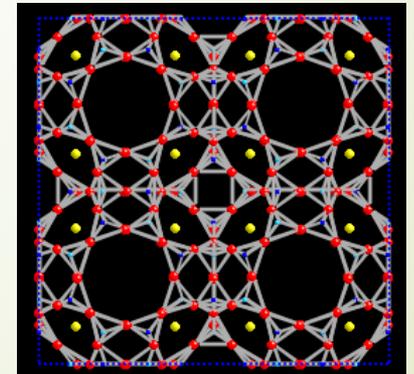


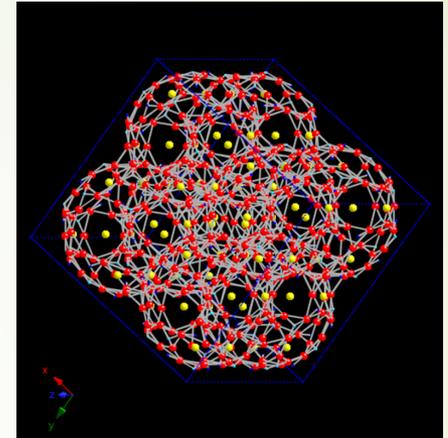
**Quasi-elastic and inelastic neutron scattering studies of  
layered silicates and zeolites  
<Great times with Bill Kamitakahara>**

**Noboru Wada  
Toyo University, Japan**



# Outline

- Personal comments
  - How we met
  - What I learned from Bill
- Introduction
  - Porous materials
  - Structures and water molecules
- Inelastic Neutron scattering
- Quasi-Elastic Neutron Scattering
- Summary





# How did we meet?

➤ NEUTRON SPECTROSCOPY OF PHONONS IN RbC8

WA **Kamitakahara**, N **Wada**... - Le Journal de ..., 1981 -  
jphyscol.journaldephysique.org

➤ Intercalate lattice dynamics in stage-1 rubidium  
graphite

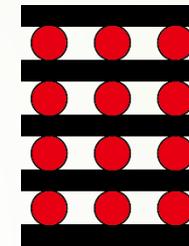
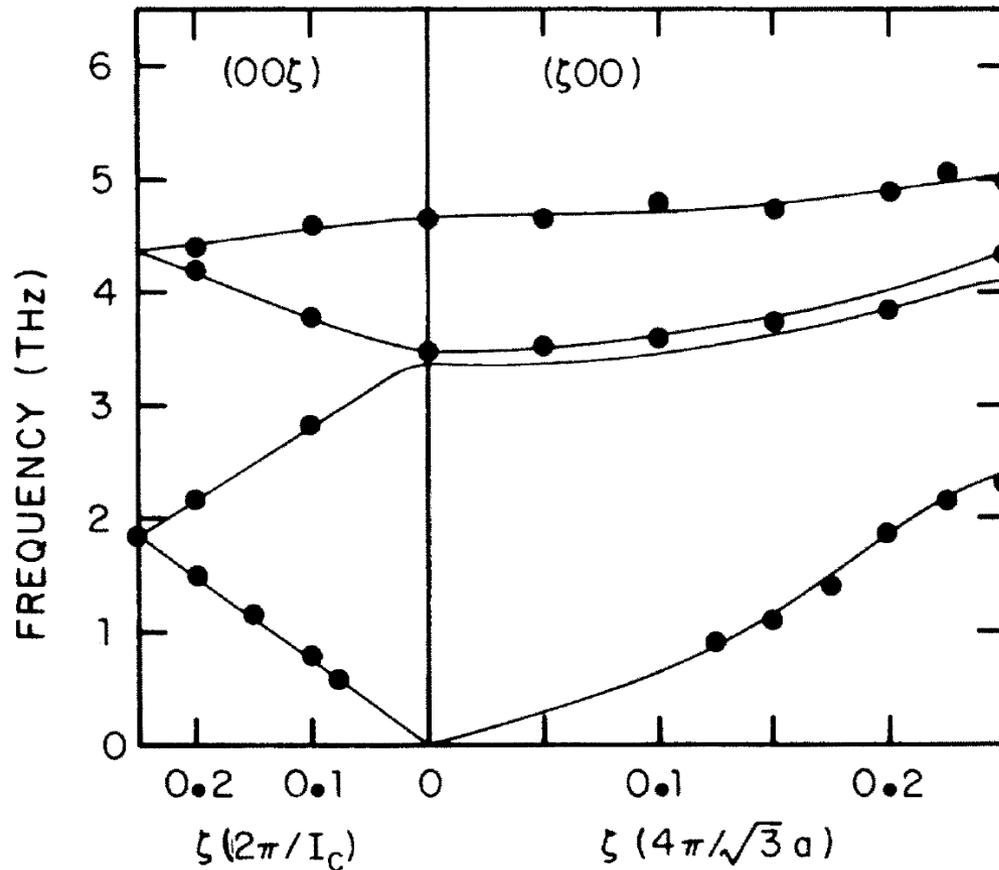
WA **Kamitakahara**, N **Wada**, SA Solin - Solid State  
Communications, 1982 - Elsevier

➤ Neutron spectroscopy of phonons in stage-1 rubidium-  
intercalated graphite

WA **Kamitakahara**, N **Wada**, SA Solin, LM Seaverson -  
Physical Review B, 1983 - APS

# Neutron spectroscopy of phonons in stage-1 rubidium-intercalated graphite

WA Kamitakahara, N Wada, SA Solin, LM Seaverson - Physical Review B, 1983 - APS



● Rb atom  
— graphene sheet

A large RbC<sub>8</sub> sample was prepared; 1.1x1.1x5.0 cm<sup>3</sup>

FIG. 2. Measured phonon dispersion curves for RbC<sub>8</sub>.

Raman Measurements of **Folded** Interlayer Shearing **Phonons** in  $KC_{12}n$  ( $n=2-6$ )  
 N Wada, MV Klein, H Zabel - Physics of Intercalation Compounds, 1981 - Springer

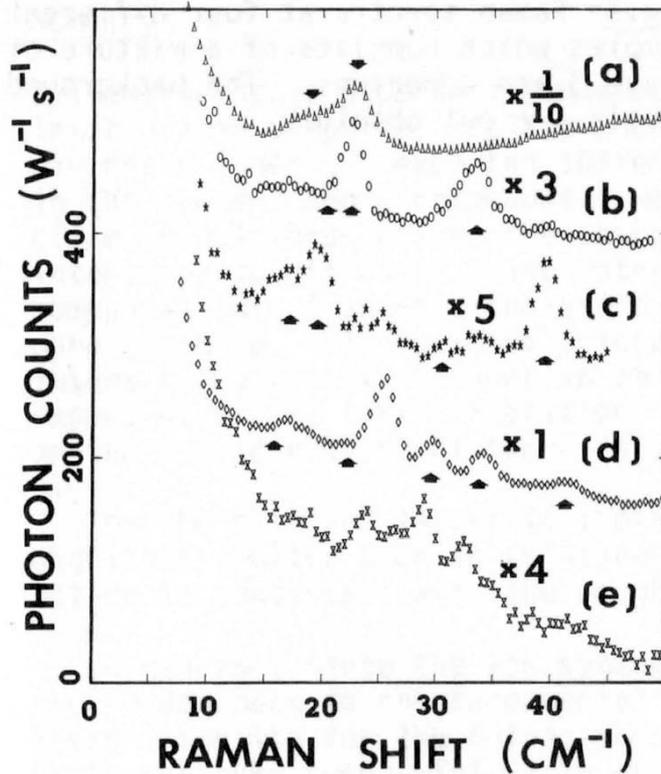


Fig.1 Raman spectra of  $KC_{12}n$  ( $n=2-6$ ) taken in the depolarized configuration at room temperature. The spectra (a) ~ (e) were taken from stage 2-6 samples, respectively. The background levels are not absolute. The signal-to-background ratios were about 1/2 in (a), 1/4 in (b), 1/6 (c) and 1/10 in the other spectra. The arrows indicate the calculated values of the phonon frequencies (see text).

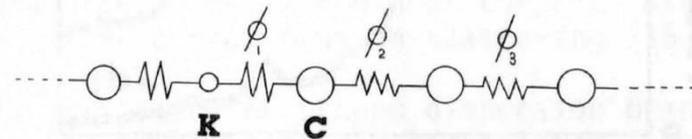


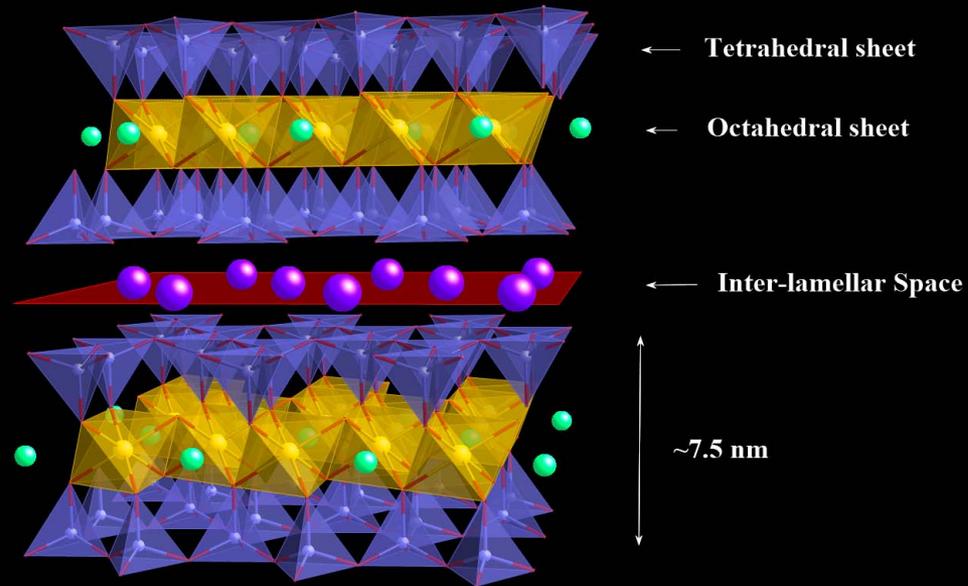
Fig.2 Schematic representation of the linear chain model.

- A triple-axis spectrometer at the [High Flux Isotope Reactor](#), ORNL.
- A triple-axis spectrometer operated by [Ames Laboratory](#) at the Oak Ridge Research Reactor, ORNL.



# Layered Silicates

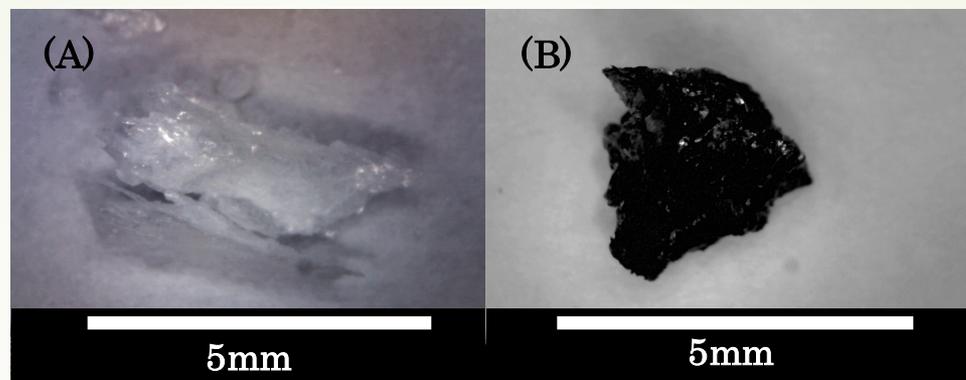
## 2:1 Layered Silicates



## Interests

- ◆ Inter-lamellar cation exchange
- ◆ Intra-lamellar cation substitution
- ◆ Hydration
- ◆ Organic-molecule intercalation
- ◆ Fluorination

# Synthesis of Taeniolite and Carbon Nano-Structures



## Inter-lamellar Cations

Organic Molecules

	$Ni^{2+}$	$Co^{2+}$	$Mn^{2+}$	$Ca^{2+}$	$Mg^{2+}$	$Na^+$	$Cs^+$	$K^+$	$NH_4^+$	$Rb^+$
DMF										
DMSO										
EG										
BA										
Py										
NMP										

