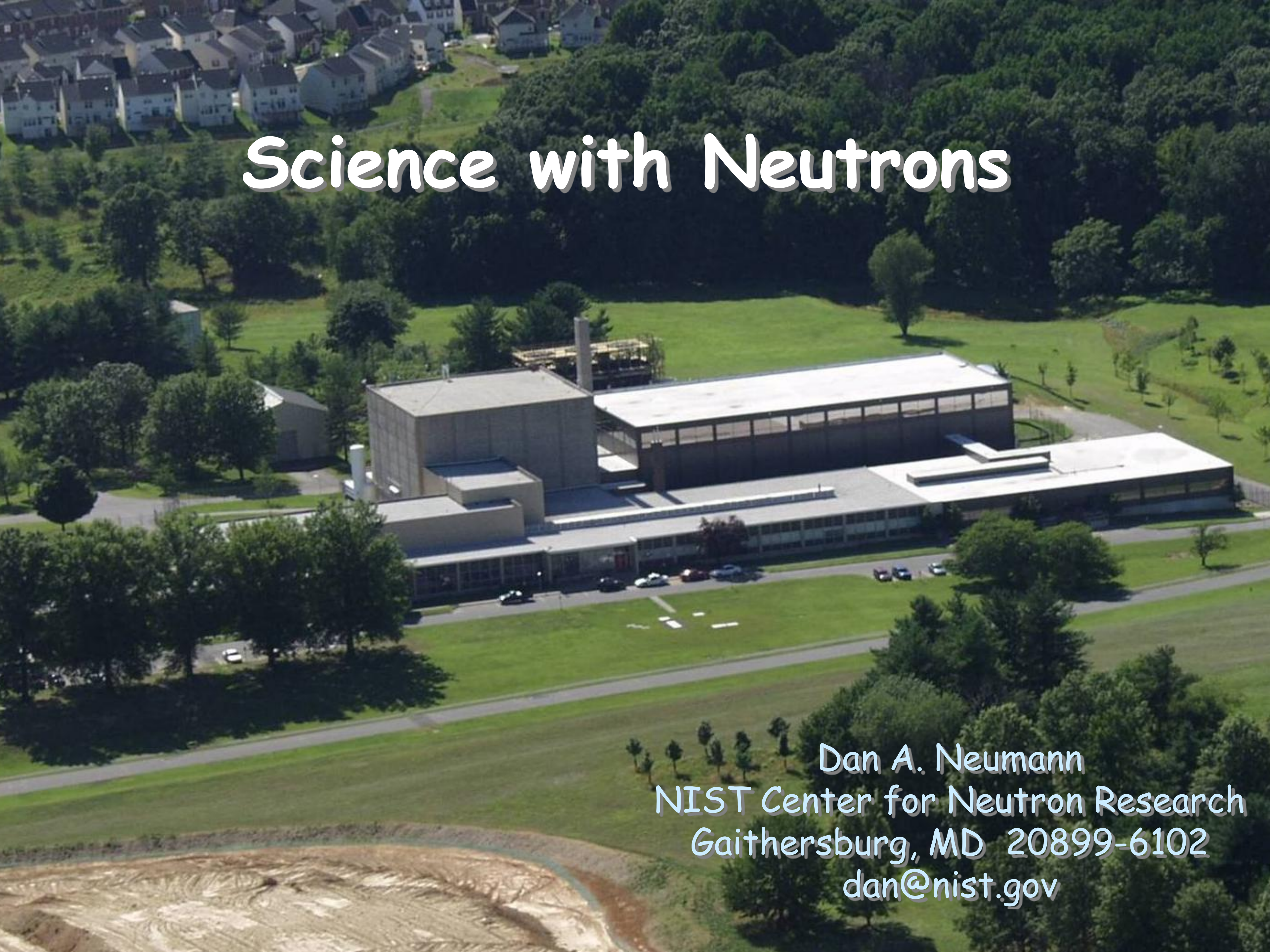


Science with Neutrons

Dan A. Neumann
NIST Center for Neutron Research
Gaithersburg, MD 20899-6102
dan@nist.gov

Why Neutron Scattering

1) Ability to measure both energy *and* momentum transfer

   Geometry of motion

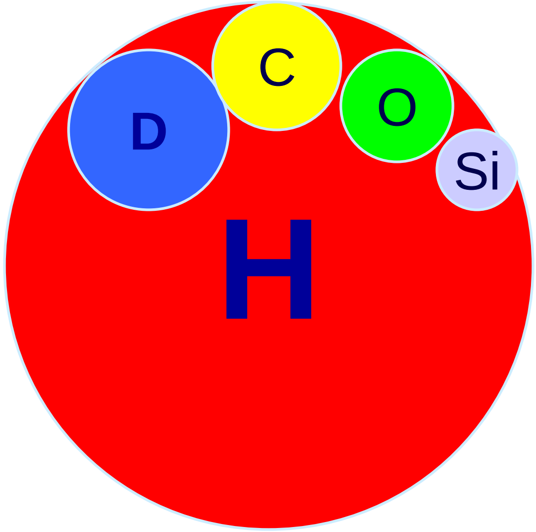
2) Neutrons scatter by a nuclear interaction => different isotopes scatter differently

   H and D scatter very differently

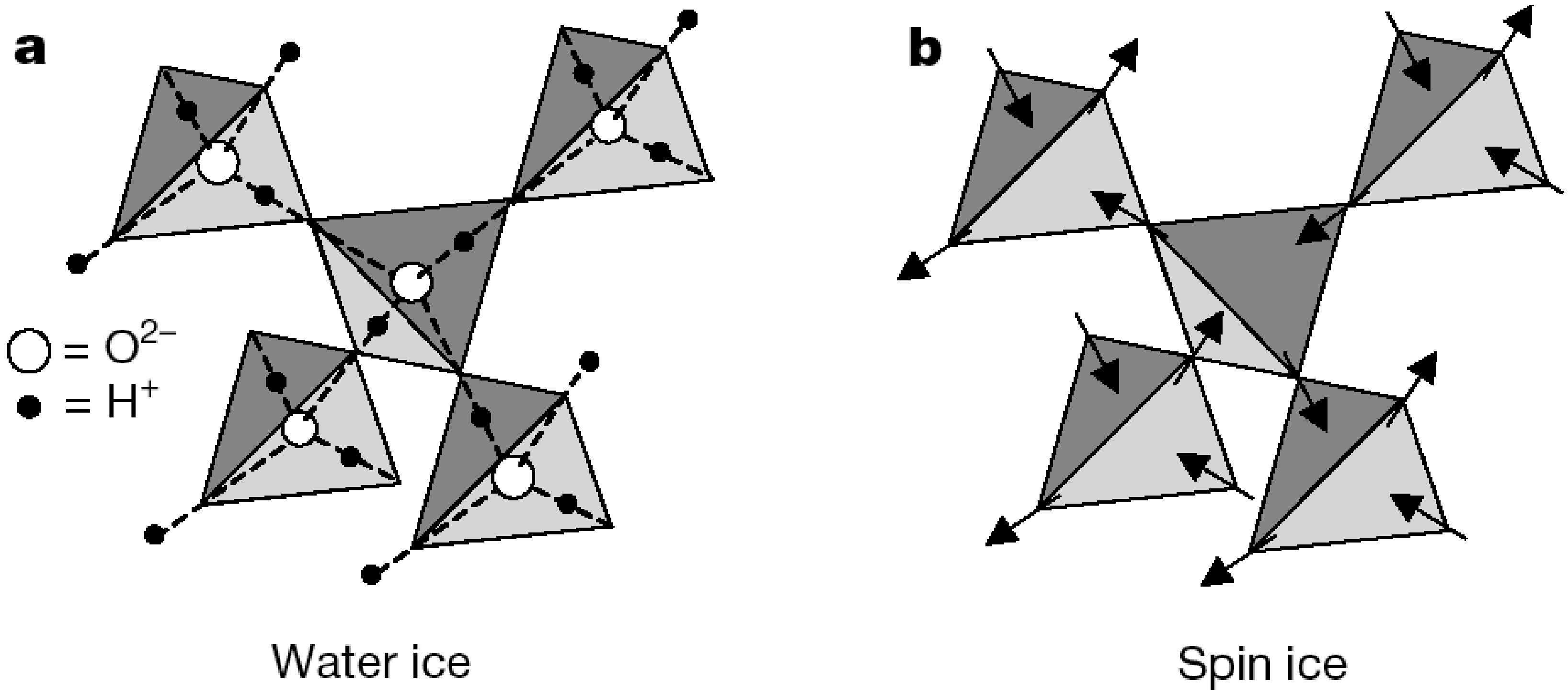
3) Simplicity of the interaction allows easy interpretation of intensities

   Easy to compare with theory and models

4) Neutrons have a magnetic moment

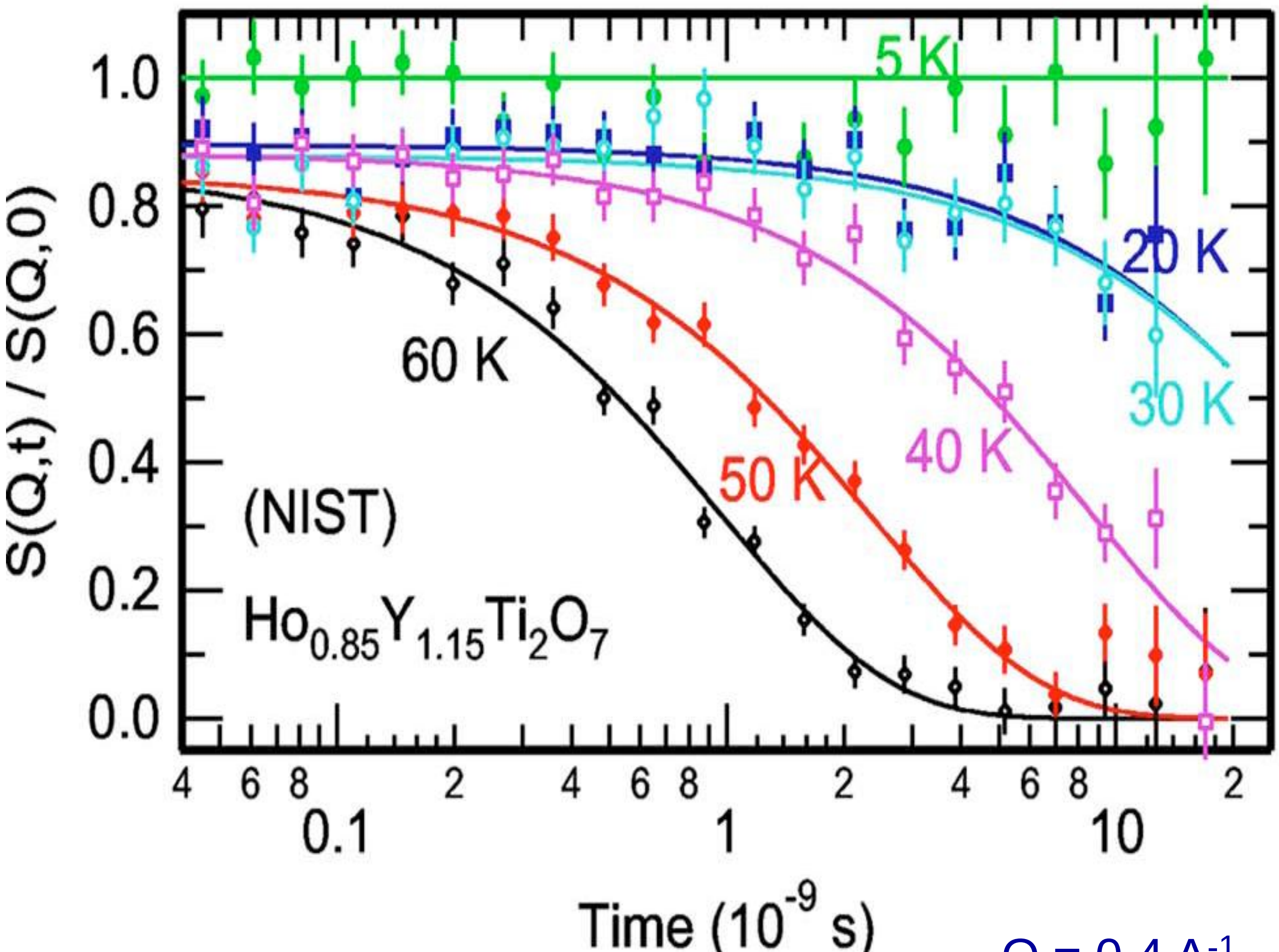


Spin Ice



Spins constrained to local <111> axes

Dynamics of Spin Ice



$$\frac{S(Q,t)}{S(Q,0)} = A \exp(-t/\tau)$$

$$\tau = \tau_o \exp(\Delta/k_B T)$$

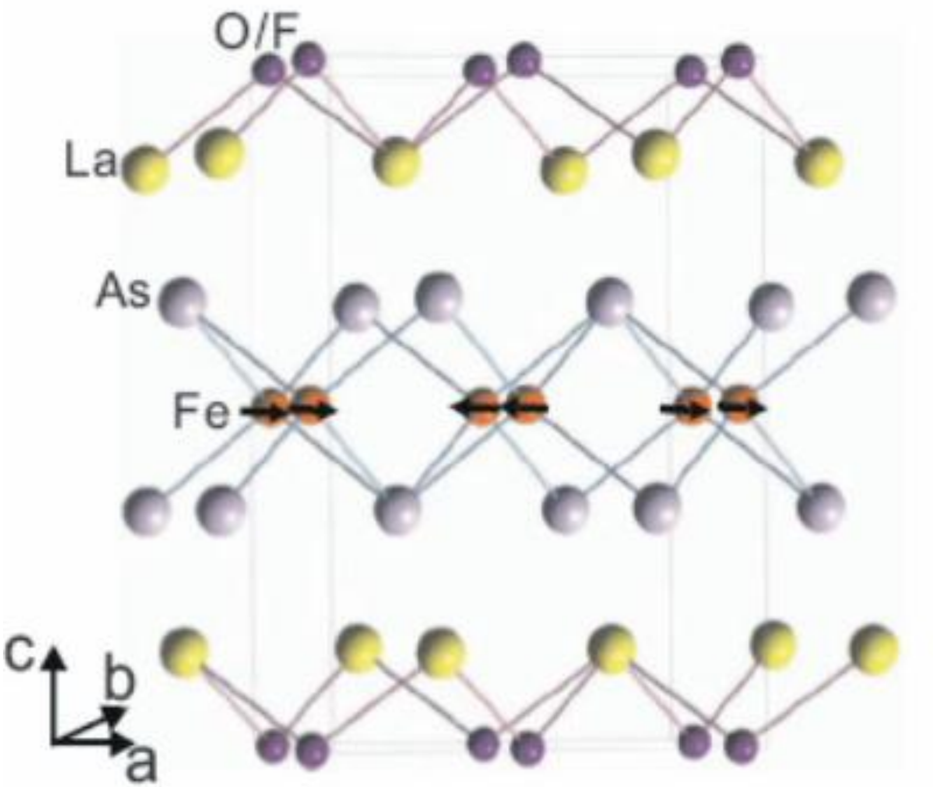
Above 40 K

Δ = 23 meV

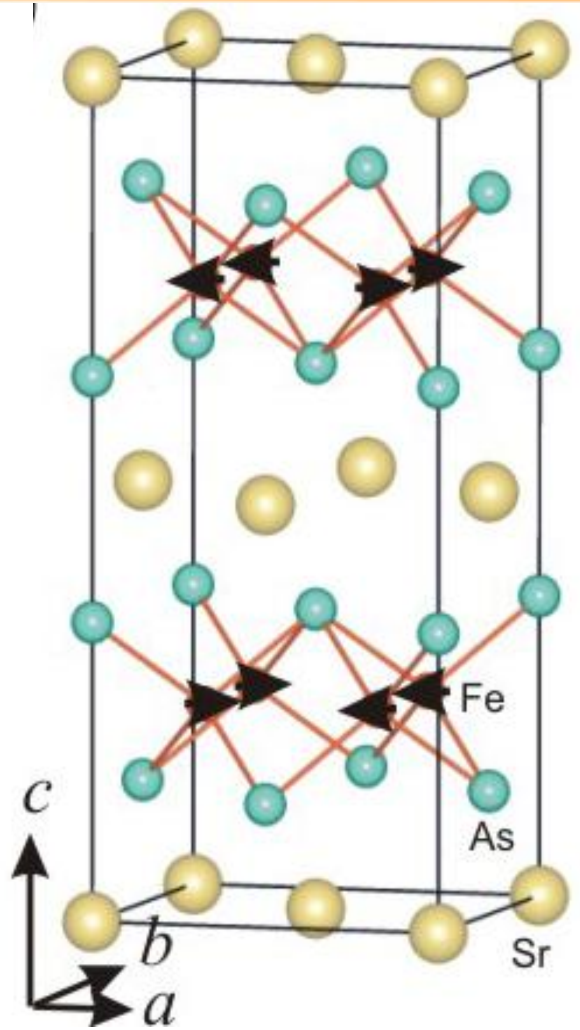
$Q = 0.4\ A^{-1}$

Ehlers *et al.*, PRB **73**, 174429 (2006).

