Neutrons at NIST

Dan Neumann
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Why Neutron Scattering

1) Neutrons scatter by a nuclear interaction => different isotopes scatter differently   H and D scatter very differently

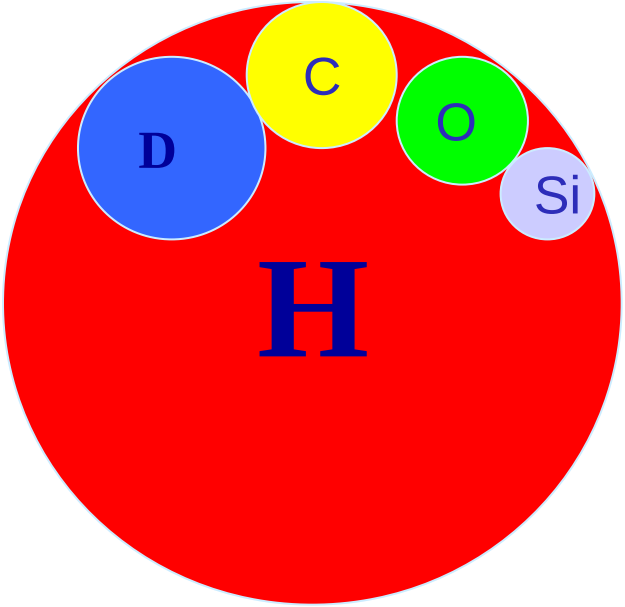
2) Simplicity of the interaction allows easy interpretation of intensities

Easy to compare with theory and models

3) Appropriate energy *and* momentum transfer

Geometry of motion

4) Neutrons have a magnetic moment



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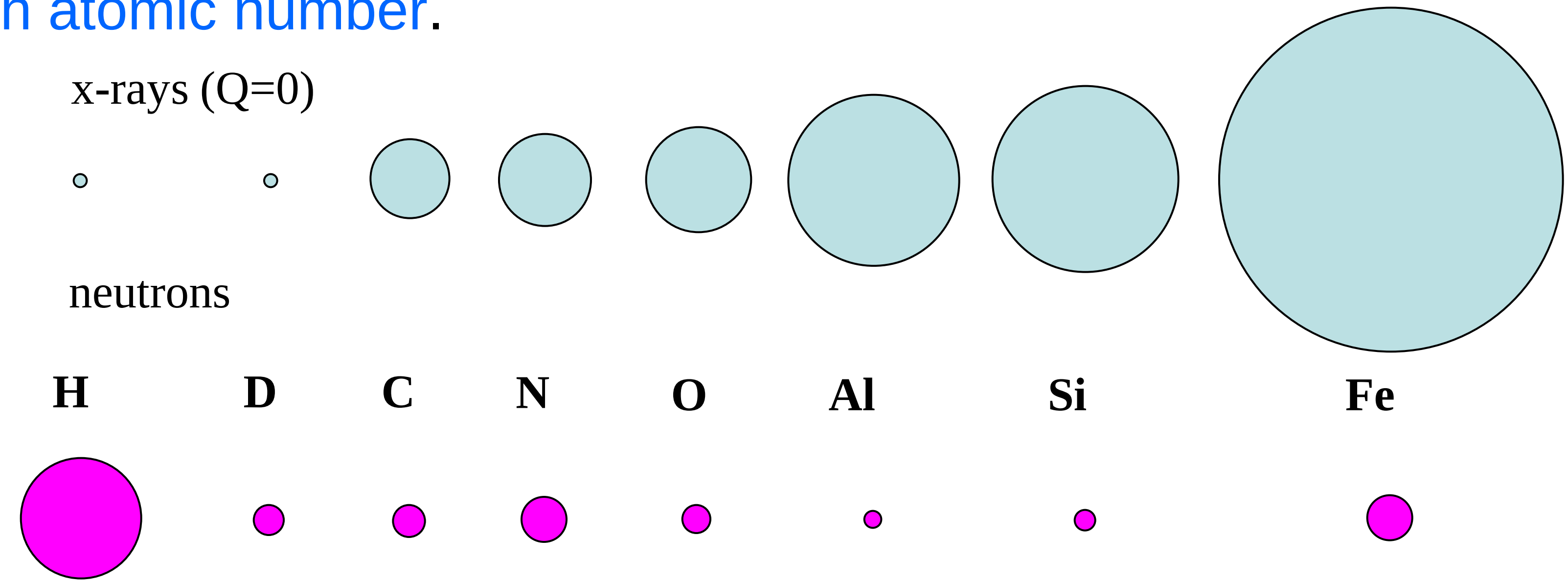
Total Scattering Cross Sections

As compared with x-ray scattering cross sections, which vary as Z^2, neutron scattering cross sections show little systematic variation with atomic number.

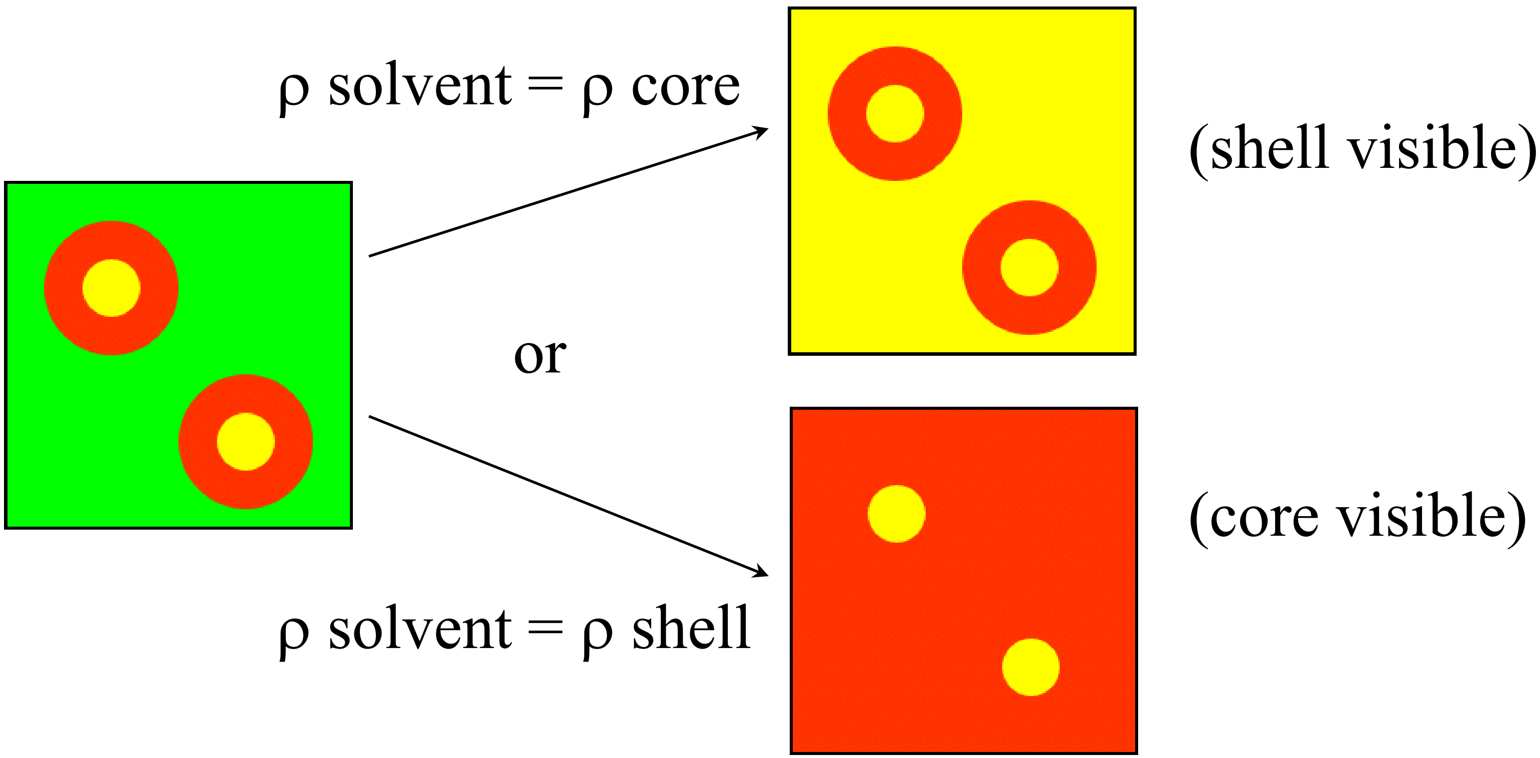


X-ray cross sections vary with scattering angle

neutron cross sections do not

Solving Multi-Phase Structures

Contrast Matching - reduce the number of phases “visible”