# X-ray-diffraction studies of hydration transitions in Na vermiculite

N. Wada, D. R. Hines, and S. P. Ahrenkiel

Phys. Rev. B **41**, 12895 – Published 15 June 1990

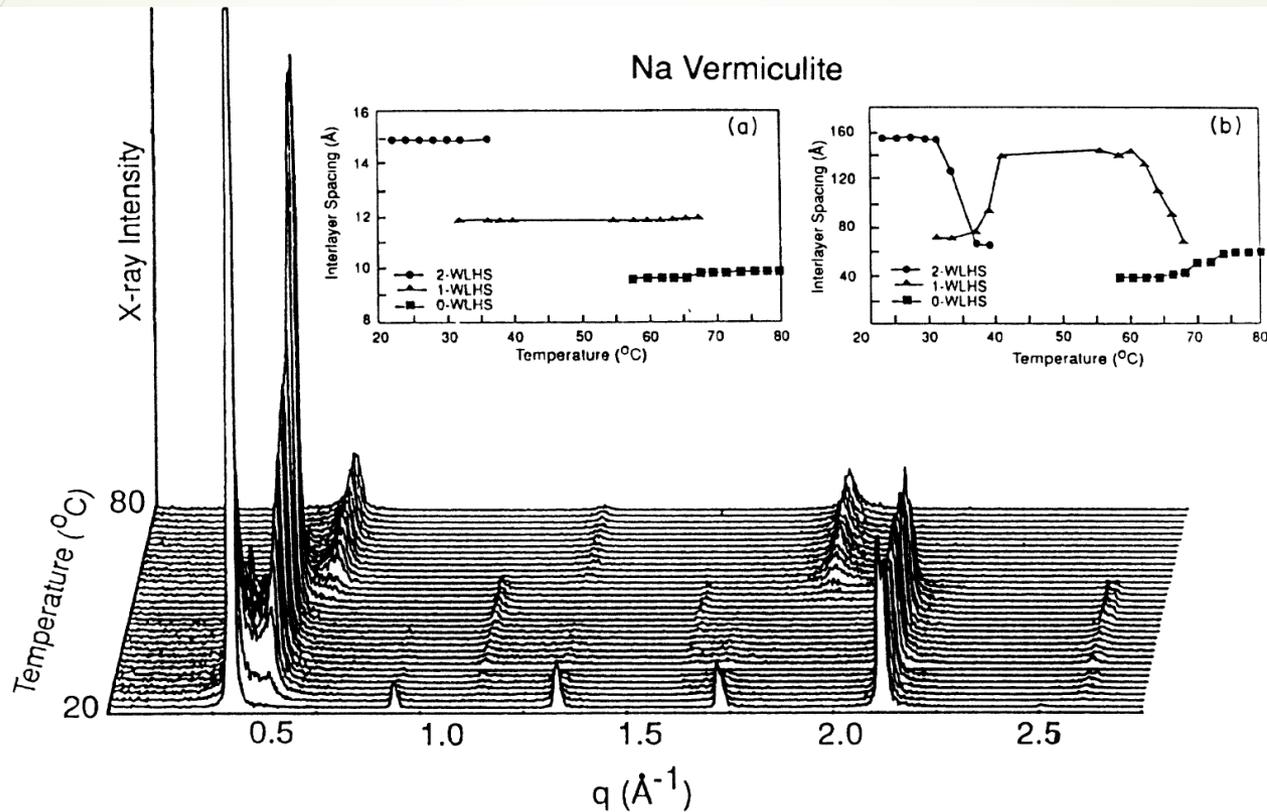


FIG. 1. (001) x-ray diffraction patterns from Na vermiculite as a function of temperature at a fixed water-vapor pressure of 19.8 Torr. Inset (a) shows the basal spacing vs temperature, whereas inset (b) shows the out-of-plane correlation length vs temperature (see text).

# Inelastic neutron- and Raman-scattering studies of muscovite and vermiculite layered silicates

N Wada, WA Kamitakahara - Physical Review B, 1991 - APS

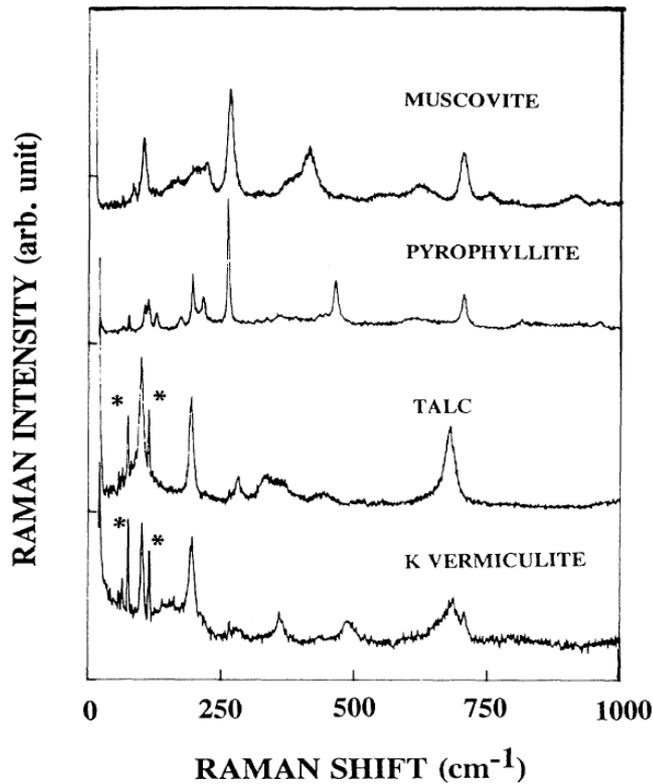


FIG. 2. Time-gated Raman spectra taken at room temperature on four layered silicates. Both muscovite and pyrophyllite are dioctahedral layered silicates, whereas talc and vermiculite are trioctahedral. The asterisks indicate plasma lines from the Ar-ion laser. The resolution was  $\sim 3 \text{ cm}^{-1}$ . Each spectrum was taken in  $\sim 1 \text{ h}$ .

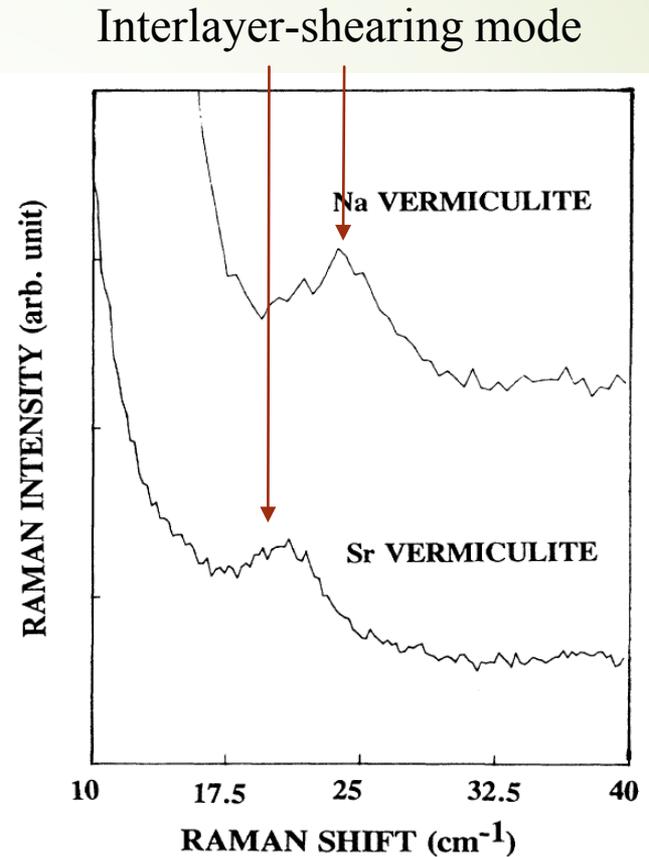


FIG. 7. Low-frequency Raman spectra for dehydrated Na and Sr vermiculite at room temperature.

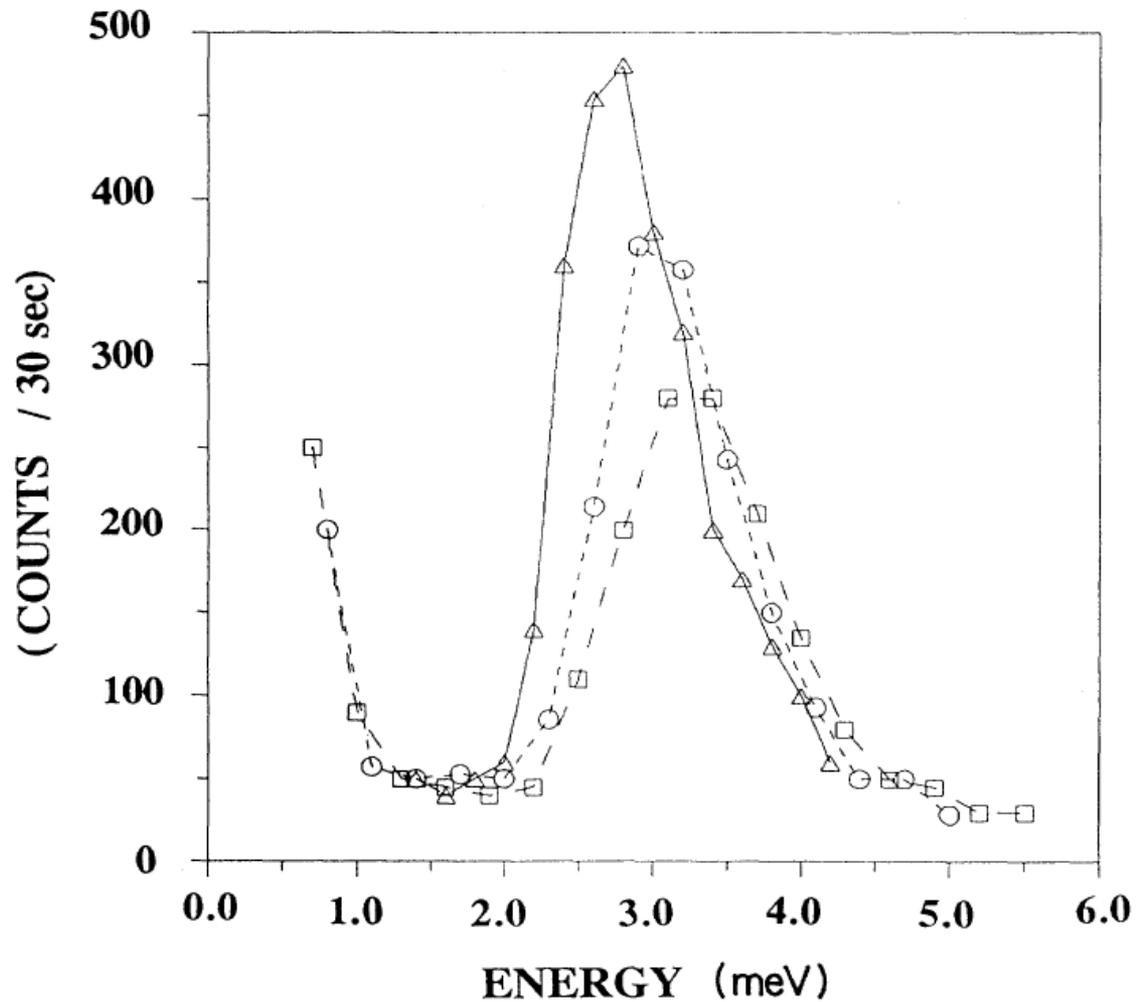


FIG. 3. Typical neutron-scattering scans for transverse phonons in muscovite at room temperature, corresponding to the TO branch in Fig. 4(a), with  $\zeta=0.4$  (triangles),  $0.3$  (circles), and  $0.2$  (squares).

