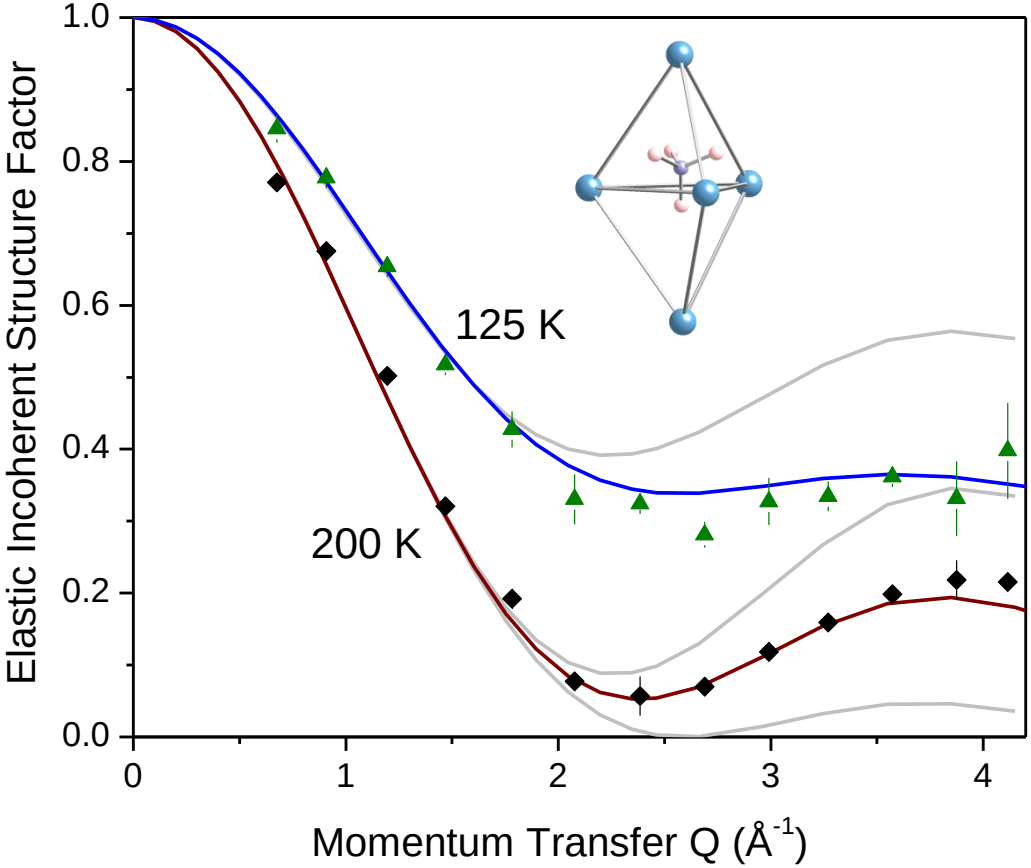
$<10^8$ anion jumps/s

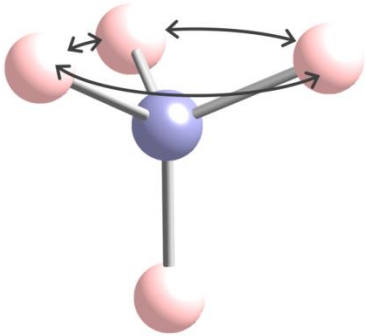
$>10^{10}$ anion jumps/s

Udovic et al. , Adv. Mat. **26**, 7622 (**2014**).

BH_4^- Dynamics of $LiBH_4$-LiI

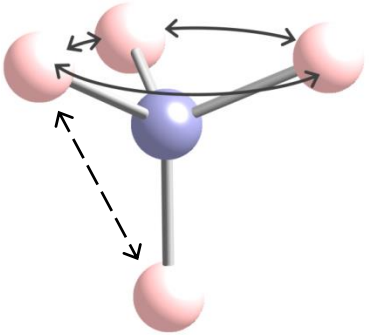
EISF's for 1:1 $LiBH_4$-LiI (hexagonal phase)





125 K

1-D rotational diffusion
(≥ 6-fold jumps)

