Proton dynamics in proton conducting perovskites investigated by neutron scattering

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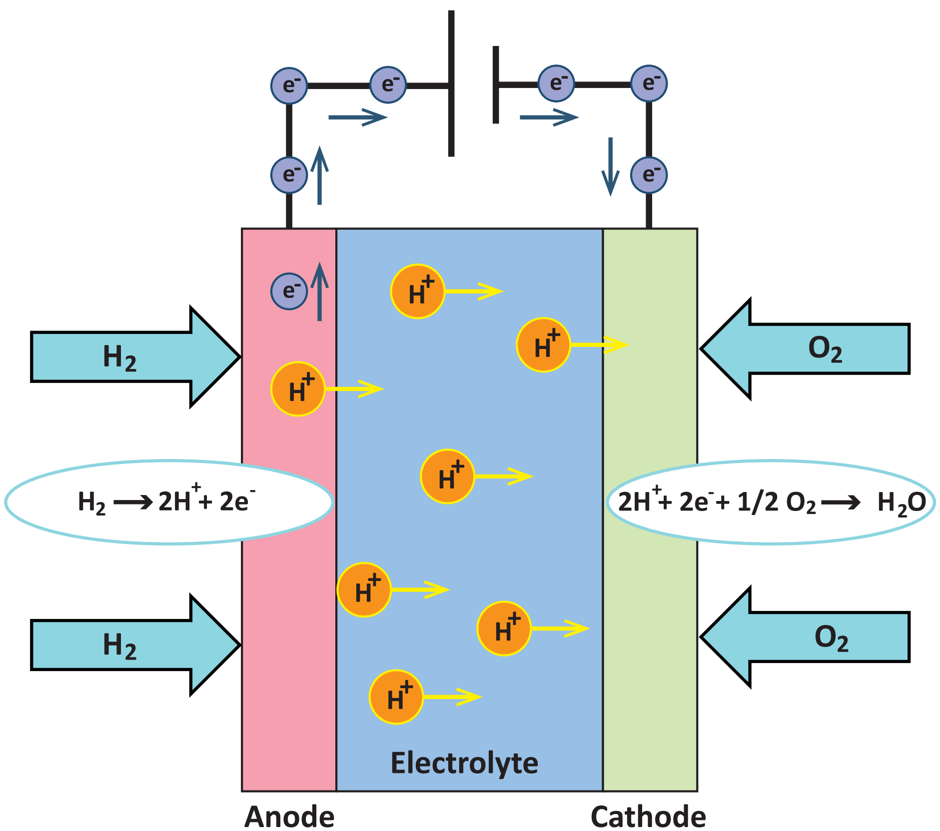
Solide Oxide Fuel Cells

Solide Oxide Fuel Cells → "clean energy"



Solid electrolyte:

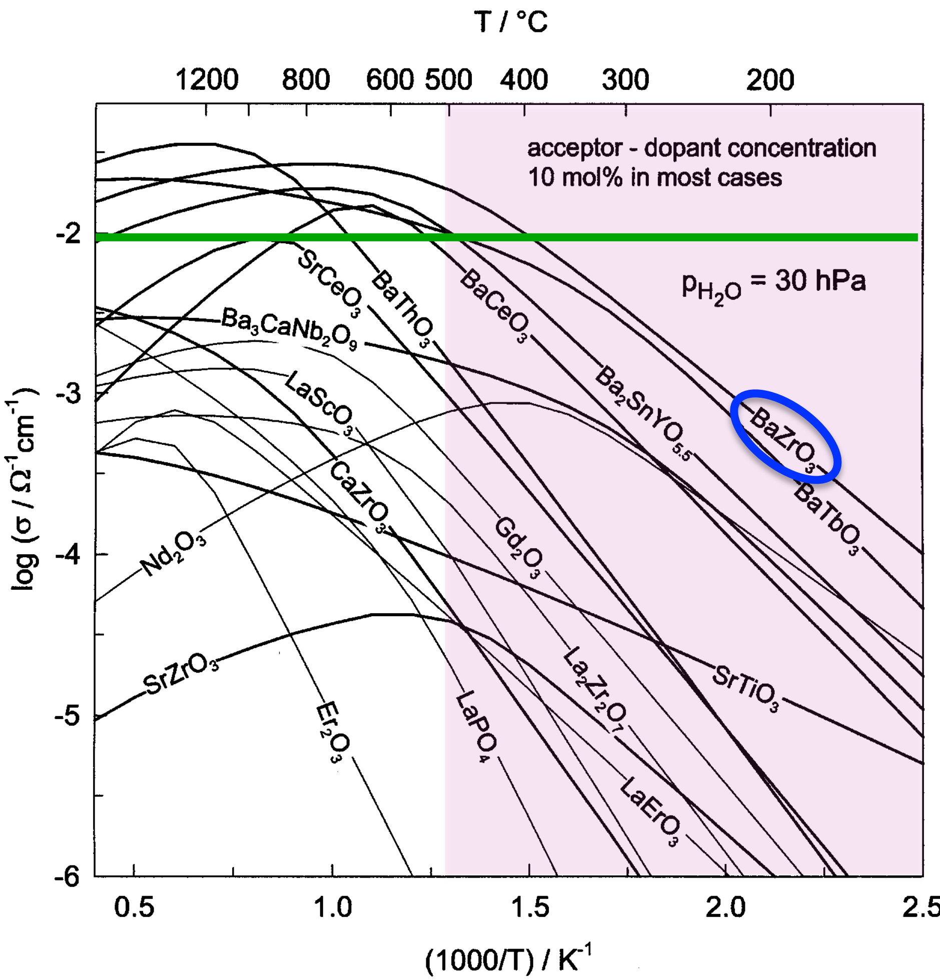
☺ great flexibility in cell design and usable fuels

Lowering the temperature of operation (T < 750 °C):

☺ more rapid start-up and shut-down
☺ less corrosion of the metallic components
☺ improve durability...

Intermediate T-range SOFCs materials

The "electrolyte gap"



(modified from Kreuer, Solid State Ionics, 145, 2001)

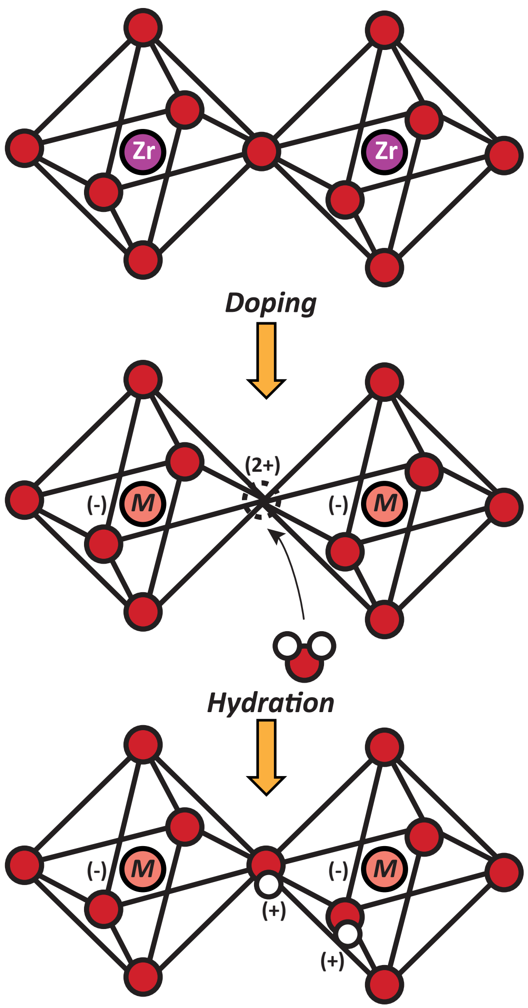
Targeted conductivities:
> 10^{-2} S cm^{-1} !

Deep **knowledge** of these materials

Tailoring **new materials** for **technological applications**

Acceptor-doped Barium Zirconates

How are the protons incorporated?



M^{3+} in B^{4+} sites

↓

oxygen vacancies

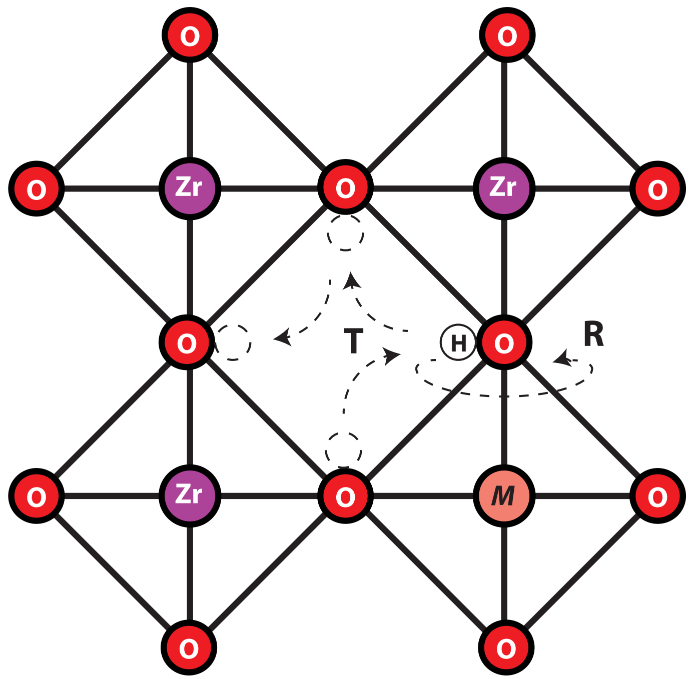
humid conditions and elevated temperatures