# Muscovite

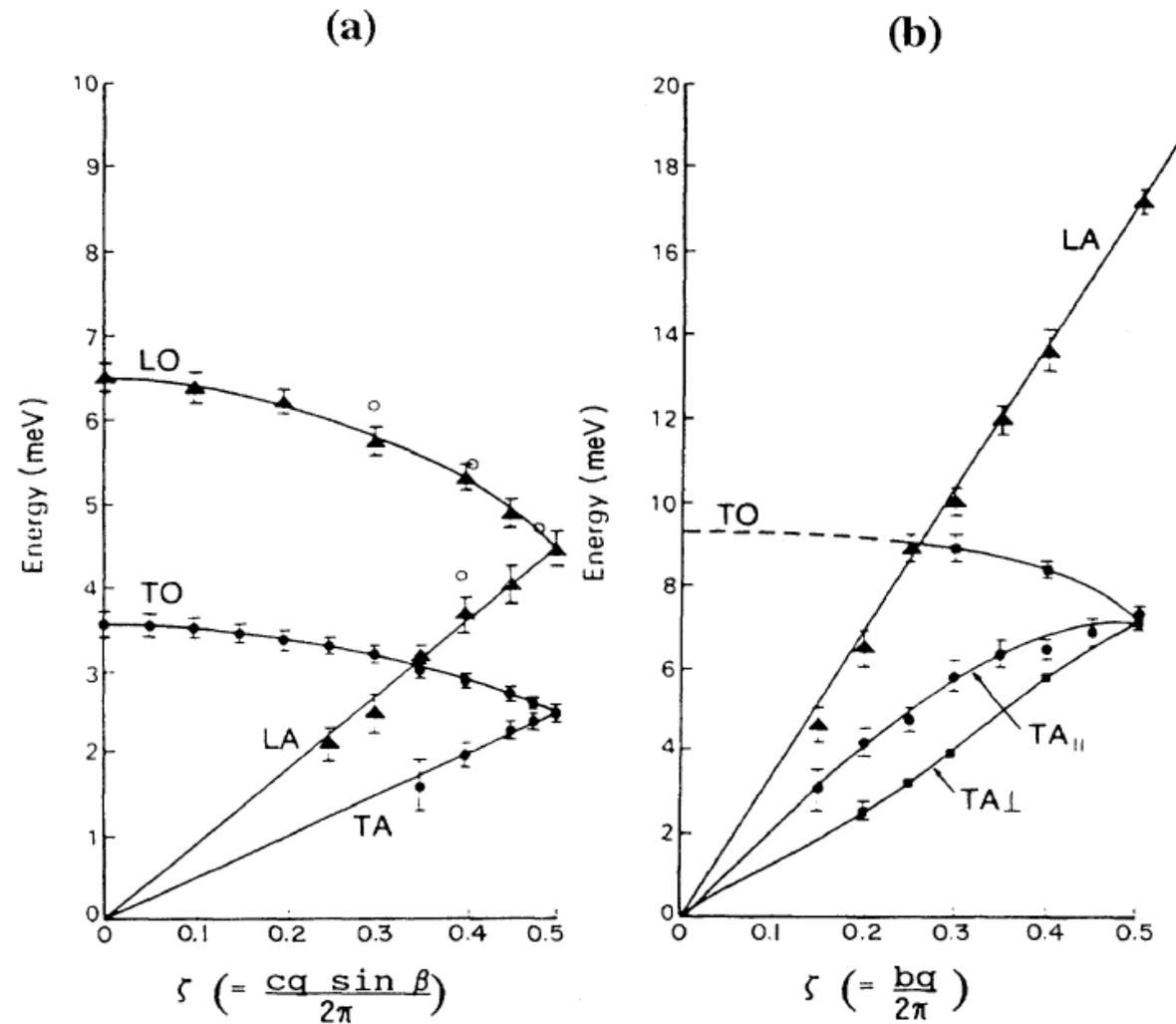


FIG. 4. Phonon dispersion curves obtained for muscovite at room temperature, with (a) phonon wave vector  $\mathbf{q}$  parallel to the  $c$  axis, and (b)  $\mathbf{q}$  parallel to the  $b$  axis. Relevant lattice parameters are  $c=20.0 \text{ \AA}$  and  $b=8.9 \text{ \AA}$  with  $\beta=96^\circ$ . The data of Cebula *et al.* (Ref. 12) are shown as open circles.

## 2-WLHS Mg vermiculite

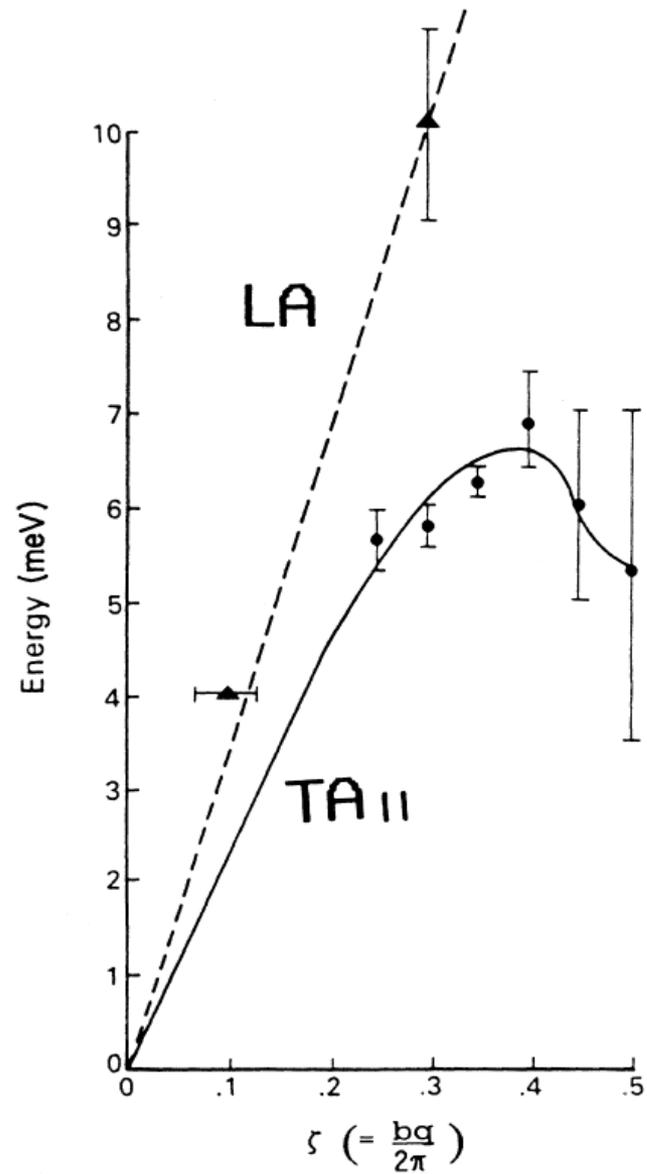
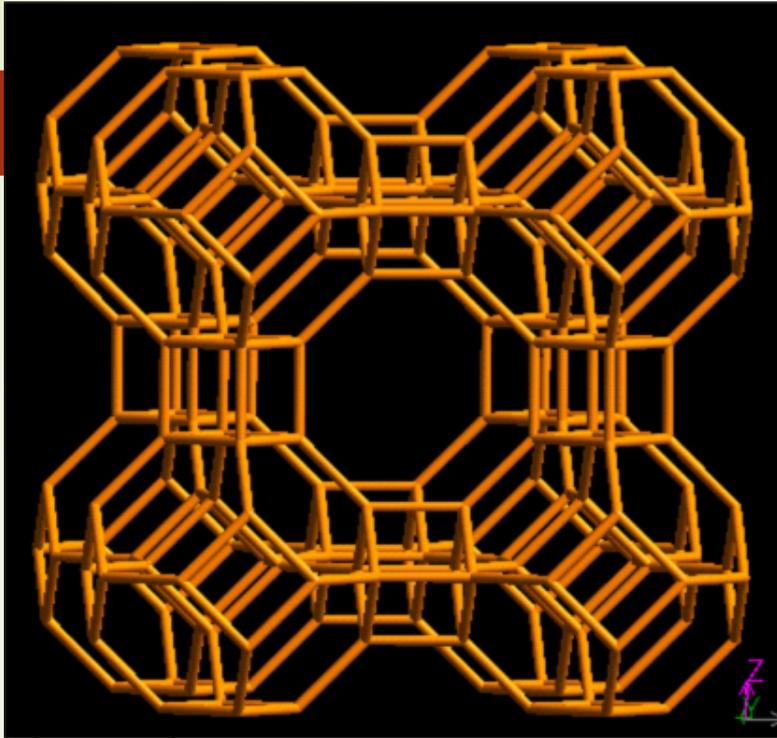


FIG. 5. Phonon dispersion curves obtained at room temperature on Mg vermiculite, for which  $c=14.36 \text{ \AA}$  and  $b=9.3 \text{ \AA}$ . The phonon wave vector  $q$  is parallel to the  $b$  axis. The polarization of the transverse acoustic (TA) phonons is parallel to the lamellae.