Fe – Pnictide Superconductors



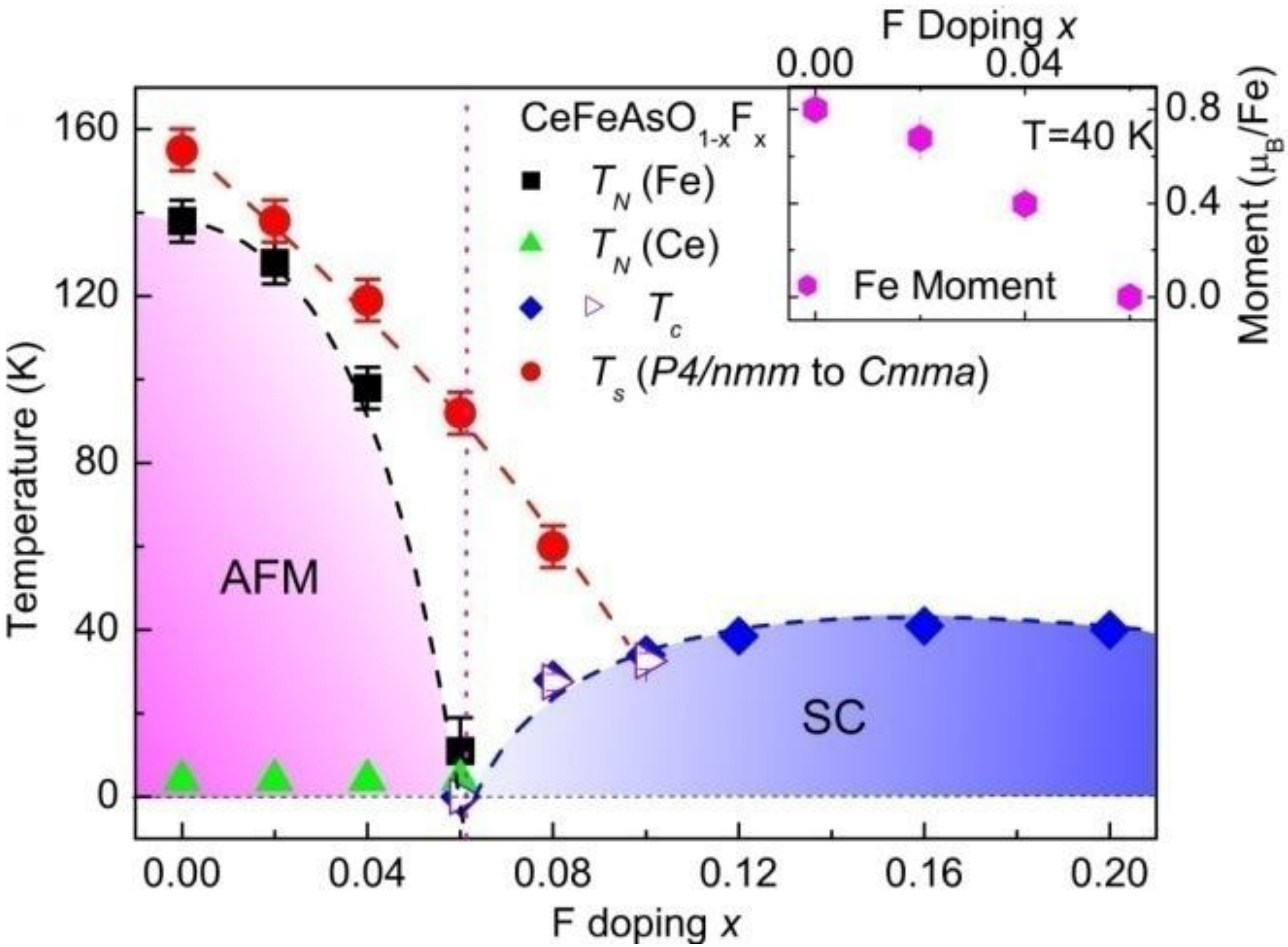
LaFeAsO



$SrFe_2As_2$

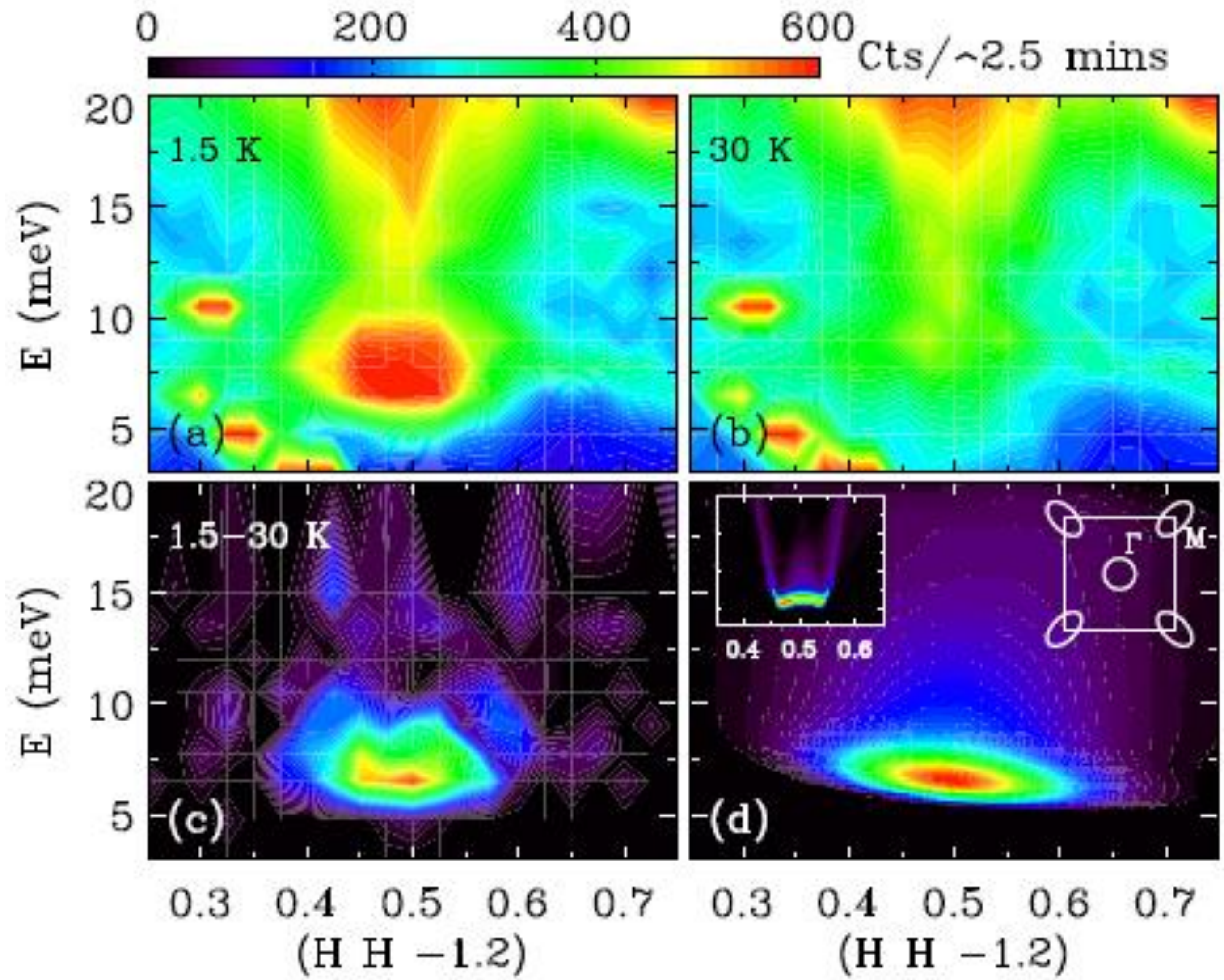
de la Cruz *et al.*, Nature **453**, 899 (2008)

Phase Diagram of $CeFeAsO_{1-x}F_x$



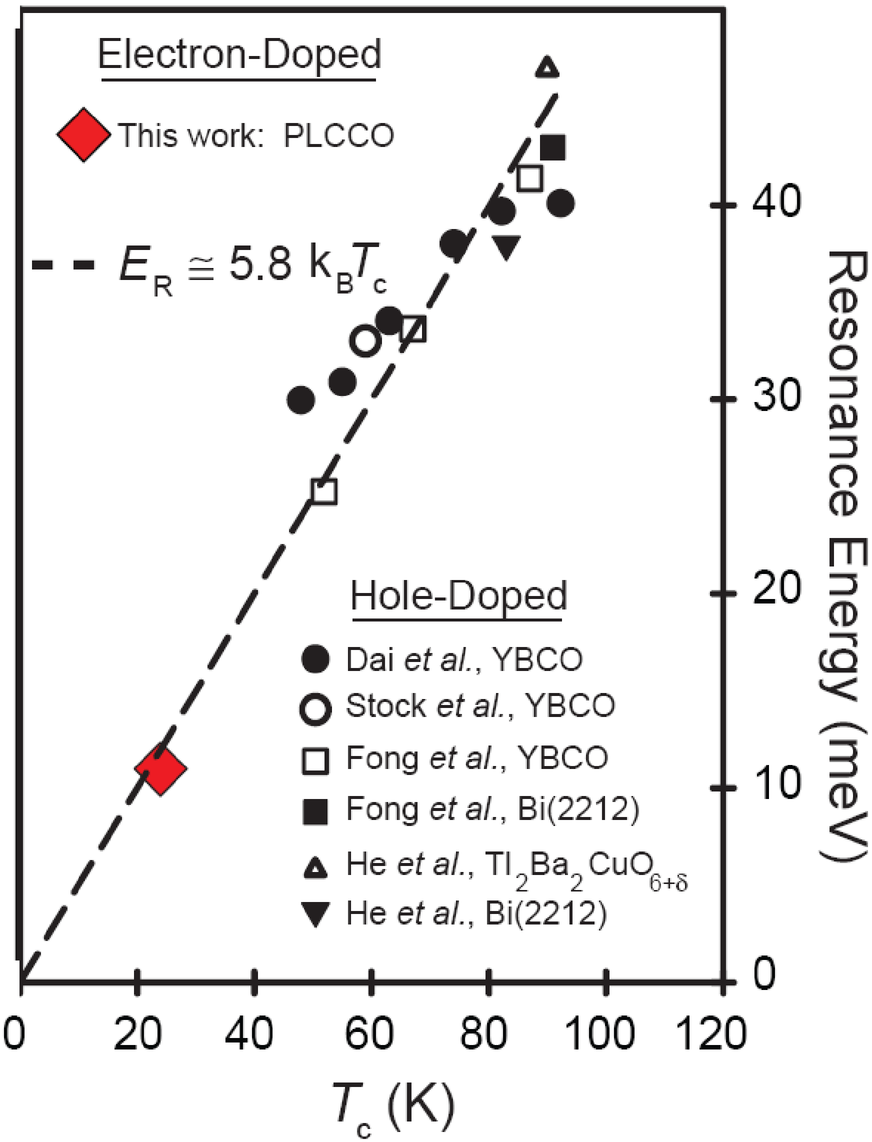
J. Zhao *et al.*, Nature Materials **7**, 953 (2008)

Spin Resonance in $Fe(Se_{0.4}Te_{0.6})$



Qiu *et al.*, (2009)

Resonance in Cuprate Superconductors

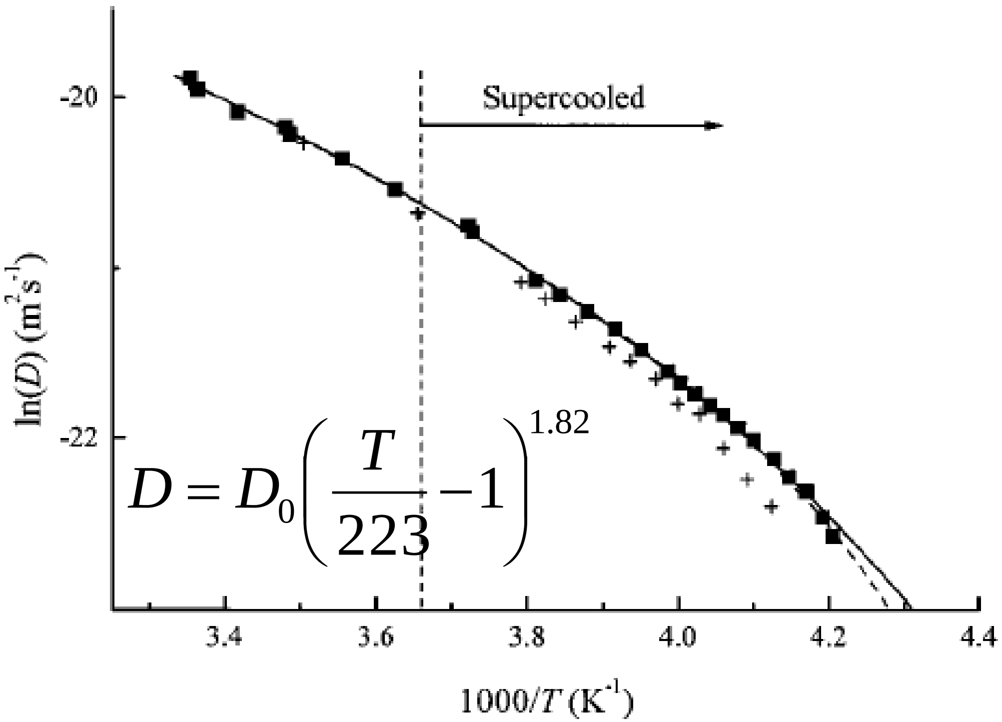


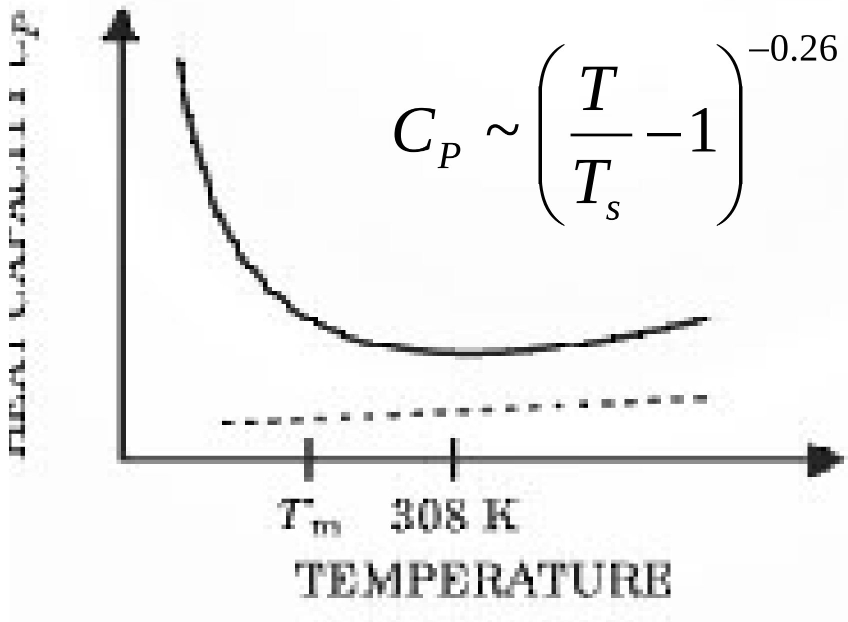
A magnetic "resonance" in YBaCuO at about 41 meV, is widely viewed to be central to high temperature superconductivity.

Neutron scattering revealed a magnetic resonance was observed in an "electron-doped" superconductor PLCCO ($Pr_{0.88}LaCe_{0.12}CuO_{4-\delta}$) at 11 meV.