↓

dissociations of water molecules

hydroxides	protons
↓	↓
fill the oxygen vacancies	bond lattice oxygens

Proton conduction mechanism



Free proton migration:

- transfer between two adjacent oxygens
- reorientation of the -OH

proton diffusion

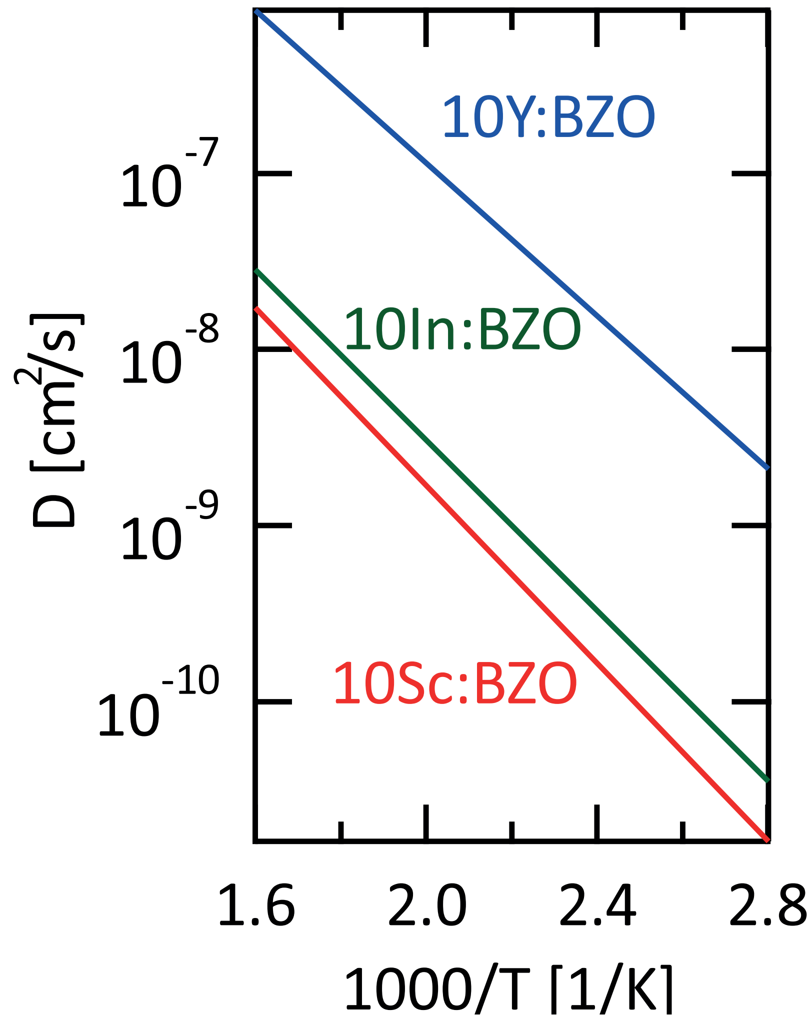
What is the effect of the dopant atom?
What are the characteristics of the motion?
Which is the rate-limiting step for proton diffusion?

Effect of the dopant atoms

$BaZr_{0.9}M_{0.1}O_3H_{0.1}$ (M= Y, In, Sc)

cubic structure

very different proton conductivities!



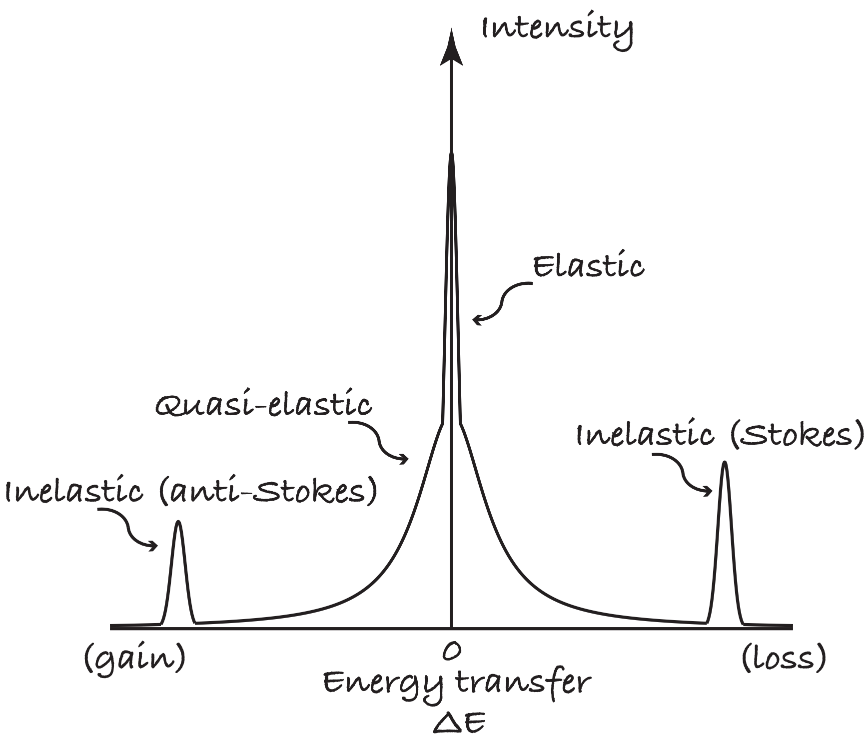
(redrawn from Kreuer, Solid State Ionics, 145, 2001)

Why neutrons?

	coherent [barn]	incoherent [barn]
H	1.7568	**80.26**
O	4.232	0.0008
Sc	19	4.5
Y	7.55	0.15
Zr	6.44	0.02
In	2.08	0.54
Ba	3.23	0.15

$$\left(\frac{d^2\sigma}{d\Omega dE_{\mathrm{f}}}\right)_{\mathrm{inc}} \propto \sum_{j}^{N} \int \left\langle e^{-i\mathbf{Q}\cdot\mathbf{r}_j(0)} e^{i\mathbf{Q}\cdot\mathbf{r}_j(t)} \right\rangle e^{-i\omega t}\mathrm{dt}$$

(R. Pynn, 1990)

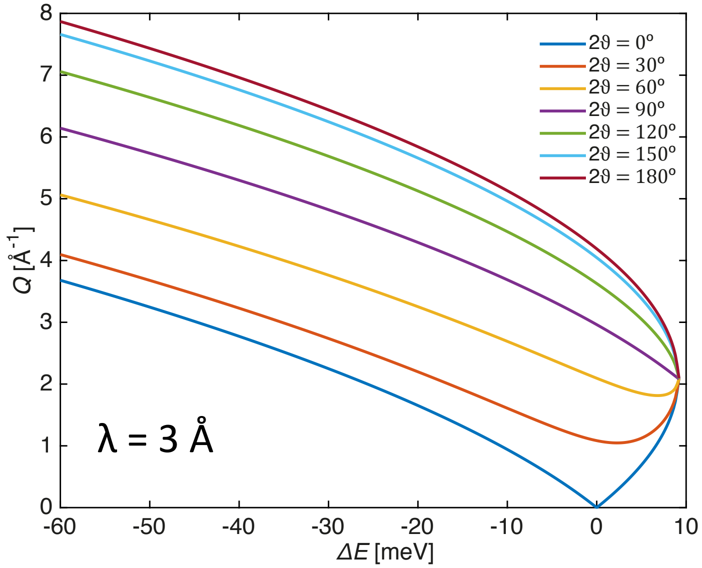


- **width → characteristic time scale**
- **if localized/confined motion → EISF → geometry**

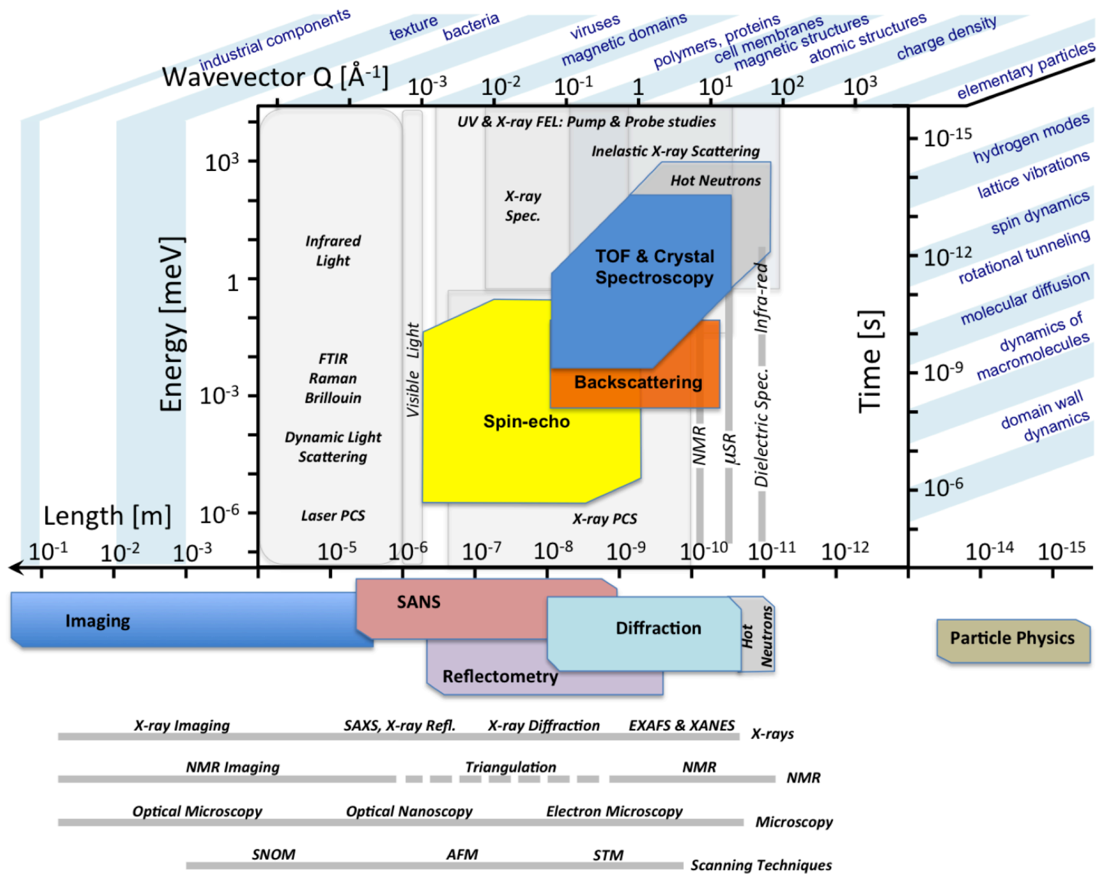
All we need is neutrons!