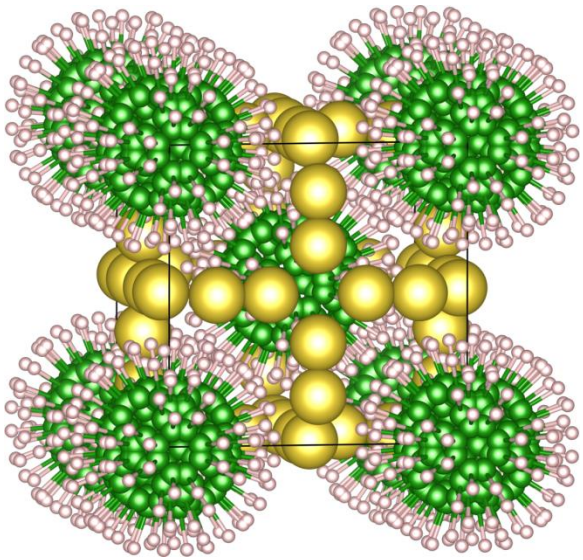


200 K

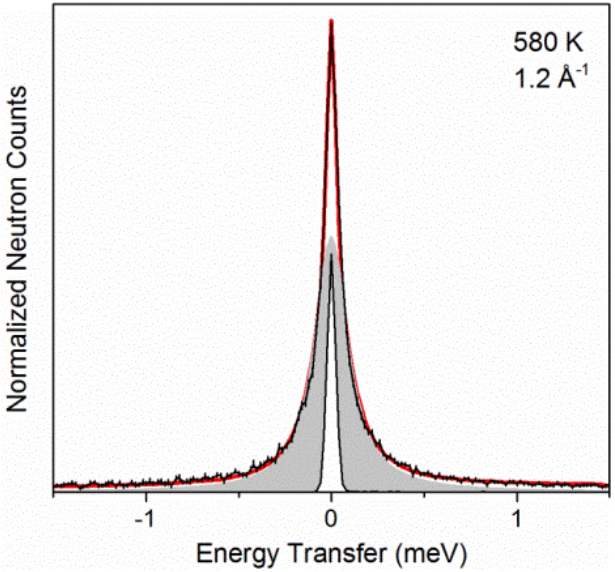
1-D rotational diffusion + axial jumps

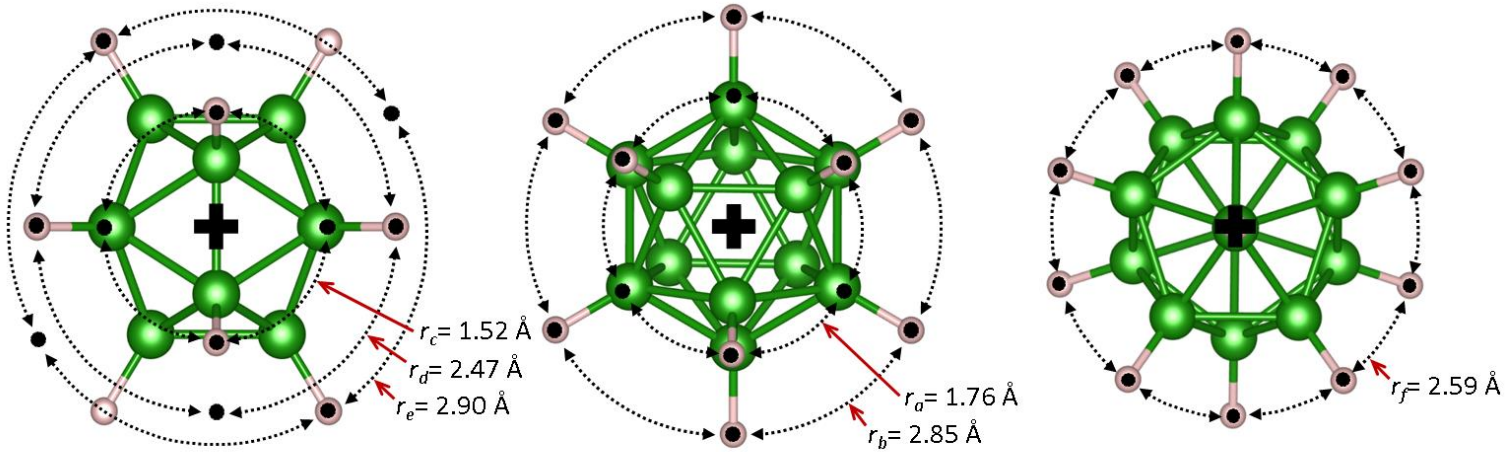
Verdal et al., J. Phys. Chem C **117**, 12010 (2013).