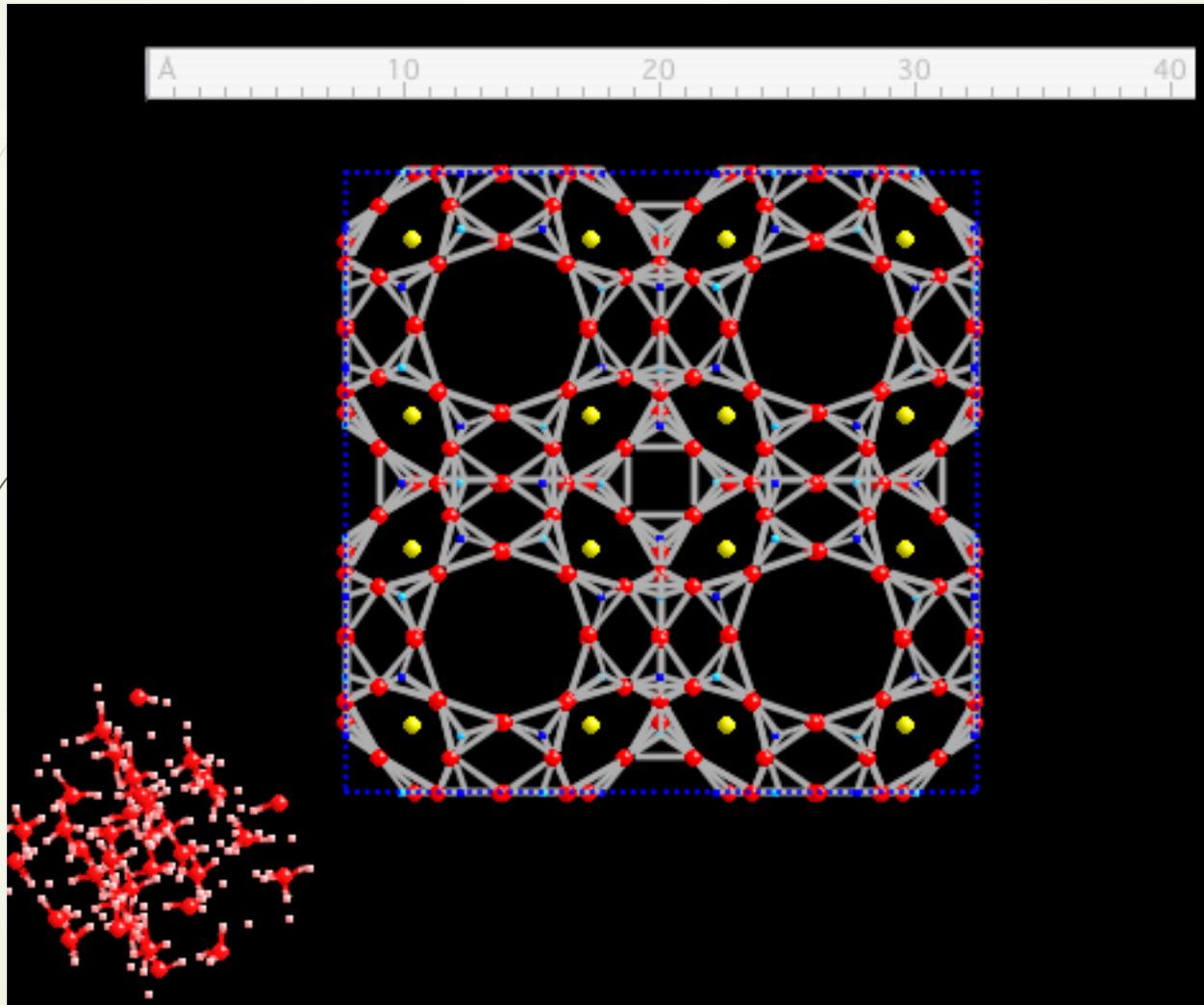


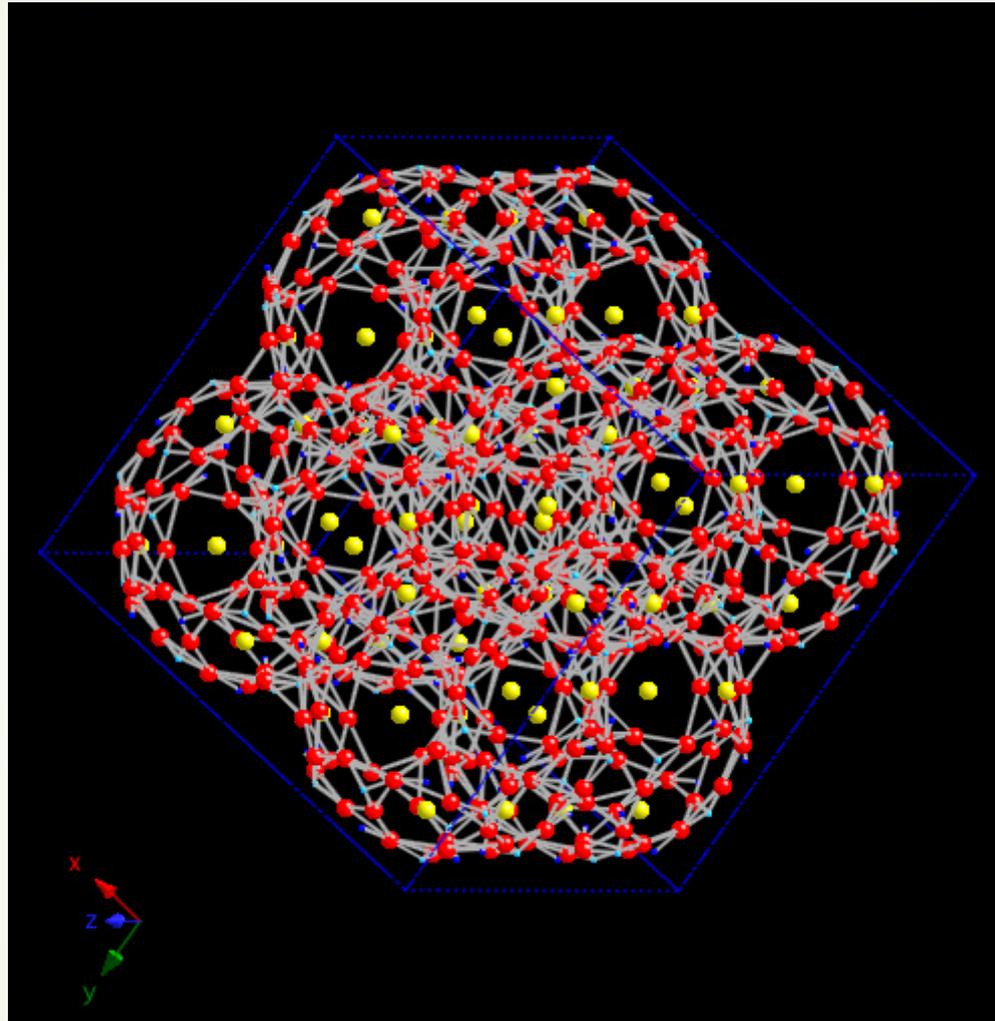
The **LTA** structure of NaA has 11 Å diameter cages, connected by 4 Å diameter openings



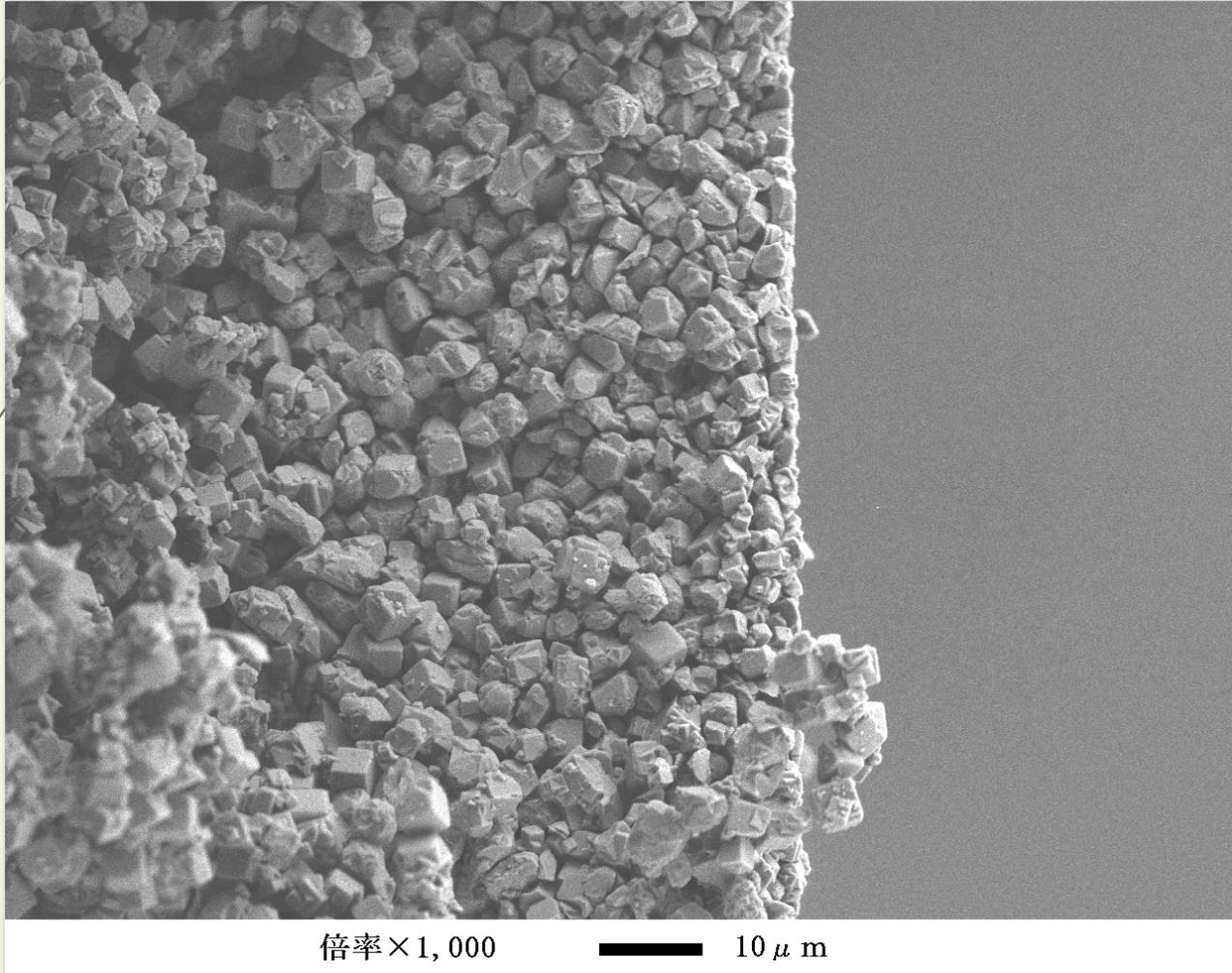
A view into the 13 Å diameter  $\alpha$ -cage of the **faujasite** structure, through the 7.4 Å diameter pore opening

# LTA with Water Molecules

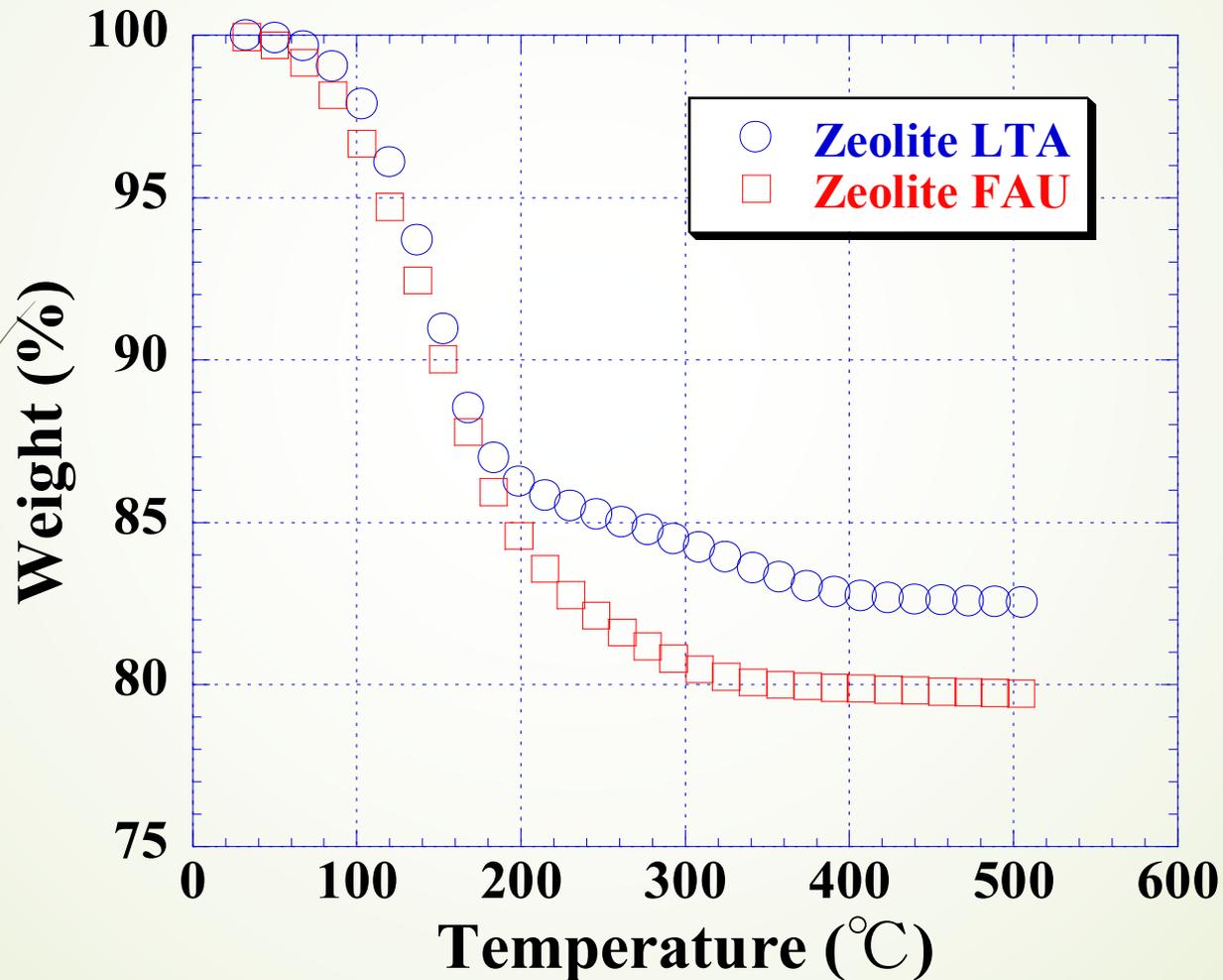




## Na-LTA Zeolite Film SEM Image



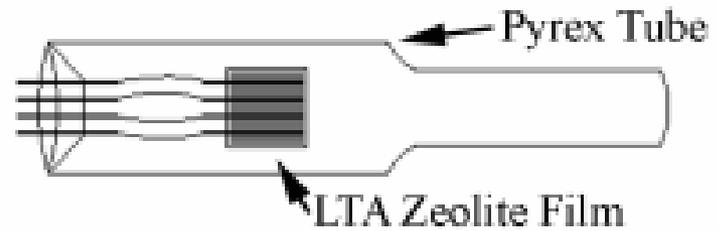
# TGA (Thermo-Gravimetric Analysis )



Resistivity ( $\Omega \cdot \text{cm}$ )