What is the effect of the dopant atom?
What are the characteristics of the localized steps and the "long-range" diffusion?
Which is the rate-limiting step for proton diffusion?

All we need is neutrons...?



(ESS Technical Design Report. 2013, courtesy of Arno Hiess)



We need several instruments and setups to combine different dynamical ranges and resolution limits to map an extensive (Q-E) space

<u>All</u> we need is neutrons…?

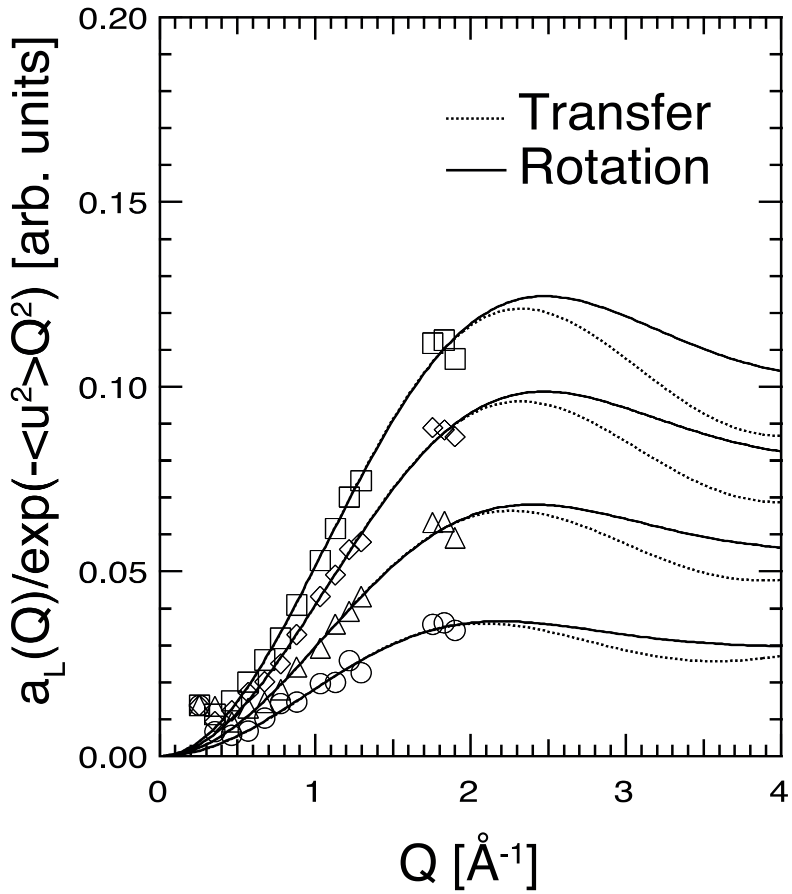
What is the effect of the dopant atom?
What are the characteristics of the localized steps and the “long-range” diffusion?
Which is the rate-limiting step for proton diffusion?

Things we need:

- *neutrons* ✓
- *instruments to map a wide dynamical range* ✓
- *tight sample cell* ✓
  (thanks Richard!)

Mechanism of the local dynamics

IN6 (2006)



M. Karlsson et al., Solid State Ionics, 180, (2009).

jump over N equivalent sites located on a circle with radius r

Transfer → N = 2

Rotation → N = 4

$$S_{inc}(Q,\omega) = A_0(Q)\delta(\omega) + \sum_{l=1}^{N-1} A_l(Q)\frac{1}{\pi}\frac{\hbar\tau_l^{-1}}{1+\omega^2\tau_l^2}$$

$$A_l(Q) = \frac{1}{N}\sum_{n=1}^{N} j_0\left(Q2r\sin\left(\frac{n\pi}{N}\right)\right)\cos\left(\frac{2ln\pi}{N}\right)$$

$$\sum_{l=0}^{N} A_l(Q) = 1$$

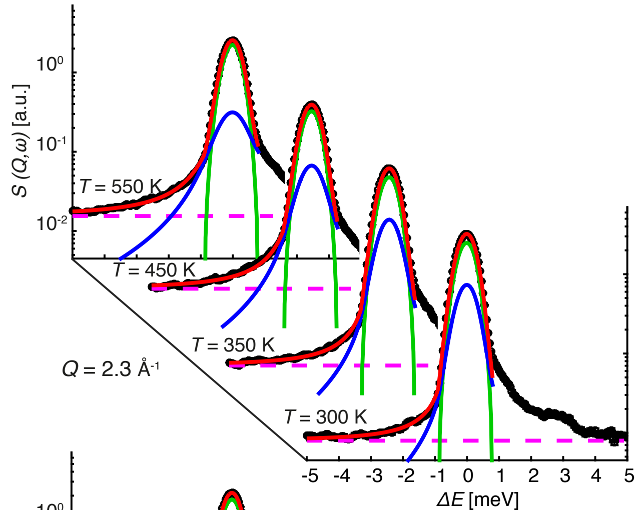
$$\tau_l^{-1} = 2\tau^{-1}sin^2\left(\frac{\pi l}{N}\right)$$

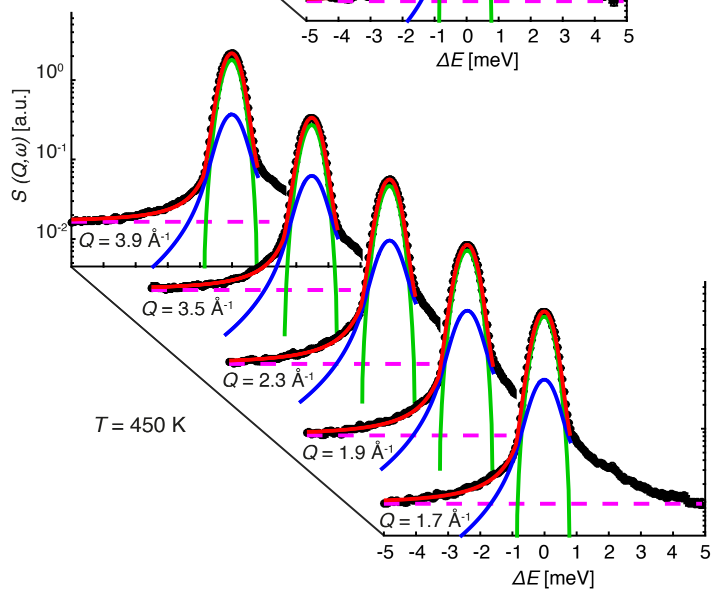
IN5 :