Wilson *et al.* Nature(2006)

Water

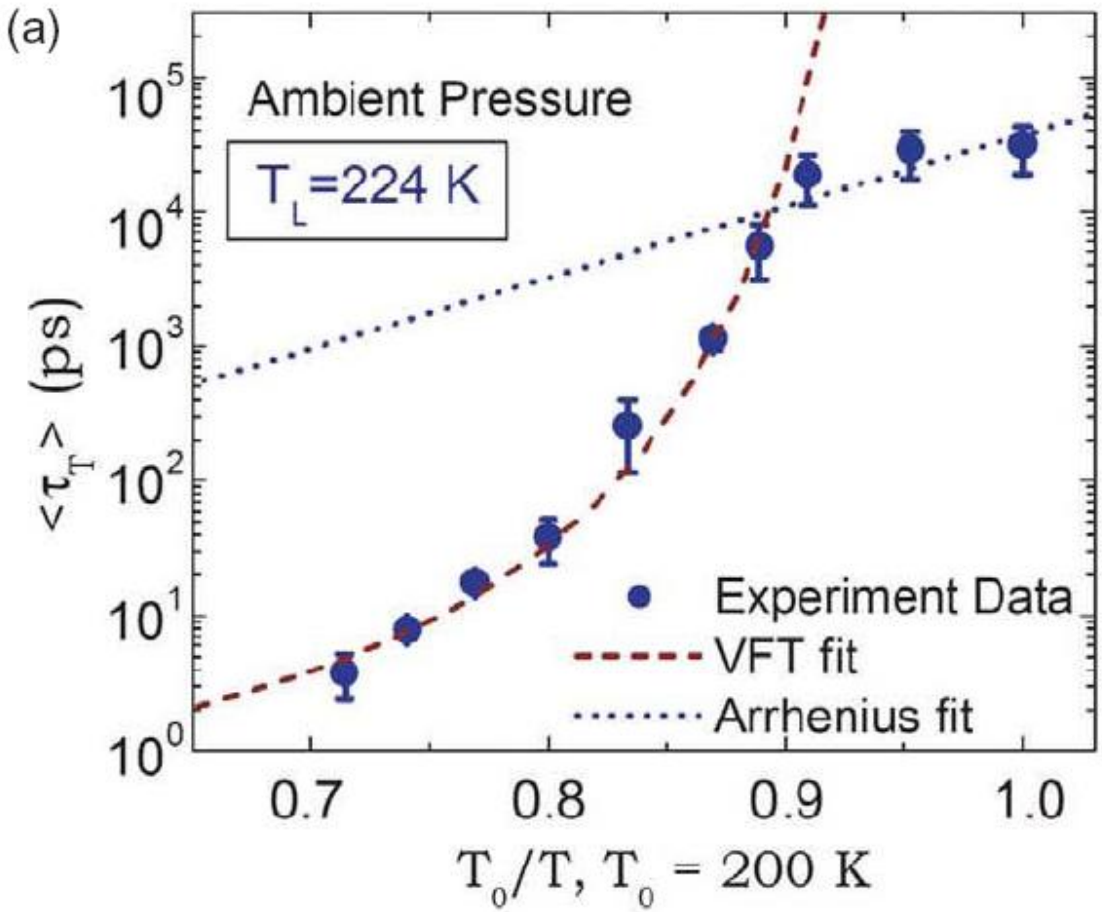




Angell et al., J. Phys. Chem., **77**, 3092 (1977)

Price *et al.*, J. Chem. Phys. A **103**, 448 (1999)

Water in Confinement



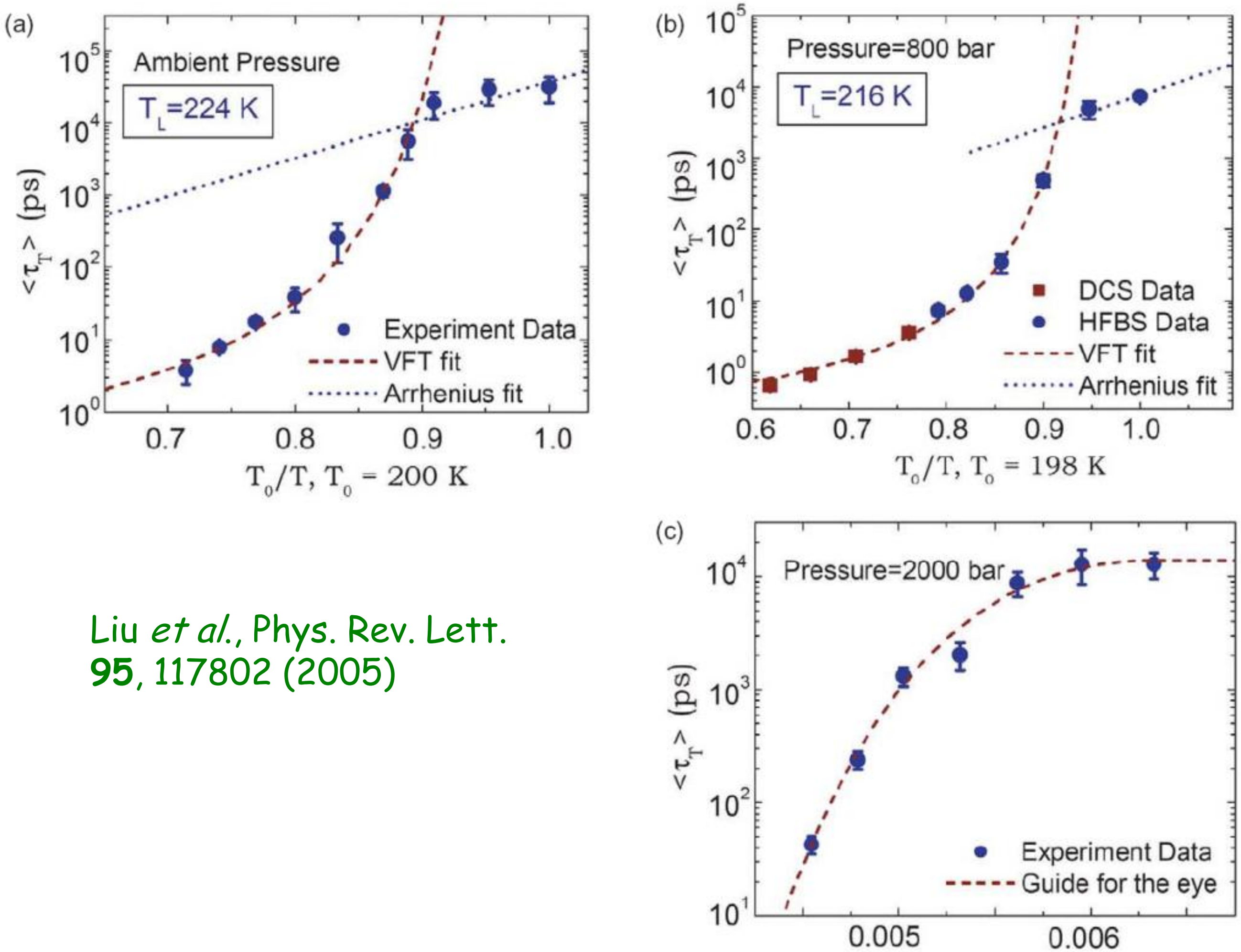
Thermodynamic measurements suggest that supercooled water should undergo a fragile-to-strong transition between two liquid phases at around 228 K. However, supercooled bulk water reaches its homogeneous nucleation point and crystallizes into ice at 235 K.

Vogel-Fulcher-Tammann law

$$\tau = \tau_o \exp[DT_o/(T - T_o)]$$

Faraone *et al.*., J. Chem. Phys., **121**, 10843 (2004)

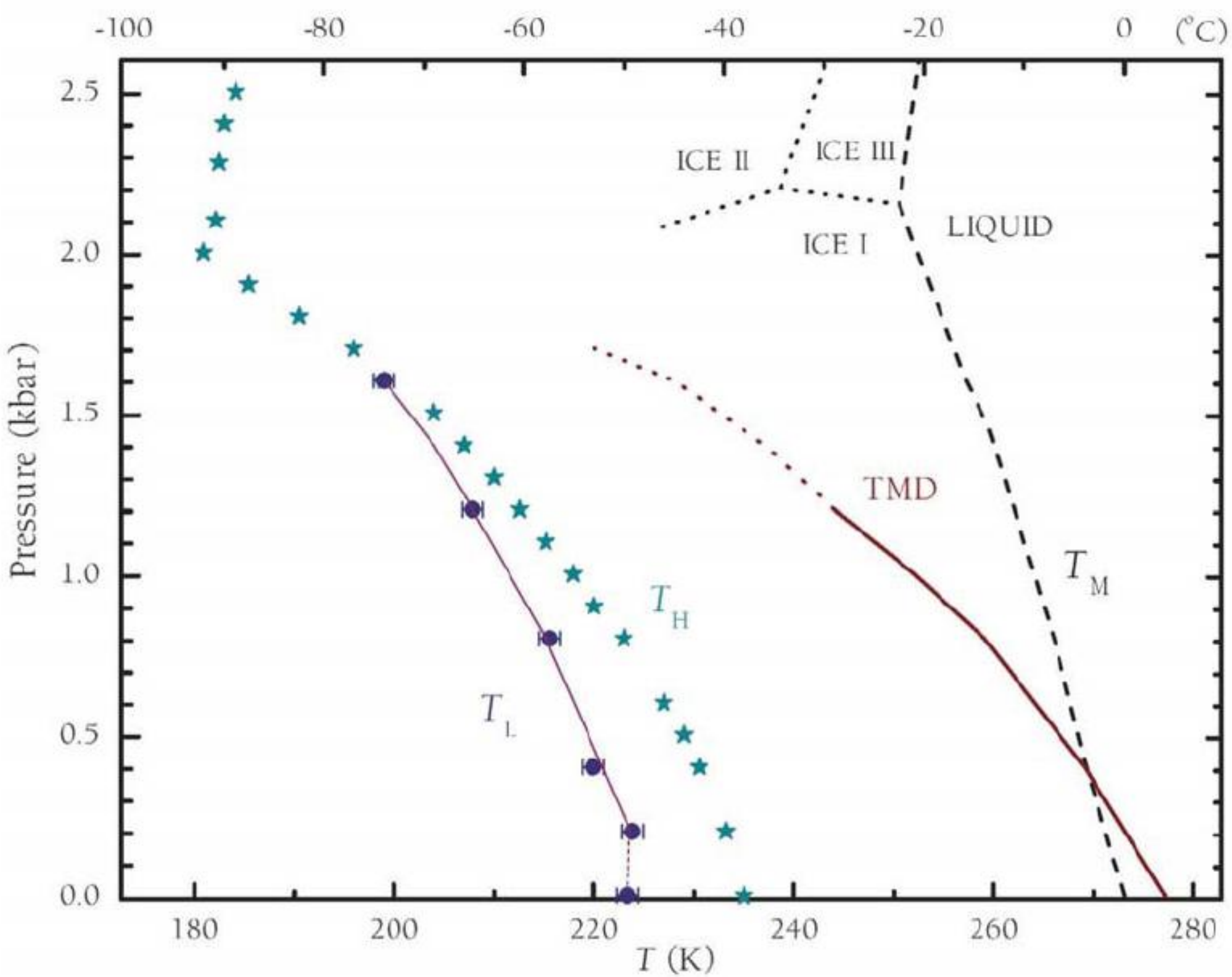
Water in Confinement



The anomalies in the thermodynamic quantities also indicate the possible existence of a low-temperature critical point near this transition temperature, but at somewhat elevated pressure.

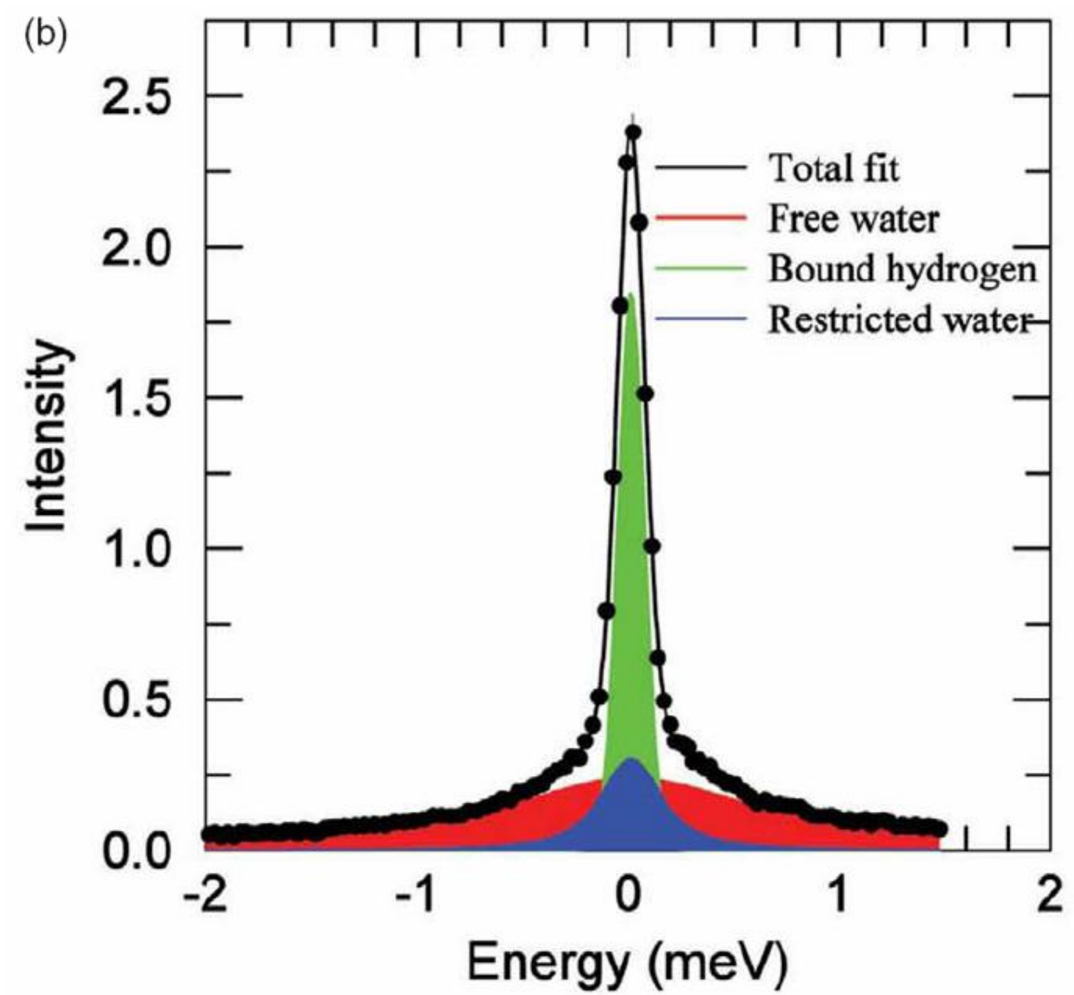
Liu *et al.*, Phys. Rev. Lett. **95**, 117802 (2005)

Water in Confinement



Liu *et al.*, Phys. Rev. Lett., **95**, 117802 (2005)

Quasielastic Scattering from Cement



Thomas *et al.*, J. Am. Ceram. Soc. **84**, 1811 (2001)

More than 800 million metric tons of Portland cement are produced each year.

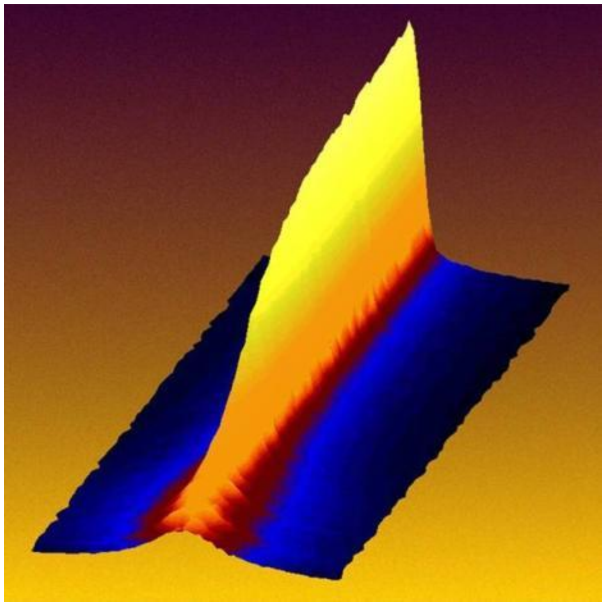
Tricalcium silicate (Ca_3SiO_5) is the most important and abundant component of Portland cement.

Dicalcium silicate (Ca_2SiO_4) is the second most abundant component.

