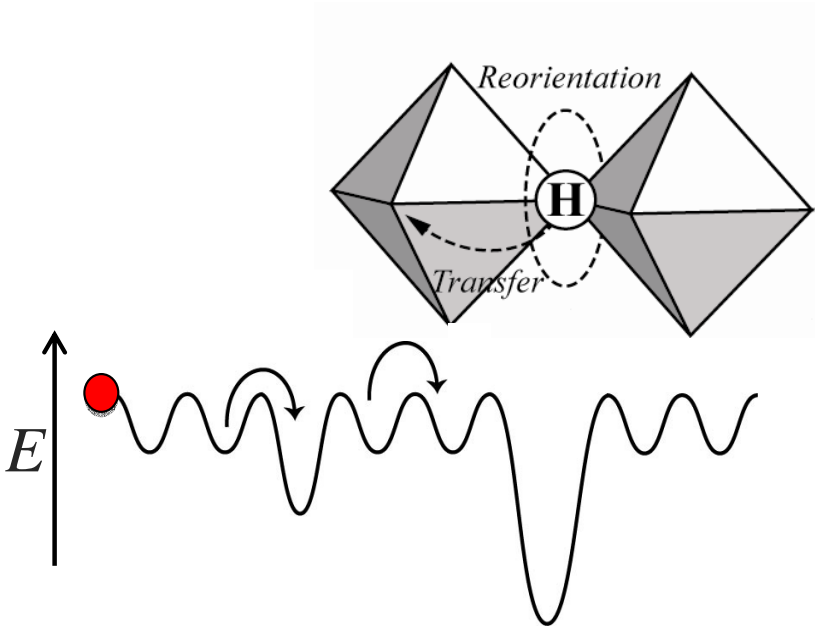
Proton dynamics in barium zirconates investigated with quasieiastic neutron scattering



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Next-generation neutrons and x-rays to appear in Sweden

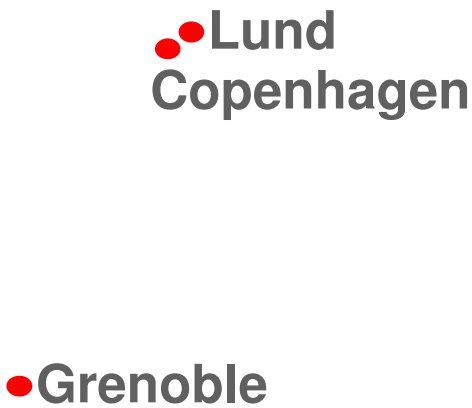
Lund city (village?) in south of Sweden, 2020

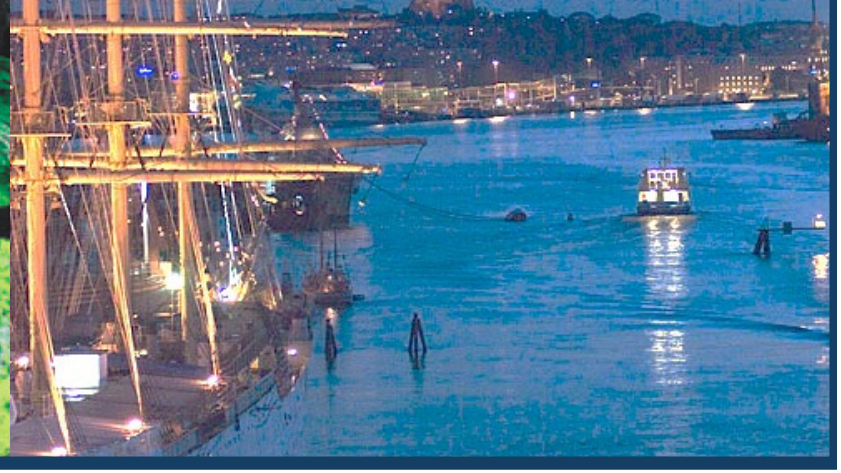
The European Spallation Source (ESS)

•Next-generation neutron facility, in operation around 2020.

The MAX IV synchrotron radiation facility

- Next-generation synchrotron source (MAX IV) close by, in operation by 2015.





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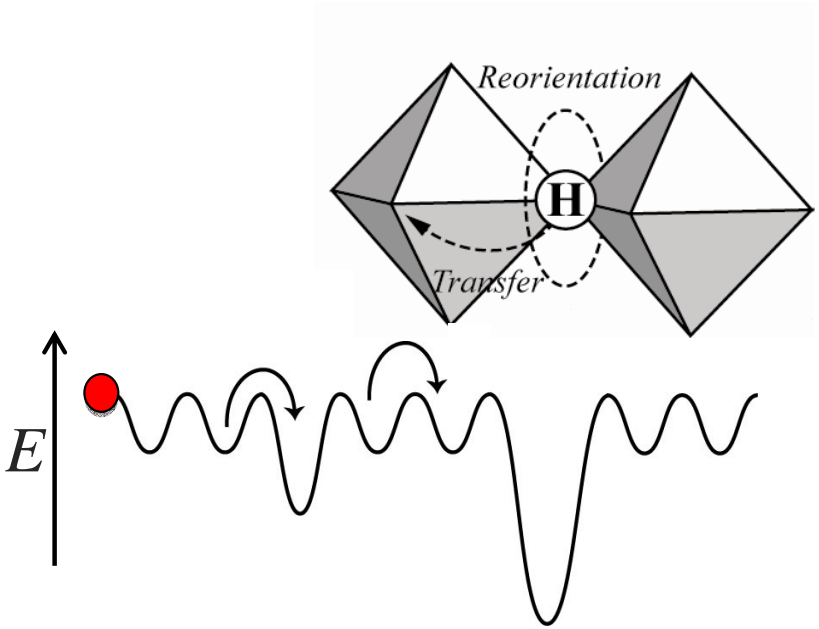

Proton dynamics

1. Vibrational motions, O-H stretches and wags, (fs)
2. Local diffusional motions (ps)
3. Long-range translational diffusion (ns)