- Incident λ = 2.5 Å, extend Q-range up to 4.7 $Å^{-1}$

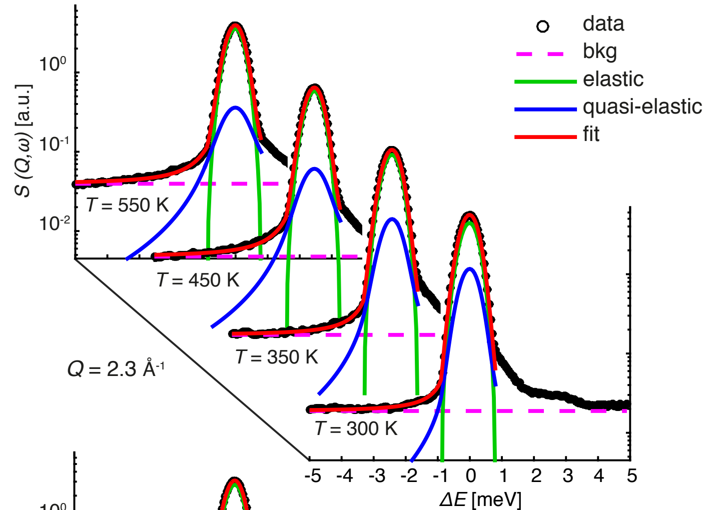
IN5 λ=2.5 Å

10Sc:BZO

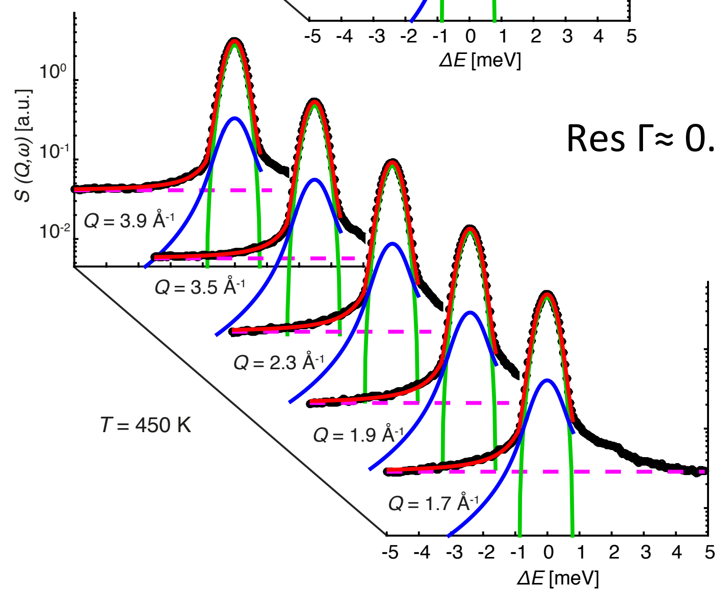




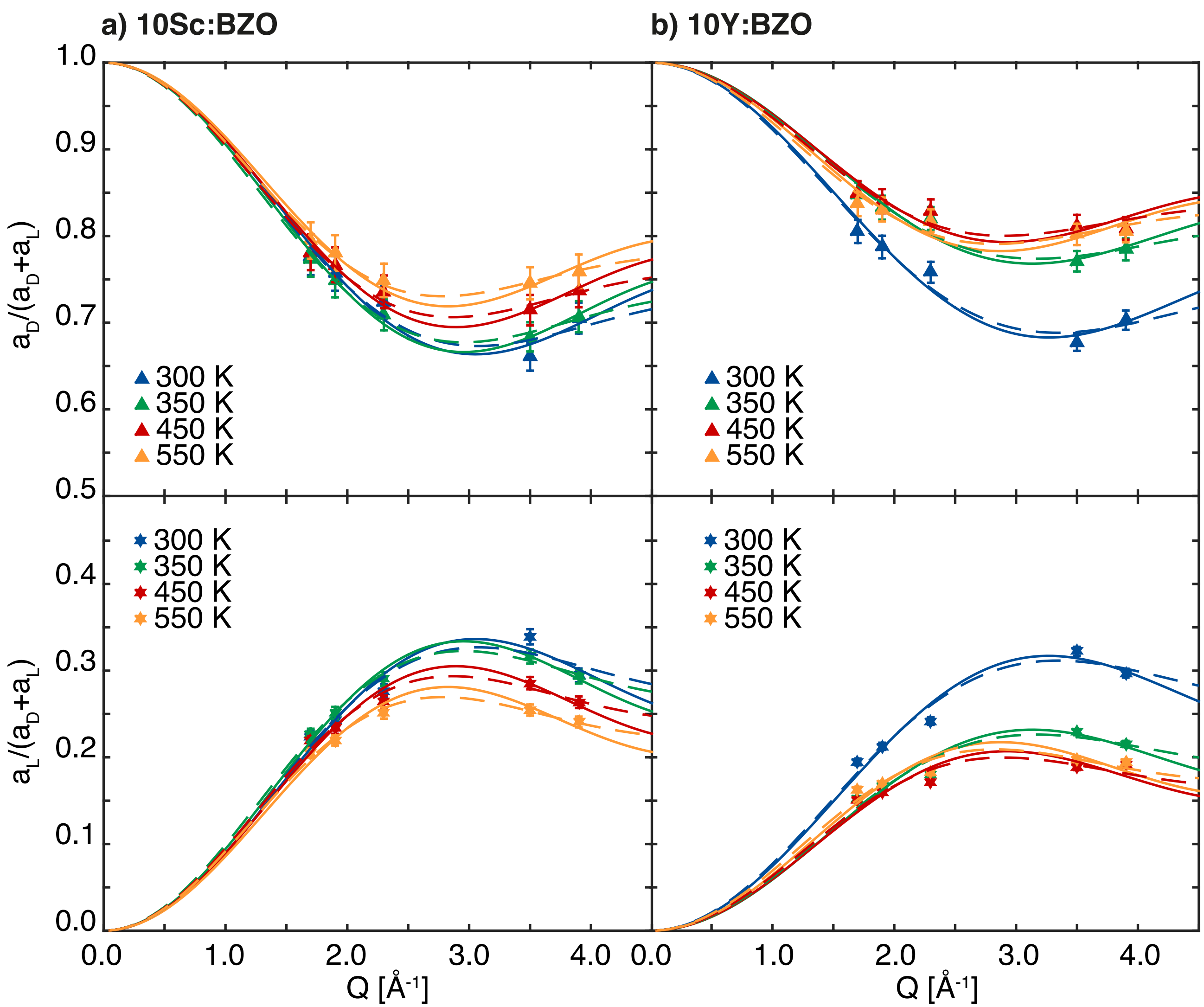
10Y:BZO



Res Γ≈ 0.62 meV



IN5 λ=2.5 Å

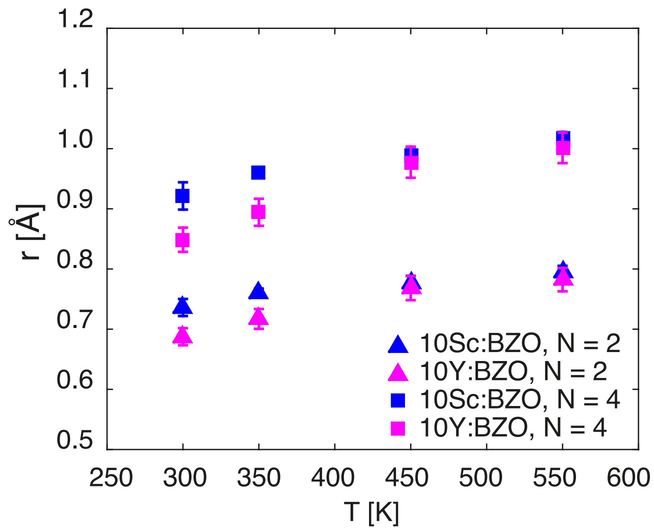


2 sites

4 sites

An additional component to take into account immobile species had to be added to the elastic part

IN5 λ=2.5 Å



transfer → hopping distance
≈ 1.4 – 1.6 Å

rotation → O-H ≈ 0.8-1.0 Å

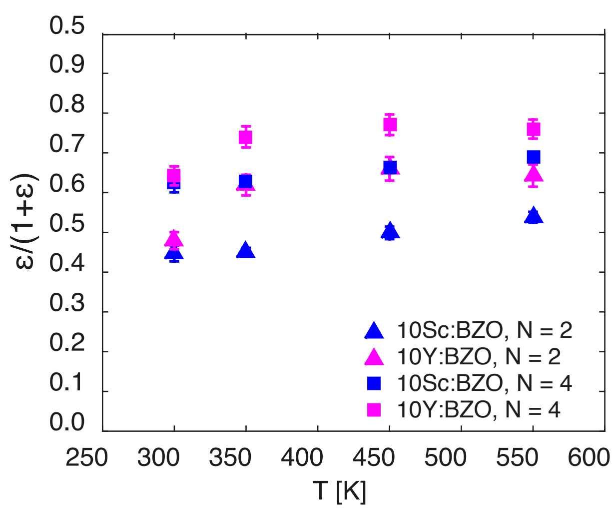
O-O ≈ 2.97 *Å*

Giannici et al. SSI 181 (2010) 122-124

O-H → 0.9 – 1.0 Å

Karlsson et al. PRB 77 (2008) 104302

Zeudmi et al. SSI 253 (2013) 195-200



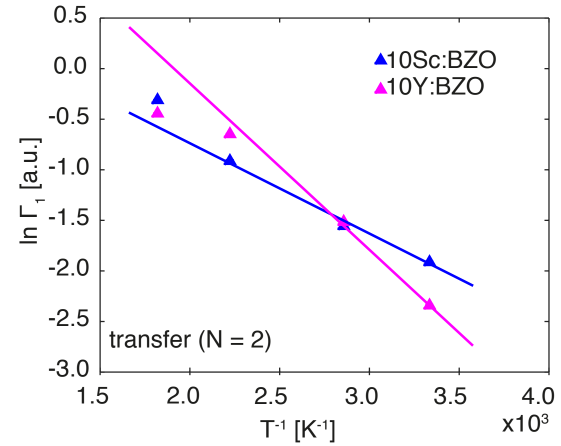
considerable fraction of immobile species

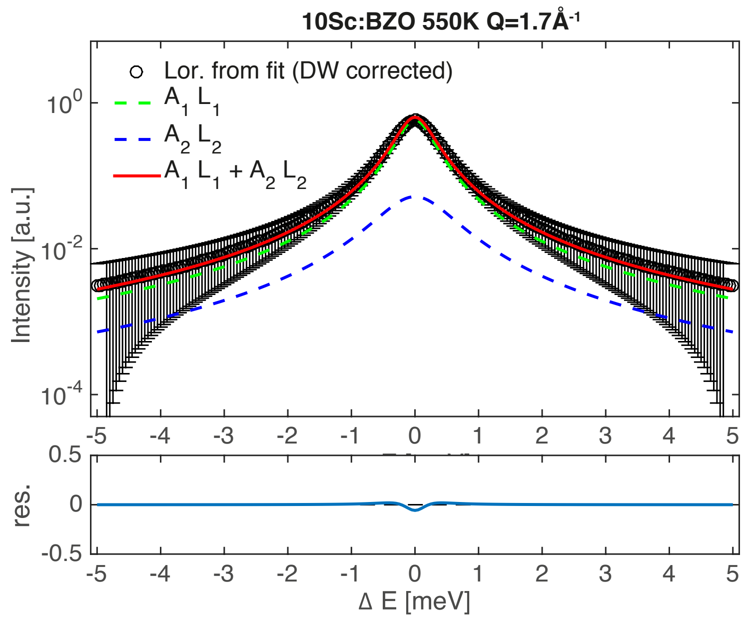
IN5 λ=2.5 Å

Mean residence time τ

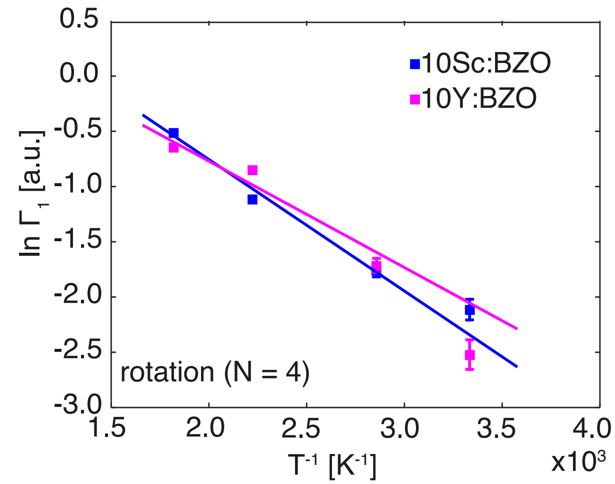
transfer: 3.606–17.8 ps (10Sc:BZO)
4.11–27.5 ps (10Y:BZO)

rotation: 2.21–11 ps (10Sc:BZO)
2.52–16 ps (10Y:BZO)