Rotational Dynamics of $B_{12}H_{12}^{2-}$ Anions



$Na_2B_{12}H_{12}$

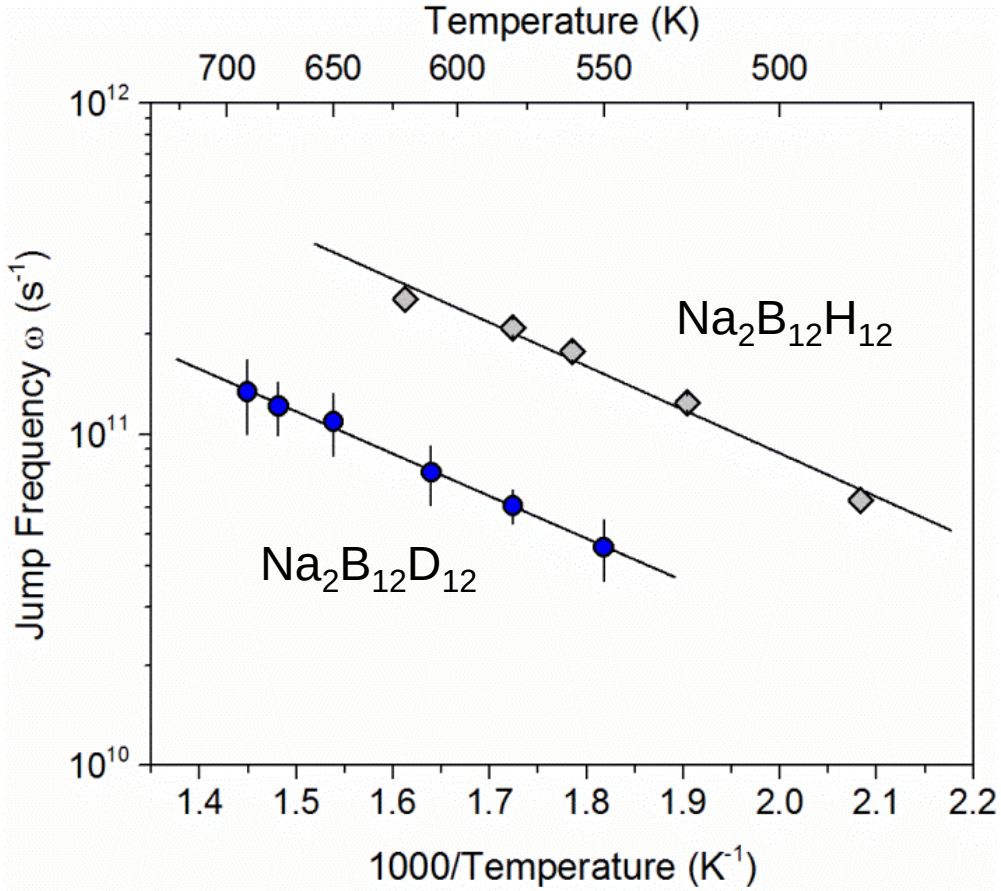




C_4 model C_6 model C_{10} model

Verdal et al., J. Phys. Chem. C **118**, 17483 (2014).