The two distinct 2-phase systems can be easily understood

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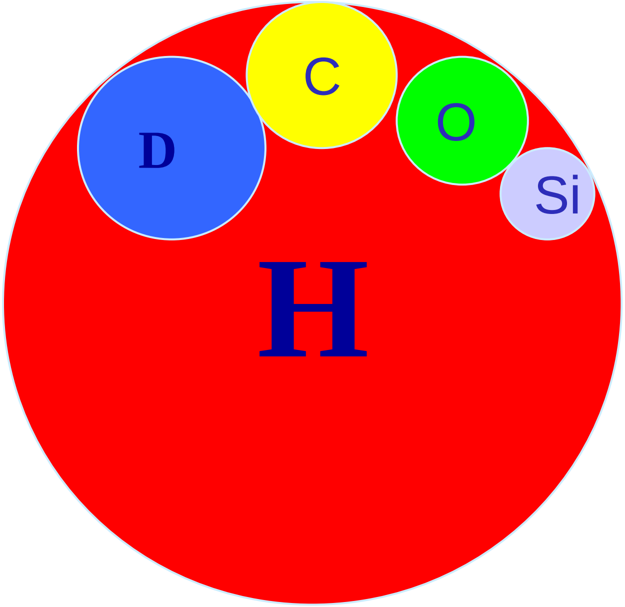

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Why Neutron Scattering

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   Geometry of motion

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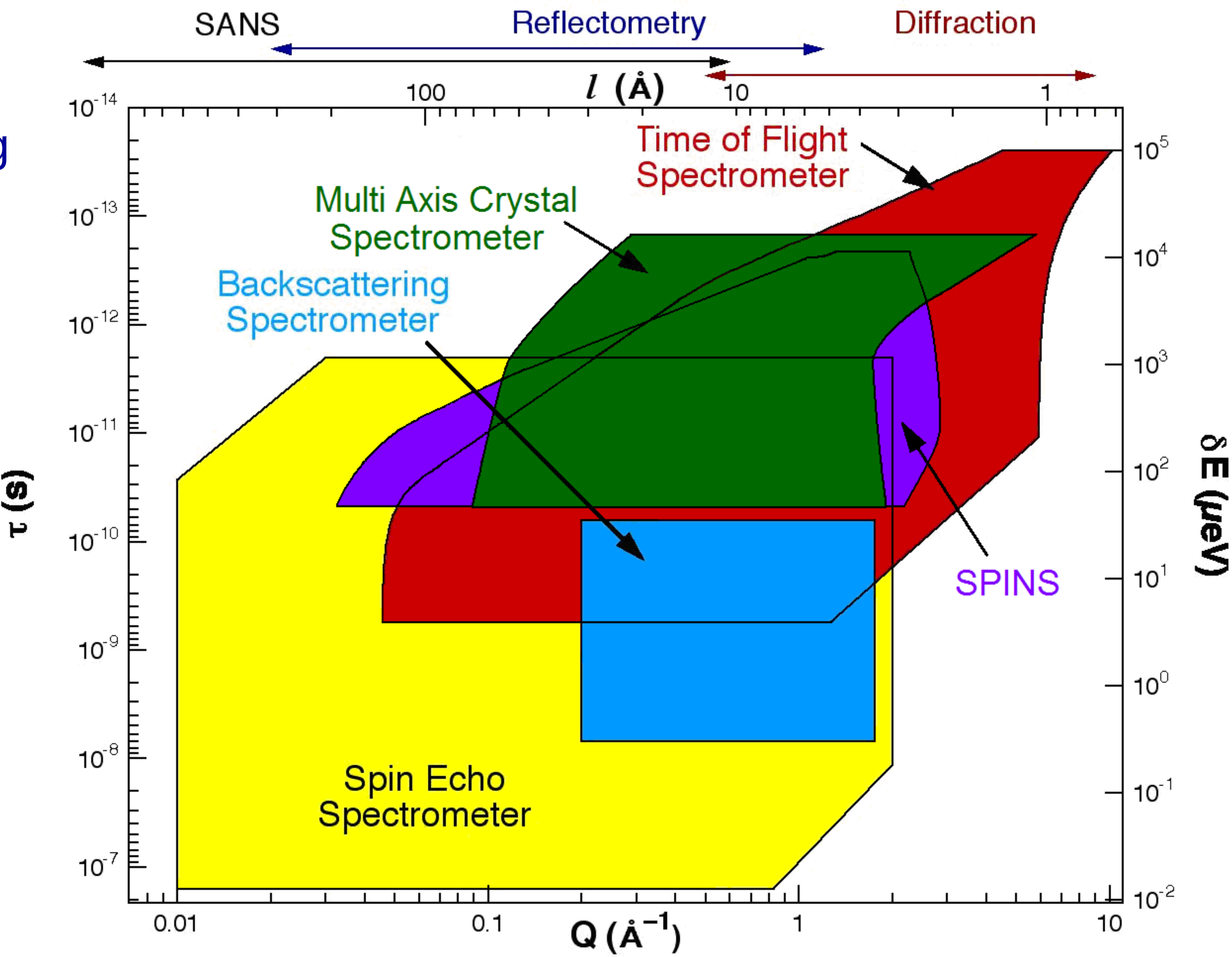
Phase Space Coverage

Neutron scattering methods probe structural features over **5** orders of magnitude

and

dynamic phenomena over **8** orders of magnitude in time



Why Neutron Scattering

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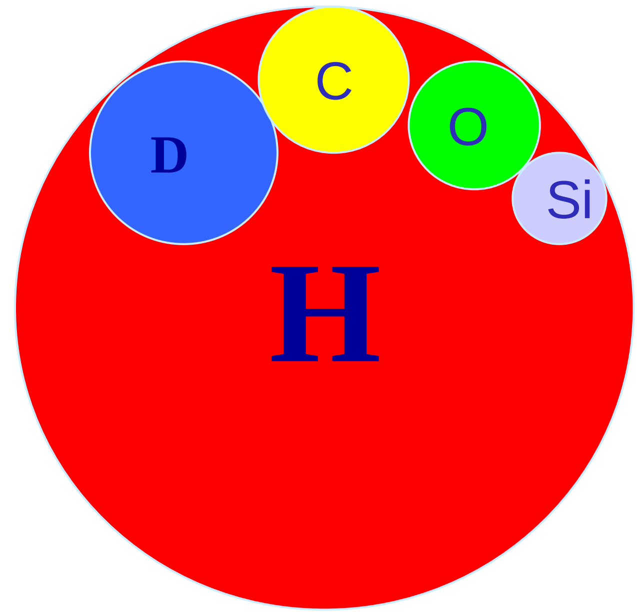

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The NIST Center for Neutron Research

20 MW Research Reactor

designed to produce neutrons, not electrical power

(power reactors are much larger ~ 3000 MW)

≈28 specialized instruments

characterization and development of new materials

chemical analysis

imaging

physics of the neutron

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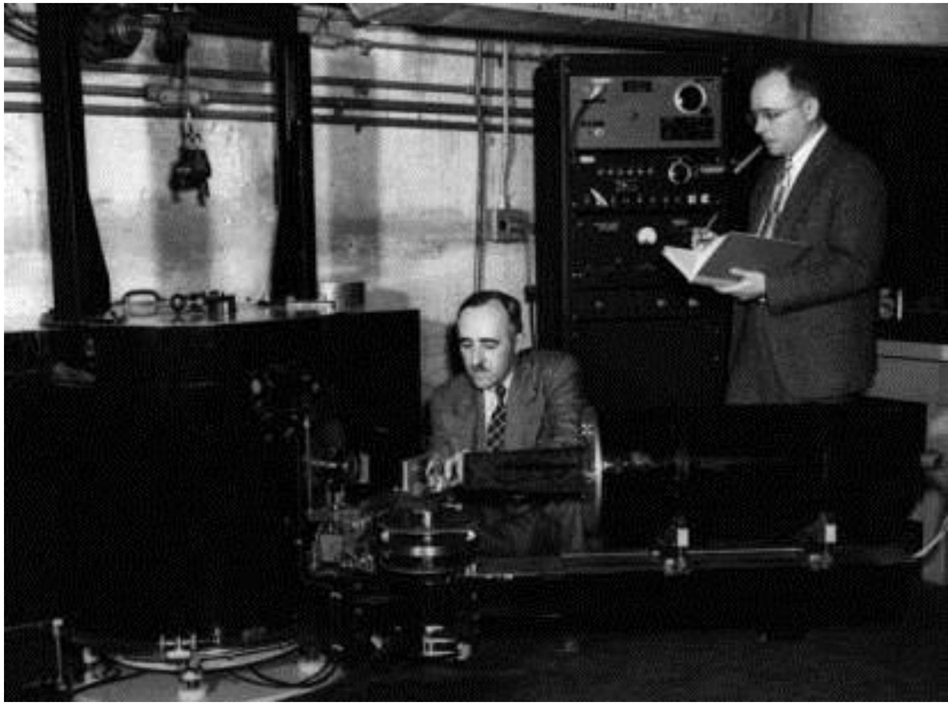
Early History