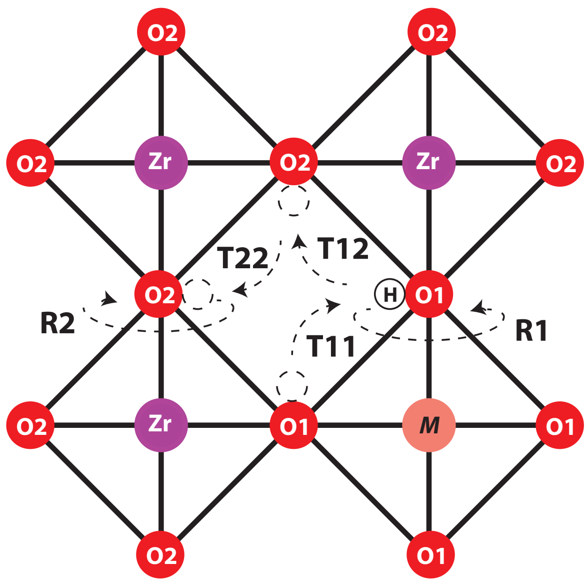


Ea ≈ 0.1 eV



Comparison with results from DFT

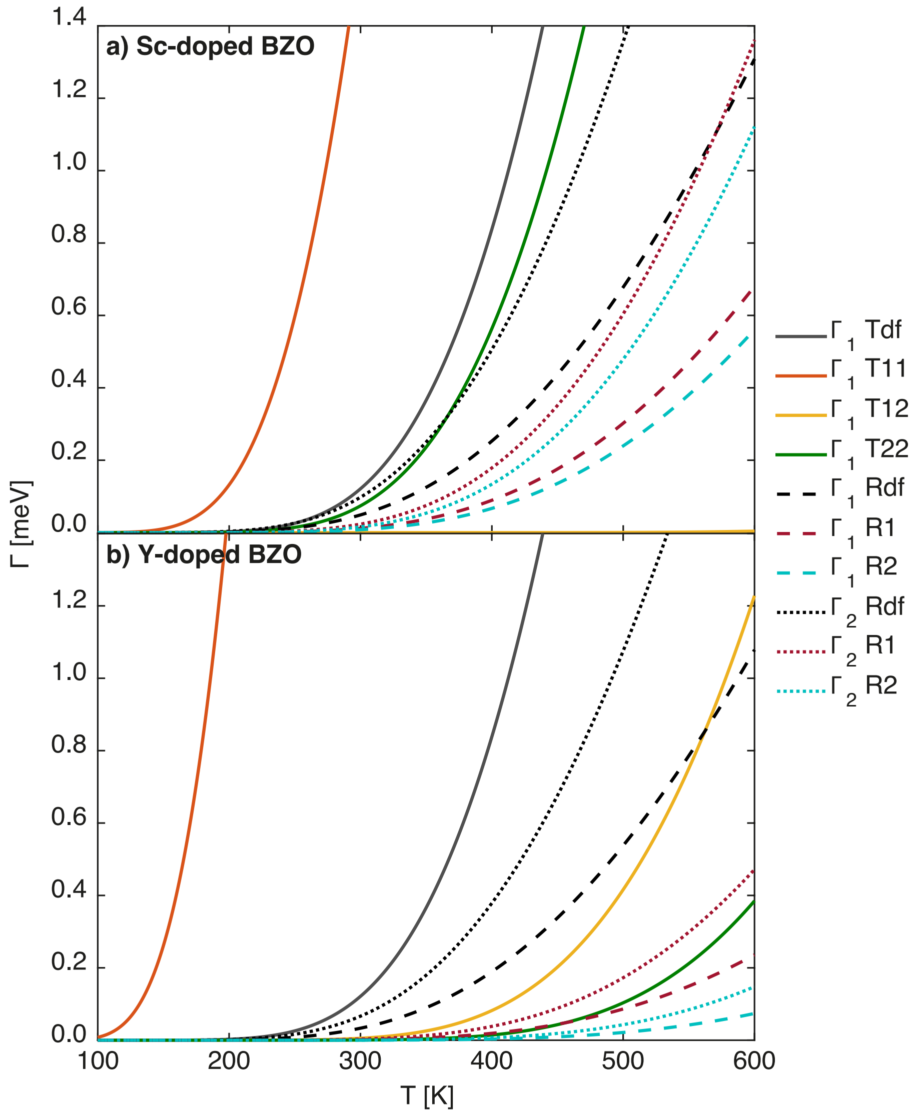
Björketun et al. Phys Rev B 76, (2007), 054307
Björketun et al SSI 176, (2005), 3035



$$\tau^{-1} = \nu_0 \exp\left(-\frac{E_a}{k_B T}\right)$$

Rotation: v_0 → OH wag (w2)
Transfer: v_0 → OH stretch

jump over 2 or 4 sites



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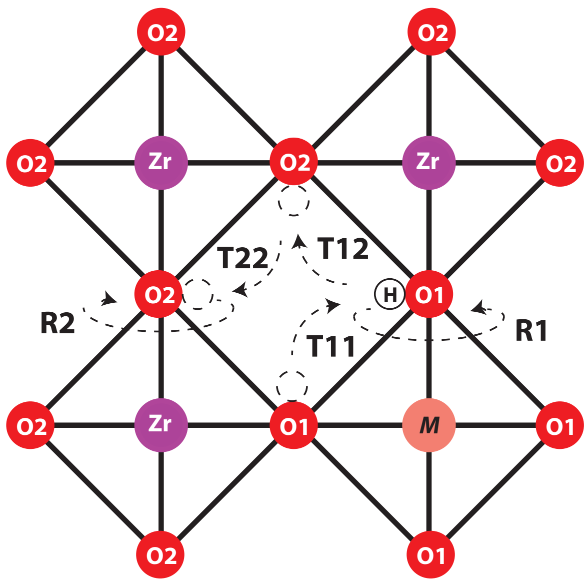

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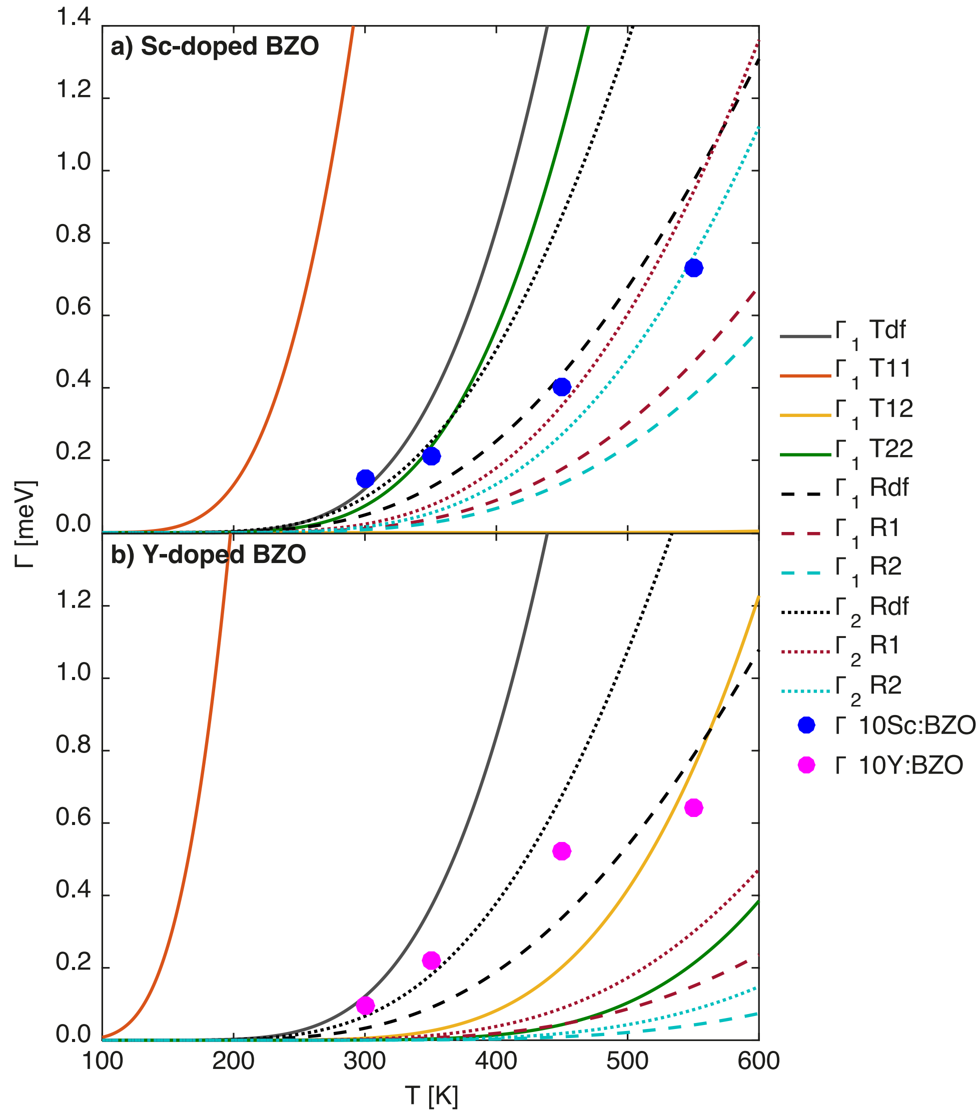
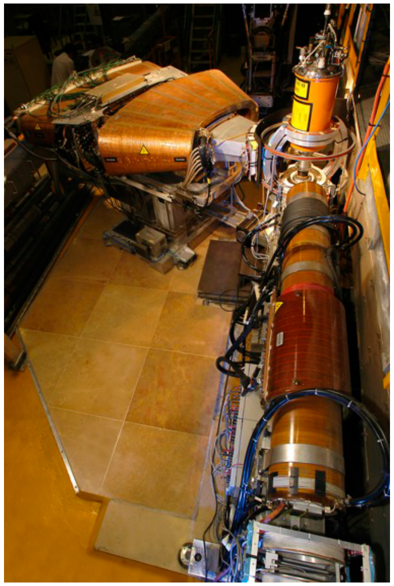