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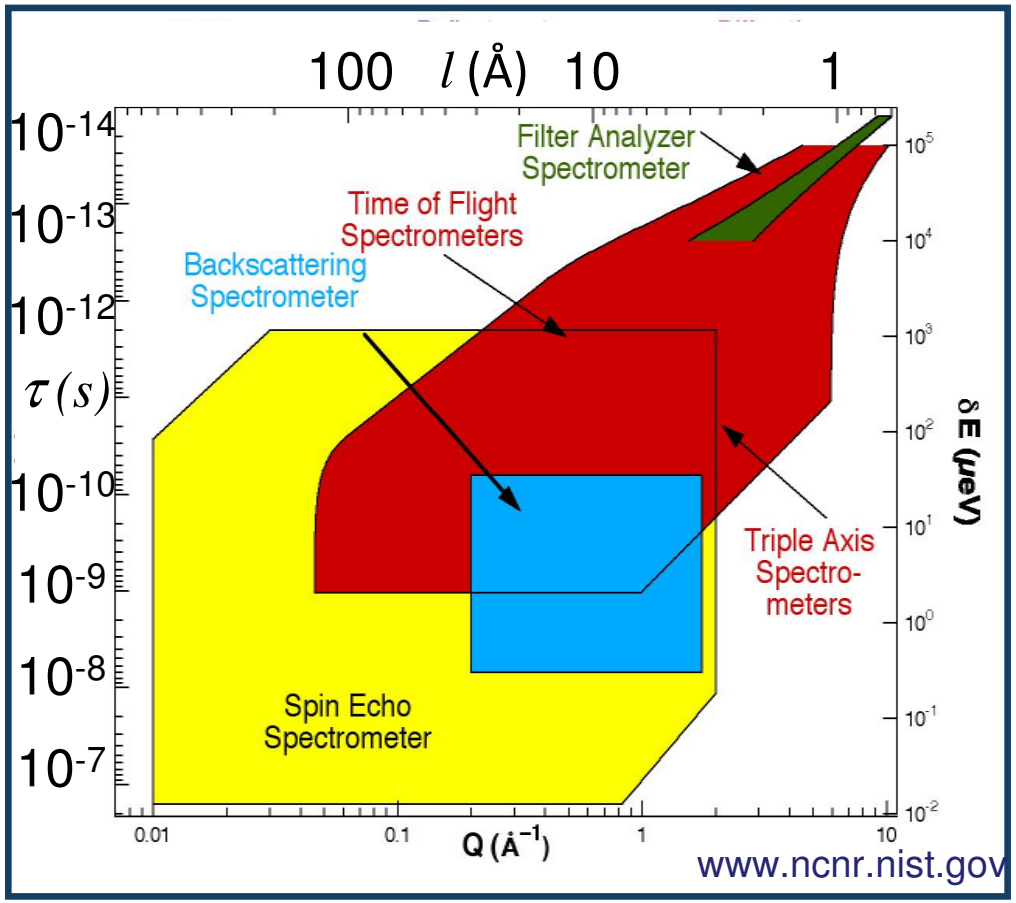
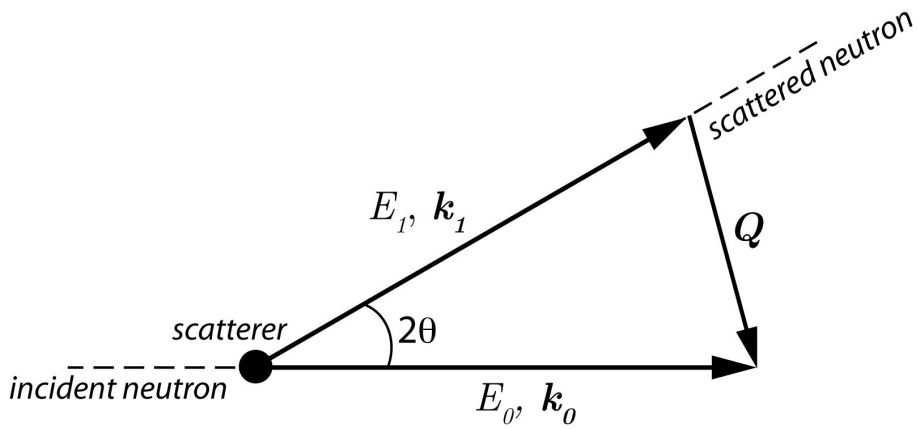
Quasielastic neutron scattering (QENS)

Time-space domain covered by different QENS methods



Quasielastic neutron scattering (QENS)

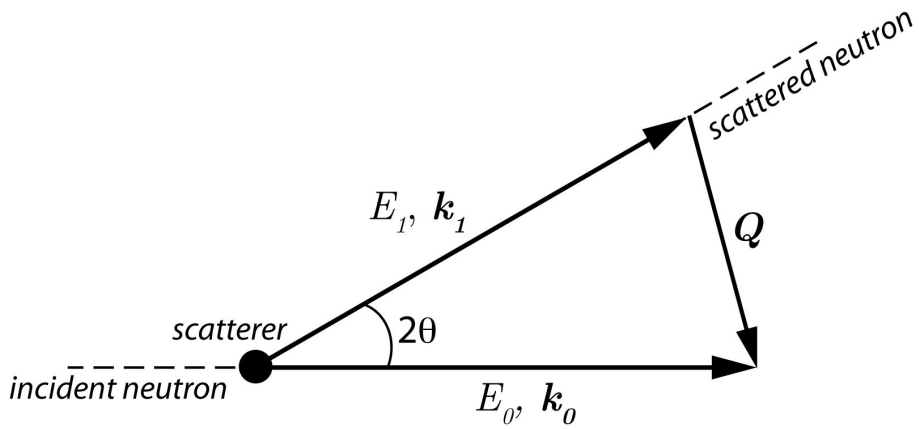
Neutron scattering in the simple picture

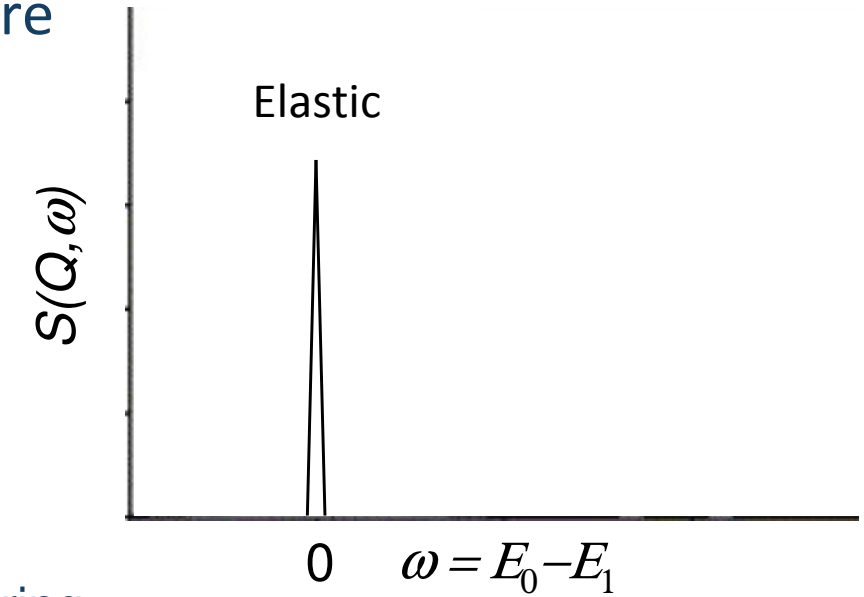


- Scattered intensity as a function of scattering angle (diffraction) gives structural information.
- Energy change gives information about dynamics in the material (in- or quasielastic scattering).

Quasielastic neutron scattering (QENS)

Neutron scattering in the simple picture





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Quasielastic neutron scattering (QENS)