Neutrons (1932) are liberated by fission of ^{235}U (1938)

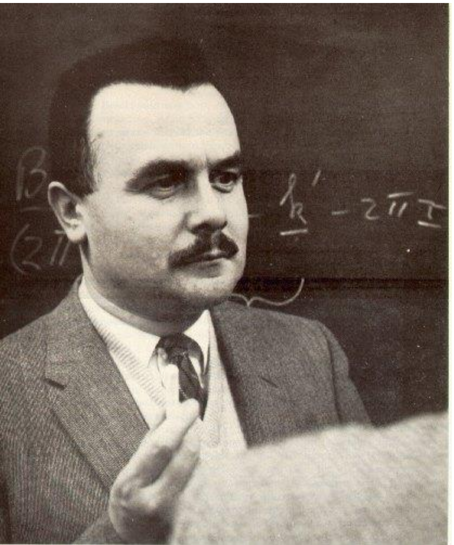
First neutron diffraction experiments were performed at the graphite reactor at ORNL (1945)

First 3-axis experiments were performed at the NRU reactor at Chalk River (1955)



Ernie Wollan **Cliff Shull**

http://diva.library.cmu.edu/Shull/access.html



Bertram Brockhouse

http://media.cns-snc.ca/history/pioneers/b_brockhouse/bbrockhouse.html

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The beginnings of the NCNR

NBS Director Allen Astin decides to build a multipurpose, high-flux research reactor at the new Gaithersburg campus (1958)

This new facility would serve the needs of the entire Washington region

$0.7 M for design in FY1961

$8 M for construction in FY1962

http://www.s9.com/Biography/Astin-Allen-Varley

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Justification

- materials research with neutron scattering
  - alliances with NOL and NRL
- elemental analysis (SRM's)
  - alliances with FBI, Geological Survey, FDA, Smithsonian
- radiation standards
- isotope production
- nuclear physics

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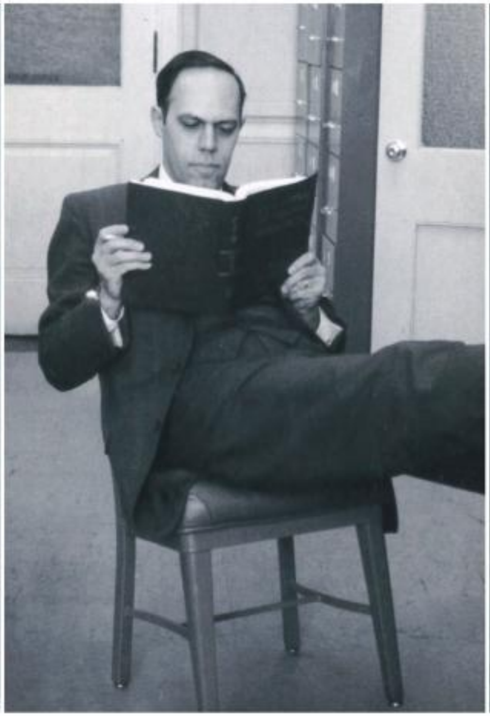
The beginnings of the NCNR

Bob Carter | Carl Muehlhause | Harry Landon



Design based on ANL's CP-5 reactor and UK's DIDO reactor

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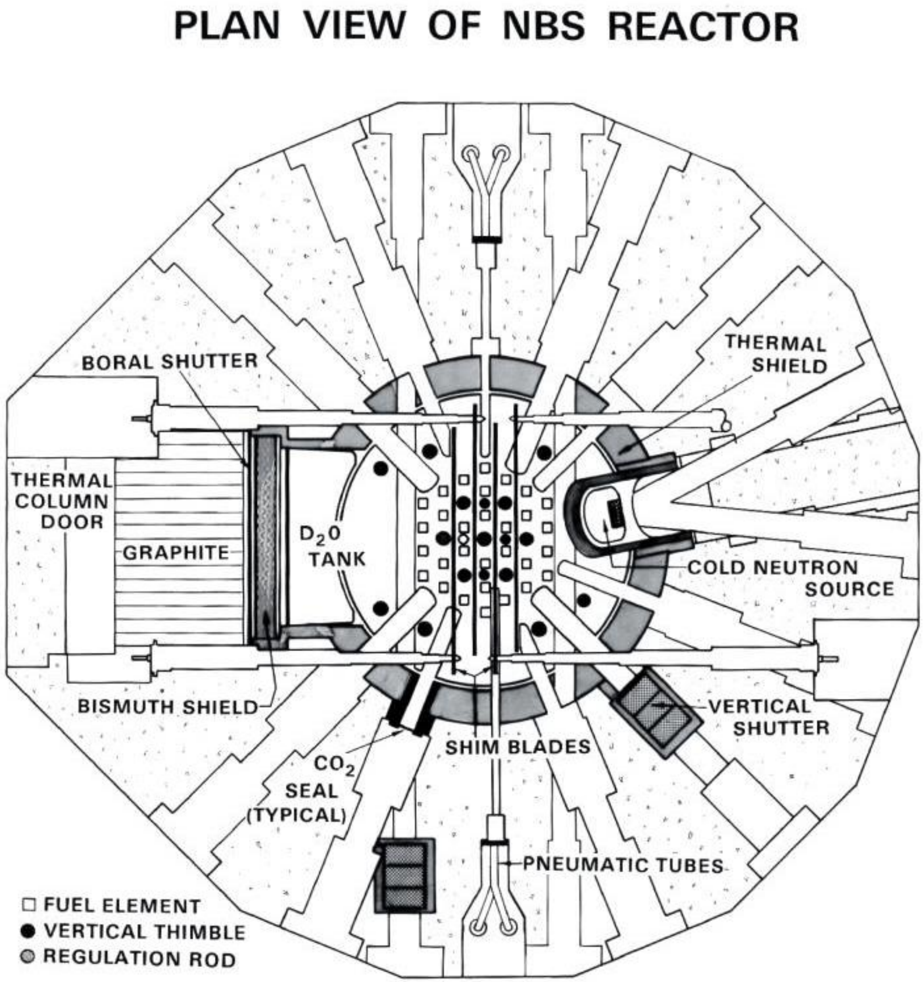
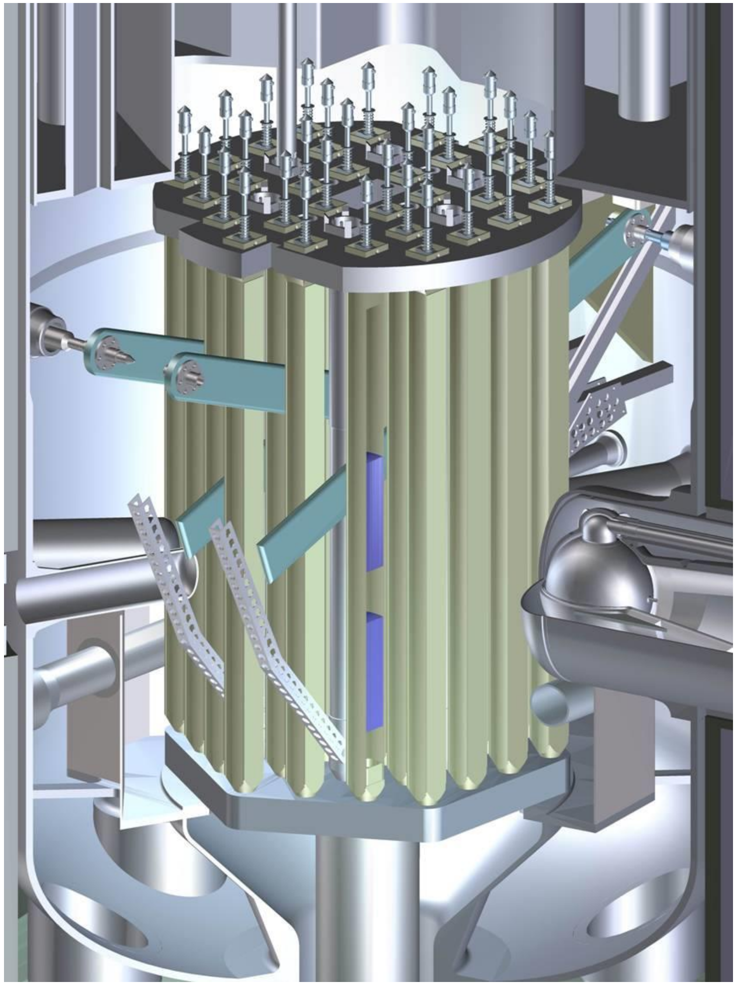