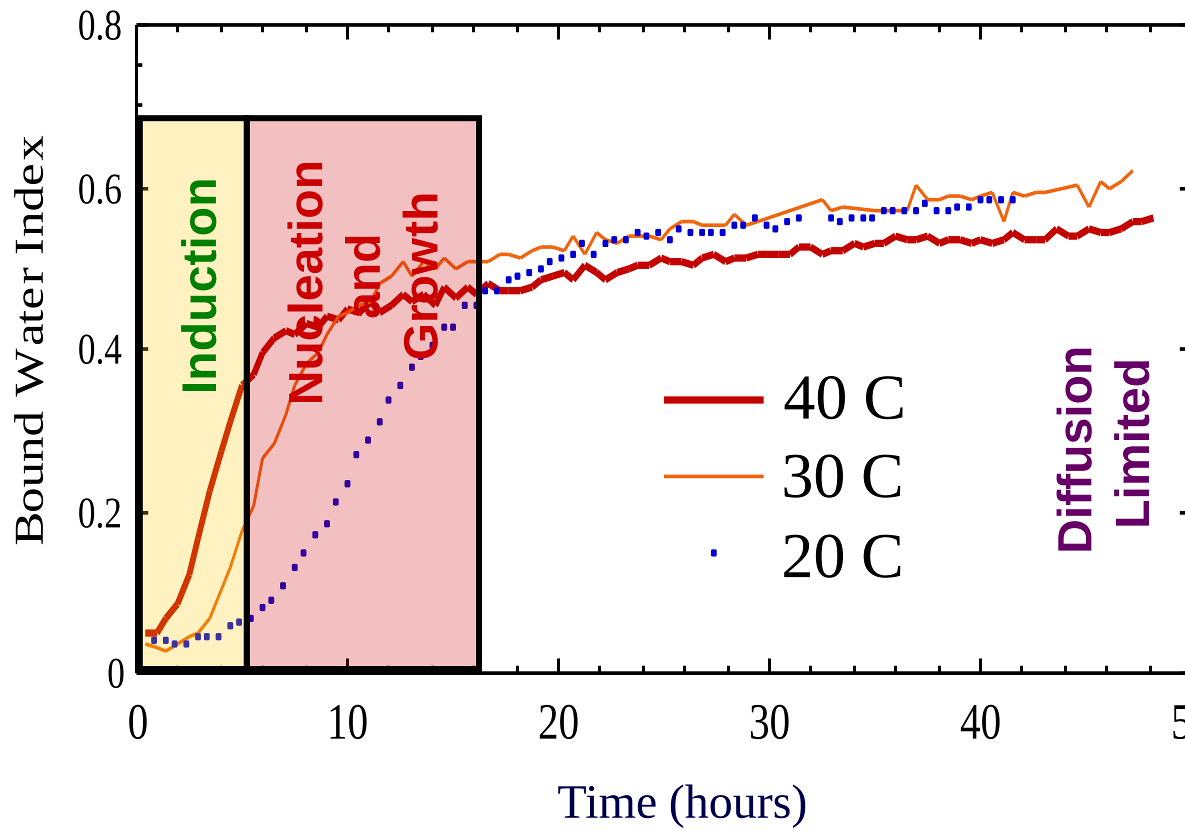
These two components typically account for approximately 80 wt.% of Portland cement.

$$BWI = \frac{Green + Blue}{Green + Blue + Red}$$

Kinetics of the Hydration of Cement

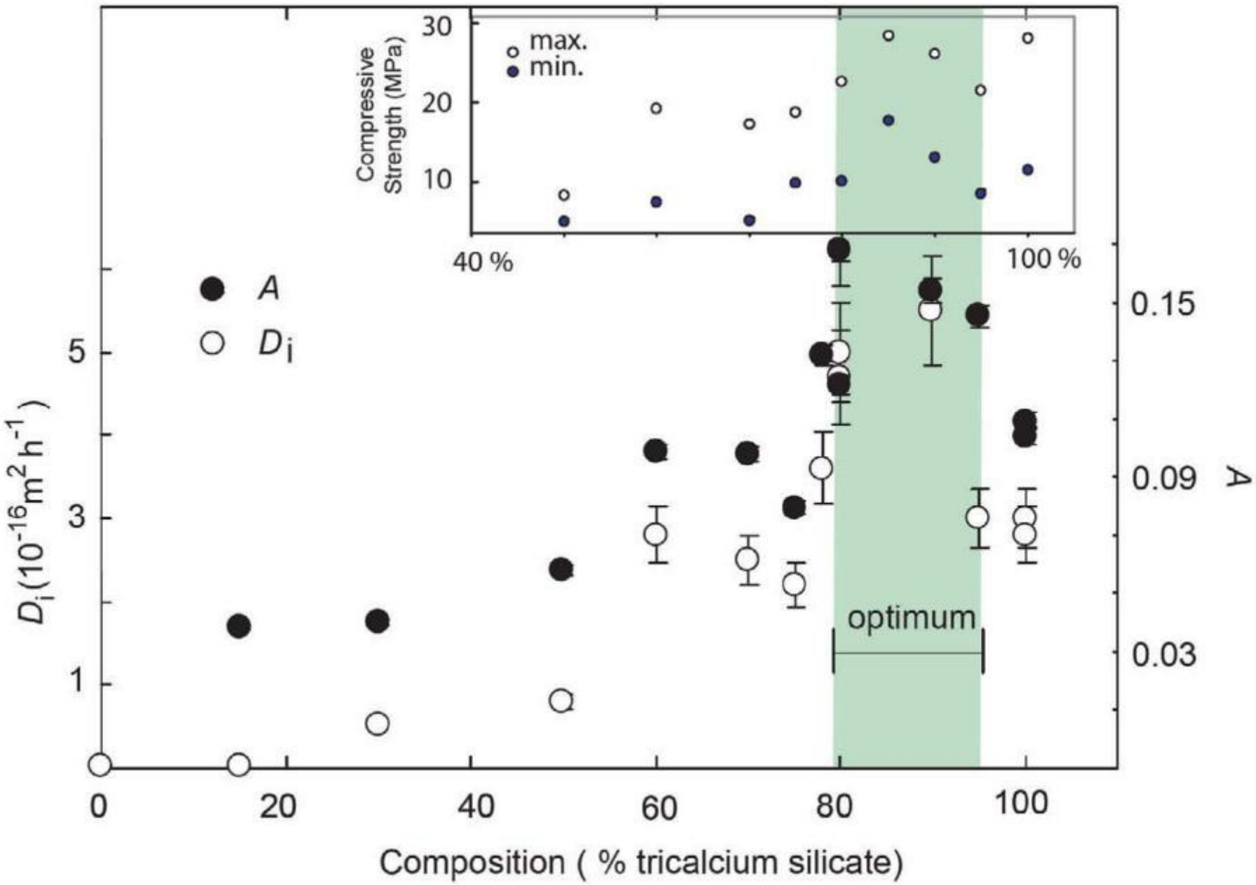


The main hydration reaction occurs over 24-48 hours. There are 3 periods.



FitzGerald *et al.*,,Chem. Mater. **10**, 397 (1998).*

Quasielastic Scattering from C3S-C2S Mixtures



Data is fit to kinetic models.

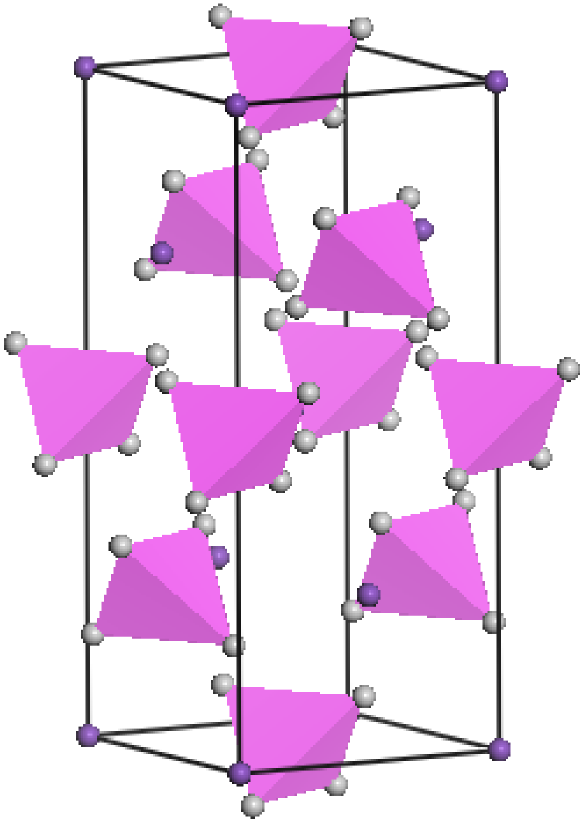
A is the amount of product that would have been formed if the "nucleation and growth" regime had continued to ∞ time.

D_i is the effective diffusion constant that controls the reaction in the "diffusion limited" regime.

Peterson *et al.*,
J. Phys. Chem. B **109**, 14449 (2005);
Physica B **385-386**, 481 (2006).

Neutron Vibrational Spectroscopy

- Understanding the binding of hydrogen is critical to developing effective materials for H storage
- Vibrational spectroscopy using neutrons is preferentially sensitive to those modes involving H motions
- Neutron spectra can easily be modeled using first principles calculations

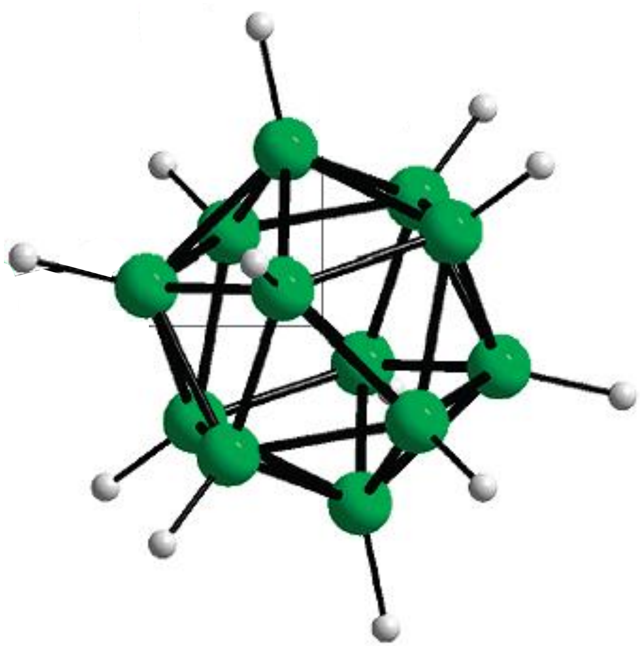


$NaAlH_4$

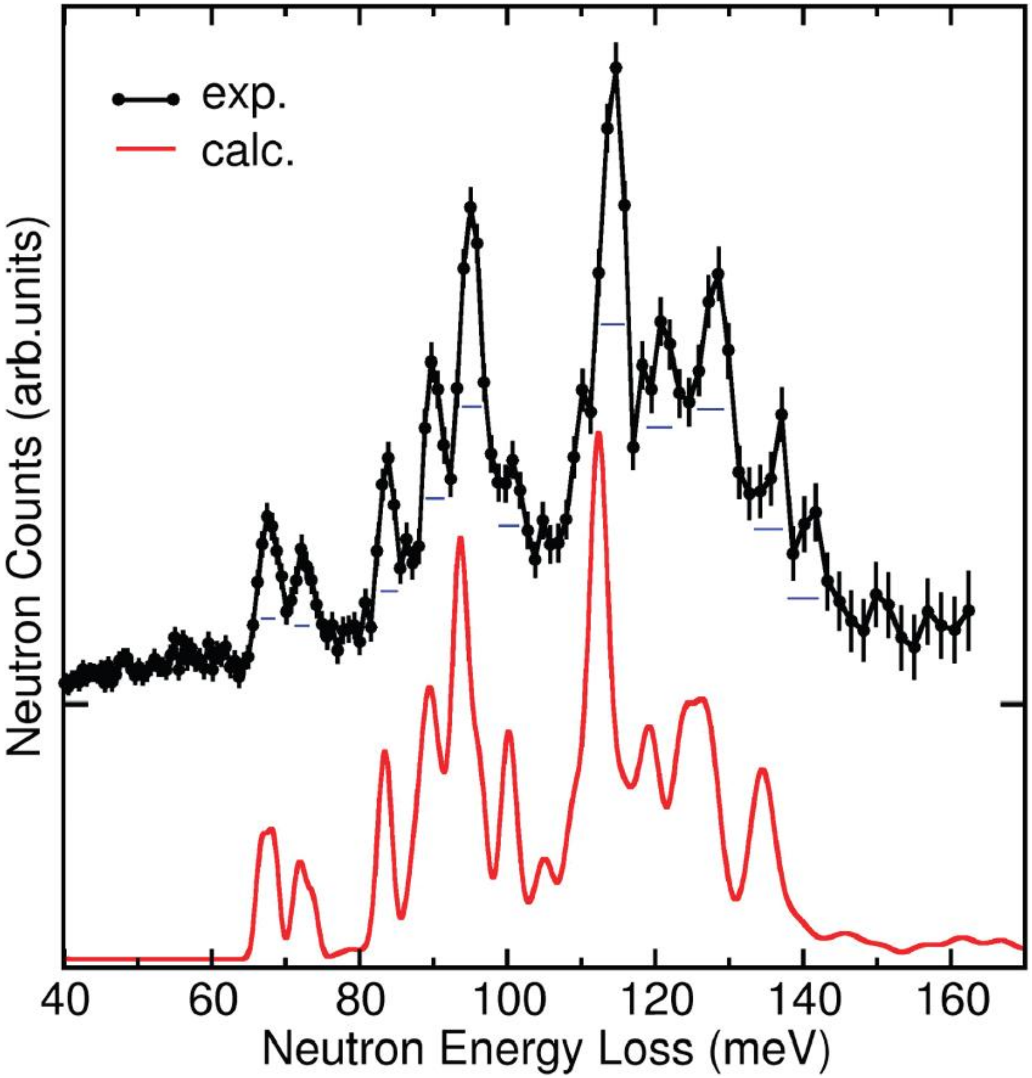
Li - Borohydride

$LiBH_4$ releases H during decomposition

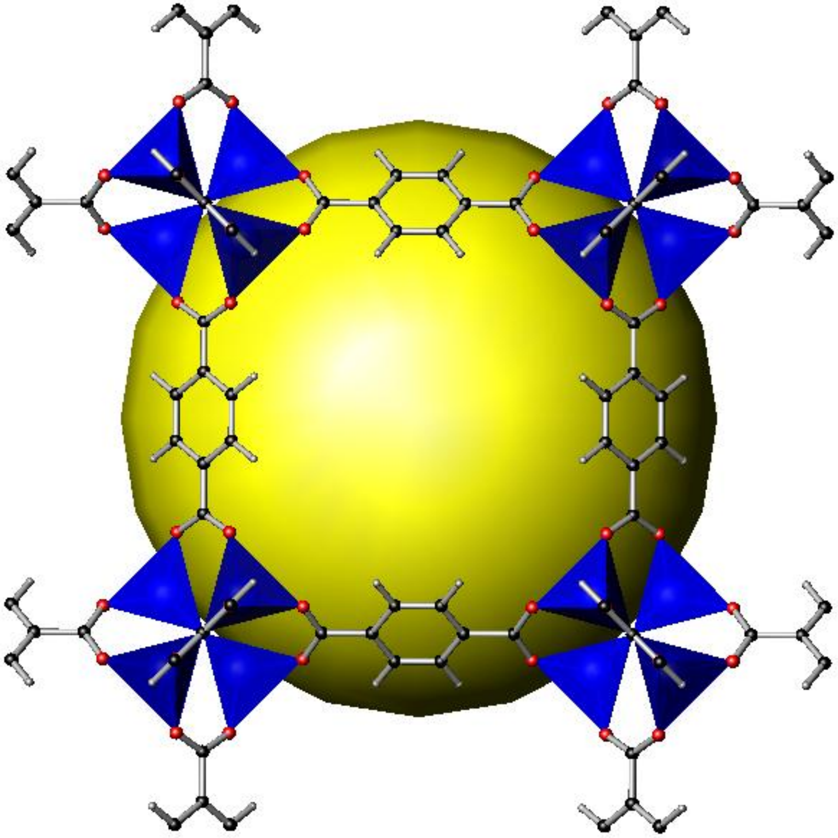
$Li_2B_{12}H_{12}$ is a stable intermediate



Her *et al*, Inorg. Chem. (2008)



Metal-Organic Framework (MOF) Materials



- MOF's consist of metal oxide clusters linked by organic linkers
  - High surface area materials
  - Crystalline nano-porous material with tunable pore size by changing the organic linker
  - Functionality of the linker can also be varied

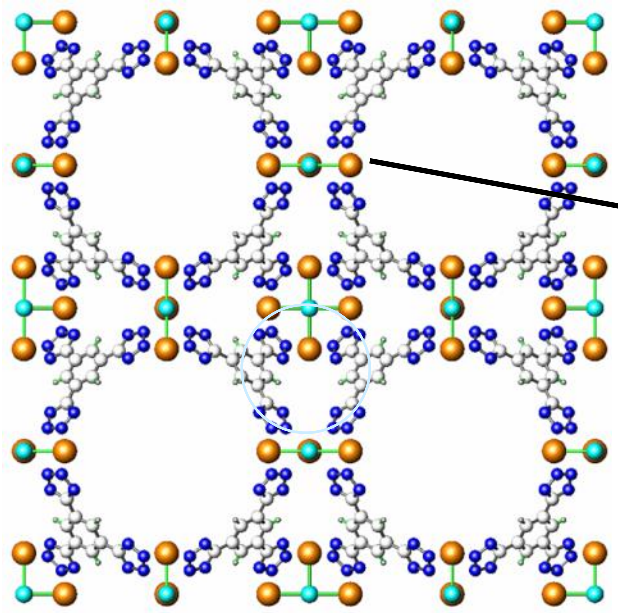
Li, et al., Nature **402**, 276 (1999).