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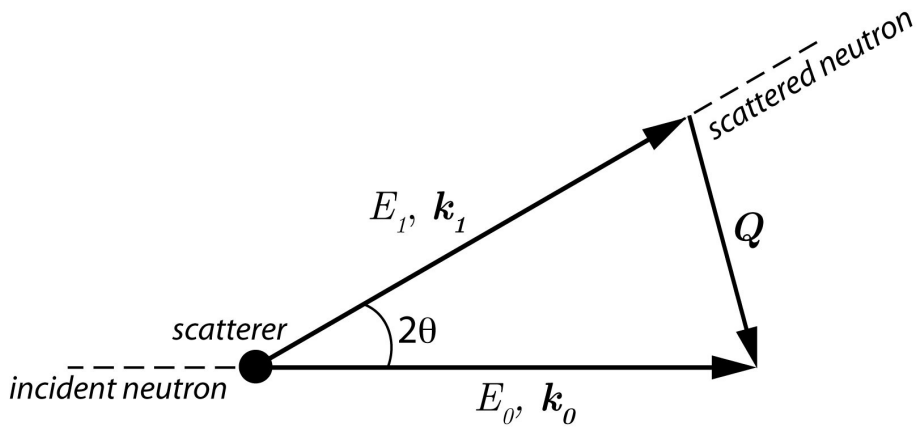
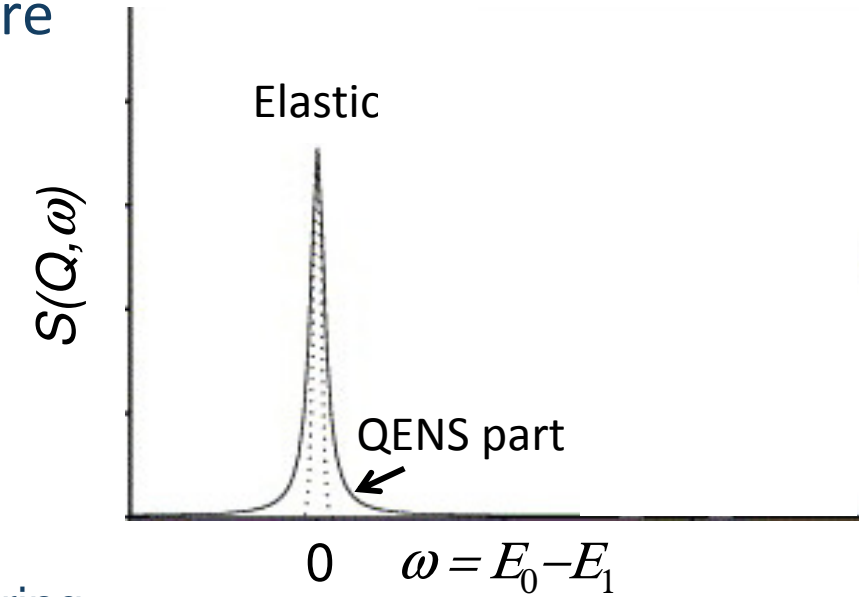


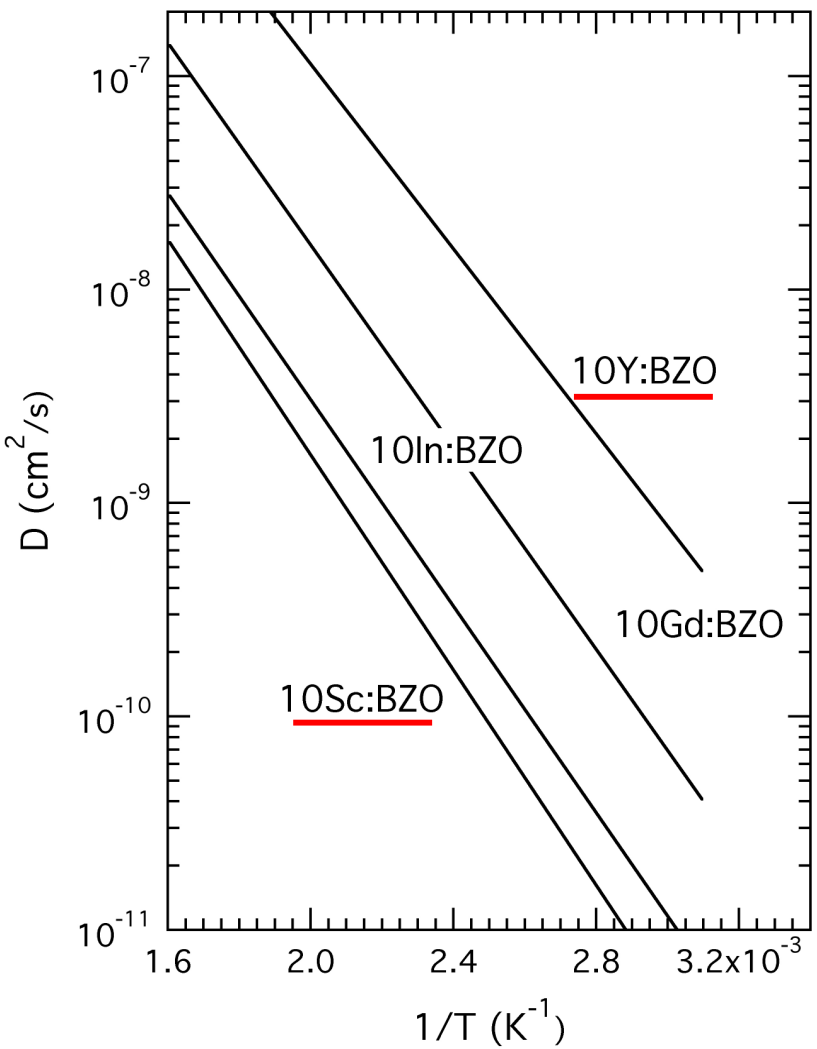


- Scattered intensity as a function of scattering angle (diffraction) gives structural information.
- Energy change gives information about dynamics in the material (in- or quasielastic scattering).

QENS on 10% Y- and Sc-doped $BaZrO_3$

Bulk proton mobility in $BaZr_{0.9}M_{0.1}O_3$ (M = Y, In, Gd, Sc), derived from conductivity exp.

(Replotted from Kreuer *et al.*, SSI 145 (2001) 295)



Fact:

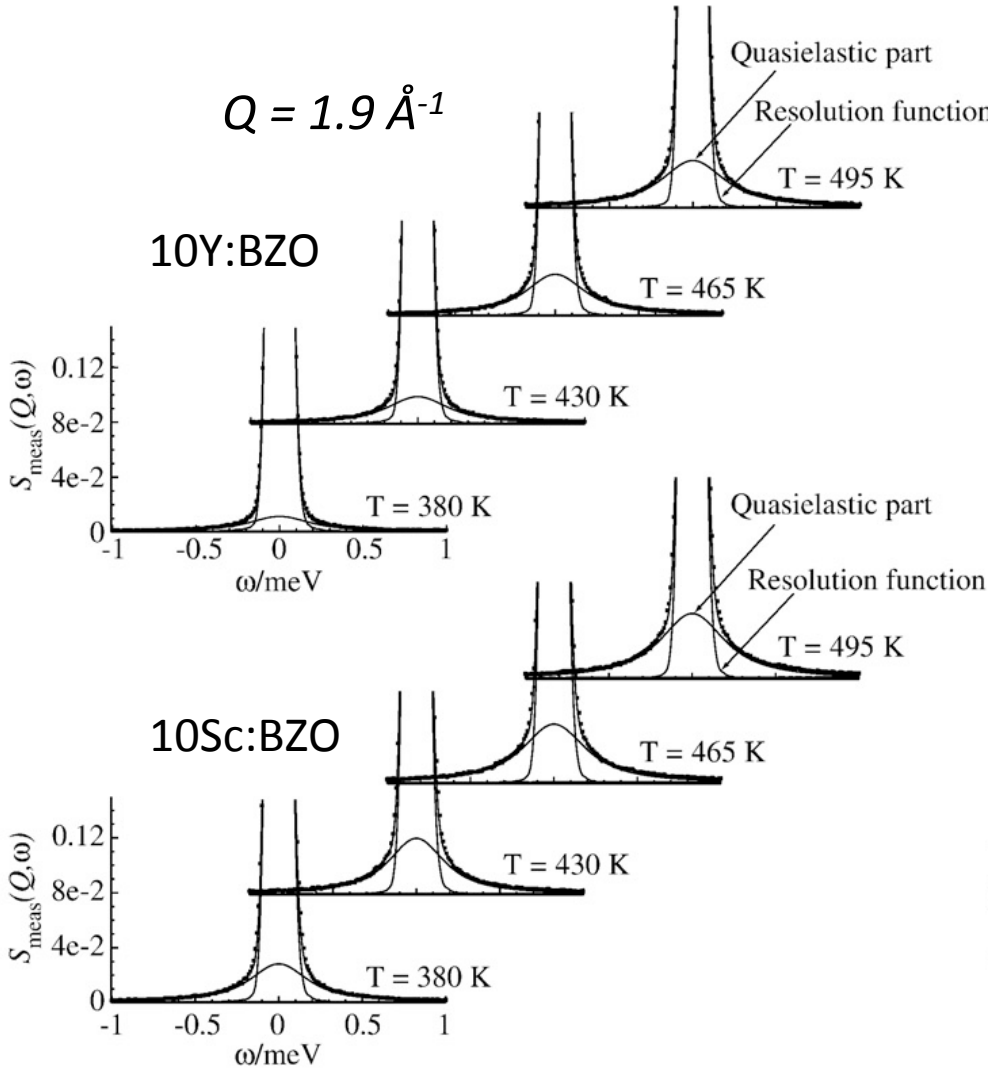
•Strong variation in the proton diffusivity, although the average crystal structure the same (cubic).