$10^5$

$10^4$



● LTA High Temp  
■ LTA Low Temp

200

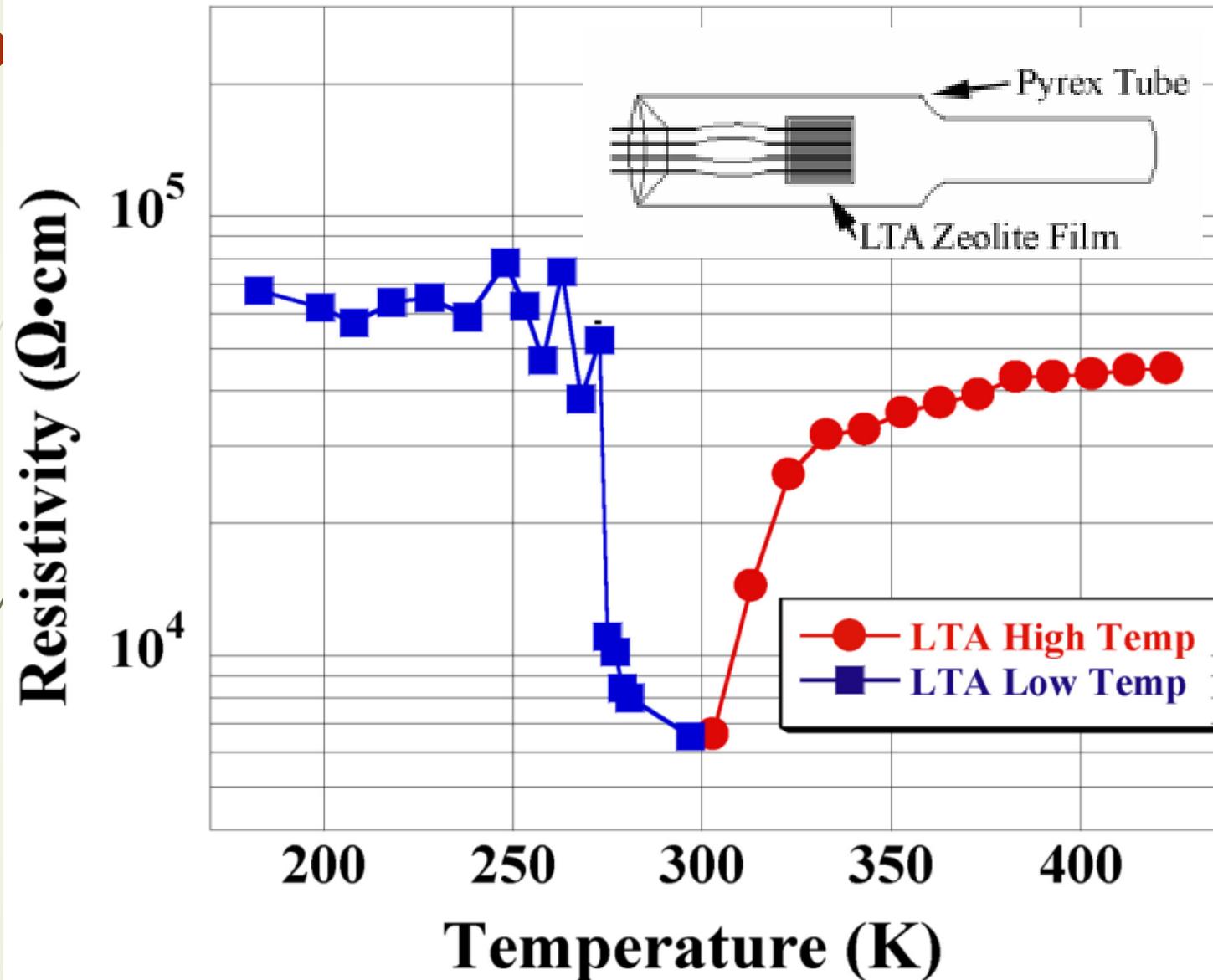
250

300

350

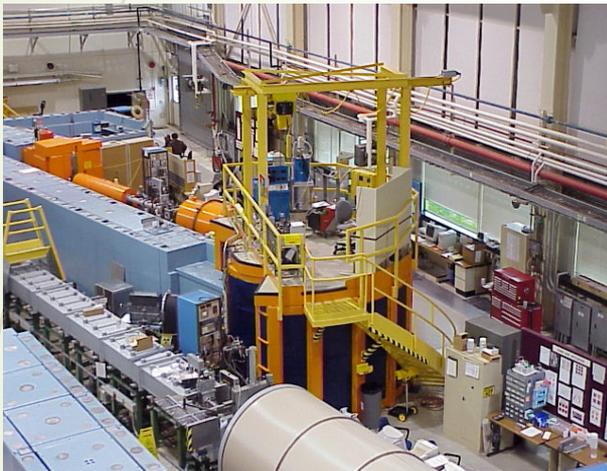
400

Temperature (K)



# QENS Experiment

The data were taken on the **High-Flux Backscattering Spectrometer (HFBS)** at NIST



With an energy resolution of  $1 \mu\text{eV}$  and a higher intensity than is available on any other neutron spectrometer at this resolution, use of the HFBS was the key factor permitting the systematic studies involved in this research.

**Our samples:** The zeolites we examined mainly had the FAU structure, with Si/Al ratios  $r=1.25, 2.75, 14.5,$  and  $180$ . We also examined the NaA zeolite ( $r=1$ ). In both cases, there are two O atoms per Si or Al atom, and one Na atom per Al atom.

# Data Analysis

**Translational jump diffusion**, decoupled from isotropic rotation of the molecules.

$$S(Q, \omega) = S_T(Q, \omega) \otimes S_R(Q, \omega) \quad (1)$$

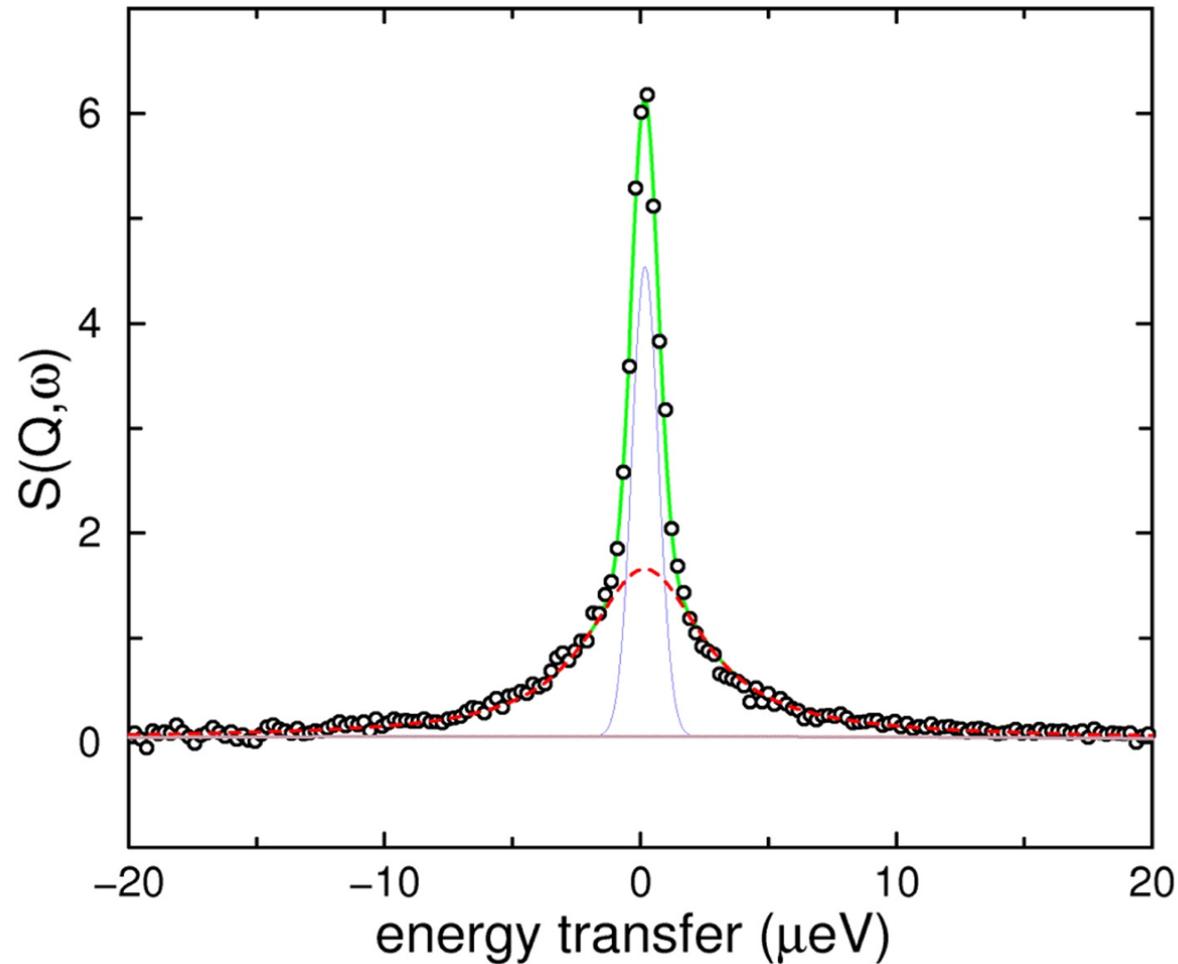
$S_T(Q, \omega) = (1/\pi)L_\Gamma(Q, \omega)$ , where the HWHM of the Lorentzian  $L_\Gamma(Q, \omega)$  is given by  $\Gamma(Q) = DQ^2 / (1 + DQ^2\tau_T)$ ,

$\tau_T \gg \tau_R$ , so that we are effectively only measuring translational motion.

We find an additional elastic component to be always present, which we ascribe to immobile water. We thus fit all spectra with a resolution-broadened elastic component plus a resolution-broadened Lorentzian.

## typical spectrum, water in FAU zeolite

NaY, H<sub>2</sub>O mass frac.=0.17, Q=0.75 Å<sup>-1</sup>, T=280K



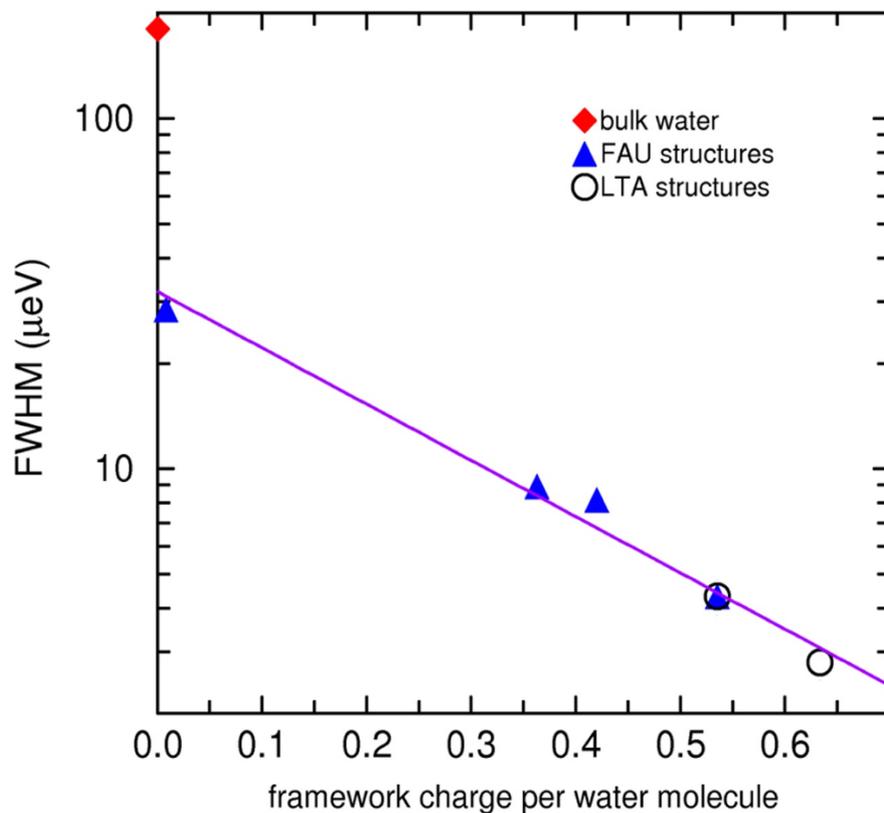
The observed scattering (circles and green line) is fitted with a resolution-limited component (blue) and a resolution-broadened Lorentzian (red).

# THE MOST IMPORTANT FACTOR AFFECTING THE DYNAMICS:

## FRAMEWORK CHARGE

The FAU structure, with **Si/Al ratios**  $r=1.25$ ,  $2.75$ ,  $14.5$ , and  $180$ . We also examined the NaA zeolite ( $r=1$ ).

effect of framework charge on QENS broadening

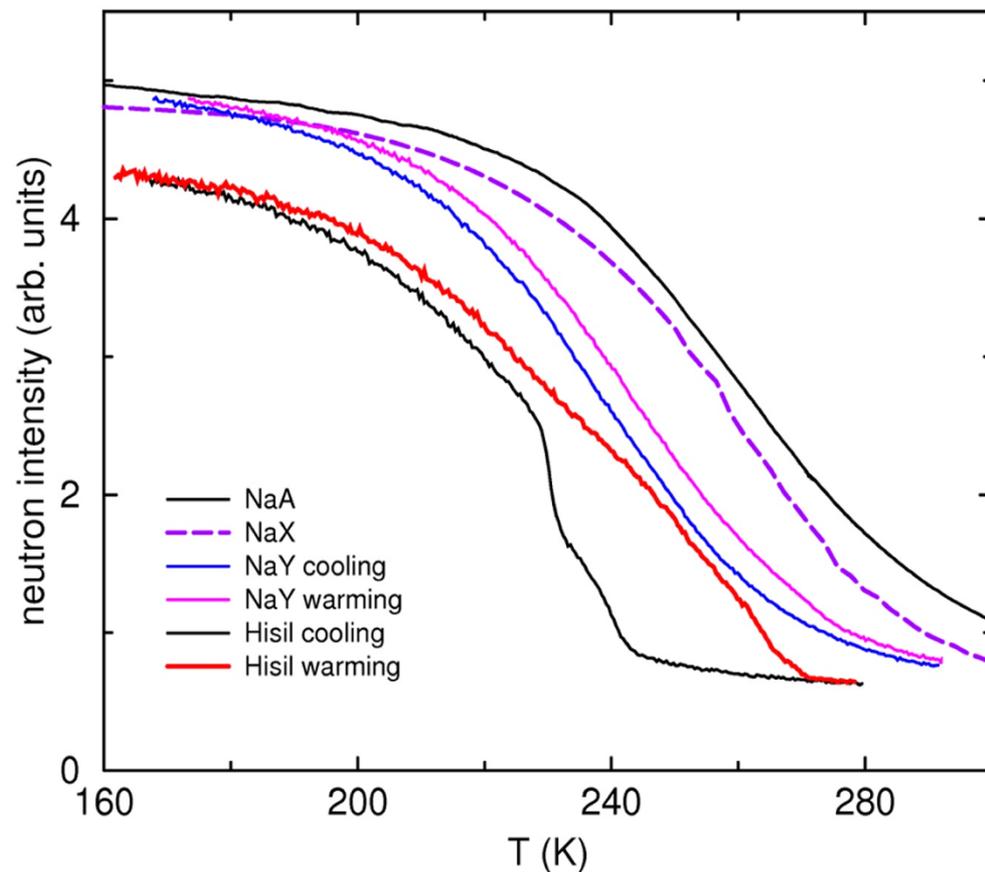


## FRAMEWORK CHARGE

- The QENS widths vary almost an order of magnitude at 300K, depending on the framework charge.