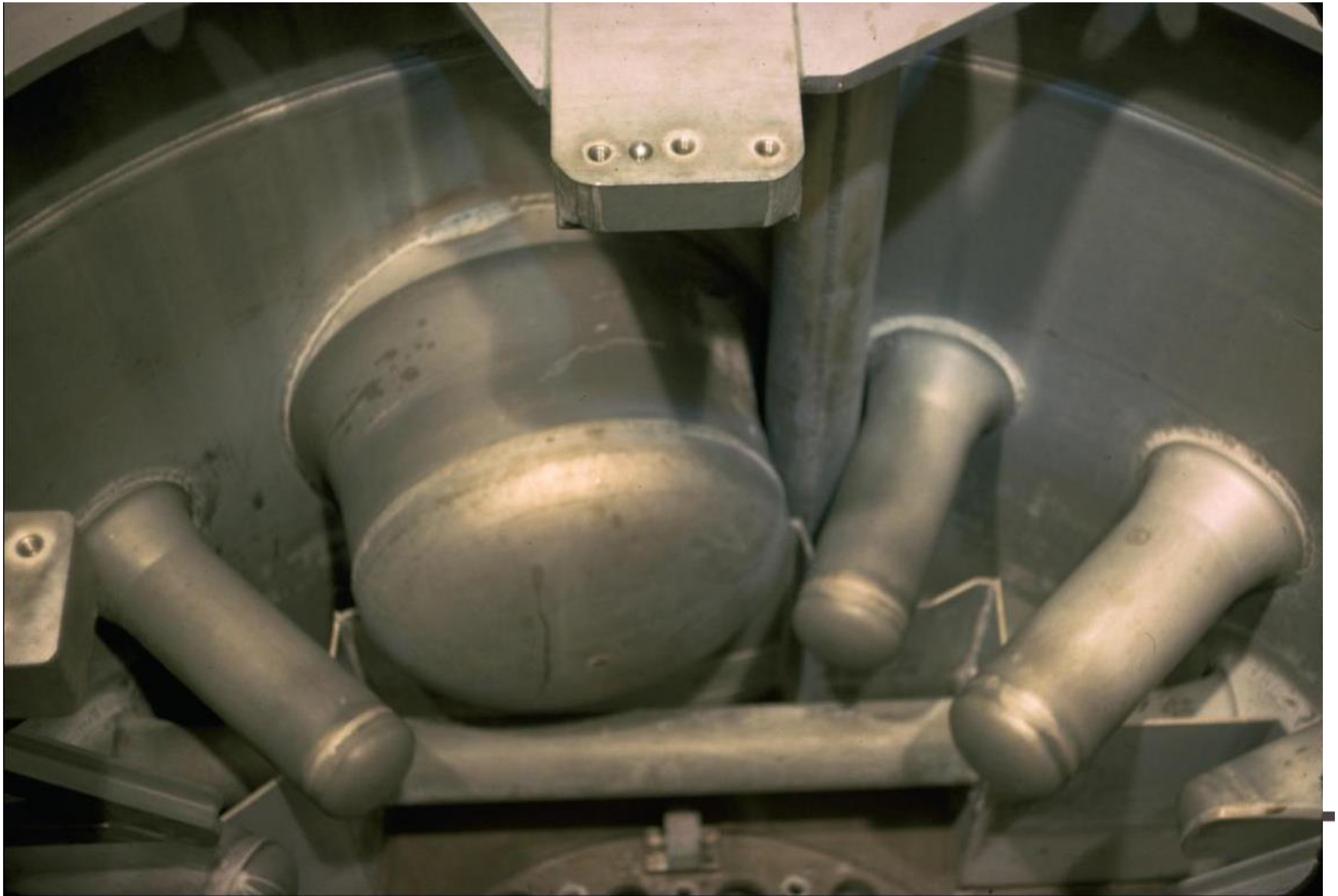
The NBSR has a large "split" core and a heavy water moderator and reflector



9 large radial beam ports

Key Decision

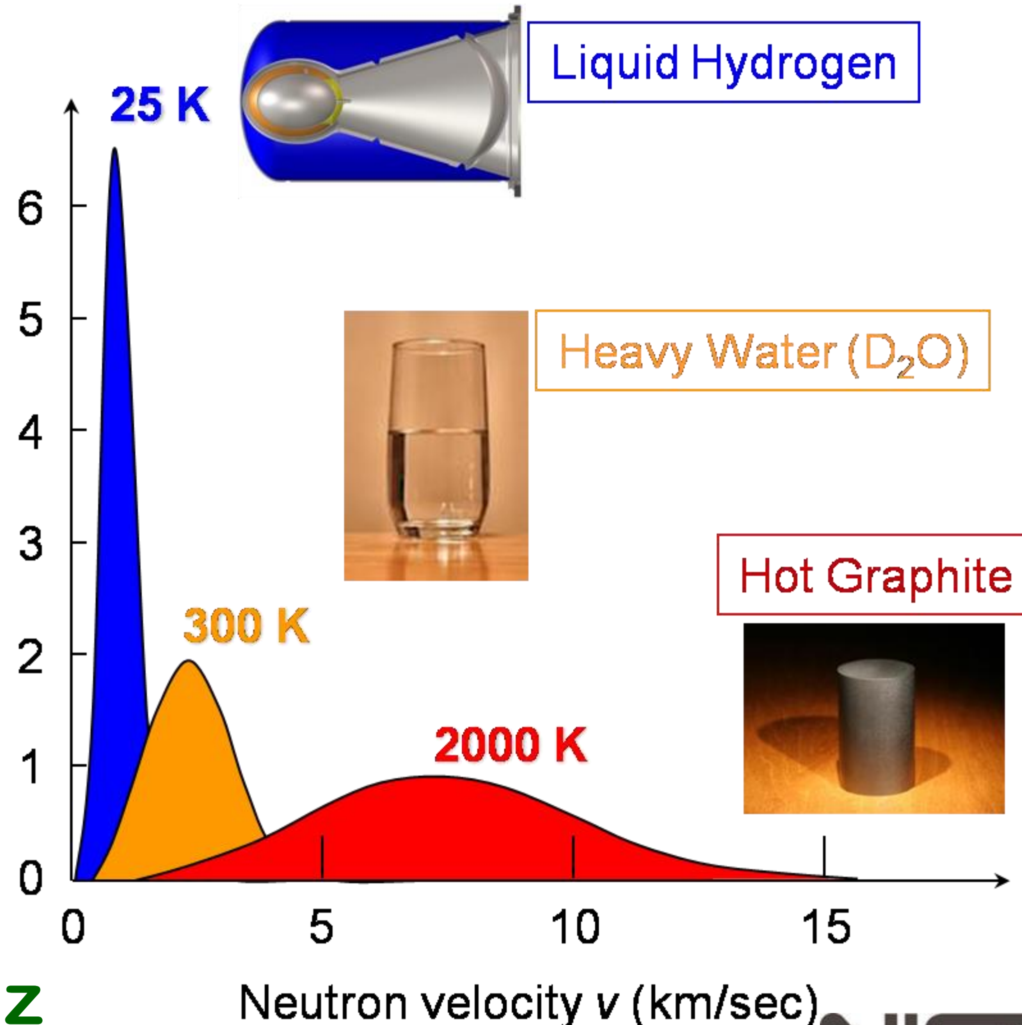
Provision for a large volume cold source