Question:

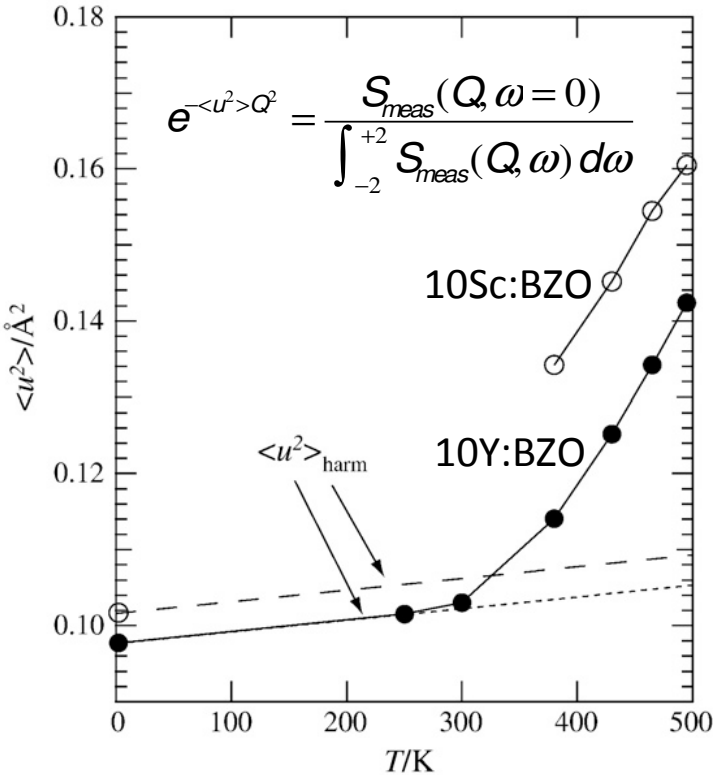
•Is there any difference in the proton dynamics on the short length-scale (1—5 Å), probed by QENS, that can explain the difference in proton mobility on the longer length-scale derived from conductivity experiments.

QENS on 10% Y- and Sc-doped $BaZrO_3$

QENS spectra at different temperatures (data from the IN6 TOF-spectrometer, ILL)



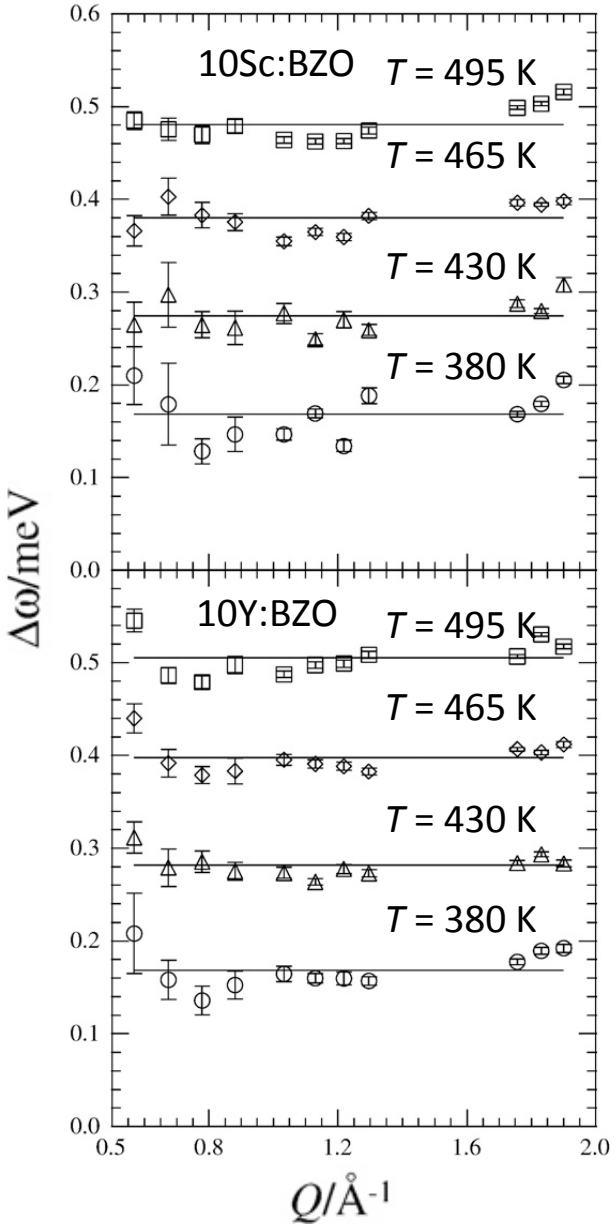
The total mean square displacement $\langle u^2 \rangle$, derived from the $S(Q,\omega)$ spectra

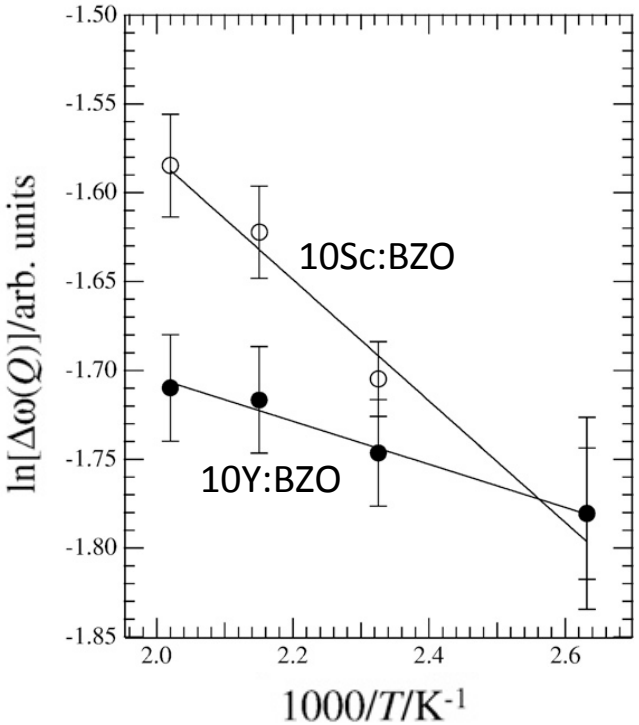


- The T-dependence of $\langle u^2 \rangle$ suggests we pick up dynamics, other than vibrational motions, at $T \approx 300$ K and above.