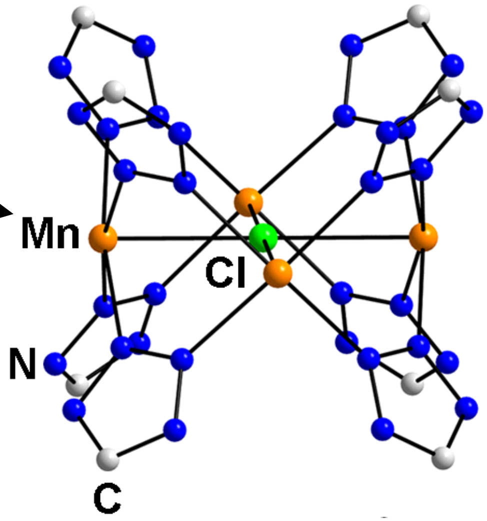
Rosi et al., Science **300**, 1127 (2003).

$Mn_{1.5}((Mn_4Cl)_3BTT_8)$

As synthesized sample: $[Mn(DMF)_6]_3[(Mn_4Cl)_3(BTT)_8(H2O)_{12}]_2 \cdot 42DMF \cdot 11H_2O \cdot 20CH_3OH$
After desolvation: $[Mn(DMF)_6]_{1.5}[(Mn4Cl)_3(BTT)_8(DMF)_{12}]$

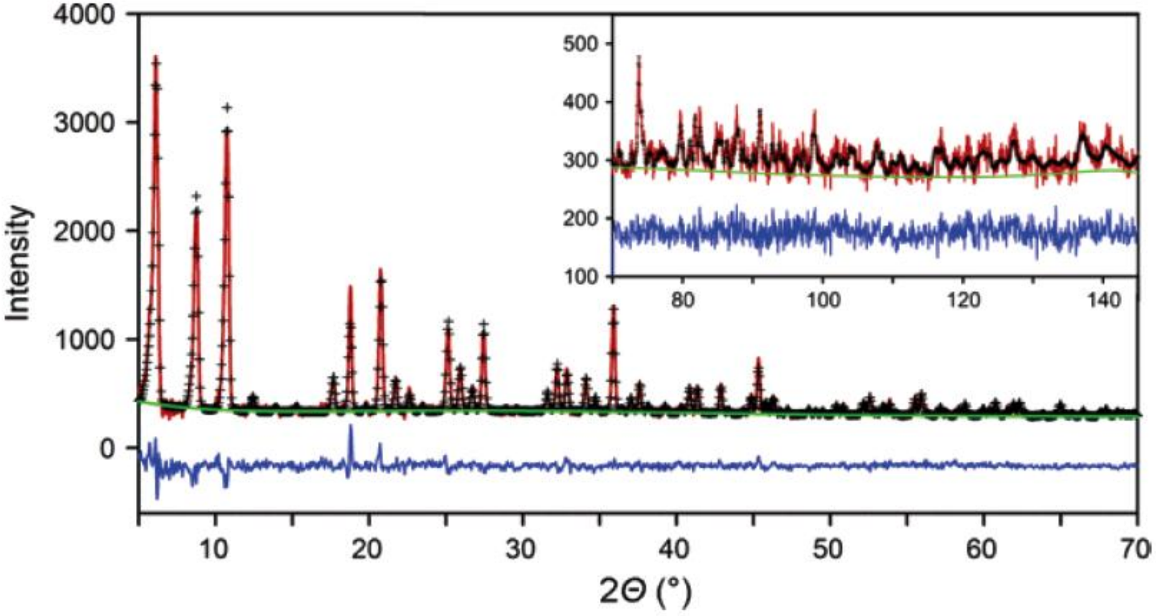
After solvent exchange and desolvation, a new material can be formed with molecular formula: $Mn_{1.5}[(Mn4Cl)_3BTT_8)]$

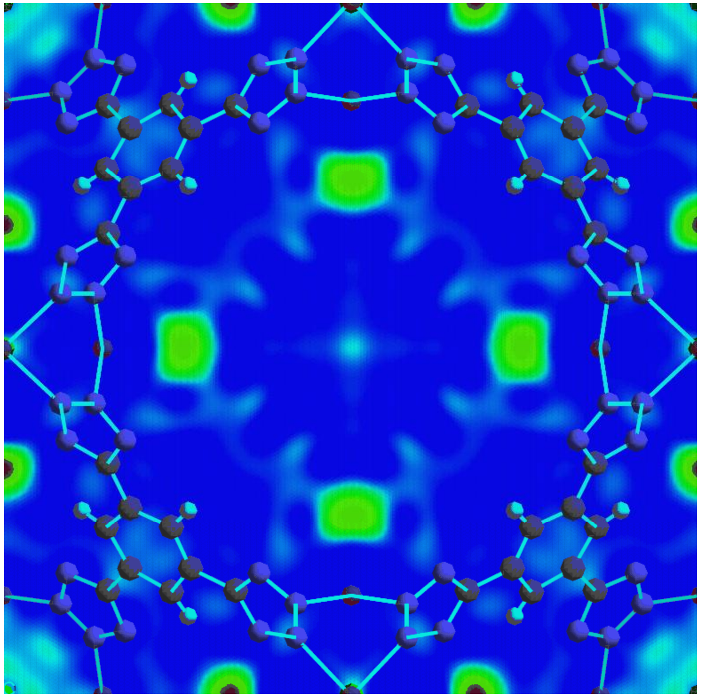




M. Dinca *et al.*, JACS **128**, 16876 (2006)

Powder diffraction patterns

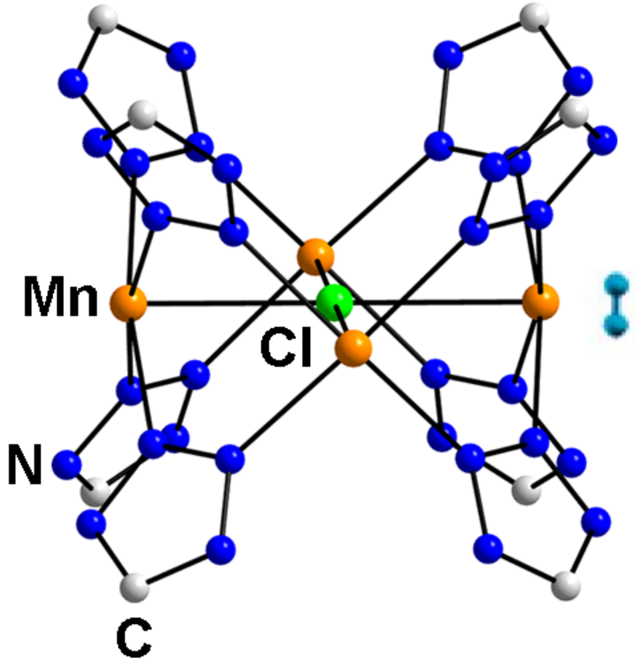




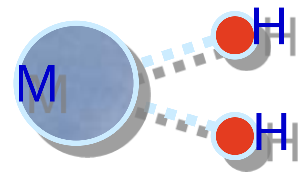
H_2 is treated as a super atom with double occupancy.
Fourier difference plot is used to visualize the initial position of H_2.

M. Dinca *et al.*, JACS **128**,16876 (2006)

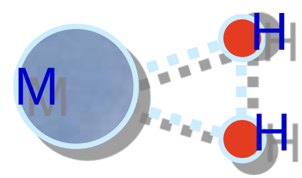
What is the Physical Picture?



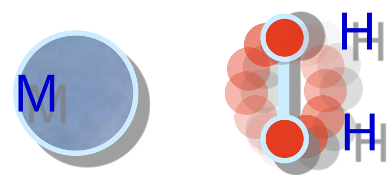
1. Metal Hydride



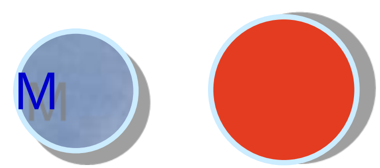
2. Kubas complex



3. Two dimensional rotor



4. Three dimensional rotor



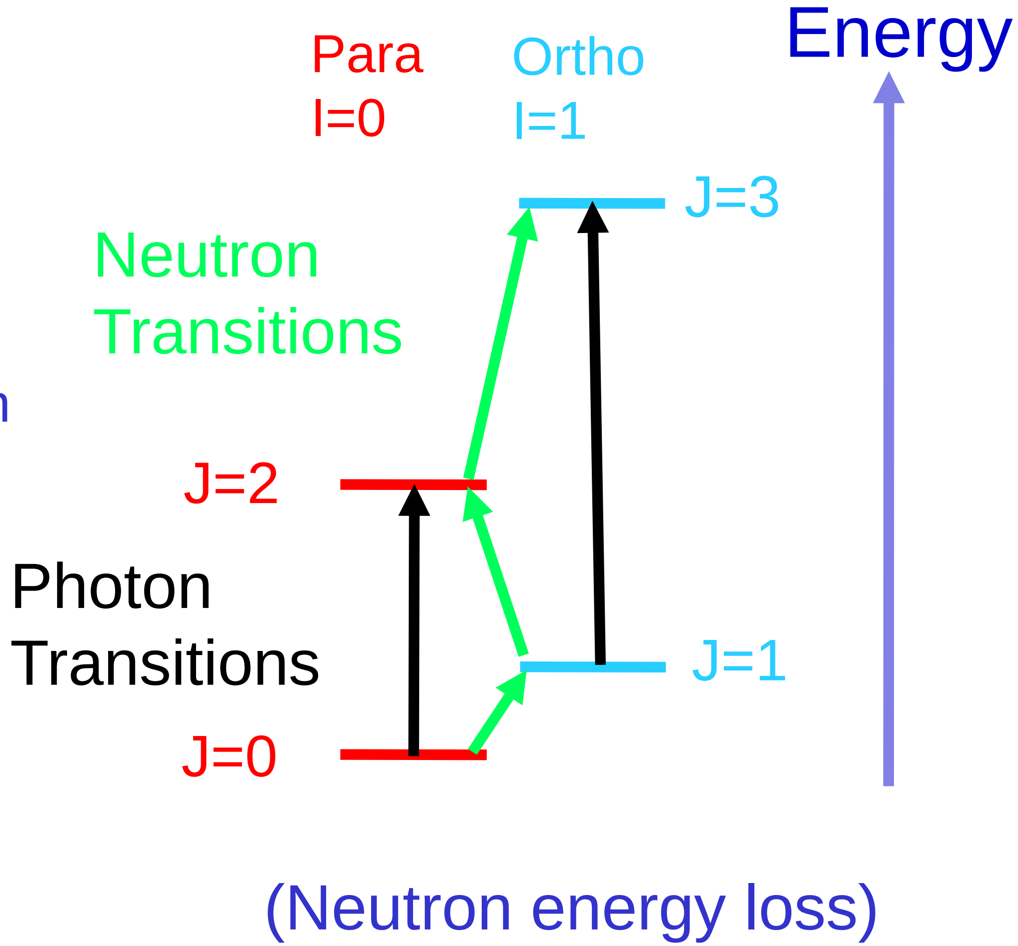
Hydrogen Rotational Transitions

Para has a nuclear spin I=0.
This constrains J to be even.

Ortho has a nuclear spin I=1.
This constrains J to be odd.

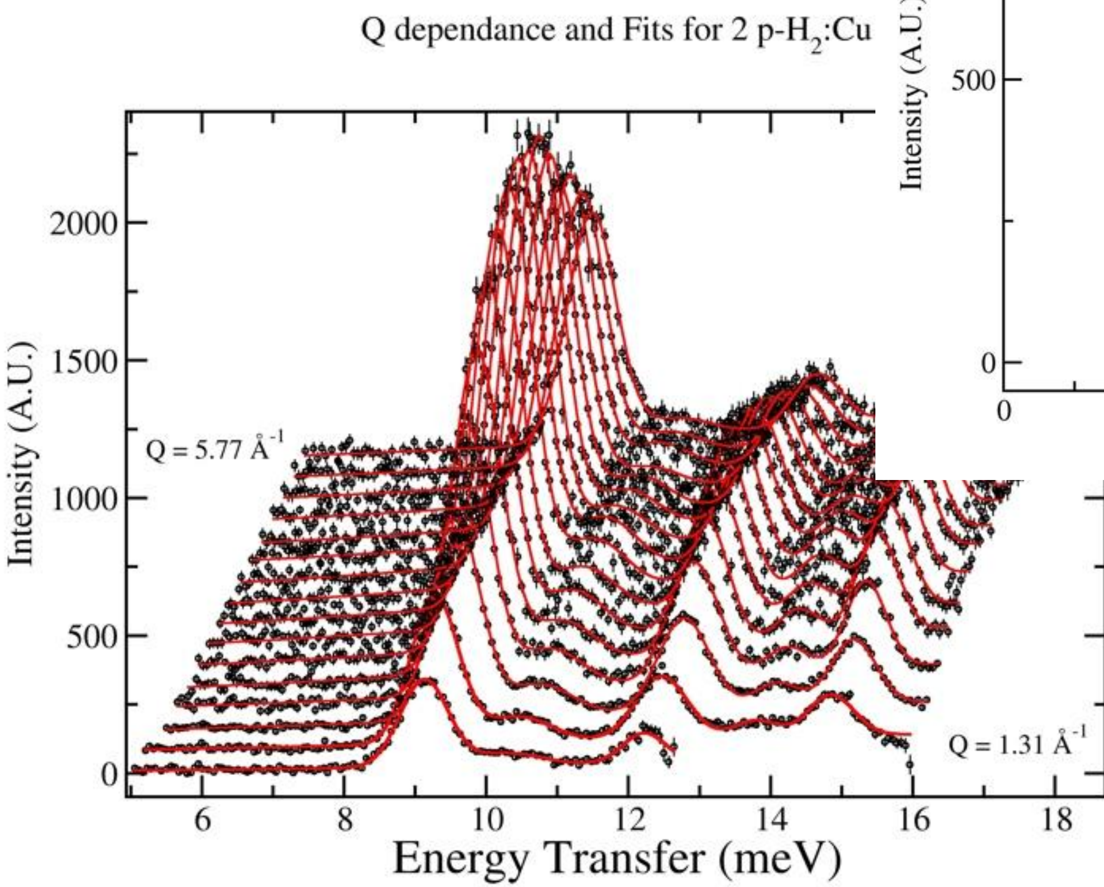
Transition between ortho and para species can occur through flipping the nuclear spin.