“Long-range” diffusion



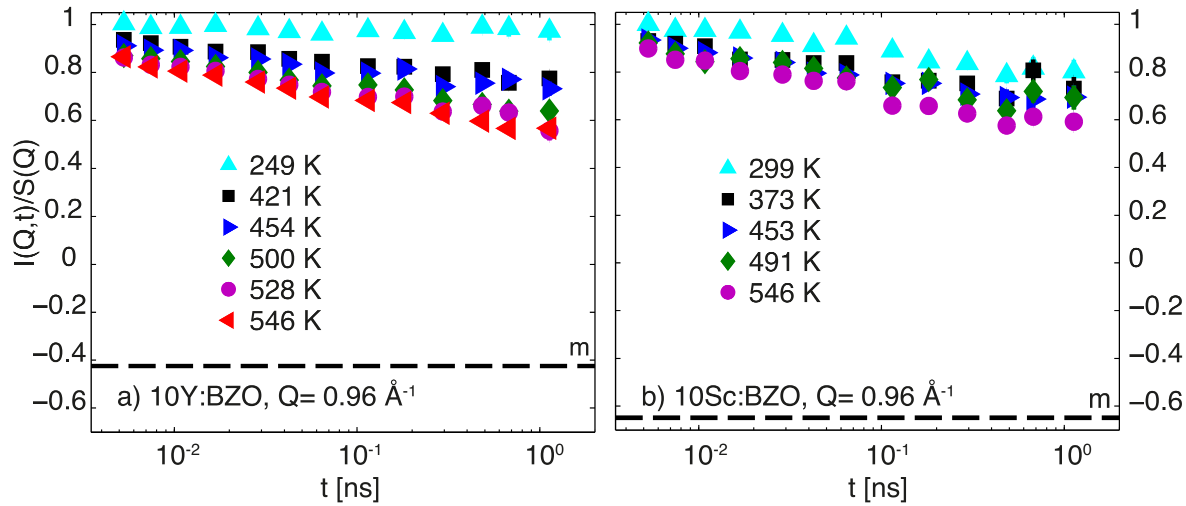
(Photo courtesy of M. Maccarini, 2011)

NSE spectrometer IN11C:

- Incident λ = 5.5 Å :
  - time range: ~5 ps-1.34 ns
  - Detector centered at:
    - 50° → Q-range ~0.7-1.2 $Å^{-1}$

- Temperature range: 250 – 563 K + 2 K measurements used as resolution.

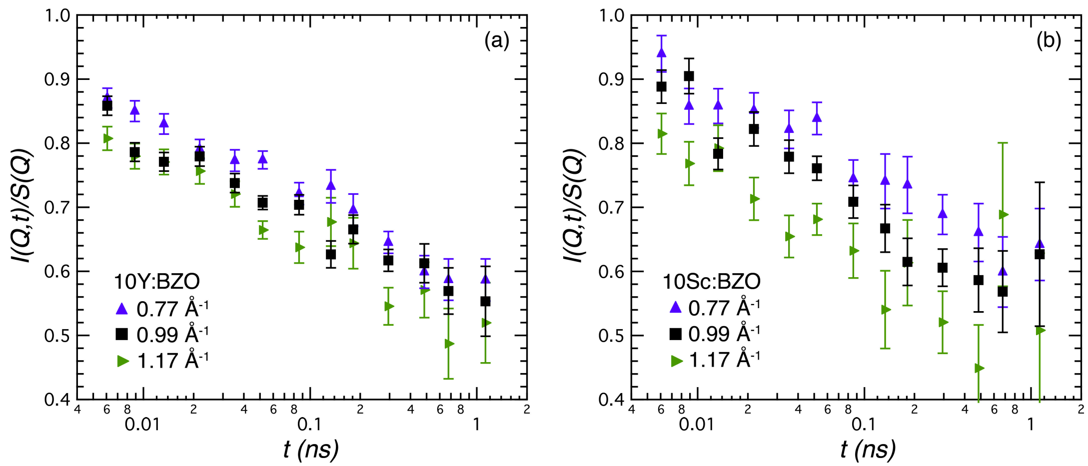
IN11 λ=5.5 Å



m → level of the complete decay in the assumption that all and only the H are moving, and that the dynamics is only incoherent

$$m = \frac{coh(Q) - \frac{1}{3}\sum_{i \neq H} inc(Q)}{coh(Q) - \frac{1}{3} inc(Q)}$$

T= 546 K



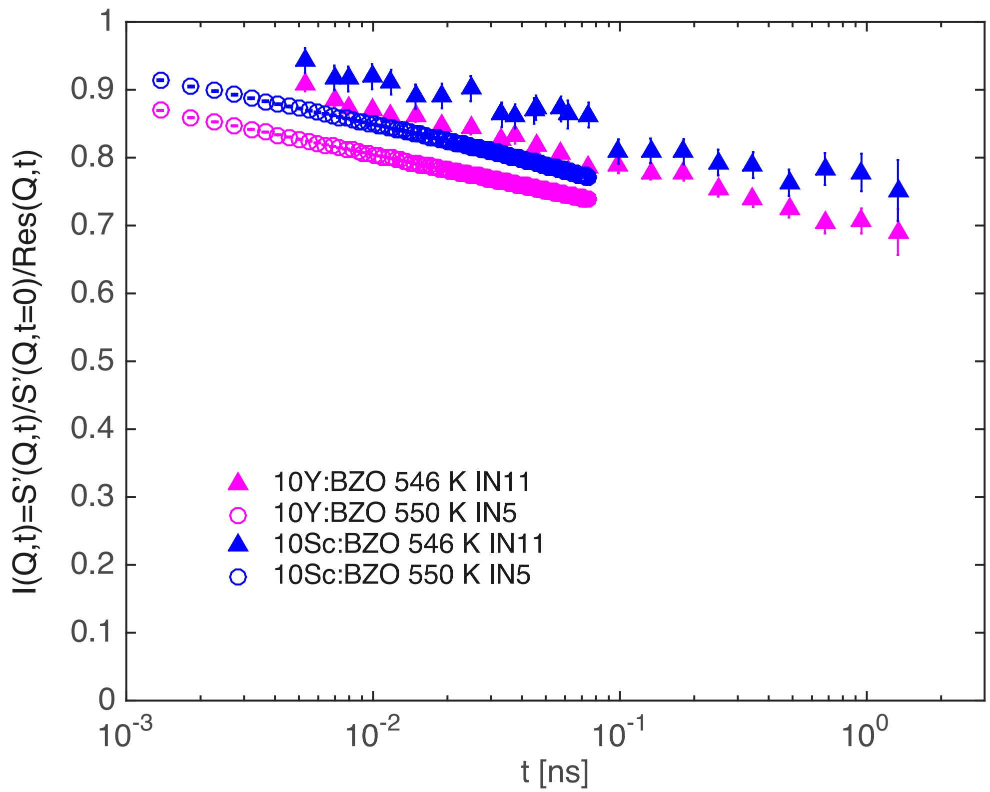
very stretched profile, no distinguishable relaxation time