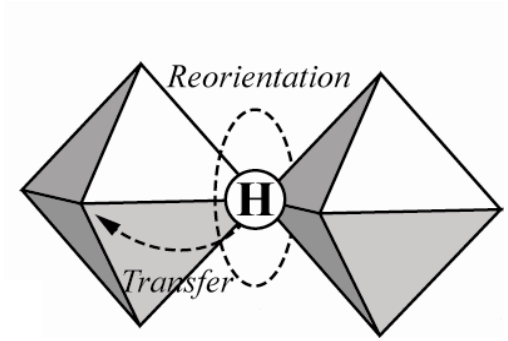
QENS on 10% Y- and Sc-doped $BaZrO_3$

Quasielastic widths *vs. Q (widths at different temperature separated by 0.1 meV)*





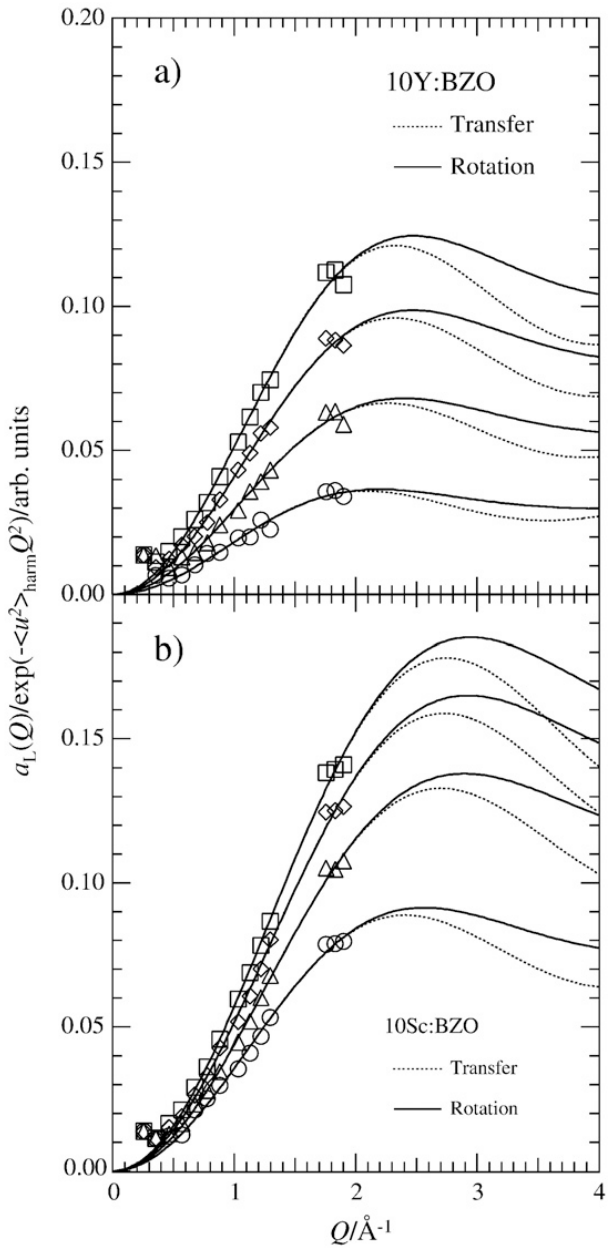
Arrhenius plot of the quasielastic widths



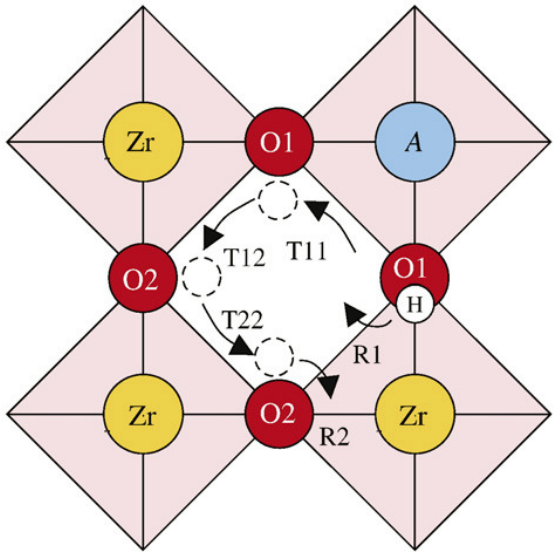
- The proton motion is **local** (since *Q*-independent) and has a characteristic time-scale of **τ ≈ 4 ps** (Y) and **6 ps** (Sc) ($\tau = \hbar/\Delta\omega$).
- *Very* small activation energies:
  E_a = 10 meV (10Y:BZO) and E_a = 30 meV (10Sc:BZO).
- Compare to E_a[Conductivity] ≈ 500 meV.

QENS on 10% Y- and Sc-doped $BaZrO_3$

Fitting to the *Q*-dependence of the quasielastic intensities



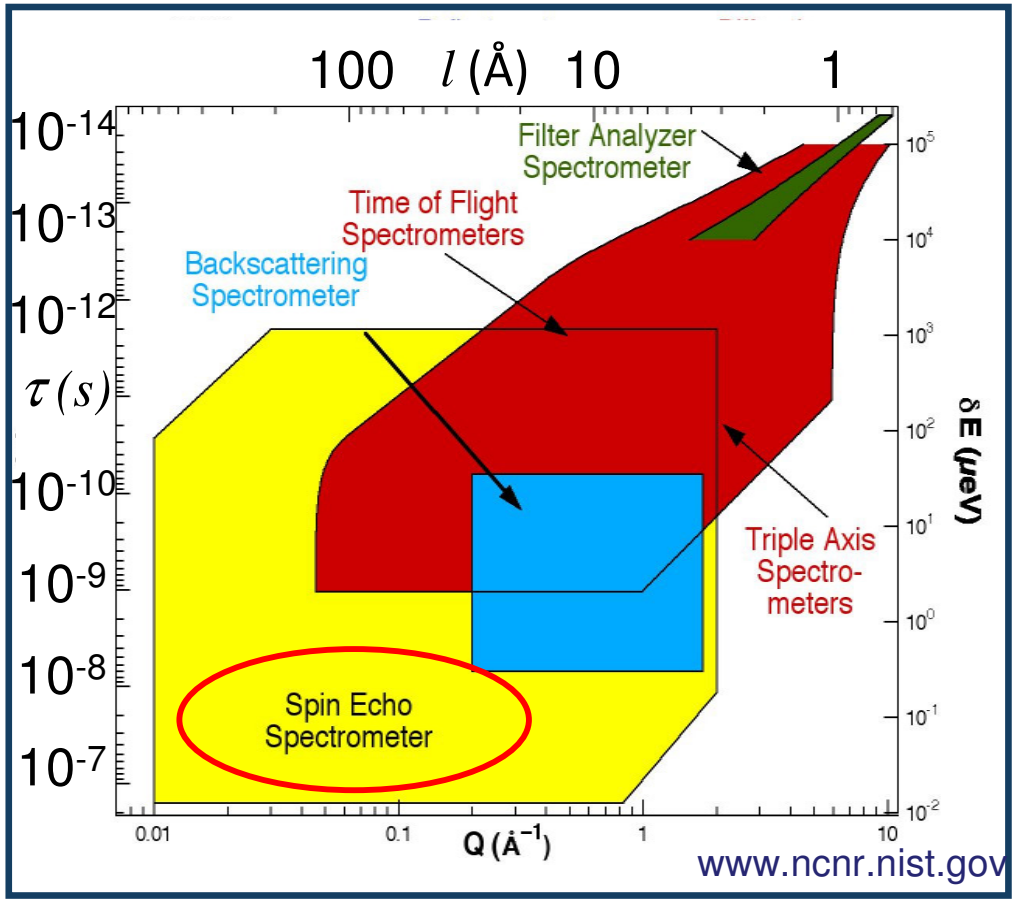
- **Jump diffusion models**
- Over two sites (proton transfer process)
- Over four sites (rotational motion of the –OH group; in a simple picture, there are four proton sites around each oxygen).
- Problem: impossible to discern the two models from each other, from the experimental data alone. Measurements to larger *Q*-values needed.
- **Comparison with jump distances and activation energy obtained from DFT calculations**
- Would suggest proton transfer close to dopant atom (T11), for both materials.