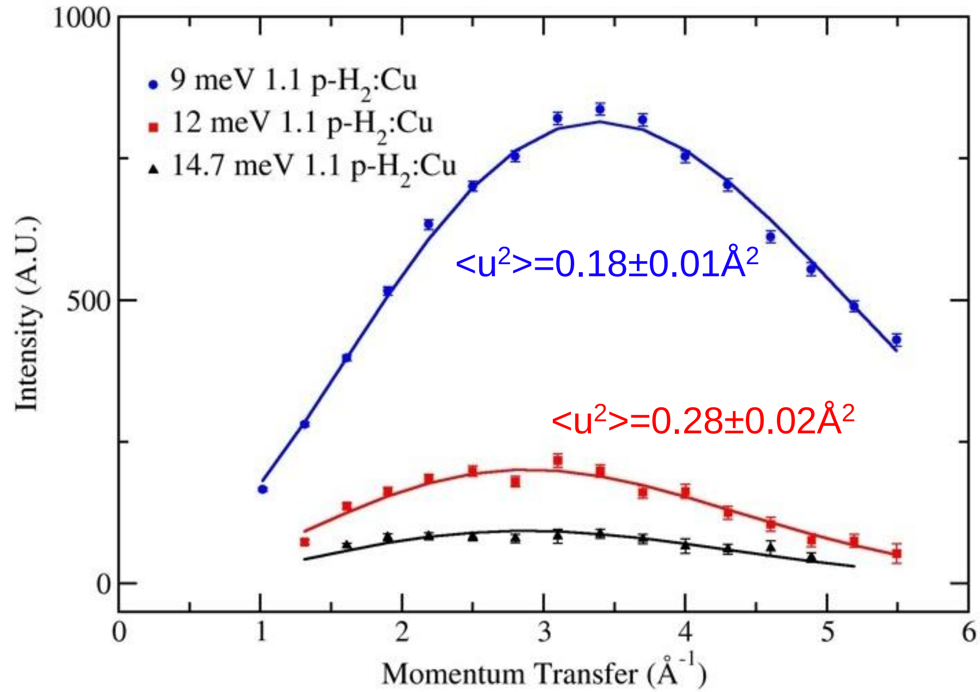
$E_J = B\,J(J+1)$, $B_{H_2} = 7.35$ meV



p-H_2 in HKUST-1

$$I(Q) \propto e^{-Q^2 \langle u^2 \rangle /3} j_1(d_{HH}Q/2)^2$$





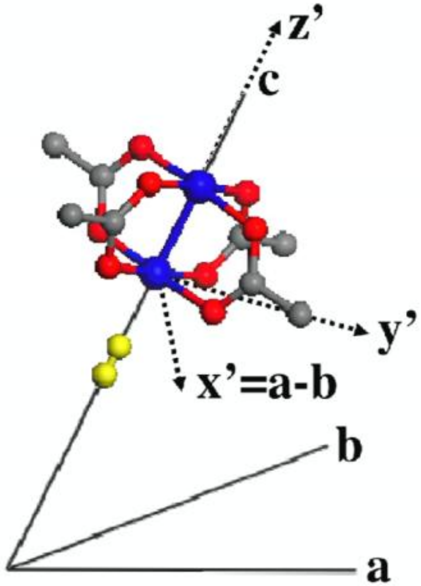
d_{HH}=0.74 Å

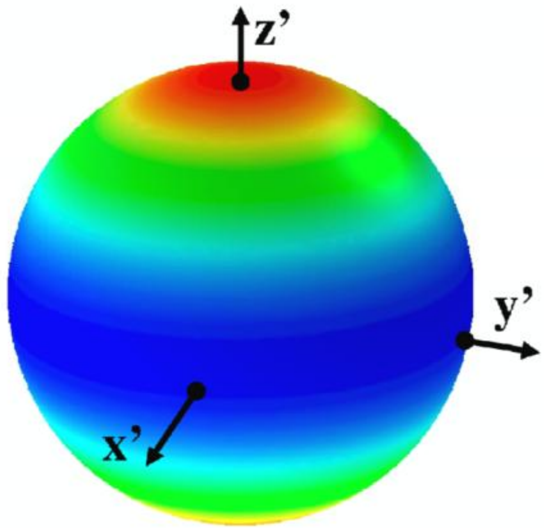
At ~5K, $\langle u^2 \rangle$ of p-H_2 =0.48 Å^2

Y. Liu *et al.*, J. Alloys Compounds **446-447**, 385 (2007)

C.M. Brown *et al.*, Nanotechnology **20**, 204025 (2009)

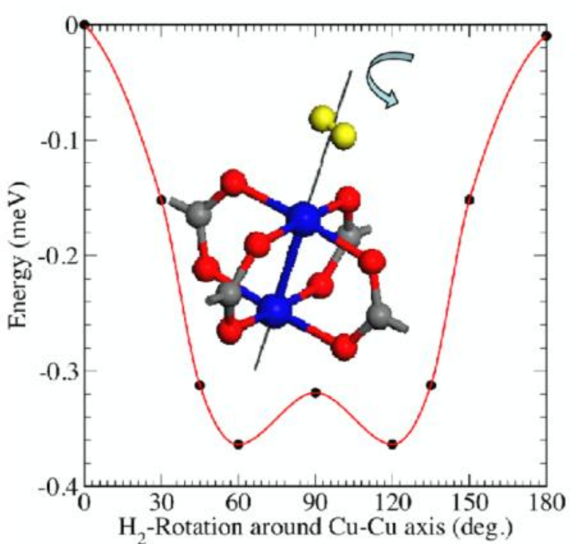
p-H_2 in HKUST-1

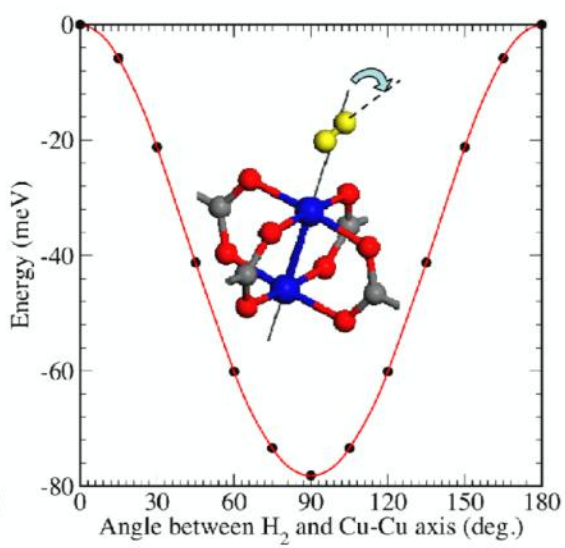




J=0 to J=1, m=±1
9.7 meV
J=0 to J=2, m=±2
36.1 meV
J=0 to J=1, m=0
37.3 meV

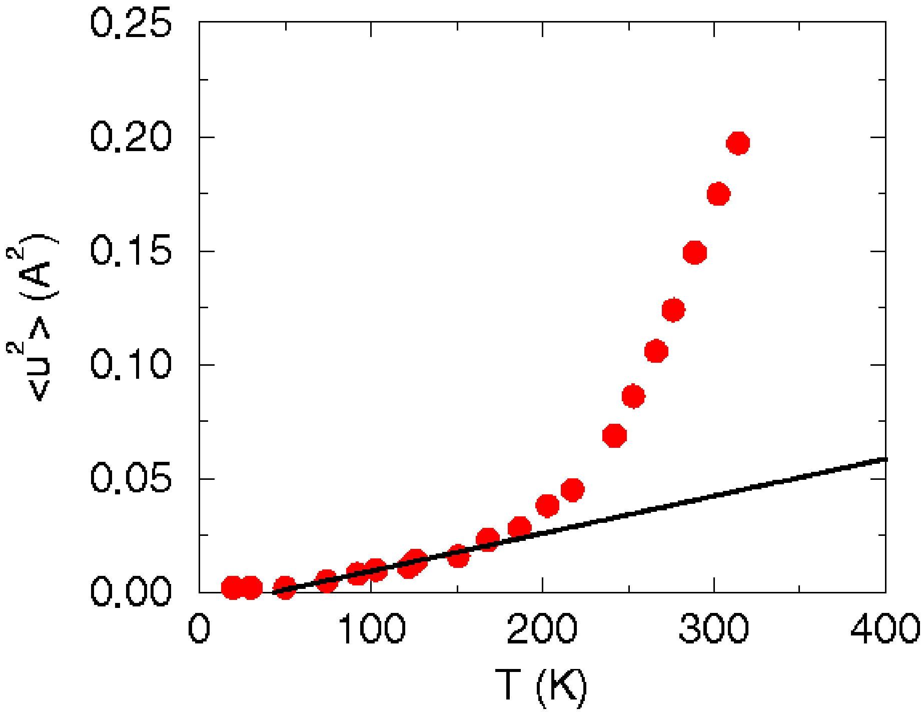
In-plane phonons
$\hbar\omega_{x'}$= 9.6 meV
$\hbar\omega_{y'}$= 13.4 meV
Out-of--plane phonons
$\hbar\omega_{z'}$= 22.9 meV

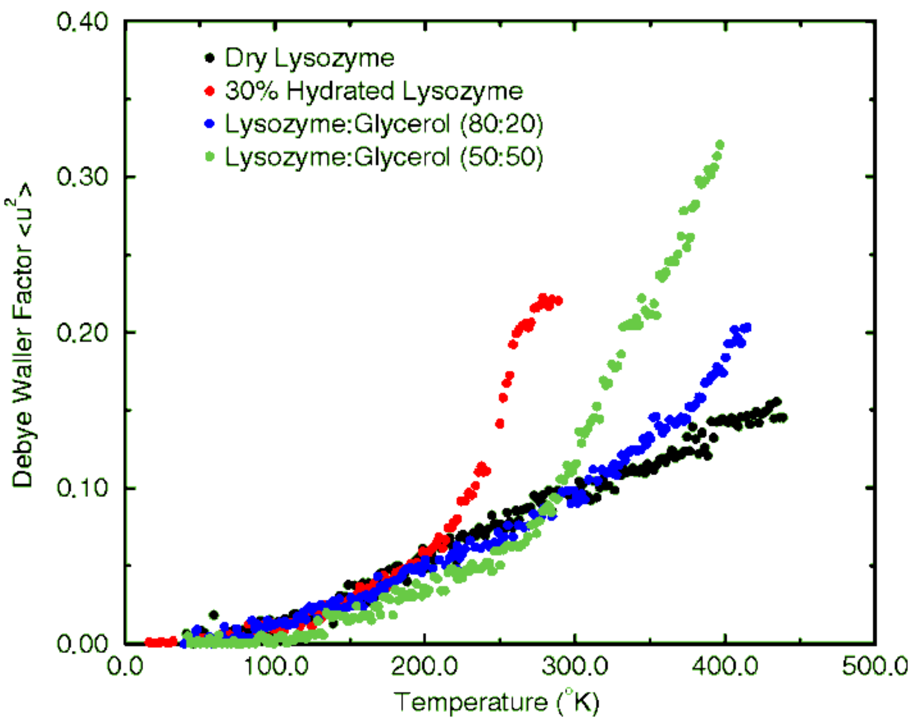




C.M. Brown *et al.*,
Nanotechnology **20**, 204025 (2009)

<u²> and Proteins





The dynamic transition in $\langle u^2 \rangle$ correlates with the onset of enzymatic activity

Doster *et al*, Nature (1989)

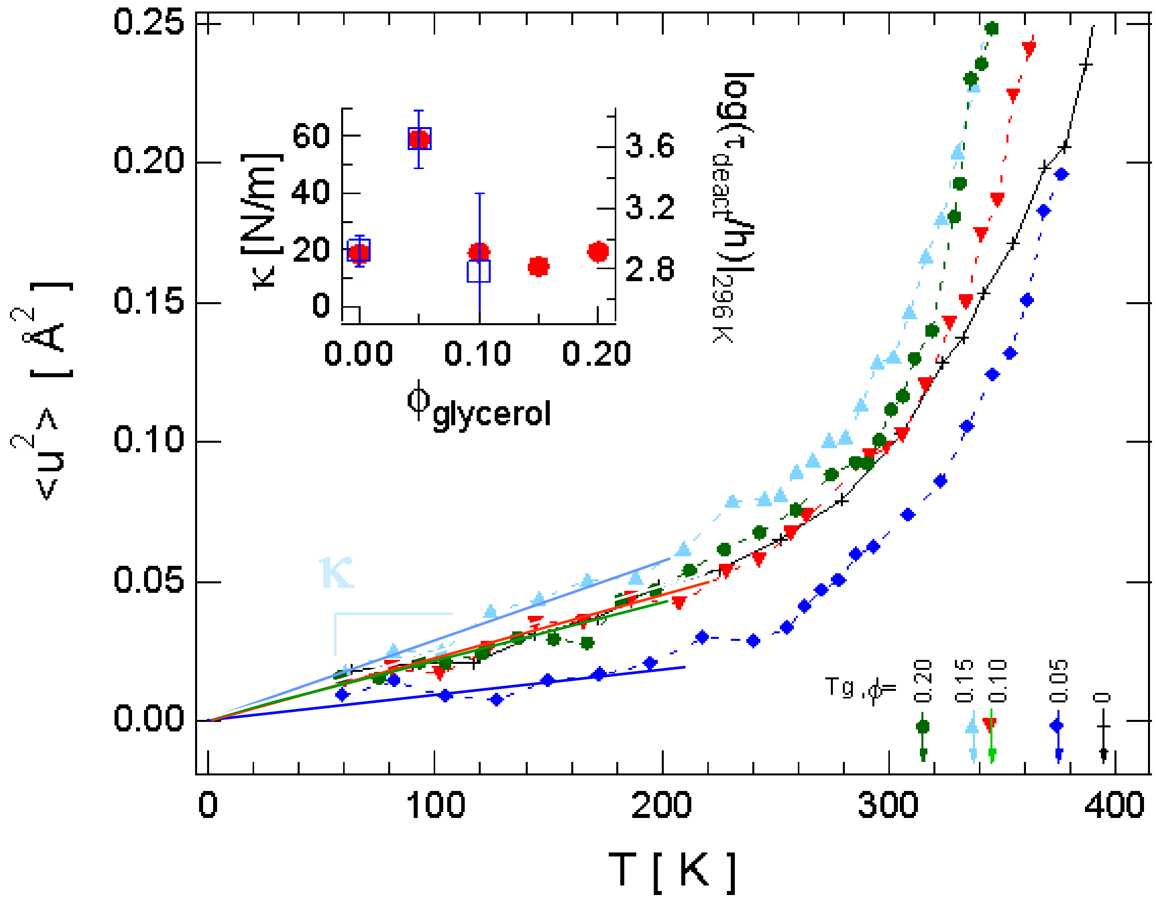
The viscous nature of glycerol retards onset of anharmonicity. The low-temperature "harmonic" region shows that glycerol stiffens the formulation.

Tsai *et al.*, Biophys. J. (2000)

QENS & Protein Preservation

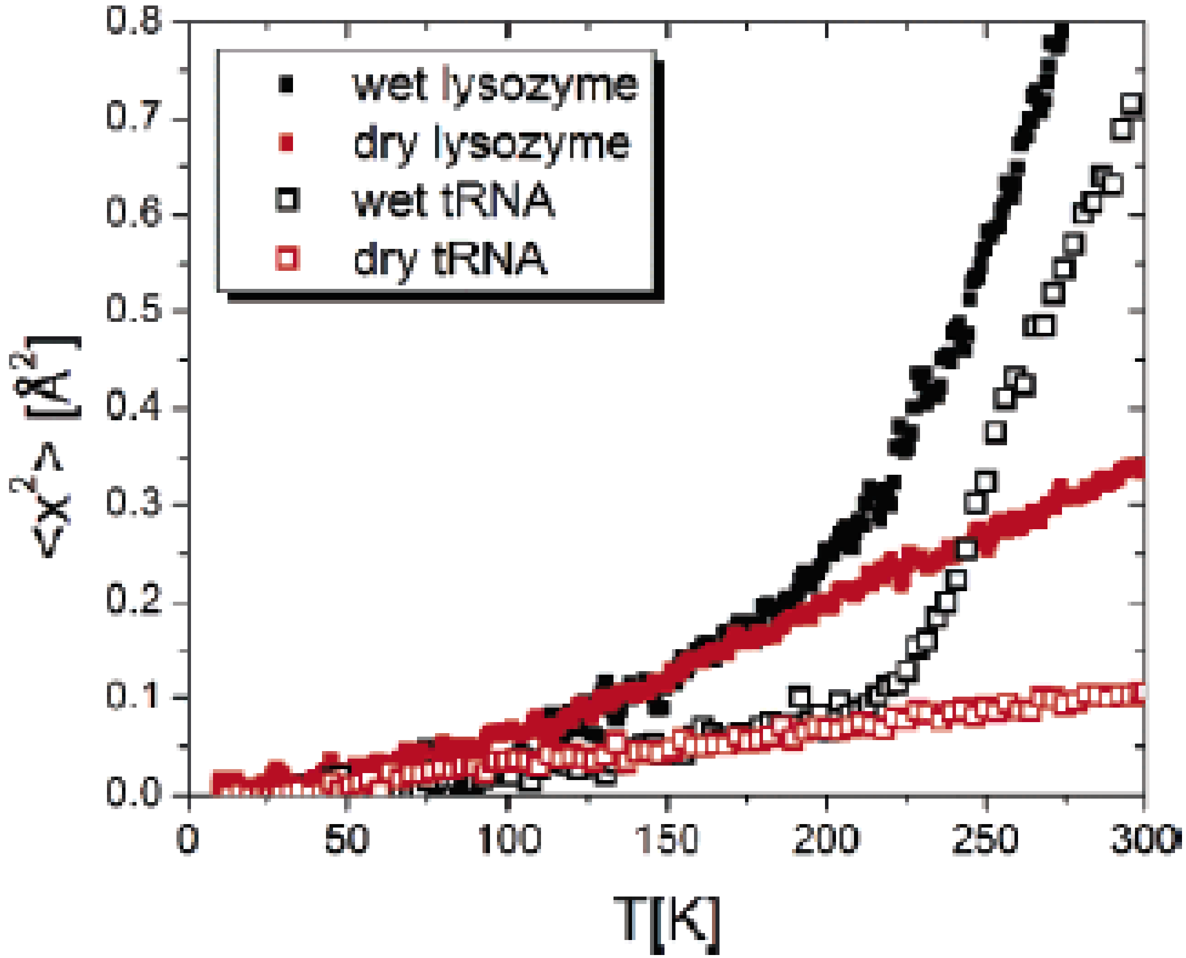
HRP and YADH preserved in trehalose with small dilutions of glycerol (trehalose with 0, 5, 10, 15, and 20 % glycerol by mass)

Soles & Cicerone, Biophys. J. **86**:3836 (2004).