QENS widths at a representative wave vector  $Q = 0.75 \text{ \AA}^{-1}$  at 300 K show a very large dependence on framework charge.

E=0 scattering from water in Na-zeolites  
Fixed window scans for  $Q=[0.5-1.7]\text{\AA}^{-1}$



## E=0 Fixed-window Scan

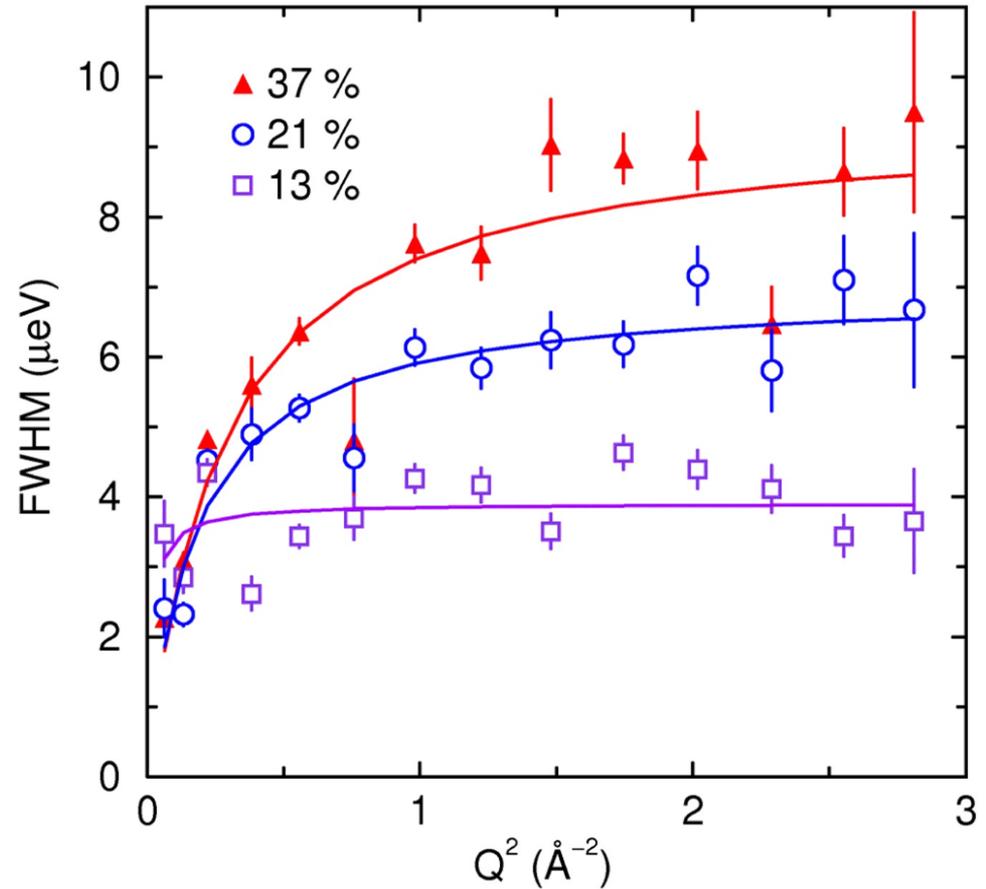
- Strong hysteresis in high-silica with a two-step structure.
- In highly-charged zeolites, the transitions are smooth, shifted to higher temperatures, and show very little hysteresis.

Fixed-window E=0 scans (rescaled to similar amplitudes) also show transitions with a marked dependence on framework charge.

**Hydration level** is a second significant factor affecting the dynamics of water

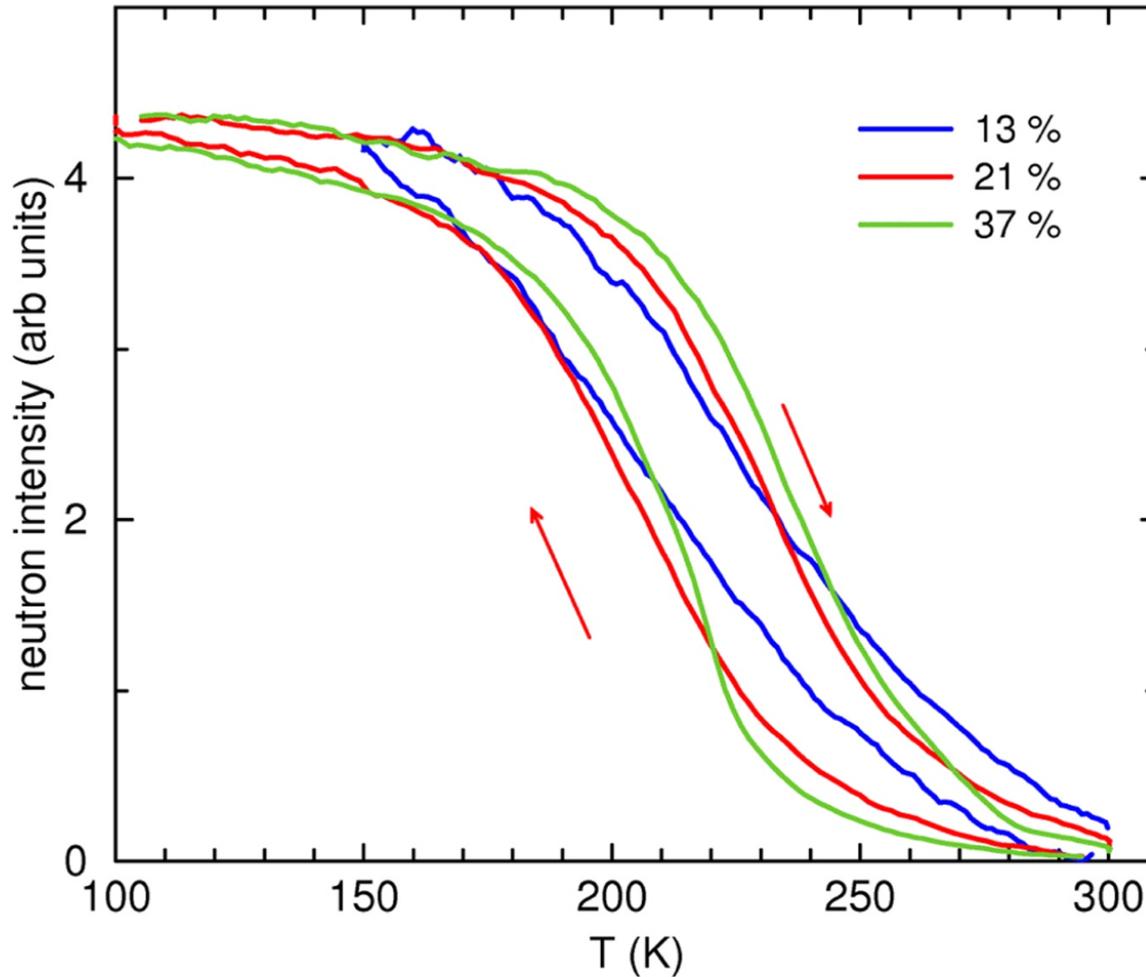
$$\Gamma(Q) = DQ^2 / (1 + DQ^2\tau_T)$$

QENS broadening for 3 hydration levels  
FAU Si/AL=14.5 260K

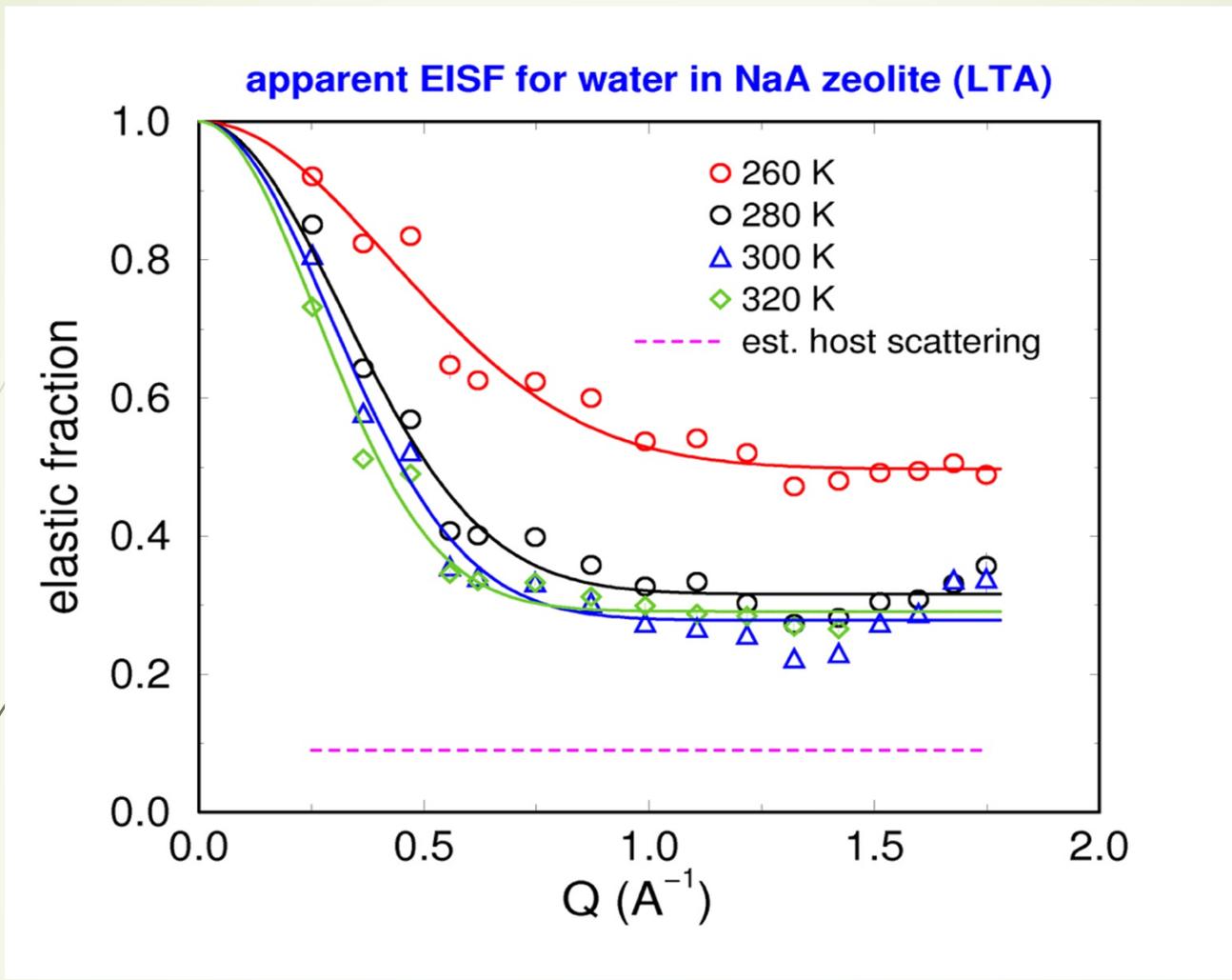


The QENS broadening increases with hydration level in a series of samples having hydration weight gains of 13, 21, and 37%.