Details found in M. Karlsson, Björketun, Wahnström *et al.*, Solid State Ionics 180 (2009) 22–28

NSE case study on $BaZr_{1-x}In_xO_{3-x/2}$ (x = 0.10 and 0.50)

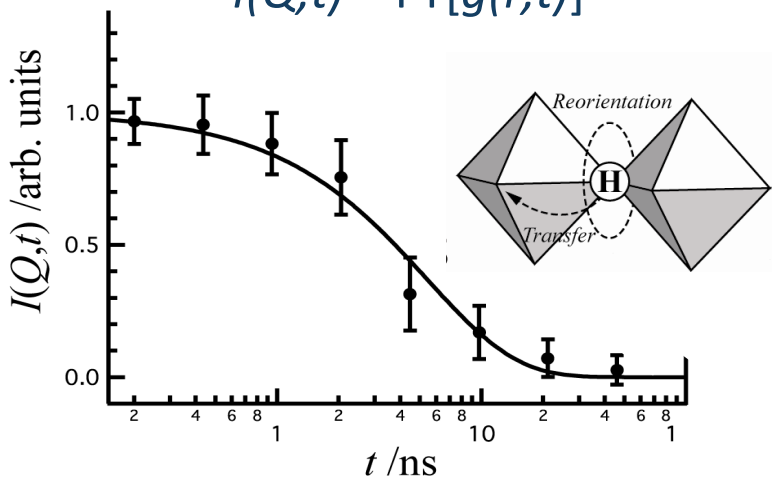
Time-space domain covered by different neutron methods



Neutron spin-echo (NSE) spectroscopy

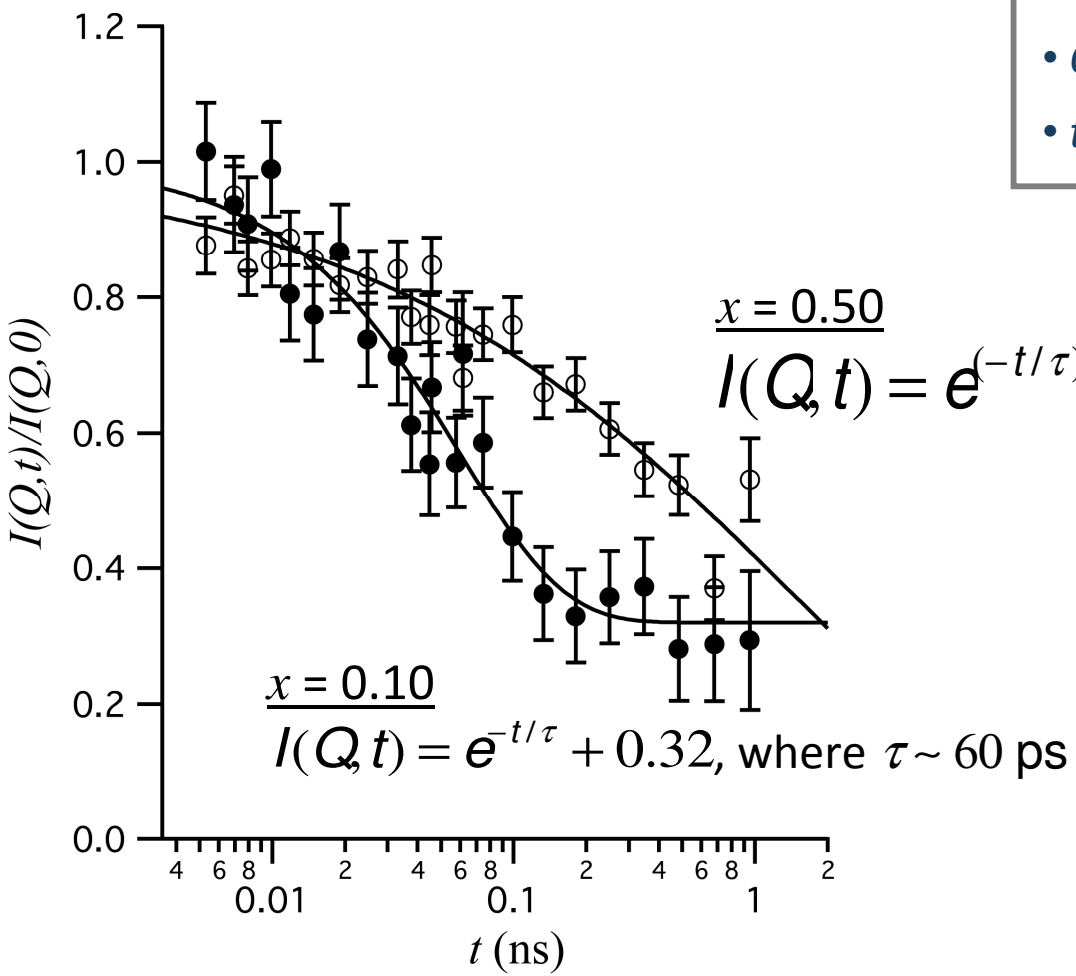
- Large accessible time-range (ps—ns); covers both local and long-range dynamics.
- Intermediate scattering function: *I(Q,t)*

$$I(Q,t) = \mathrm{FT}[g(r,t)]$$



NSE case study on $BaZr_{1-x}In_xO_{3-x/2}$ (x = 0.10 and 0.50)

***I(Q,t)* at *T* = 500 K and *Q* = 1.05 Å^{-1}**



$\beta \sim 0.50$, $<\tau> \sim 1$ ns, E_a = 0.75 eV

Data from the IN11 spectrometer at ILL

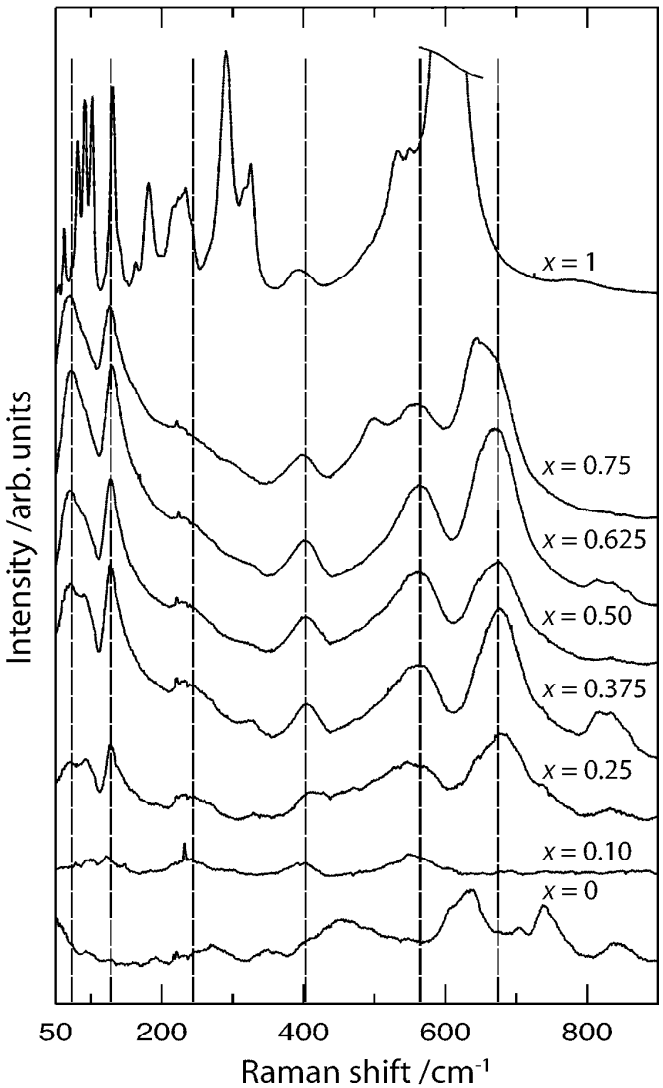
- *T*-range: 470—525 K
- *Q*-range: 0.83—1.26 Å^{-1} (r ~ 5—7.5 Å)
- *t*-range: 5 ps–1.3 ns

- The NSE data suggests local process for x = 0.10, with a well defined time scale.
- For x = 0.50, a wide distribution of diffusional rates is observed. E_a = 0.75 eV (high?).