Reorientational Jump Frequencies in $Na_2B_{12}H_{12}$



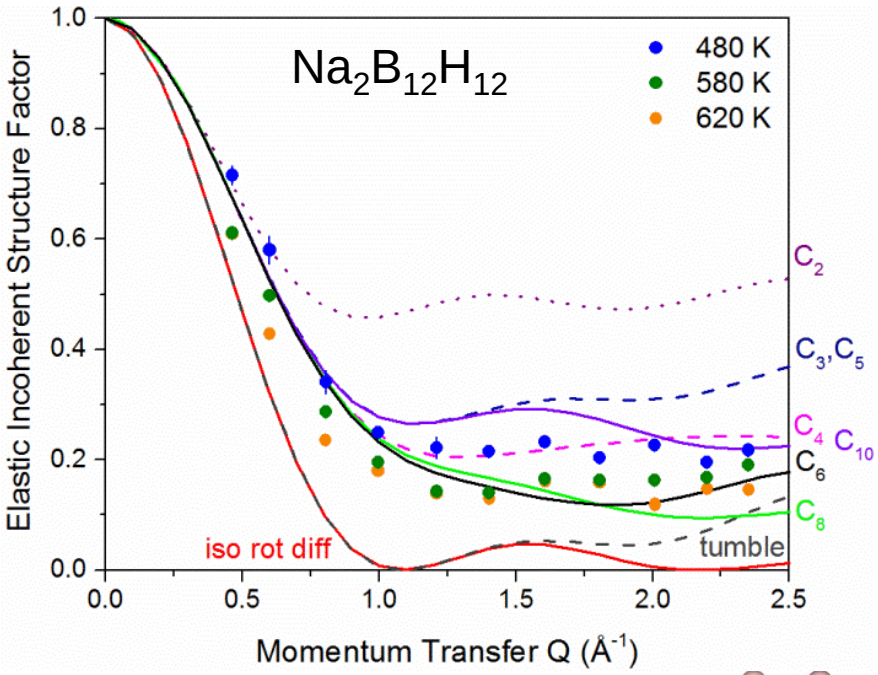
10^{11}-10^{12} anion jumps/s

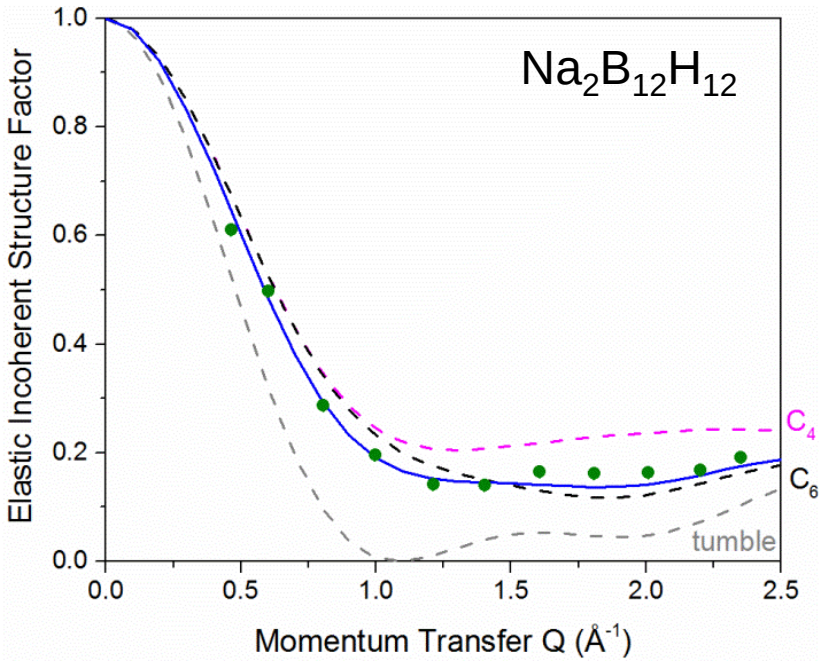
10^{8}-10^{9} cation jumps/s

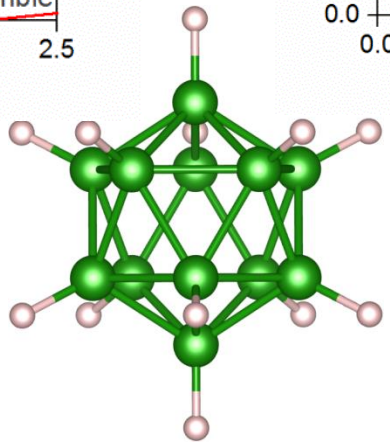
An activation energy of 260(20) meV is in agreement with that from NMR. Jump frequencies for $B_{12}H_{12}^{2-}$ are ~3x higher than those for $B_{12}D_{12}^{2-}$ anions and orders of magnitude higher than Na^+ cation diffusive jump frequencies.

Verdal et al., J. Phys. Chem. C **118**, 17483 (2014).

Rotational Dynamics of $B_{12}H_{12}^{2-}$ Anions







- uniaxial C_4 jumps – 480 K
- uniaxial C_6 jumps – 620 K

model with 50% C_6, 30% C_4, and 20% 3-D tumbling

Despite a variety of possible reorientational mechanisms as a result of the disordered Na^+ sublattice, anion reorientations in $Na_2B_{12}H_{12}$ tend to be predominantly **uniaxial** in nature.

Verdal et al., J. Phys. Chem. C **118**, 17483 (2014).