no strong Q-dependence

IN5 λ=8.0 Å

- energy range: ~-6-0.76 meV
- Q-range: 0.6-1.2 $Å^{-1}$
- Res Γ = 20 μeV

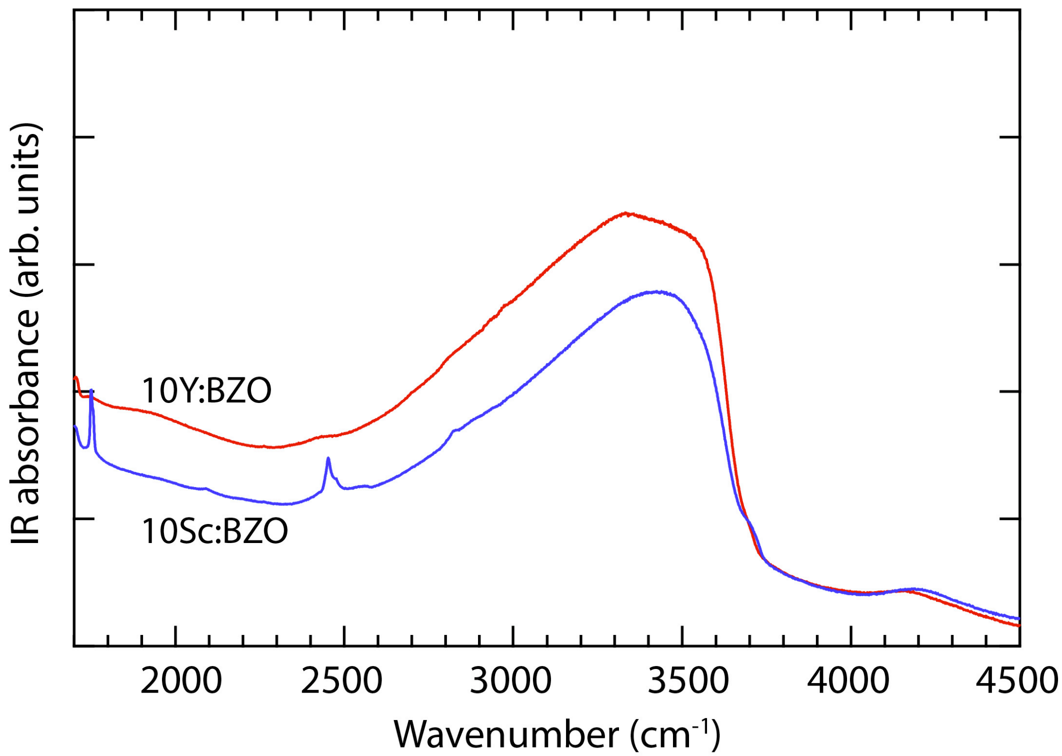
  Comparison of IN5 FT data (Q=1.0 Å) and IN11, rescaled for the level m



Heterogeneity of H sites

INFRARED MEASUREMENTS

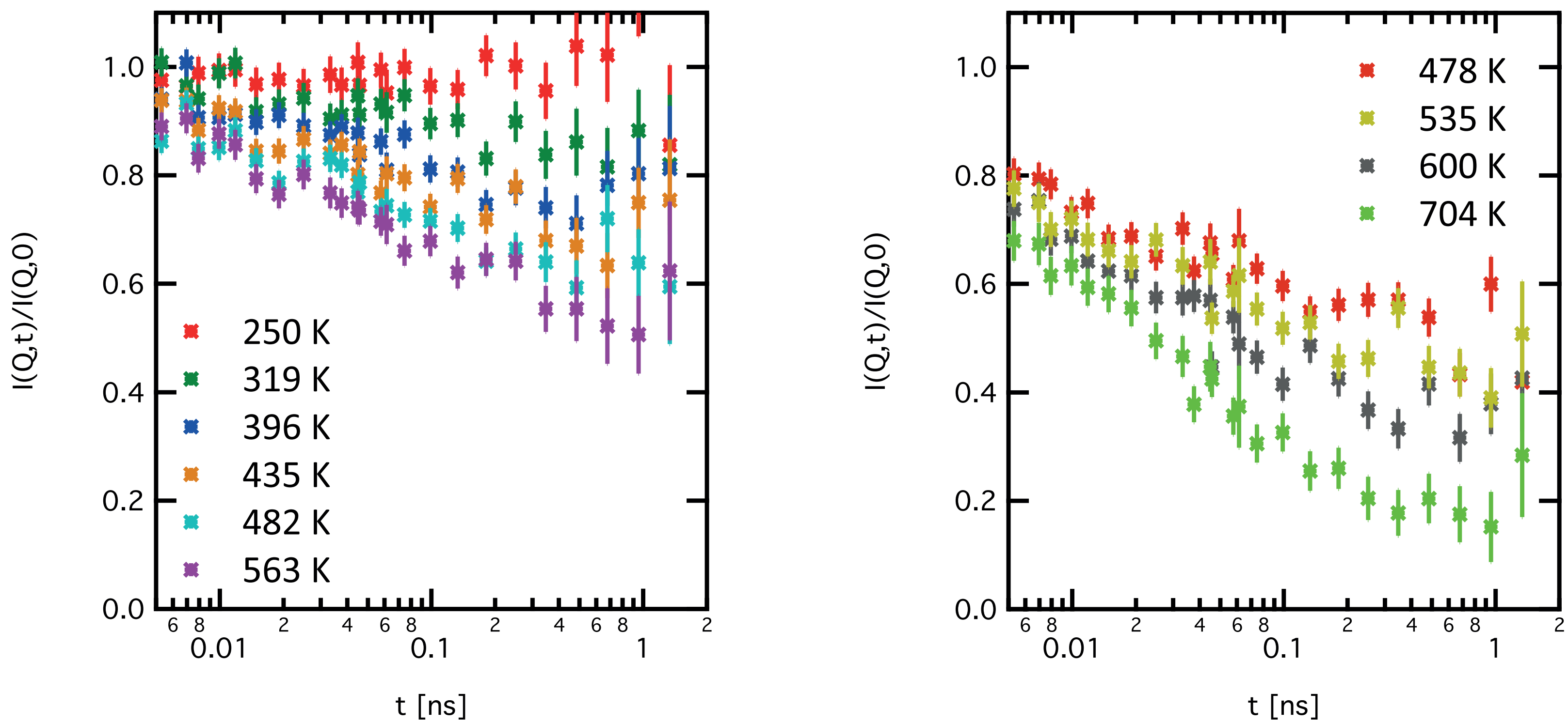
→ broad O-H stretching band related to a distribution of different proton sites



Samples and reproducibility

10Sc:BZO

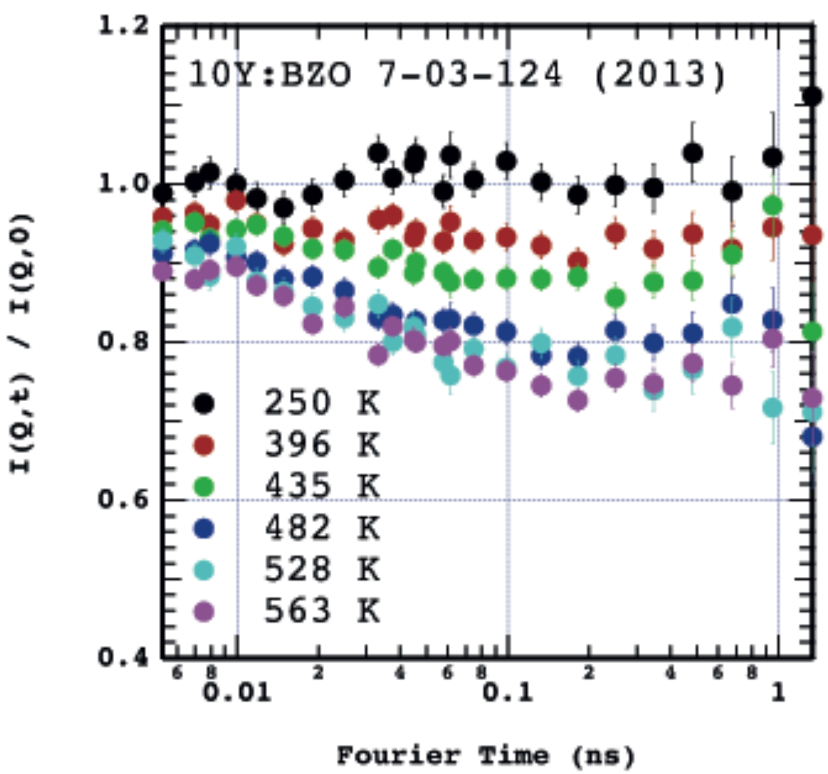
Same material, different samples. 2013 vs 2010 IN11 C