Moderating Neutrons

Maxwellian Distribution

$$\Phi \sim v^3 e^{(-mv^2/2k_BT)}$$



1 meV ≈ 12 K ≈ ¼ THz

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Hot, Thermal and Cold Neutrons

Hot neutrons – wavelengths ~ 0.7 Å (170 meV)

Thermal neutrons - wavelengths ~ 2 Å (20 meV)

Cold neutrons - wavelengths ~ 6 Å (2.3 meV)

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The NBSR goes critical (1967)

Allen Astin, Harry Landon, Carl Muehlhause, Bob Carter, Irl Schoonover

10 MW achieved &
regular operations (1969)

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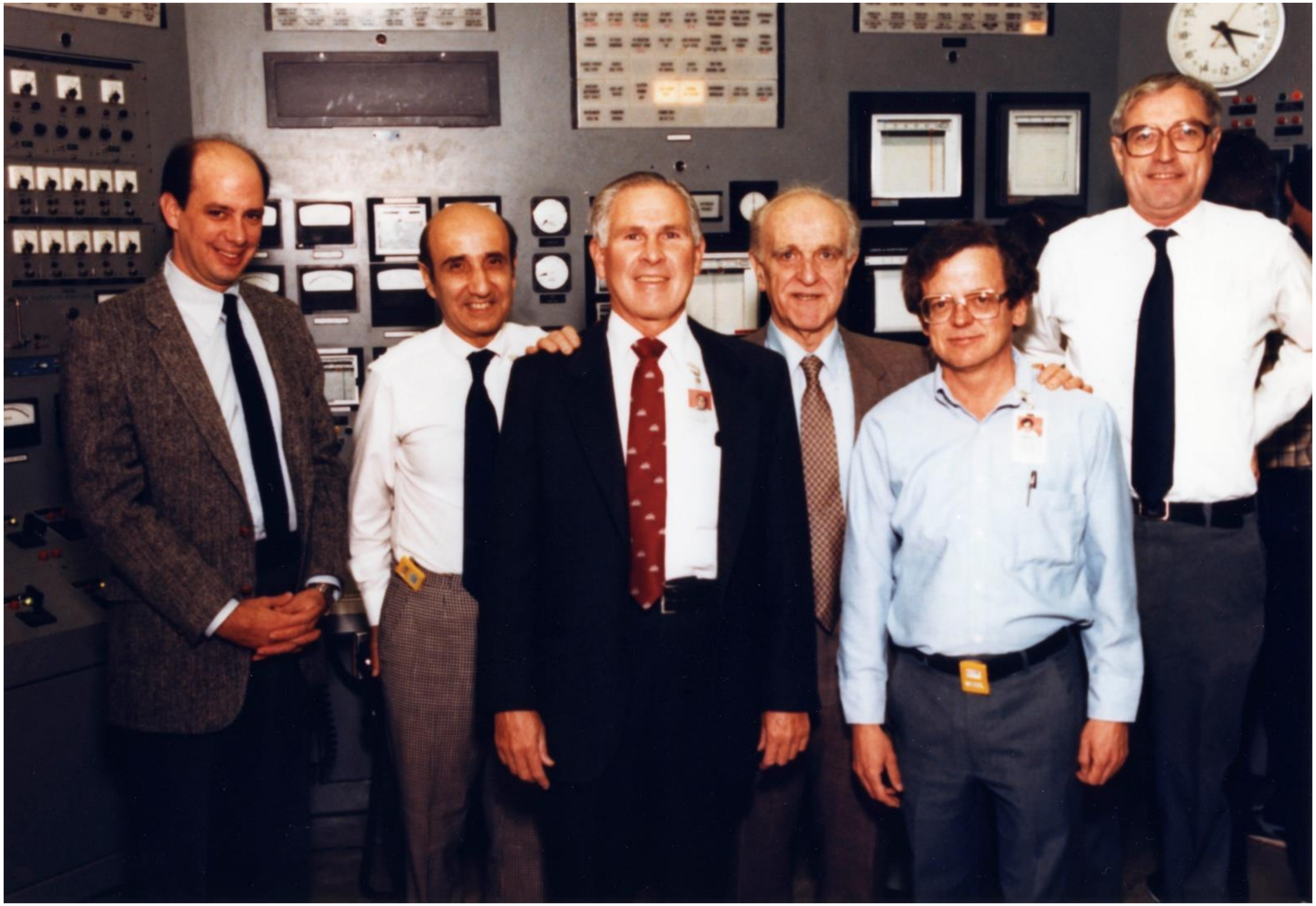
Increase to 20 MW - funded (1979)



Ray Kammer, Tawfik Raby, Bob Carter, Ernie Ambler, Mike Rowe, Jack Rush

20 MW achieved & the NBSR relicensed (1985)

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The first cold neutron scource

In FY 1985, funding was provided for the first cold source at the NBSR - a D_2O ice source – serves the SANS instrument (1987)

Still no guide hall

In spite of this, Exxon signed an agreement with NBS to share the cost of developing the first competitive SANS instrument in the US (1985)

Seitz-Eastman Panel

By 1983 there were many proposals for new and upgraded facilities for materials research (including an NBS proposal for a cold neutron facility at the NBSR)

Jay Keyworth asked the NRC to set up what became known as the Seitz-Eastman Panel

The committee reviewed 12 proposals for facilities and ranked the proposals in priority order

(6 were eventually built)

Seitz-Eastman Panel (1984)

Cold neutron facilities at NBS and BNL received the highest recommendation for new capabilities at existing facilities

(APS received the highest recommendation for new facilities, followed by ANS, ALS, and SNS)

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Success! (FY 1987)

Lyle Schwartz, Clarence (Bud) Brown, Connie Morella, Ernie Ambler, Mike Rowe

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1989

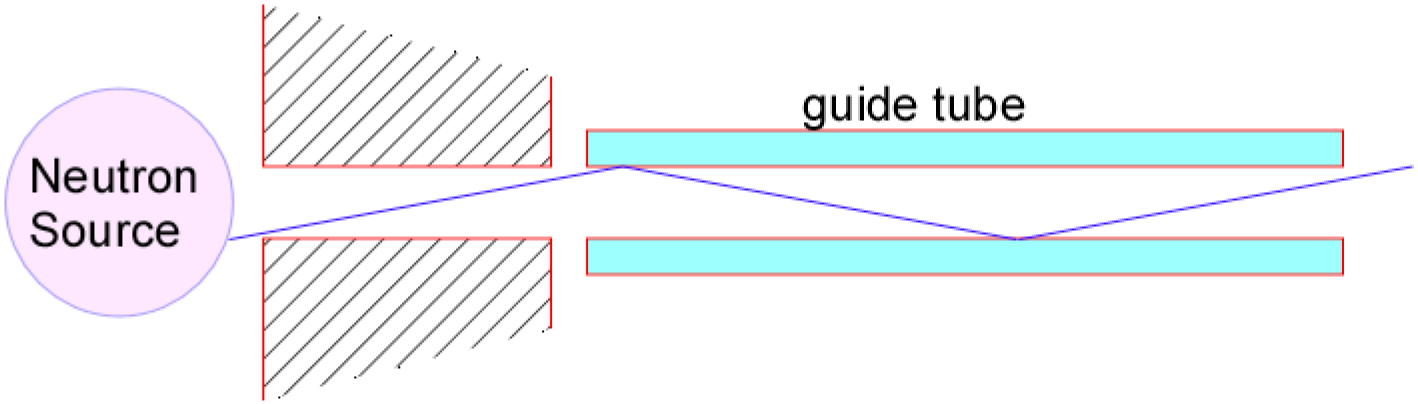
Neutron Guides

Neutron guides are the neutron analog of fiber optic cable

Developed in Europe

The large cold source volume allowed NIST to develop the largest guide area of any facility