rescaled fixed window scans for 3 hydration levels  
FAU Si/Al ratio=14.5

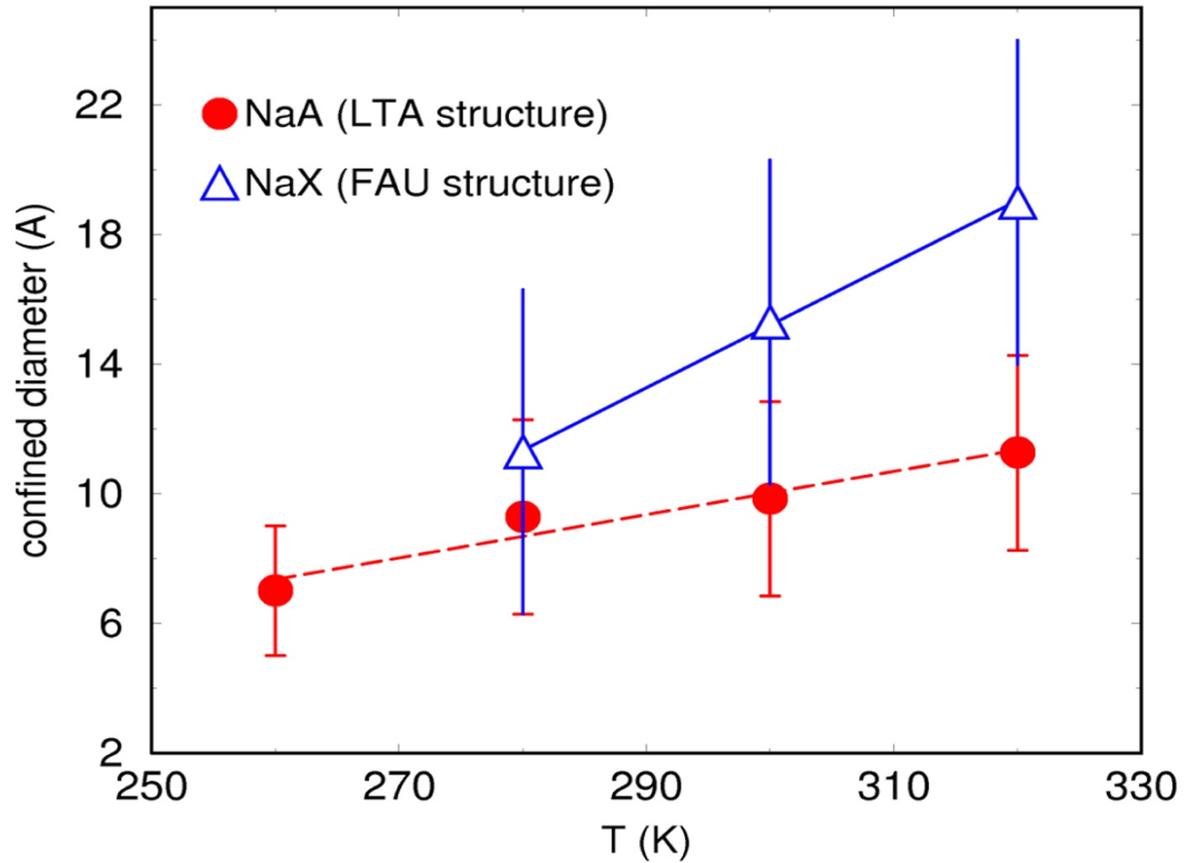


E=0 scans in temperature show that the freezing transition does not change in temperature as hydration is increased, but does become sharper.



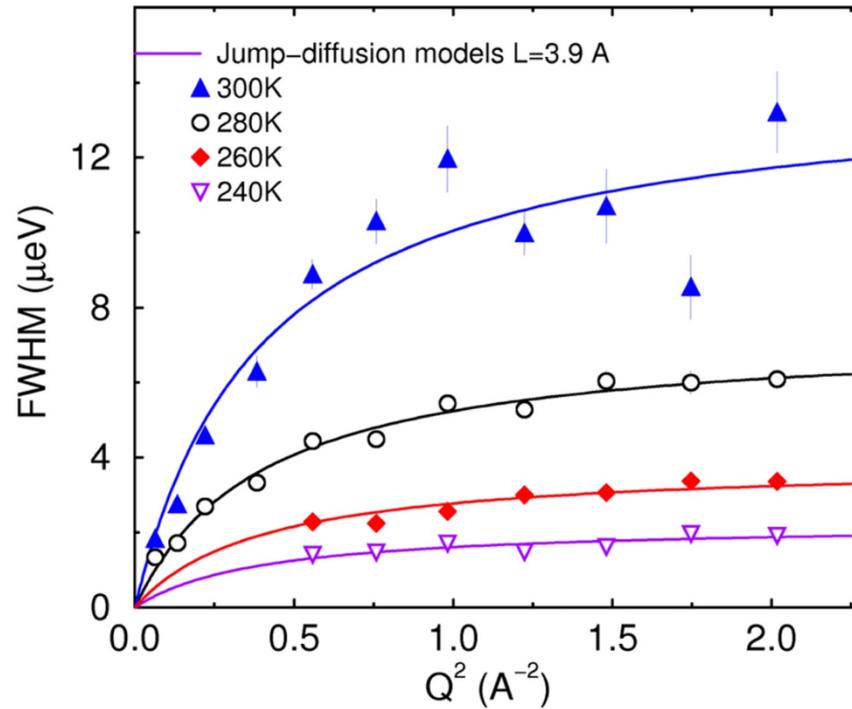
These data, for 0.18 mass fraction of water in NaA Zeolite, illustrate both confined diffusion and the presence of immobile water.

confined diameter = (FWHM of Q-width /  $2\pi$ )



The confinement diameters derived from the Q-width of the apparently elastic scattering are consistent with LTA and FAU pore sizes

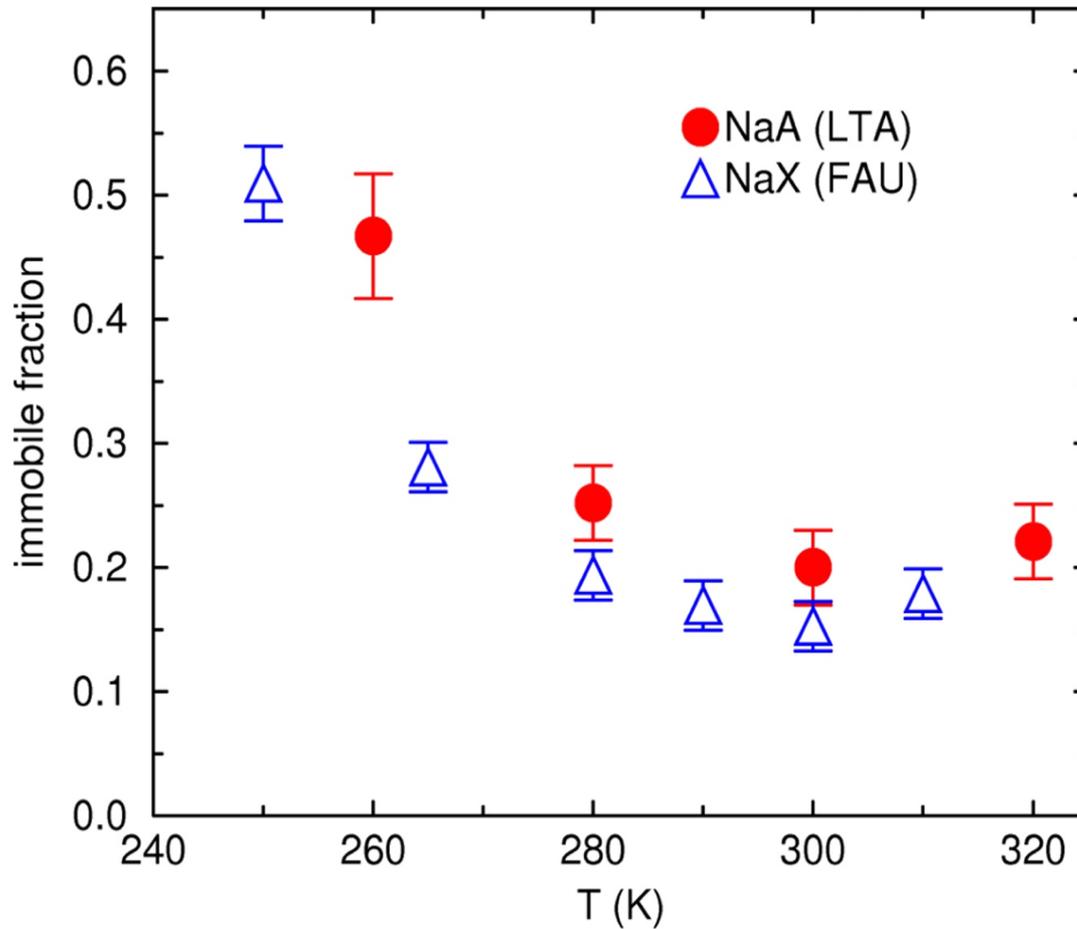
QENS widths in hydrated NaY zeolite  
Si/Al ratio=2.75 H<sub>2</sub>O massfraction=0.17



$$\Gamma(Q) = DQ^2 / (1 + DQ^2\tau_T)$$

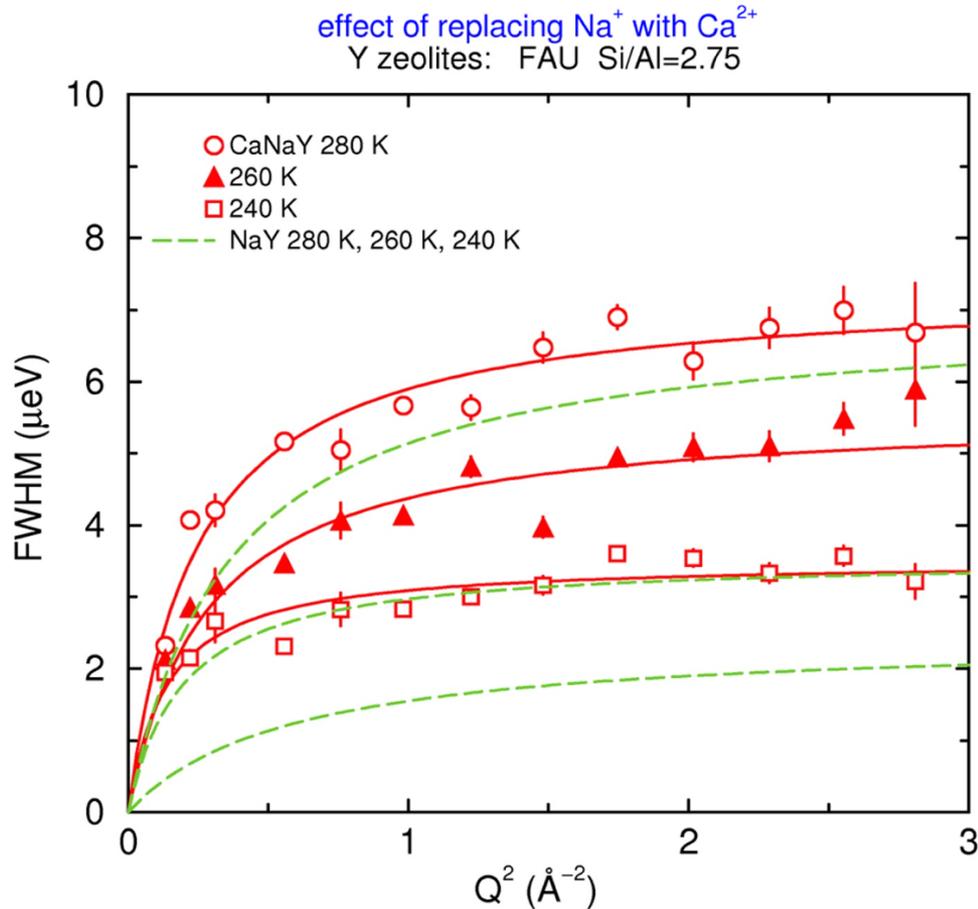
The Q dependence of the observed QENS widths can be fitted well with simple jump diffusion models. The data above on 0.17 mass fraction water in NaY zeolite are typical.

immobile water fraction for H<sub>2</sub>O in NaA and NaX



The immobile water fraction is slightly smaller for water in NaX than in NaA, but shows a similar temperature dependence.