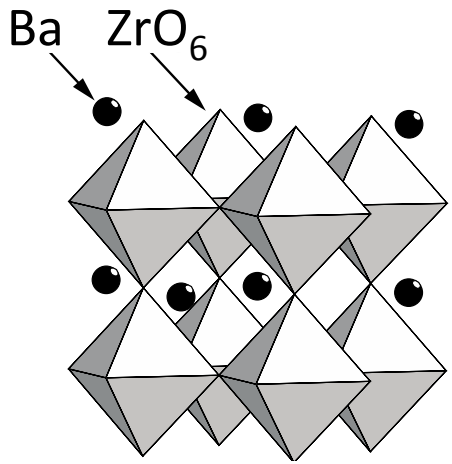
Further data analysis in progress

Raman study on $BaZr_{1-x}In_xO_{3-x/2}$ (x = 0—1)

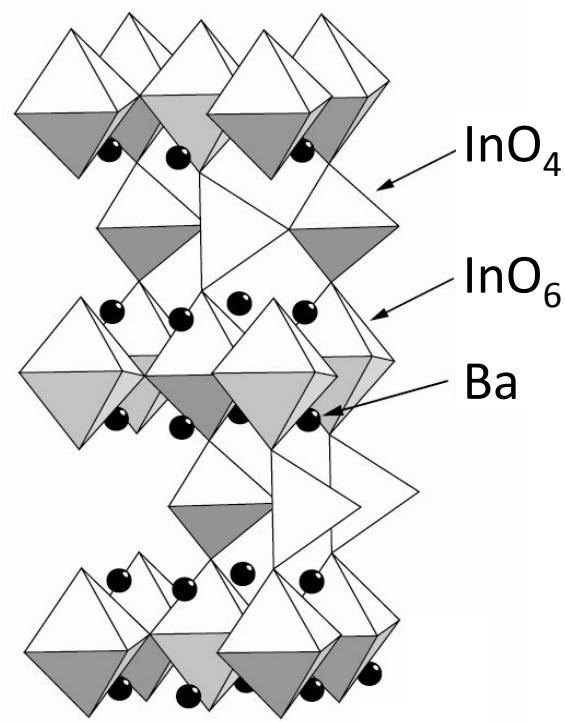
Dopant induced local structural distortions revealed by Raman spectroscopy



- The presence, and growth, of Raman bands suggest the presence of local distortions of the average cubic structure. The Raman spectrum of a "perfectly" cubic perovskite is featureless.
- Structure goes from perovskite-like (x= 0—0.75) to brownmillerite-like (x > 0.75) with increasing x.



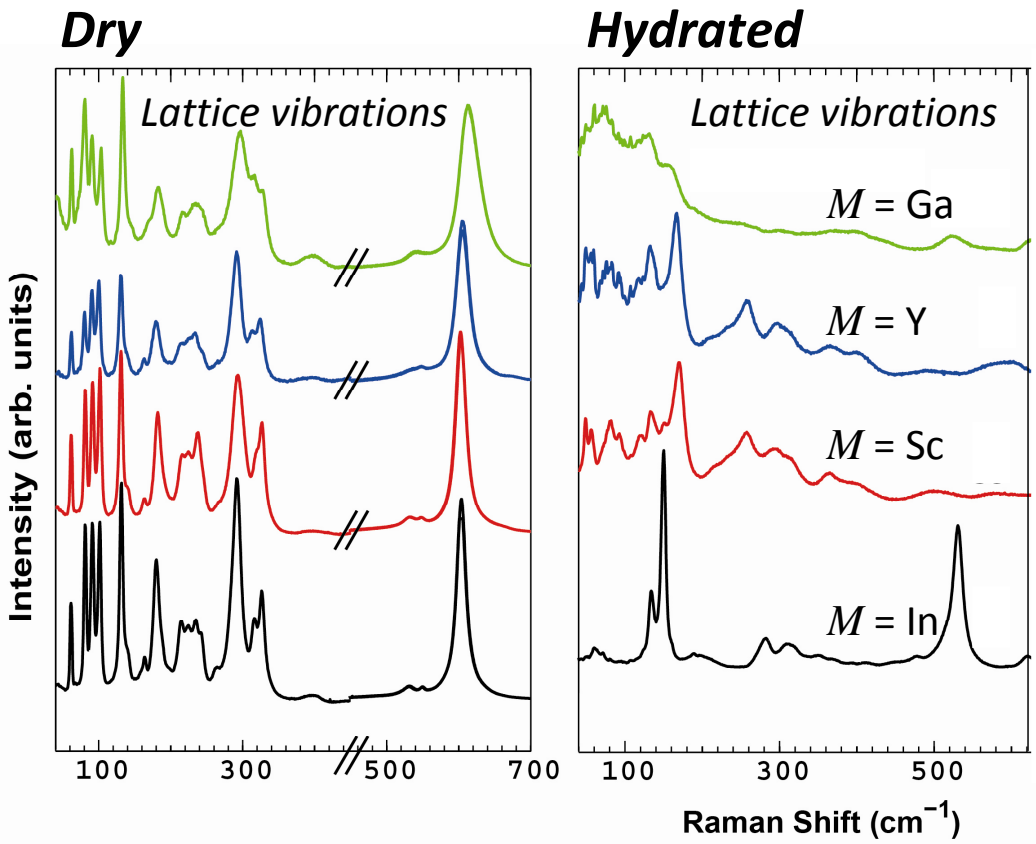
$BaZrO_3$ (x = 0)



$Ba_2In_2O_5$ (x = 1)

Karlsson et al., Chem. Mater. ***20*** *(2008) 3480*

Recent Raman case study on $Ba_2In_{1.85}M_{0.15}O_5$ (M = In, Sc, Y and Ga)



- **Dehydrated samples:** Raman spectra essentially the same. Small structural differences.
- **Hydrated samples:** Raman spectra dissimilar. Larger structural differences.

  ”Proton configurations”: more well defined for un- and Ga-doped materials, than for Sc- and Y-doped.