NIST was also the first to employ “supermirror” guides



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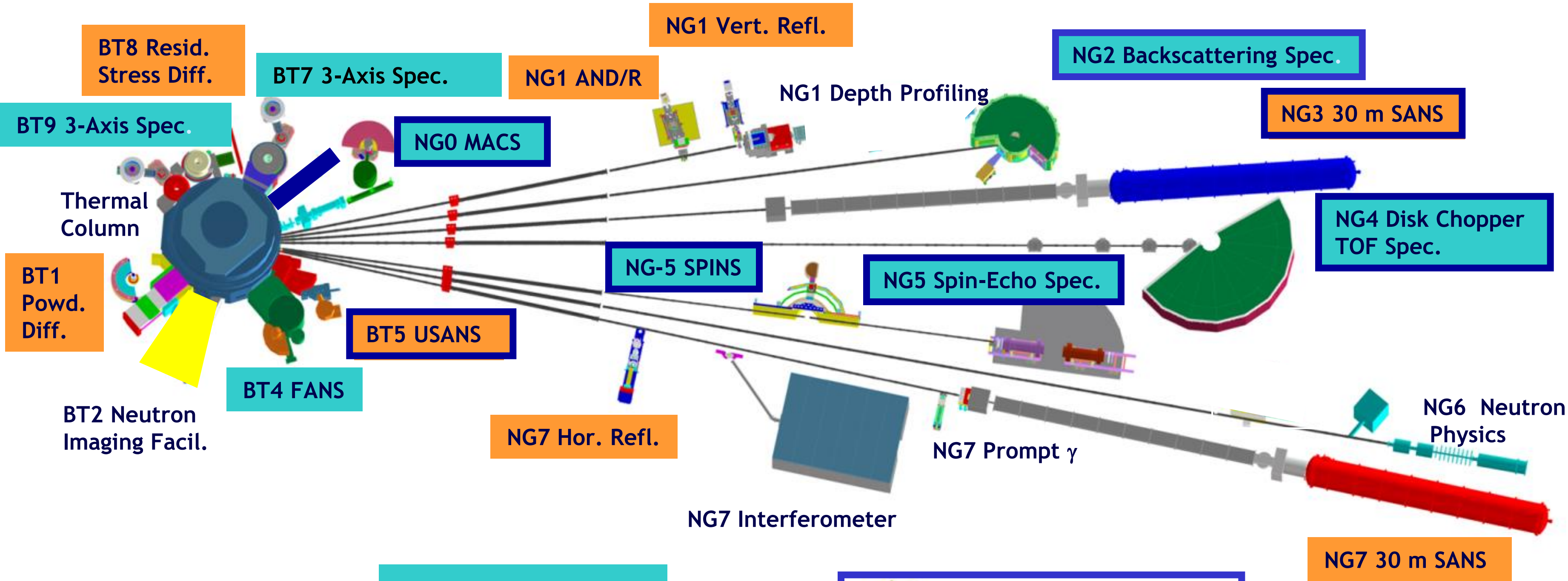
Installation of Guides 5, 6, and 7

1989 or 1990

The NCNR (2010)



Diffraction Instruments

Spectrometers

Other Neutron Methods

CHRNS Center for High Resolution Neutron Scattering NIST

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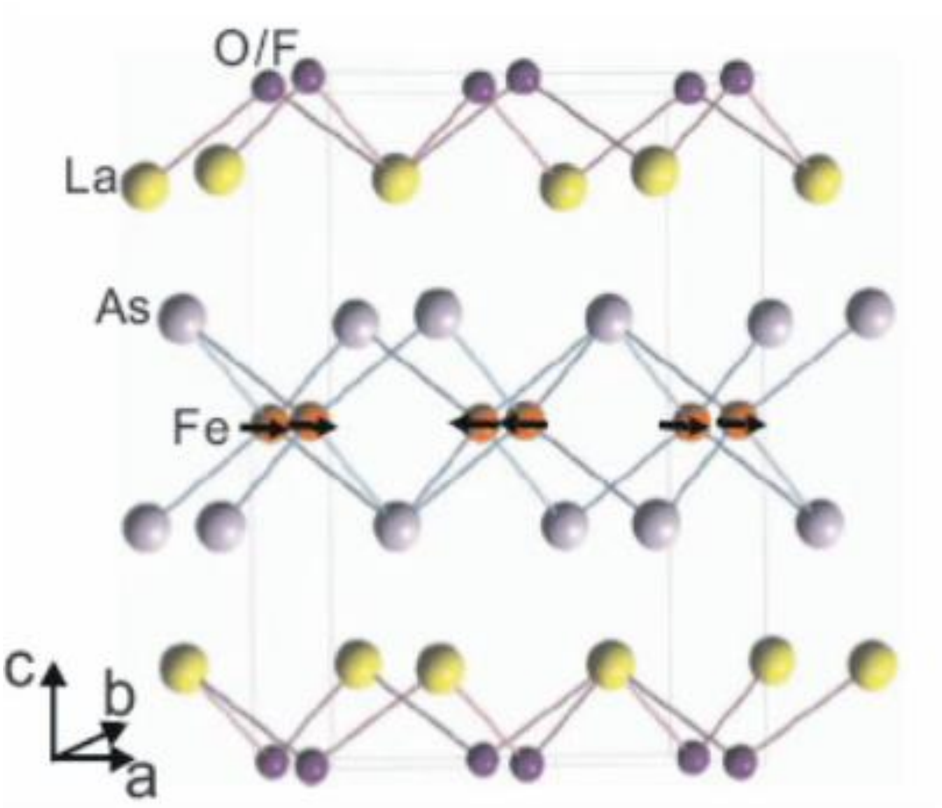
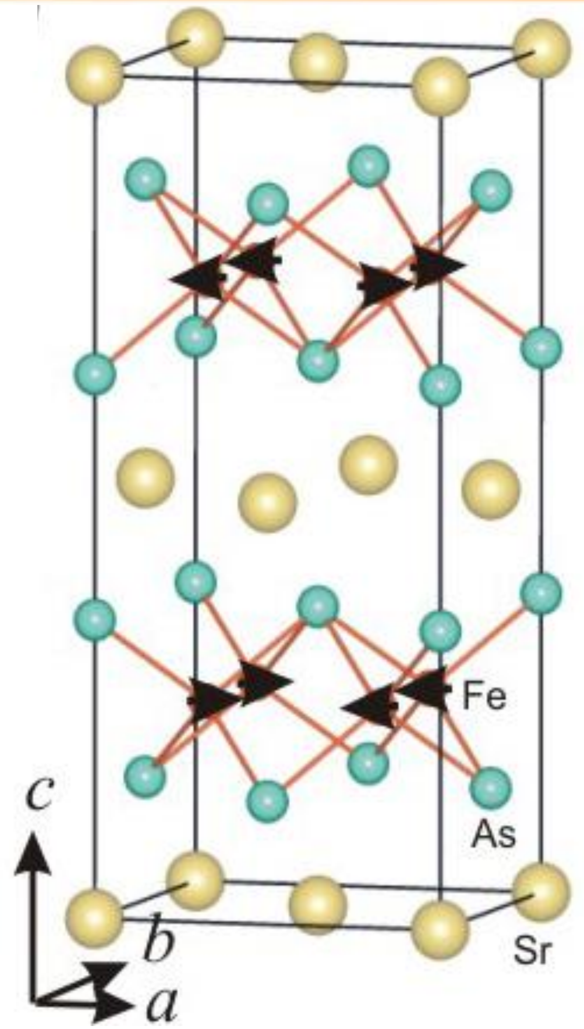
Fe – Pnictide Superconductors