- Small additions of glycerol to trehalose greatly suppresses $\langle u^2 \rangle$
- Neutron scattering predicts long term enzyme stability
  => pharmaceutical preservation

$\langle u^2 \rangle$ and RNA



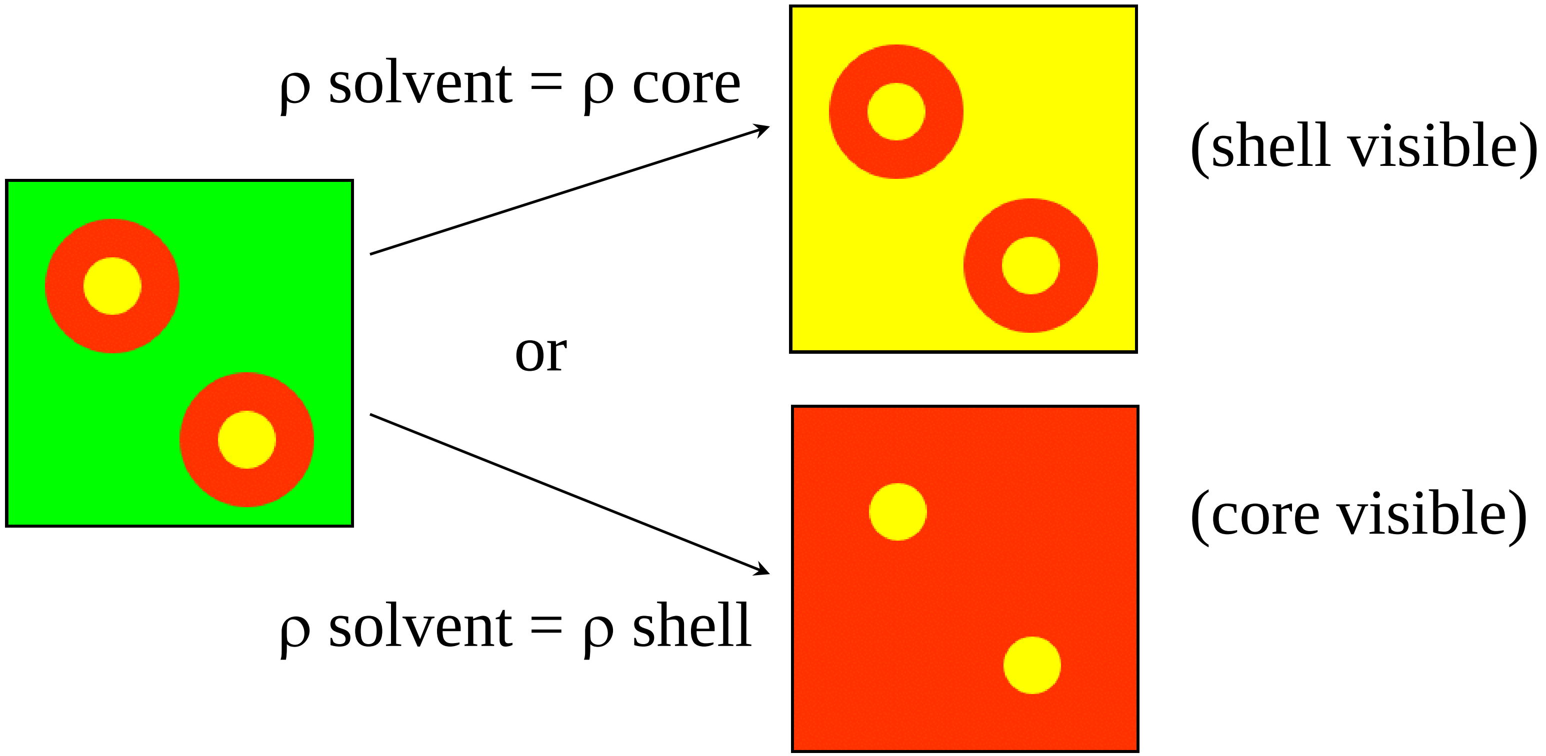
The dynamics of solvent molecules controls the the dynamic transition in RNA as well as proteins.

G. Caliskan *et al.*, JACS **128**, 32 (2006).

CHRNS NIST

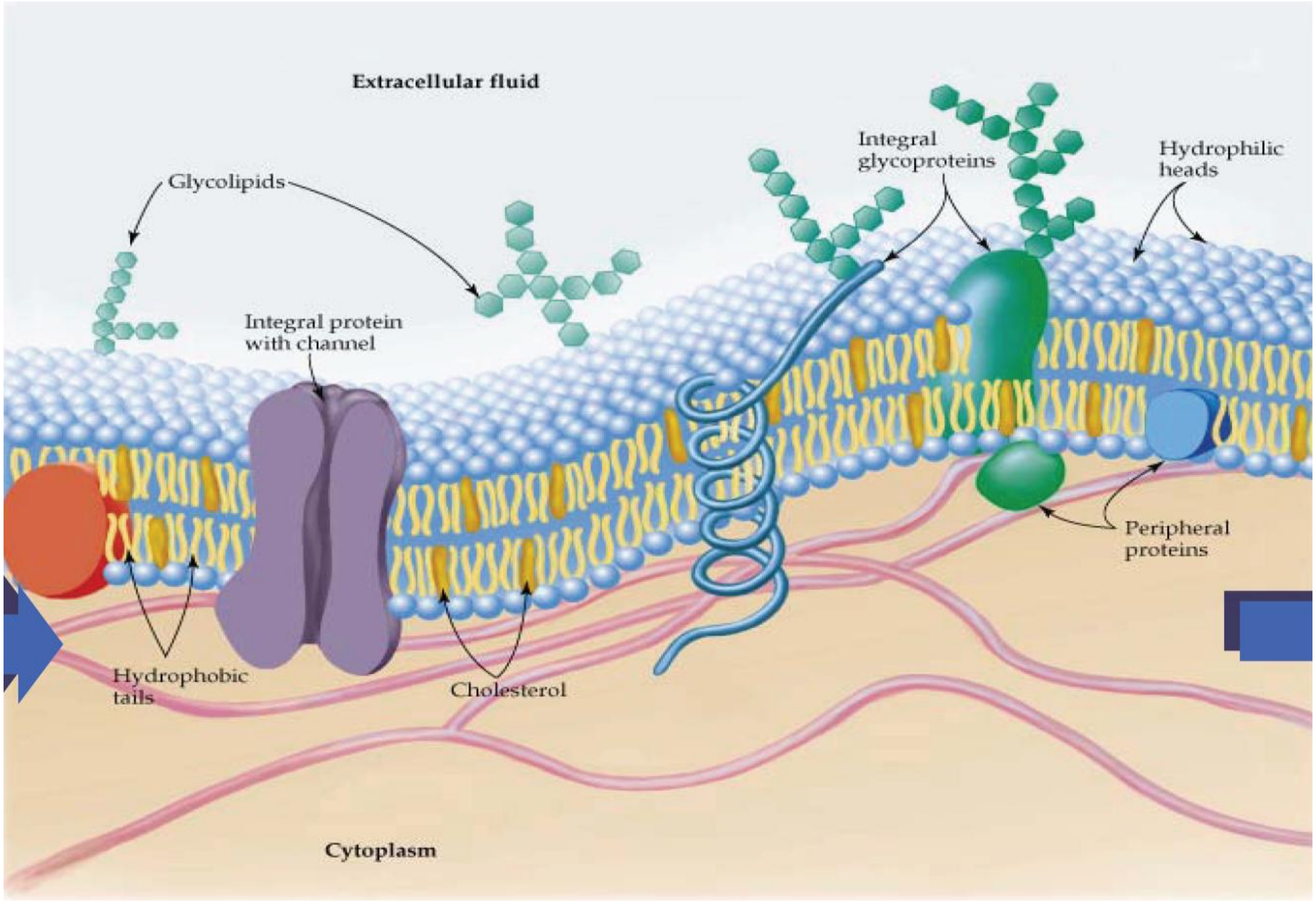
Contrast Variation using Deuteration

Contrast Matching - reduce the number of phases "visible"