For more about this, see Poster #13 (Thursday), Bielecki *et al.*

Acknowledgements

Collaborations:

-Group of Göran Wahnström (Dept. Applied Physics, Chalmers) – (Theoretical modeling)
-Group of Sten Eriksson (Chemistry Dept., Chalmers) – (Synthesis, hydration, TGA, diffraction *etc.*)
-Marek Koza, Peter Fouquet, Marco Maccarini (ILL, France) – (QENS)
-Johan Bielecki (Dept. Applied Physics, Chalmers) – (Raman spectroscopy)

Experiments:

-**ILL (France)** [QENS]
-**Chalmers, Dept. Applied Physics** [Raman spectroscopy]

Funding:

-Swedish Research Council (VR), 2011-
-VR and the European Spallation Source (ESS), 2008-2010
-Swedish Graduate School in Materials Science (NFSM), 2003-2007

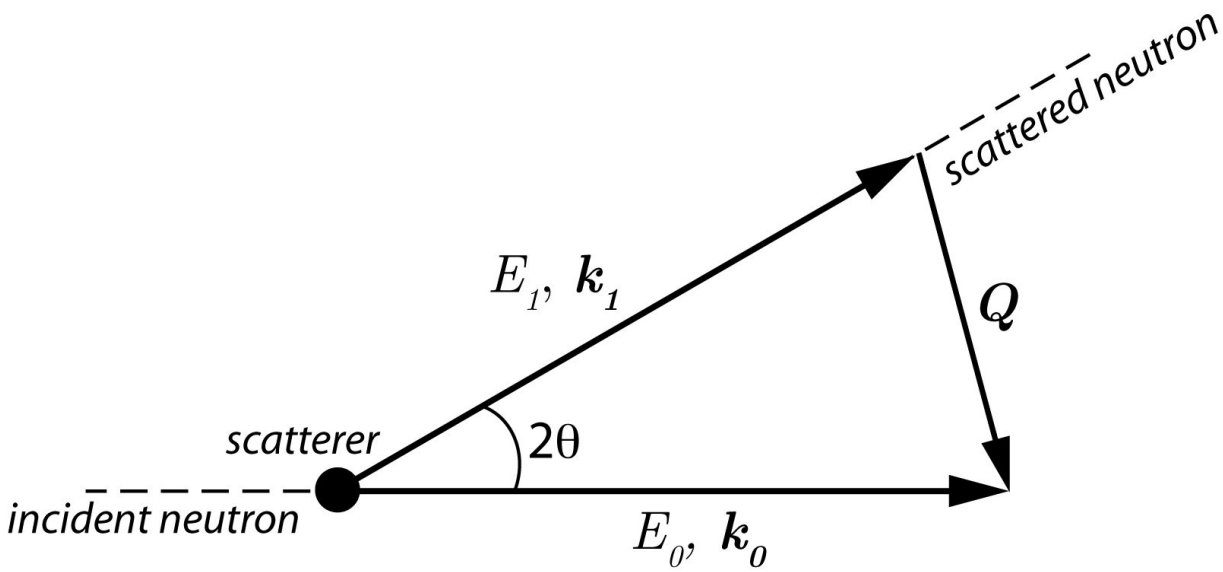
References:

-M. Karlsson *et al*, Solid State Ionics 180 (2009) 22–28 (QENS)
-M. Karlsson *et al.*, J. Phys. Chem. C 114 (2010) 3292 (QENS:Spin-echo)
-M. Karlsson, “Perspectives of neutron scattering on proton conducting oxides” (To appear in Dalton Trans.)

Thank you for your attention!

Neutron scattering

Scattering geometry



$$k = \frac{2\pi}{\lambda}$$

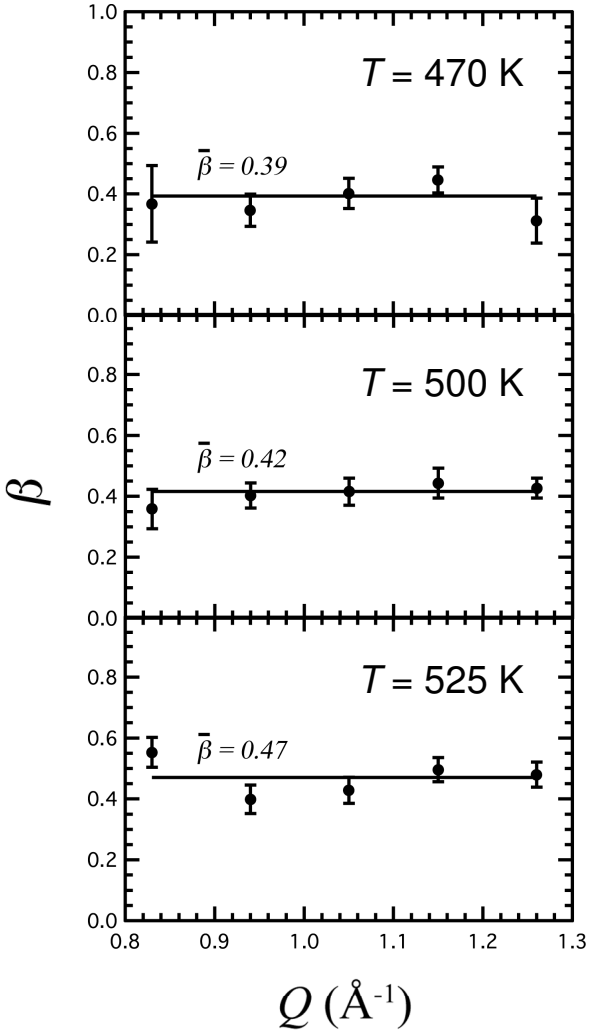
$$Q = k_0 - k_1$$

$$E = \frac{(\hbar k)^2}{2m_n}$$

$$\Delta E = \hbar\omega = E_0 - E_1$$

Neutron spin-echo results: In-doped $BaZrO_3$ (x = 0.50)

Stretching parameter

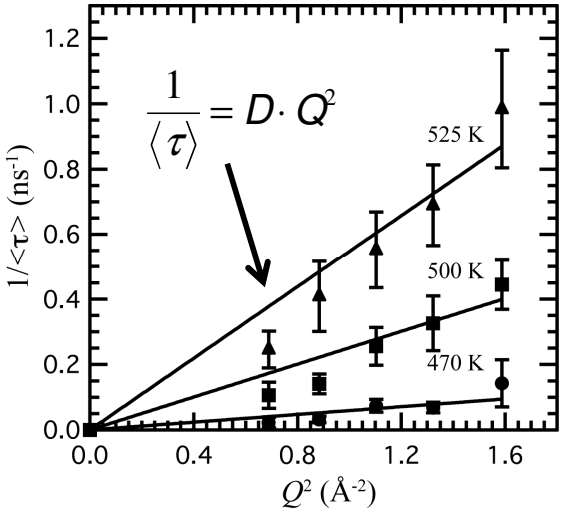


$$I(Q,t) = e^{(-t/\tau)^{\beta}}$$

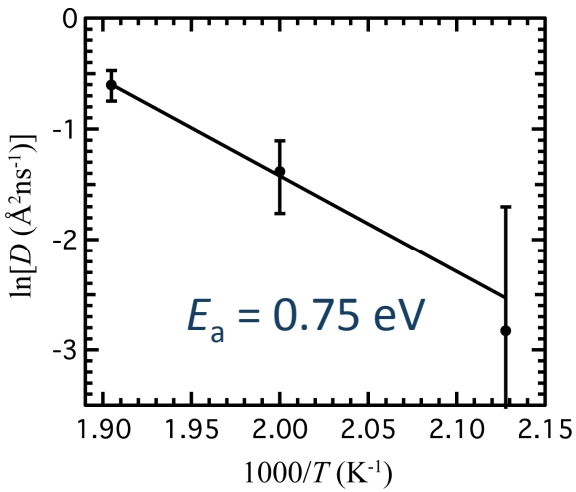
$$\langle \tau(Q) \rangle = \frac{\tau(Q)}{\bar{\beta}} \Gamma\left[1/\bar{\beta}(Q)\right]$$

$$\frac{1}{\langle \tau \rangle} = D \cdot Q^2$$

Average relaxation rate



Effective diffusion coefficient



Karlsson et al., J. Phys. Chem. C ***114*** *(2010) 3292*