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

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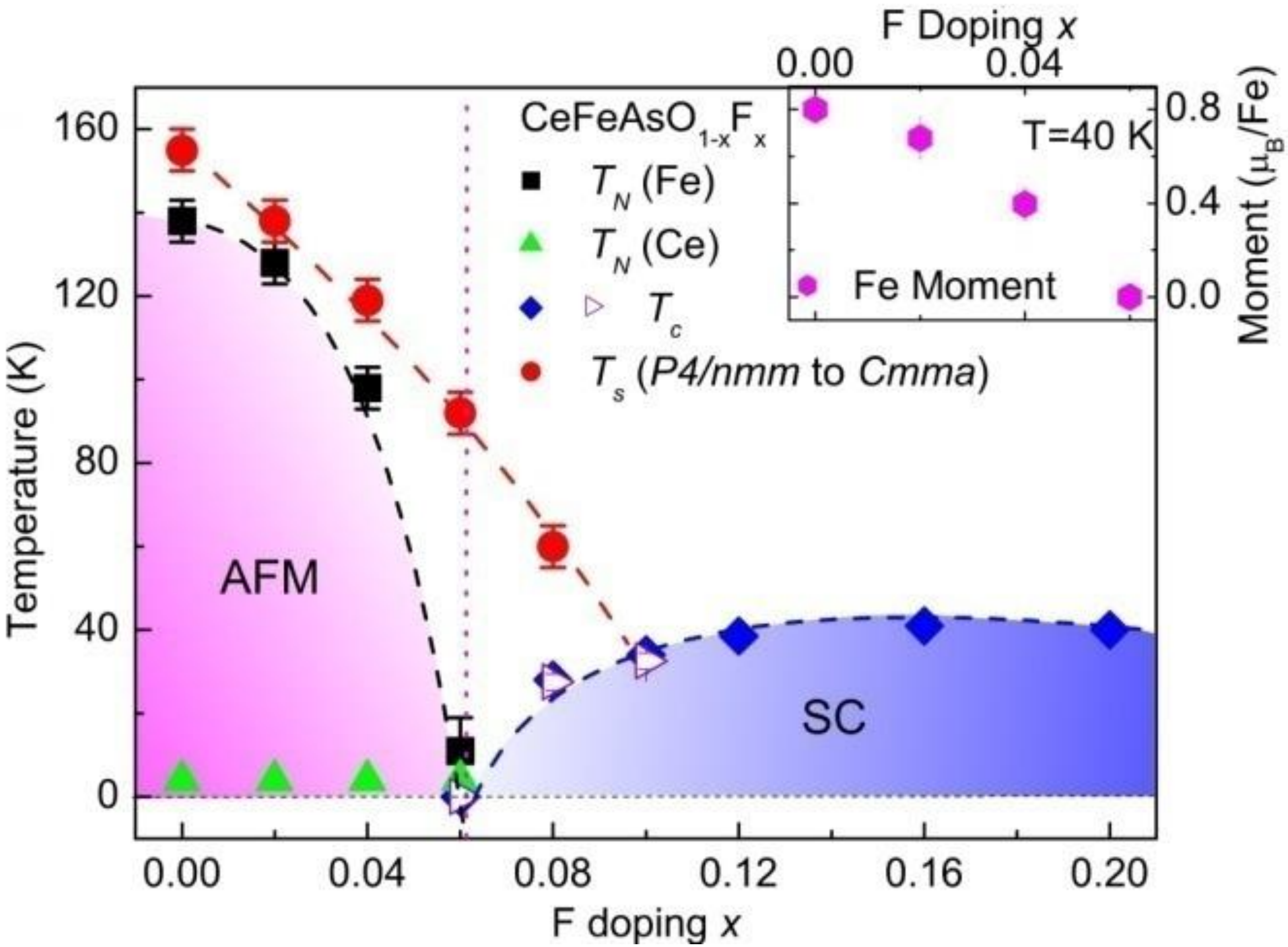
Phase Diagram of $CeFeAsO_{1-x}F_x$



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

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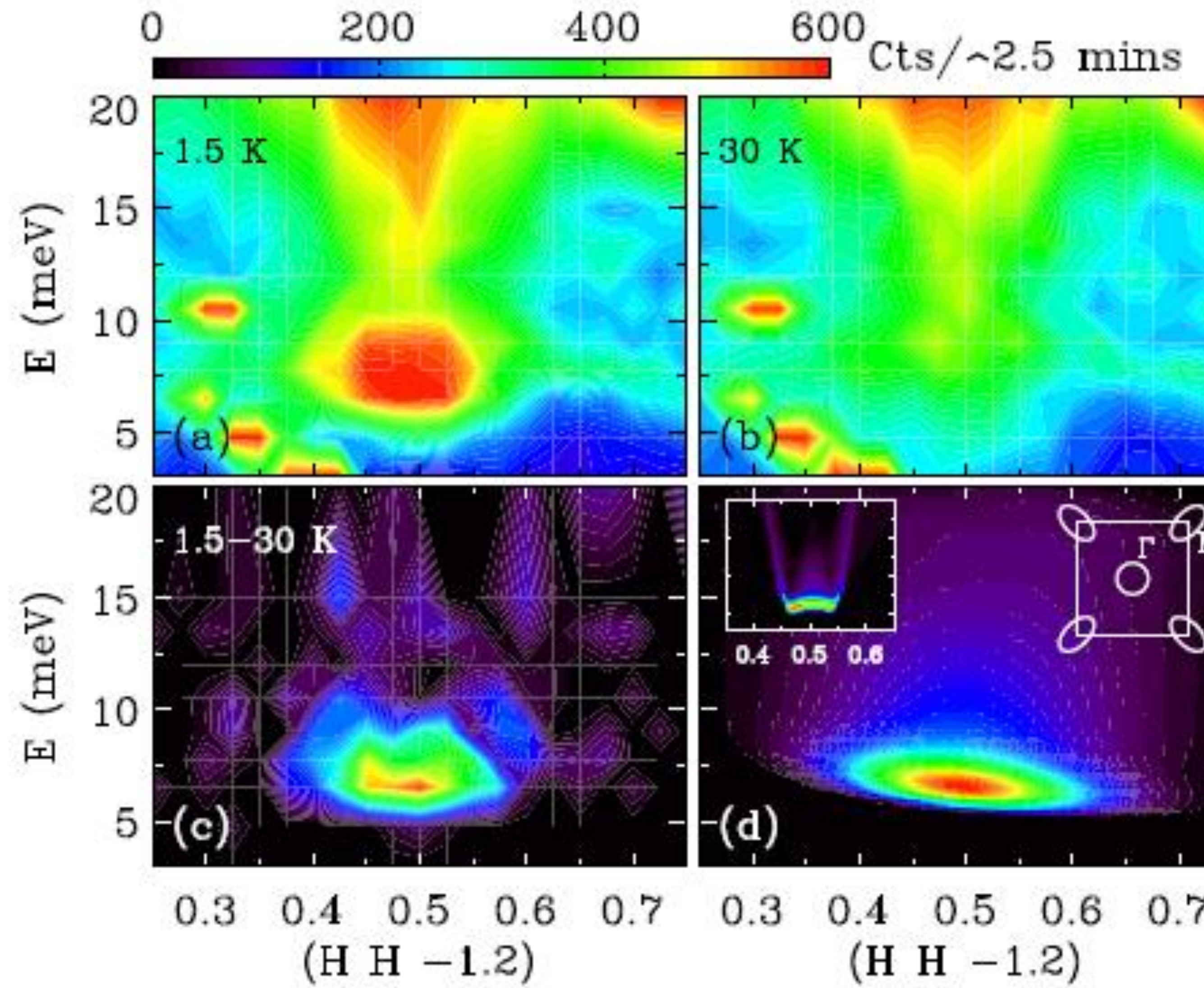
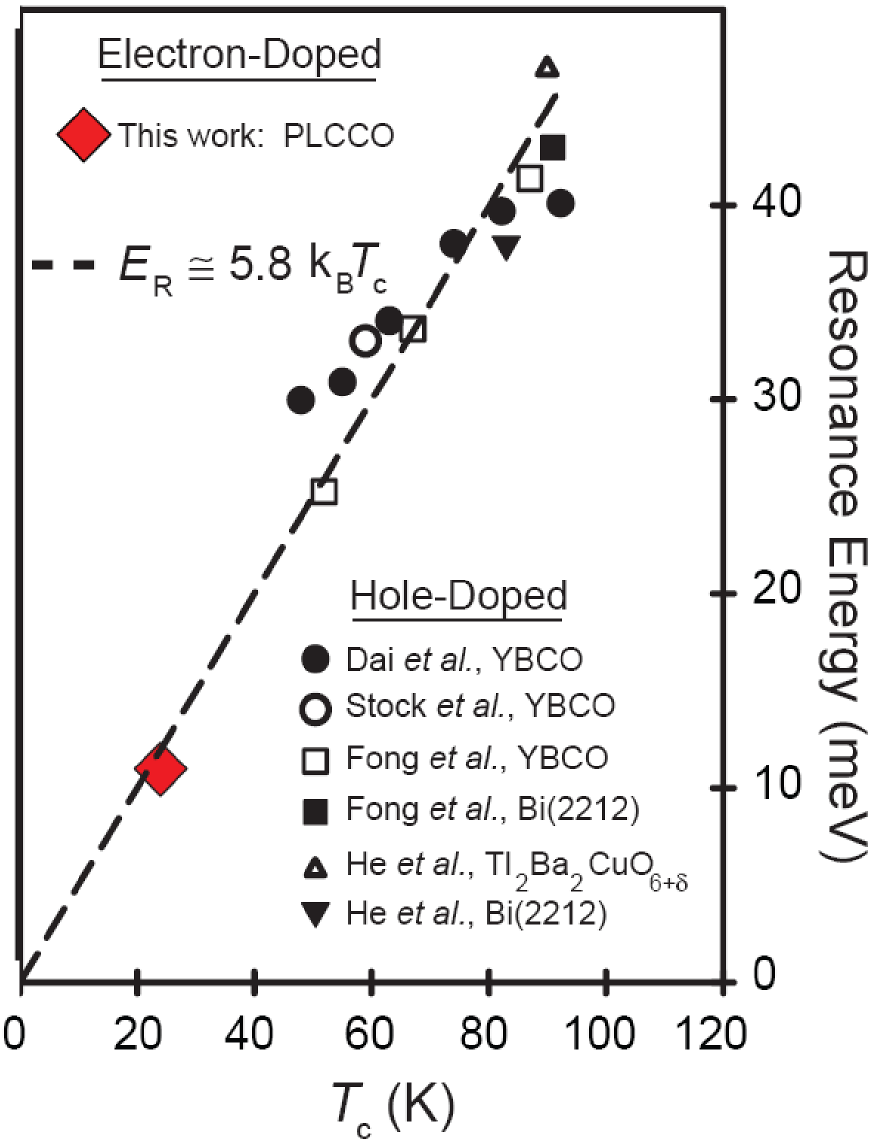
Spin Resonance in $Fe(Se_{0.4}Te_{0.6})$