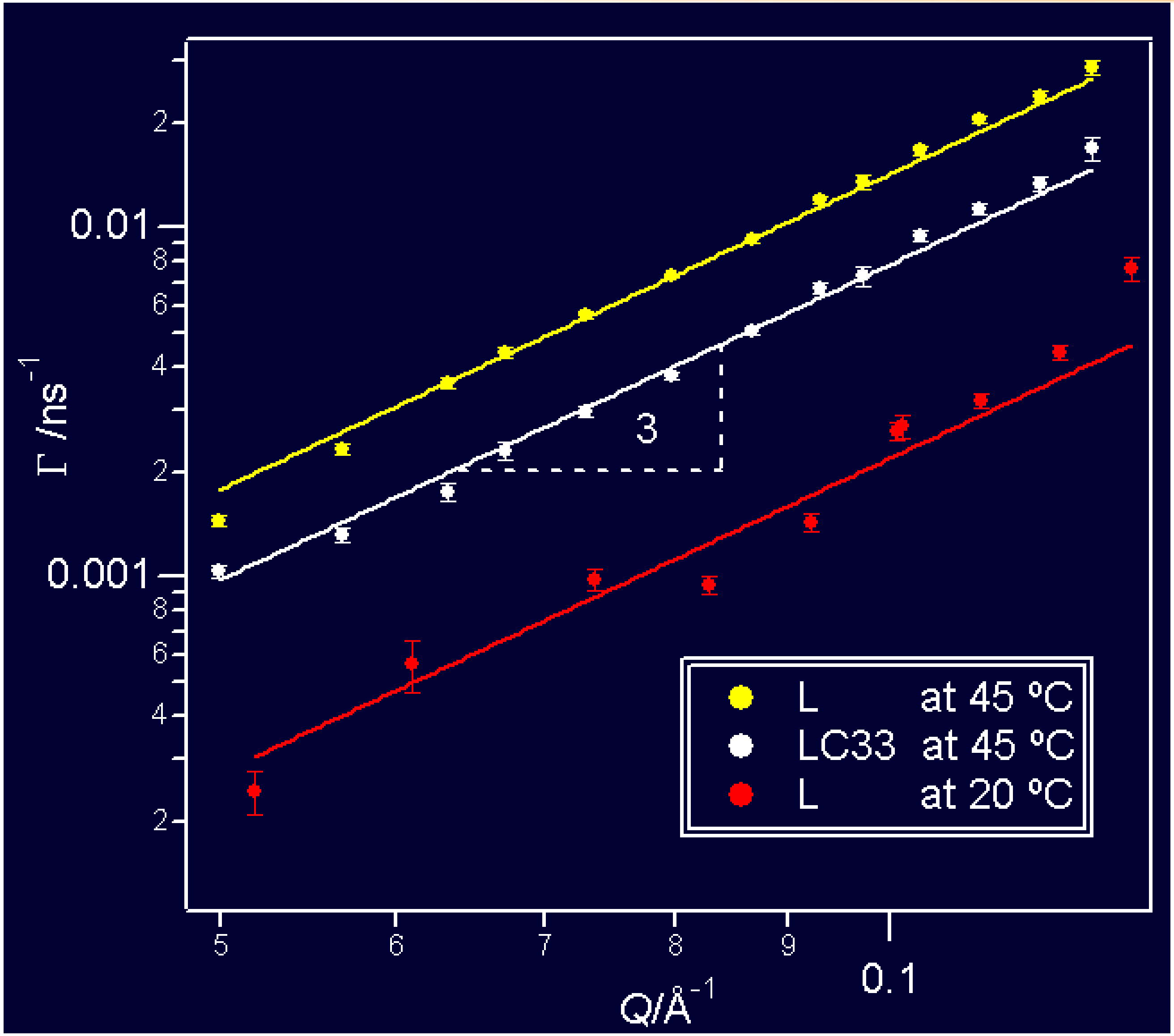


The two distinct 2-phase systems can be easily understood

Phospholipid Membranes

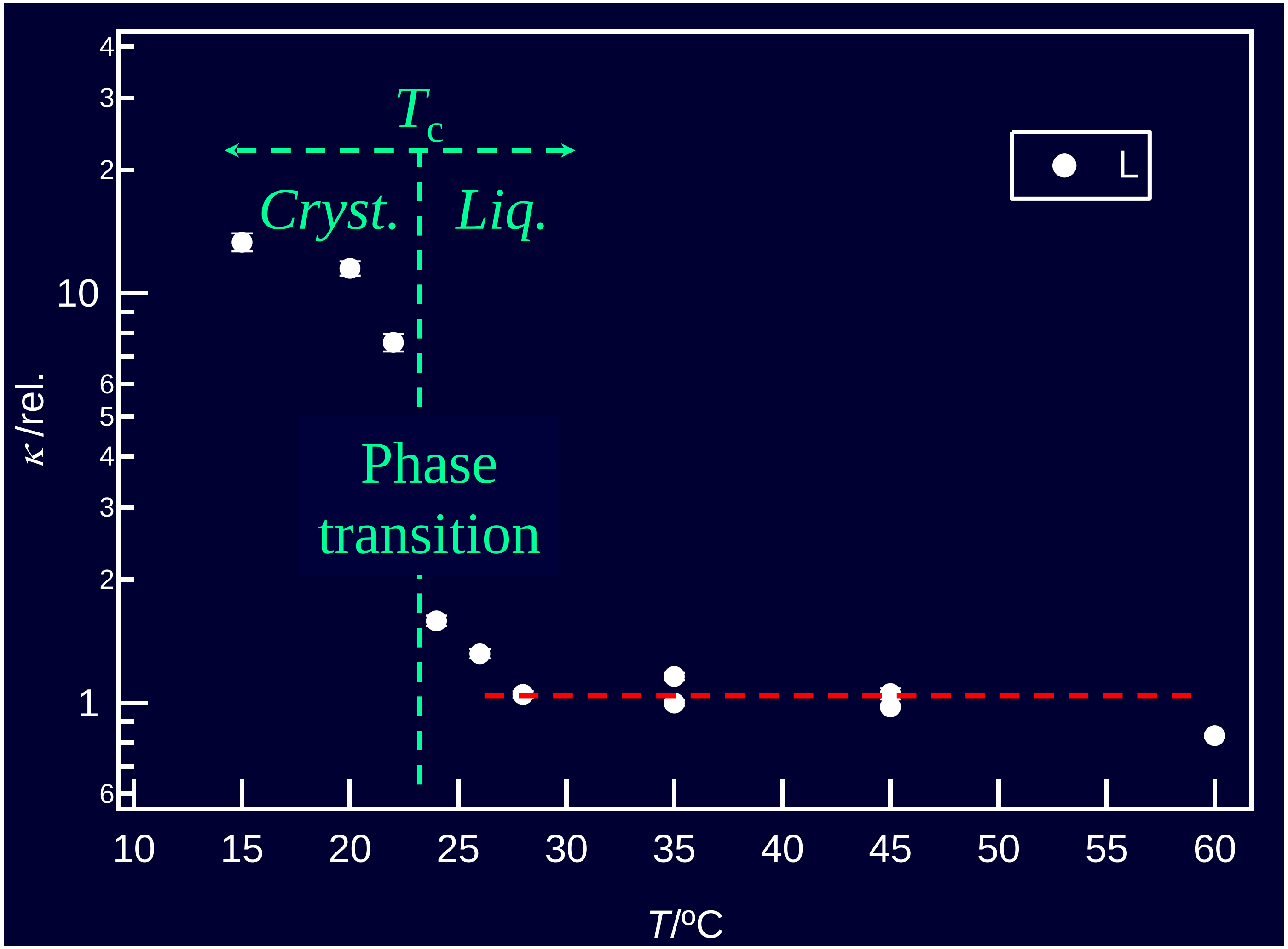


Relaxation rate of $S(Q,t)$

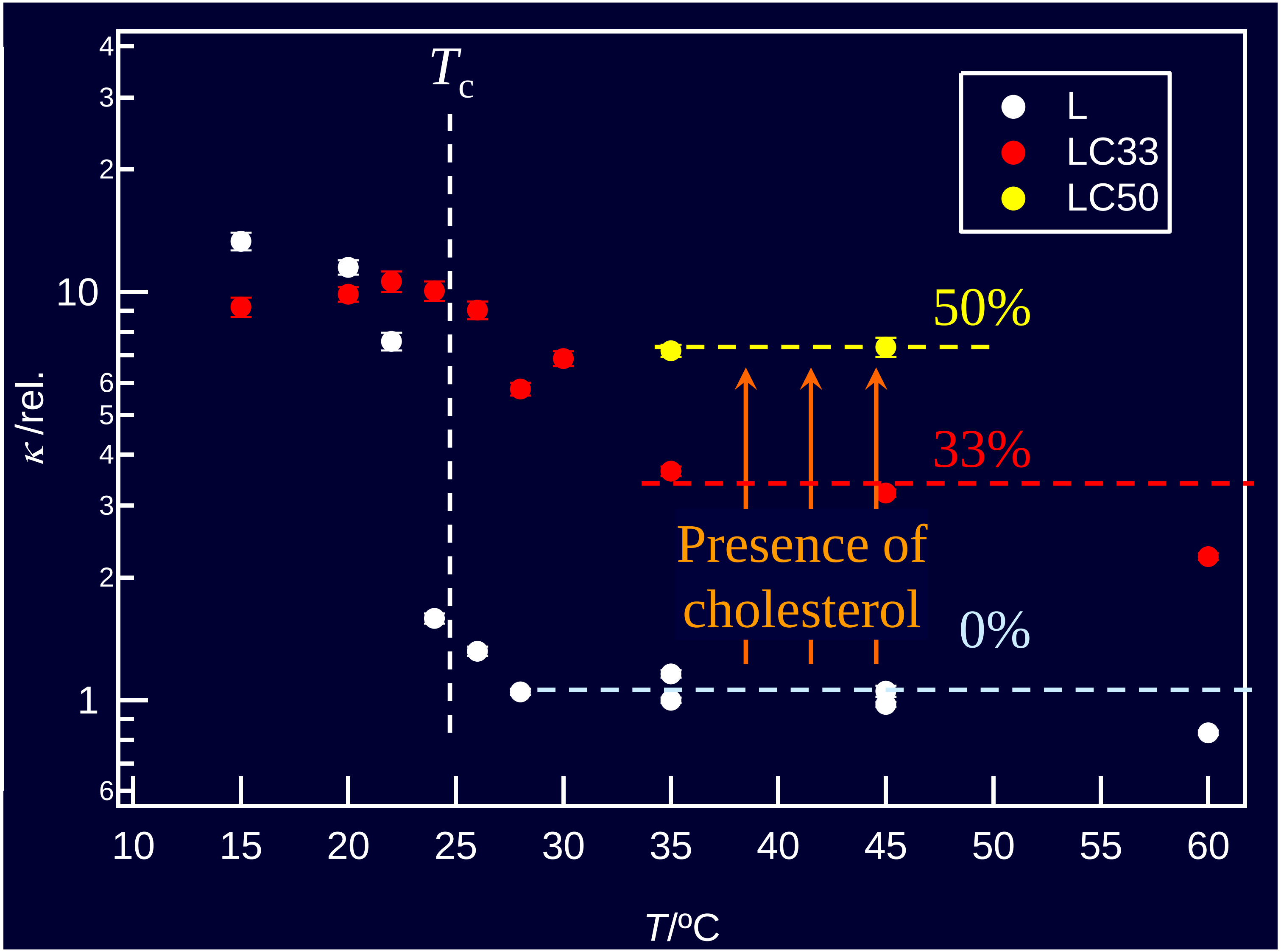


$$\Gamma \propto \sqrt{\frac{k_B T}{\kappa}}\,\frac{k_B T}{\eta}\,Q^3$$

Temperature Dependence of κ



Vesicles with Cholesterol



Why Neutron Scattering

1) Ability to measure both energy *and* momentum transfer

    Geometry of motion

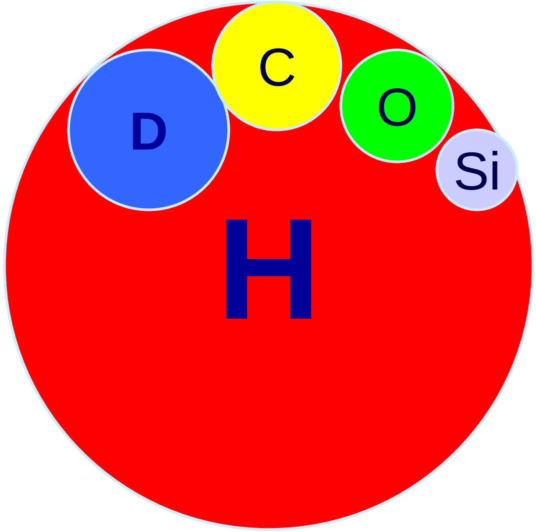
2) Neutrons scatter by a nuclear interaction => different isotopes scatter differently

    H and D scatter very differently

3) Simplicity of the interaction allows easy interpretation of intensities

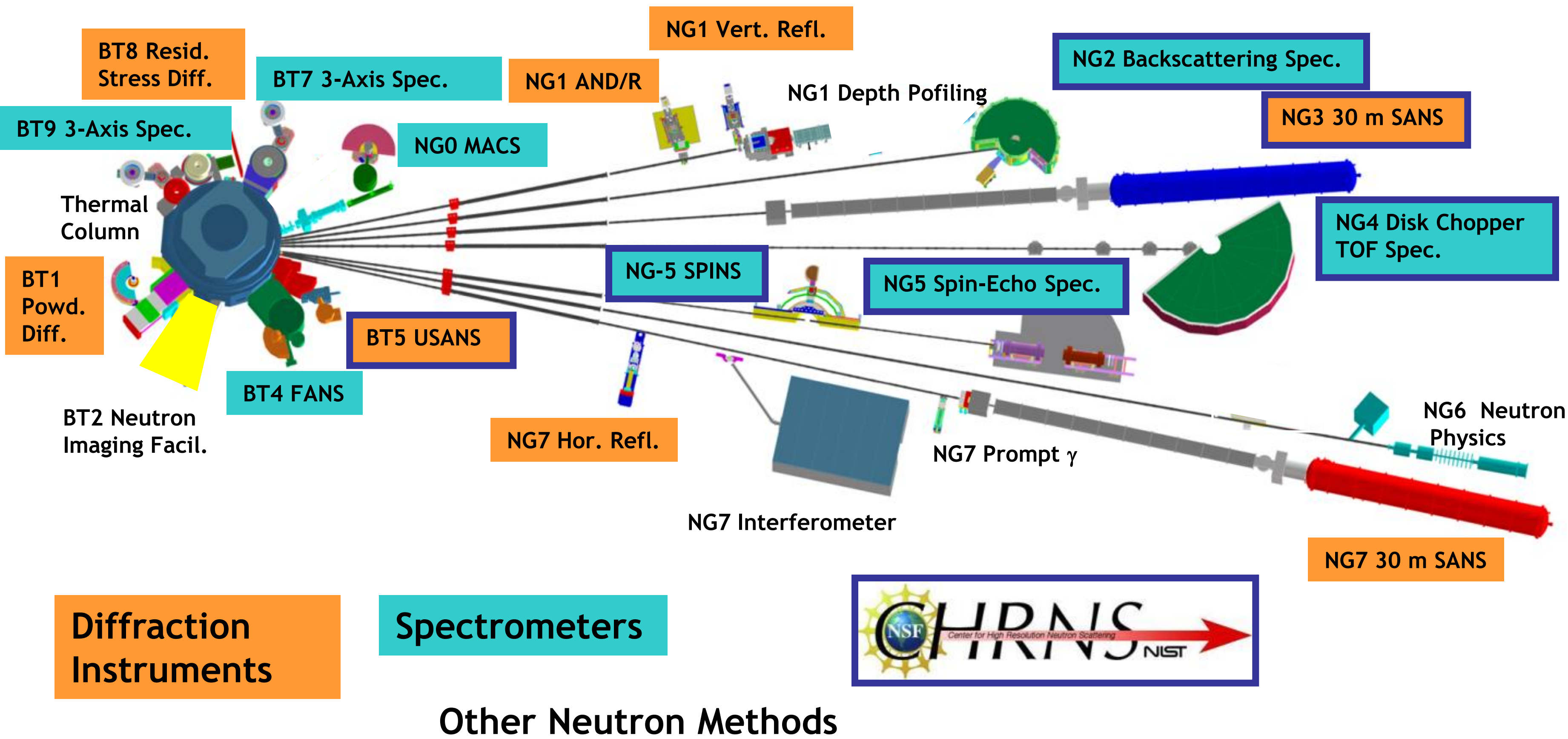
    Easy to compare with theory and models

4) Neutrons have a magnetic moment



The NCNR Has 25 Operating Neutron Beam Instruments Tailored to Specific Needs …

www.ncnr.nist.gov



Expansion Activities

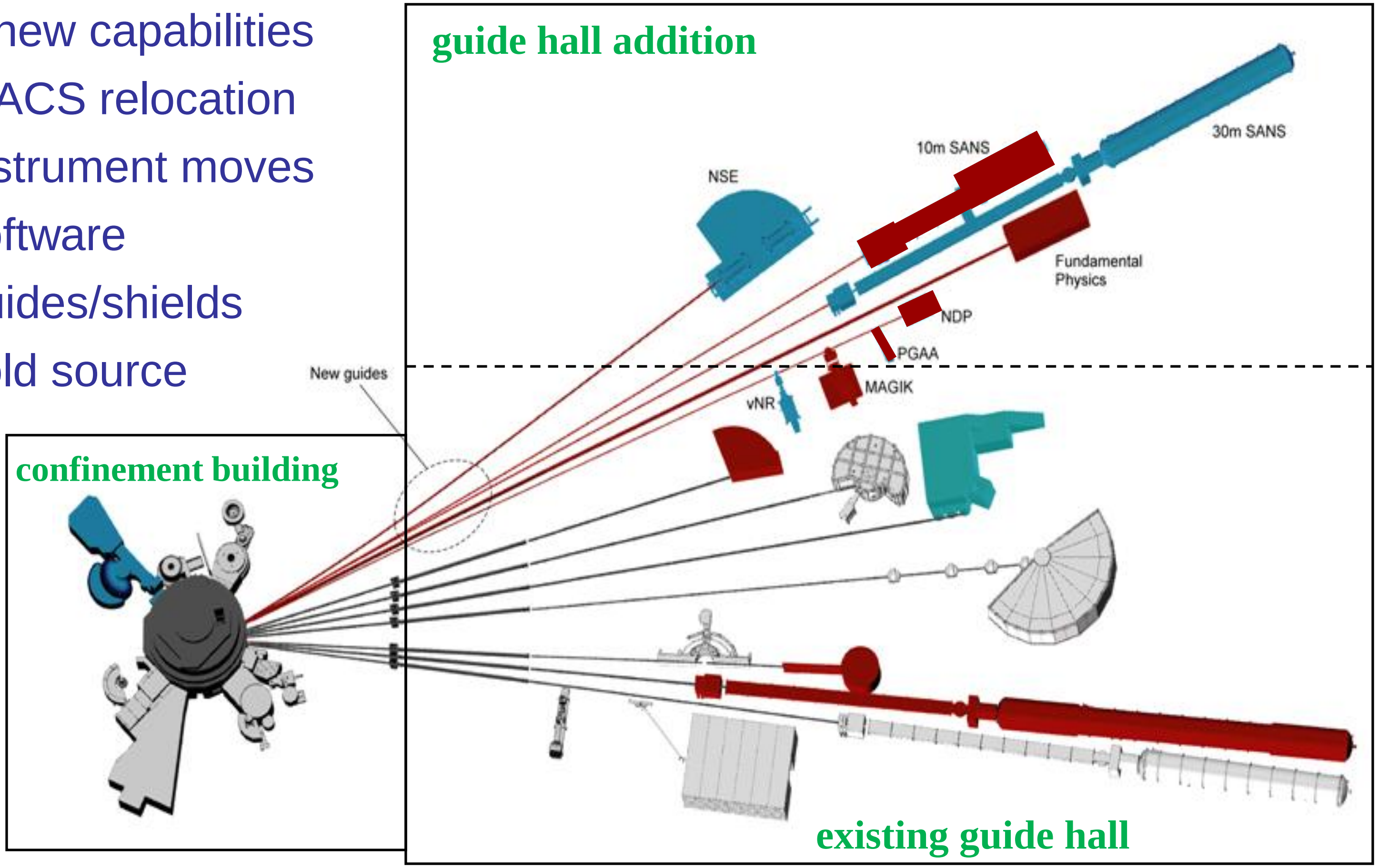
- New Cold Source
- Construction
- Instrument development
- Beam delivery
- Reactor reliability enhancements

NIST

NCNR Expansion

Many sub-projects:

5 new capabilities
MACS relocation
instrument moves
software
guides/shields
cold source



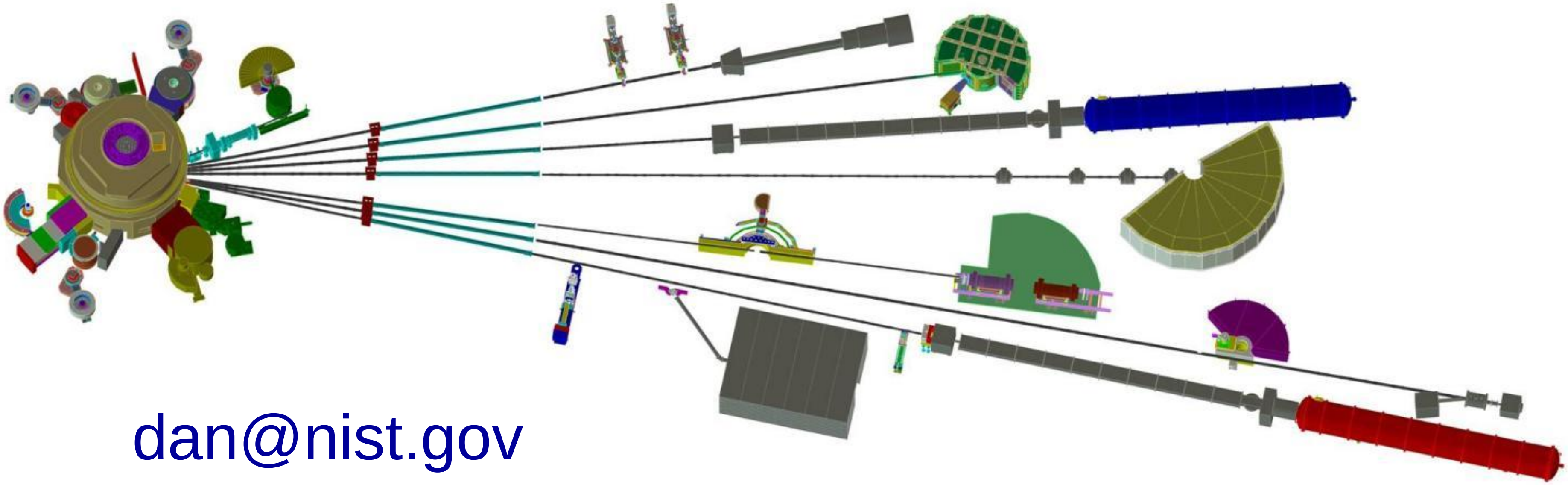
Major areas of activity:

Construction
Cold source
Guide systems
Shield systems
Instruments
Control room upgrade

NIST

Neutron methods are extremely versatile

Which type of instrument might be useful in your research?



dan@nist.gov

www.ncnr.nist.gov