Journal of Solid State Chemistry 184 (2011) 2635–2639

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Detection of dynamical transitions in hydrogenous materials using transmission measurements with very cold neutrons

Nina Verdal [a,*], Terrence J. Udovic [a], John R.D. Copley [a], John J. Rush [a,b]

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[b] Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742-2115, USA

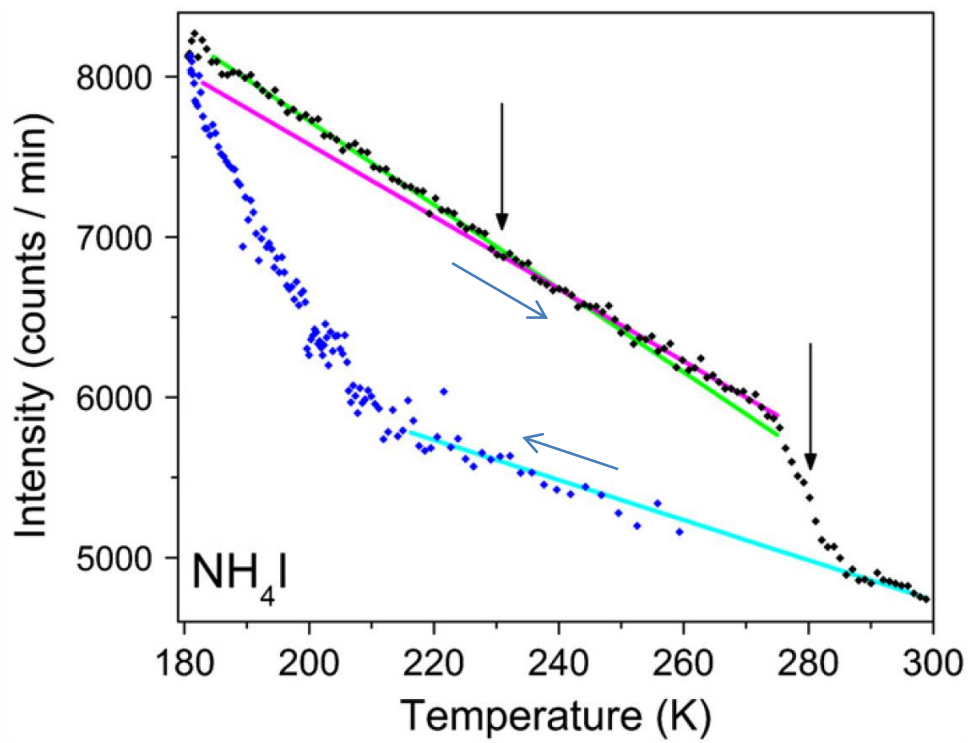
DCS

30 Å neutrons

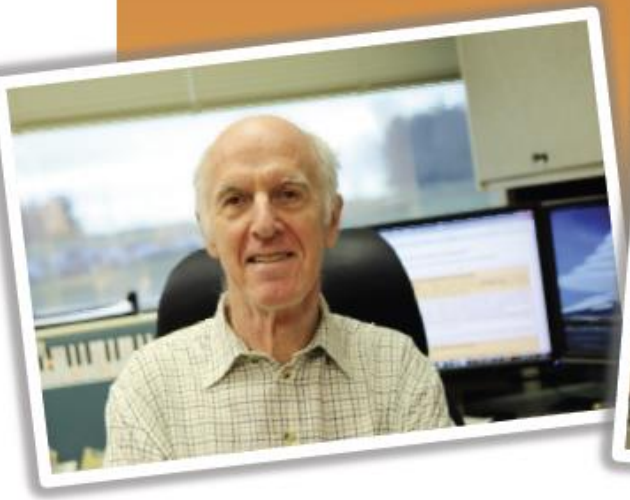
2500 rpm – 23 kcts/min

It was predicted and demonstrated that total cross section measurements with long wavelength neutrons were very sensitive to the total inelastic scattering that results from neutron-energy-gain scattering processes involving large amplitude vibrational or rotational modes in hydrogenous materials.

T.I. Taylor, R.R. Smith, W.W. Havens, Science 120 (**1954**) 789.
J.J. Rush, T.I. Taylor, W.W. Havens, Phys. Rev. Lett. 5 (**1960**) 507–509.
J.J. Rush, T.I. Taylor, W.W. Havens, J. Chem. Phys. 35 (**1961**) 2265–2266.
J.J. Rush, T.I. Taylor, W.W. Havens, J. Chem. Phys. 37 (**1962**) 234–238.
J.J. Rush, T.I. Taylor, J. Phys. Chem. 68 (**1964**) 2534–2537.
J.J. Rush, J. Chem. Phys. 47 (**1967**) 3936–3943.
P.S. Leung, J.J. Rush, T.I. Taylor, J. Chem. Phys. 57 (**1972**) 175–182.



40 years of Neutron Scattering

A Symposium Honoring

John Copley, William Kamitakahara and David Mildner