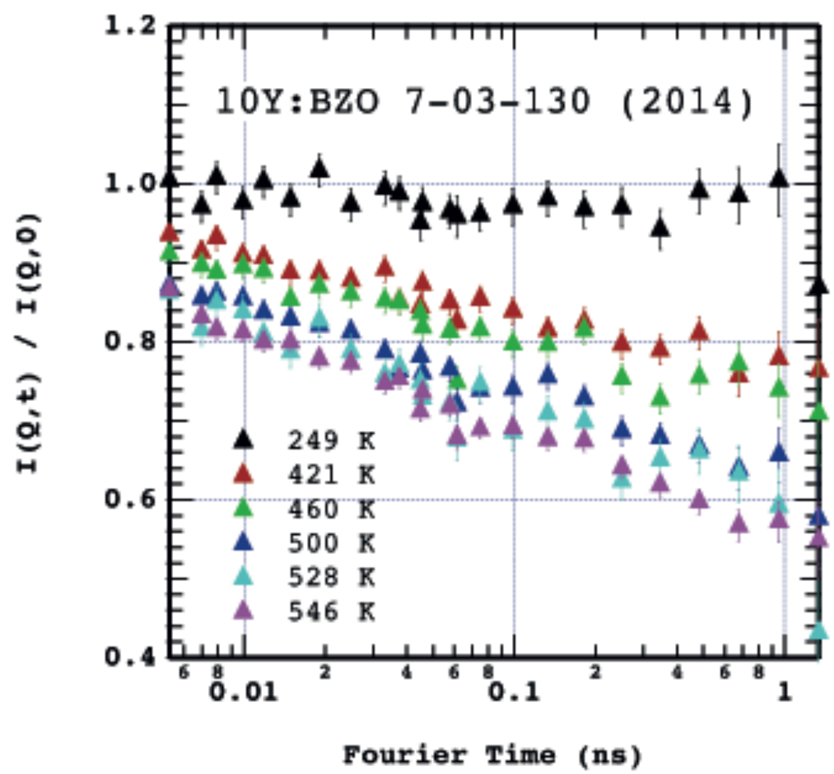


Samples and reproducibility

10Y:BZO

Same sample batch. 2013 vs 2014 IN11 C



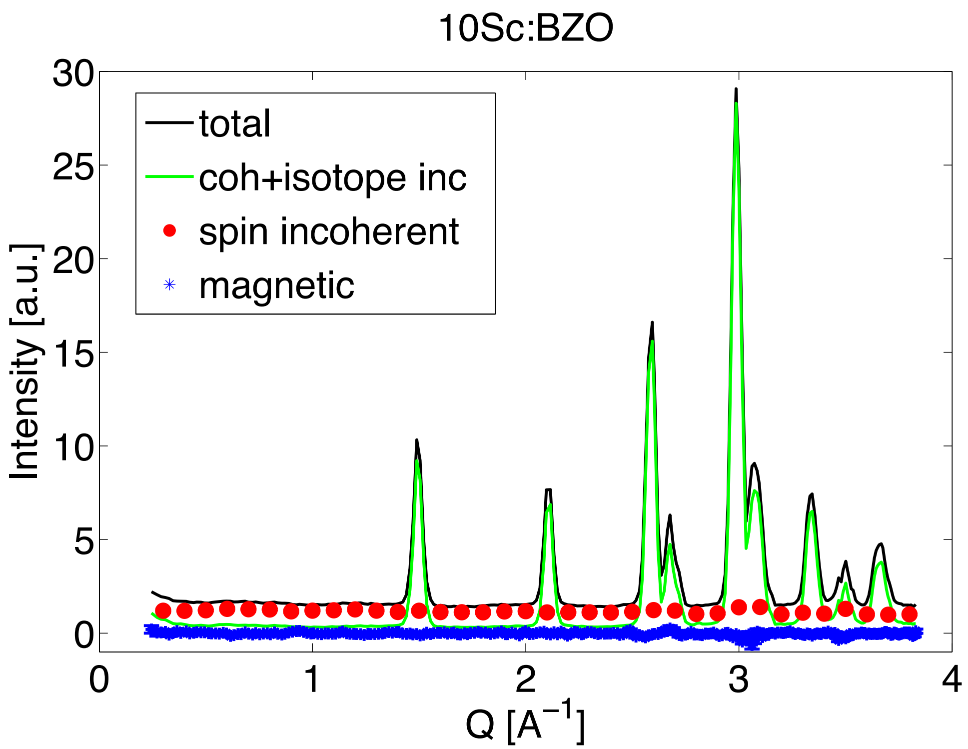


Hydrogen content: D7

diffraction with polarisation analysis

- Separation of magnetic, nuclear and spin-incoherent cross sections
- Corrections + calibration with Vanadium with known mass → H content

non-destructive measurement!



100% hydrated samples:
H content = dopant level [mol/mol]

0.1 mol $_H$ / mol $_{Ba}$

10Sc:BZO: 0.18 mol H/mol Ba
10Y:BZO: 0.36 mol H/mol Ba

agreement with TGA

Hydrogen content: open questions

- **The protonation process is not fully understood yet.**
- **Hydration level ⟷ protonation conditions and sample characteristics.**
- **Difficult to reach the full theoretical content of “bulk” protons.**
- **Presence of hydrogens in samples after high temperature (900-1000 °C).**

Which is the nature of these “extra protons”?

Surface water, complex hydroxycarbonates… ?

Which is the effect of the dopant atom on hydration?

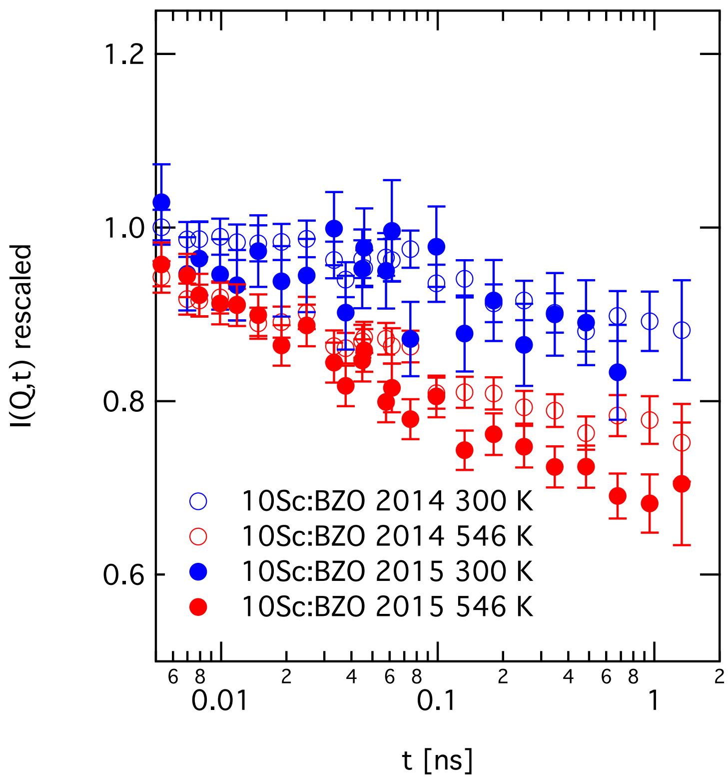
(How) do they influence the observed dynamics?

P. Colomban et al. The European Physical Journal Special Topics, 213, (2012).
P. Colomban et al. Journal of Raman Spectroscopy, 44, (2013).
M. Pionke et al. Solid State Ionics, 97, (1997).
I. Ahmed et al. Journal of the American Ceramic Society, 91, (2008).

Samples and reproducibility

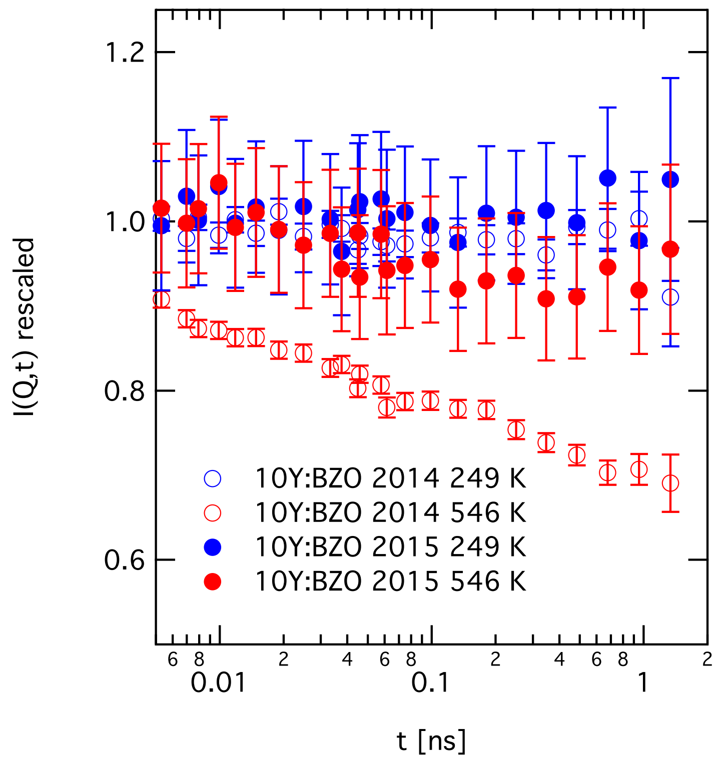
Samples were heated at 190 °C for several hours

10Sc:BZO: 0.15 mol H/mol Ba (D7)



10Y:BZO: 0.06 mol H/mol Ba (D7)

unfortunate combination of coh/inc → polarization almost 0 in Q-range



All we need is neutrons…?

What is the effect of the dopant atom?
What are the characteristics of the localized steps and the "long-range" diffusion?
Which is the rate-limiting step for proton diffusion?

Things we need:

- *neutrons* ✓
- *instruments to map a wide dynamical range* ✓
- *tight sample cell* ✓ *(thanks Richard!)*
- *well characterized samples and procedures for synthesis and hydration which limit the amount of "impurities" and "variables"*

Conclusions

- **We observed a localised proton dynamics with characteristic times in a range of *ca* 2-30 ps and energy barrier of the order of 10^2 meV.**
- **The geometry of the dynamics is compatible with the fundamental steps of the diffusion: transfer between neighbouring oxygens and reorientation of the –OH group.**
- **The high resolution measurements revealed proton dynamics extremely stretched, that cannot be characterized by a unique relaxation time.**
- **The presence of a considerable fraction of immobile species is suggested.**
- **The differences between the different systems cannot be correlated with the large difference in proton conductivities.**

Neutrons: enjoy responsibly!

Next steps and perspectives

In-doped samples xIn:BZO x=10-25

- Backscattering data from IN16b
- Spin-echo data from IN15 (10In:BZO)
- TOF data from TOFTOF
- polarised diffraction from D7

Some ideas for the future…

- S(Q,ω) measurements with polarised neutrons
- Measurements with in-situ hydration

→ special sample environment

Al-Wanish et al. Review of Scientific Instruments 86 (2015) 095102

Acknowledgments

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- Seikh Rahman

- Wiebke Lohstroh
- Zachary Evenson

- Moureen Kemei
- Ram Seshadri

And of course…

Thank you for your attention !!!

Bill Watterson's Calvin&Hobbes: en.wikipedia.org/wiki/Calvin_and_Hobbes

Questions?

Comments?

Ideas???