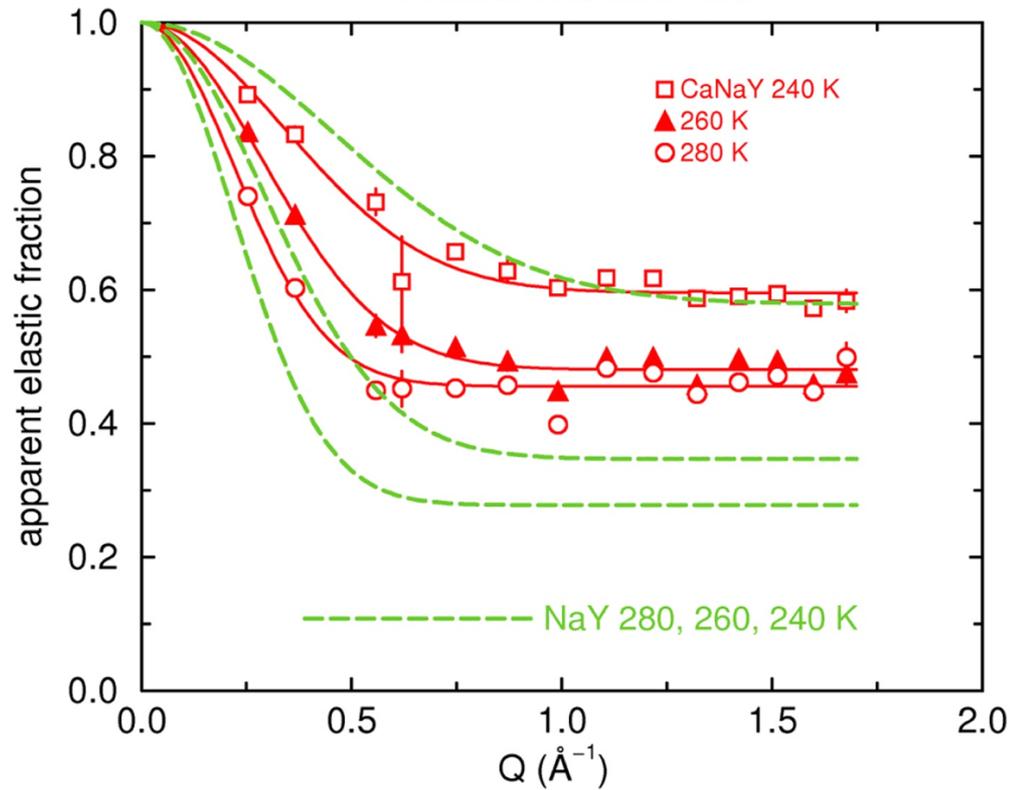
## Substituting the cation ( $\text{Ca}^{2+}$ for $\text{Na}^+$ ) also has an effect



We examined a Y zeolite (Si/Al ratio of 2.75), in which 2/3 of the Na atoms originally present were exchanged with half the number of Ca atoms. We observed significant, but not dramatic, effects on water dynamics, comparing CaNaY and NaY samples hydrated to 0.18 mass fraction of water.

The QENS widths are not changed much by Ca substitution, but show a smaller temperature dependence.

effect of replacing  $\text{Na}^+$  with  $\text{Ca}^{2+}$   
Y zeolites: FAU Si/Al=2.75



Ca substitution increases the fraction of the water that is immobile within the resolution of the instrument.

## ➤ Summary

**A simple translational jump diffusion model could be applied to understand our QENS results.**

**Framework charge** is perhaps the most important, strongly influencing the rapidity of diffusion and its temperature dependence.

**Hydration level** is also an important factor. QENS widths are roughly proportional to it.

**Cation substitution** also has effects, but the trends are less obvious within our limited data.

## OTHER NOTEWORTHY CHARACTERISTICS OF THE DATA

### IMMOBILE WATER

There is a  $Q$ -independent component to the elastic scattering, indicating that a fraction (10-30%) of the water contributing to the scattering is immobile within the resolution of the instrument. The immobile fraction rises as the sample is cooled, but changes only slowly at higher temperatures.

### CONFINEMENT

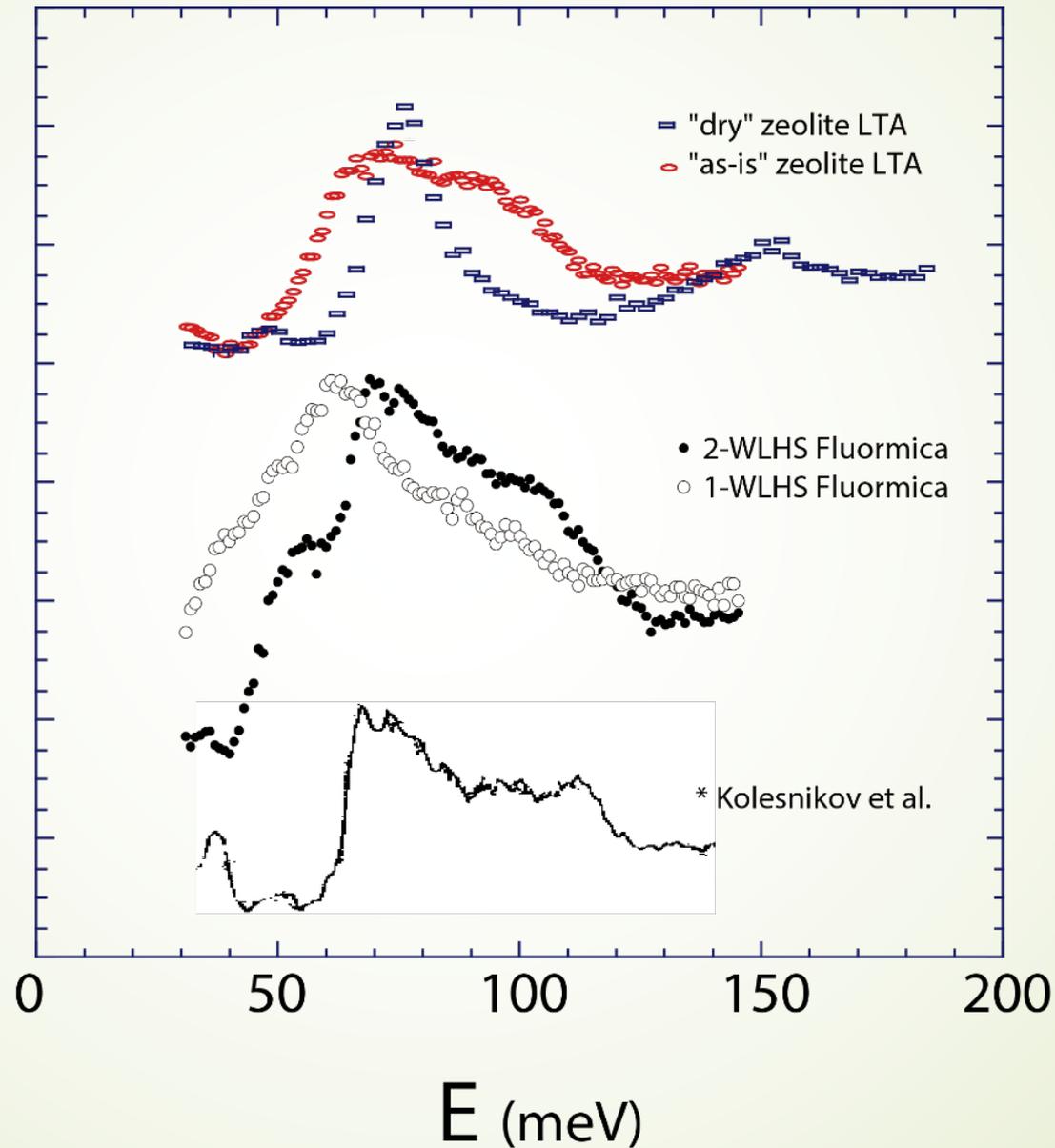
The intensity of the apparently elastic scattering rises sharply at small  $Q$ , indicating that the QENS we observe arises largely from the diffusive motion of molecules within the zeolite  $\alpha$  cages. The small- $Q$  scattering must have a QENS width due to inter-cage diffusion, but the latter is too narrow to be observed with  $1 \mu\text{eV}$  resolution.

### JUMP DIFFUSION

The QENS widths tend to saturate at large  $Q$ , indicating jump-like motions for translational diffusion within a cage.

Librational mode spectra taken using a filter analyzer neutron spectrometer (FANS)

NEUTRON INTENSITY (ARB. UNITS)





- ▶ Neutron spectroscopy of water dynamics in NaX and NaA zeolites

WA **Kamitakahara**, N **Wada** - Physical Review E, 2008 - APS

- ▶ Dynamics of intercalated water molecules in synthetic layered silicates

WA **Kamitakahara**, N **Wada** - Molecular Crystals and Liquid ..., 2000 - Taylor & Francis

- ▶ Structural, lattice-dynamical and magnetic properties of alkali-metal intercalated vermiculite

..., Y Omura, N **Wada**, WA **Kamitakahara**... - ... Crystals and Liquid ..., 1998 - Taylor & Francis

# Conclusions

The **phonon dynamics** of non-hydrated mica samples can be studied by inelastic neutron scattering. However, hydrated layered silicates are rather difficult to study because of their crystallinity and hydrogen atoms.

By QENS, the **dynamics of water molecules** in layered silicates and zeolites were found to be influenced by framework charge, hydration level, cation substitution.

## **Future work**

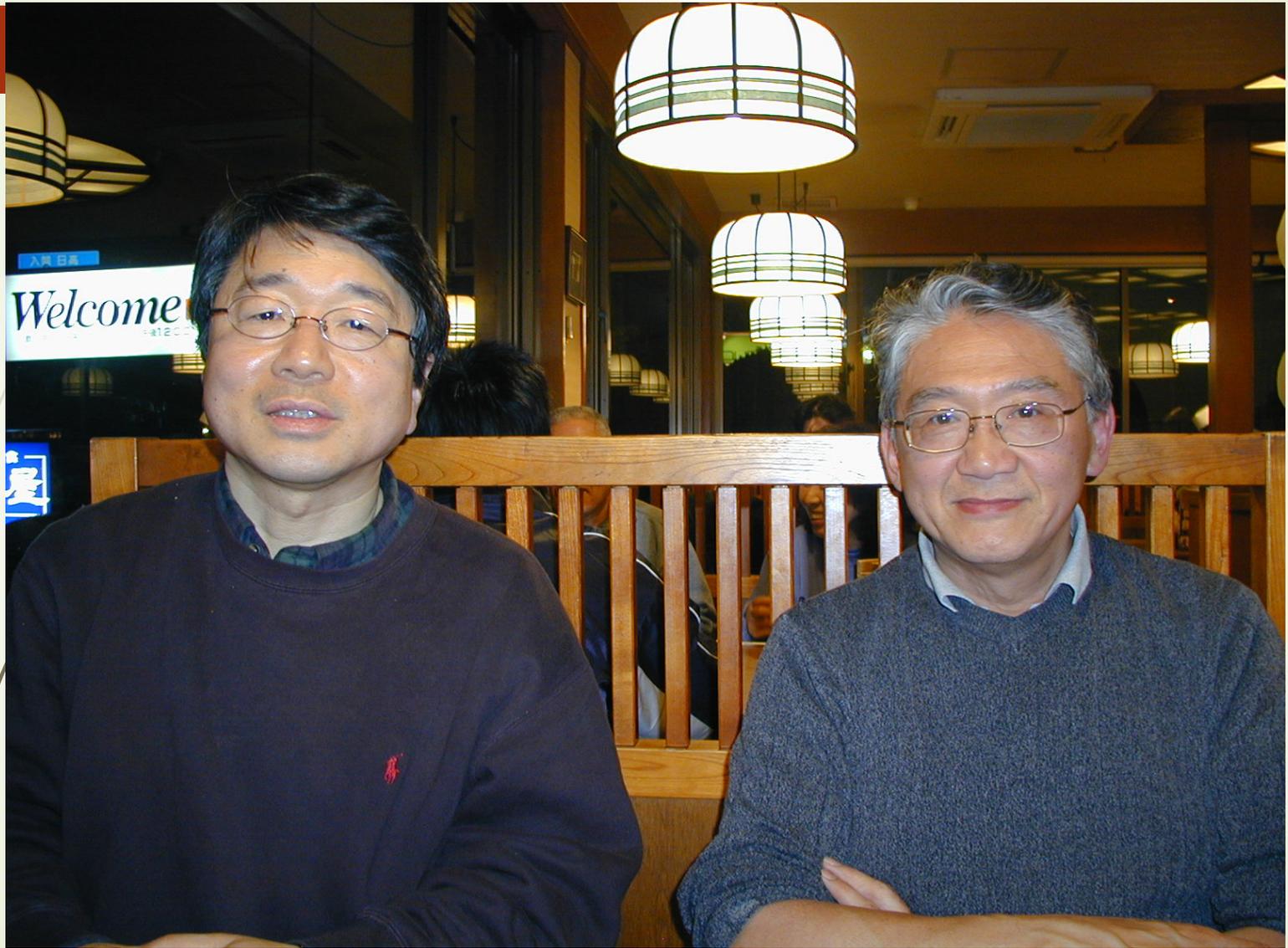
Zeolites with high Si/Al ratios may be of interest in terms of “**water dynamics in confined geometry**.”

**Synthetic clays** may provide an interesting playground to intercalation and 2D physics.

















**Thank you  
for your attention!**