Qiu *et al.*., (2009)

Superconductivity



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

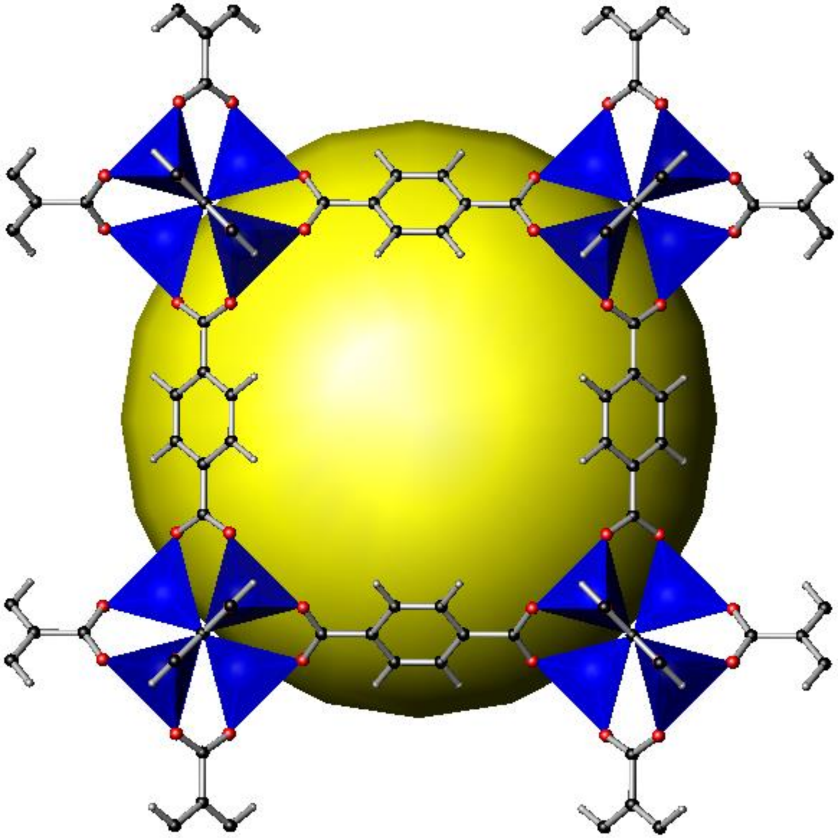
Neutron scattering revealed a magnetic resonance was observed in an "electron-doped" superconductor PLCCO ($Pr_{0.88}LaCe_{0.12}CuO_{4-\delta}$) at 11 meV.

Wilson *et al.* Nature(2006)

Metal-Organic Frameworks (MOF)

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



H. Li, M. Eddaoudi, M. O'Keeffe, O.M. Yaghi, Nature **402**, 276 (1999).

N. Rosi, M. Eddaoudi, D. Vodak, J. Eckert, M. O'Keeffe, O.M. Yaghi, Science **300**, 1127 (2003).

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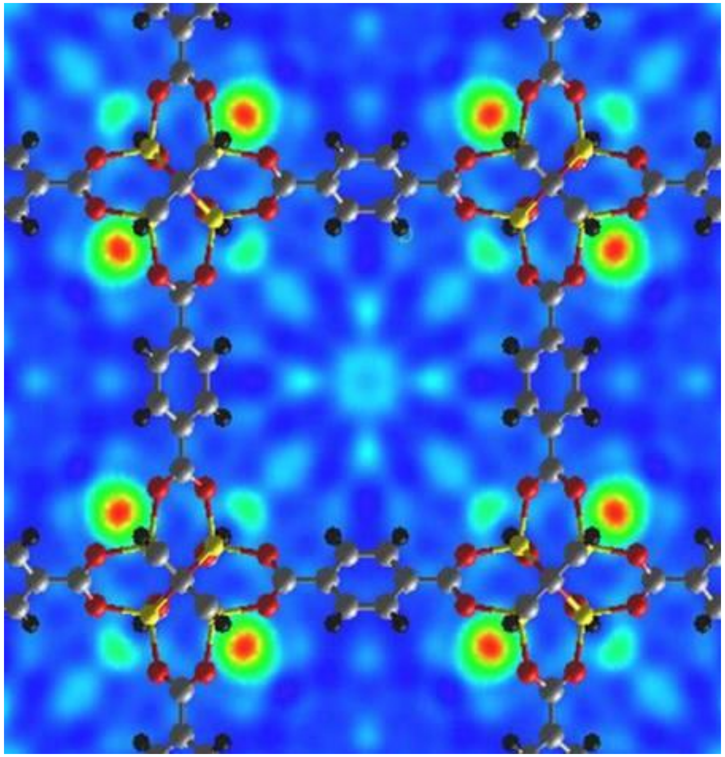
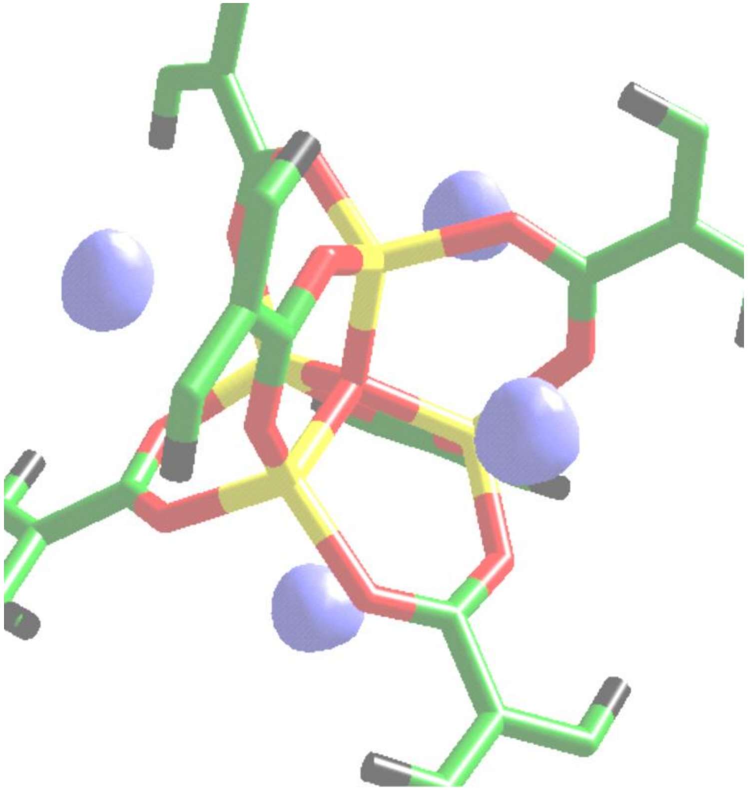
Locations of the H_2 Molecules

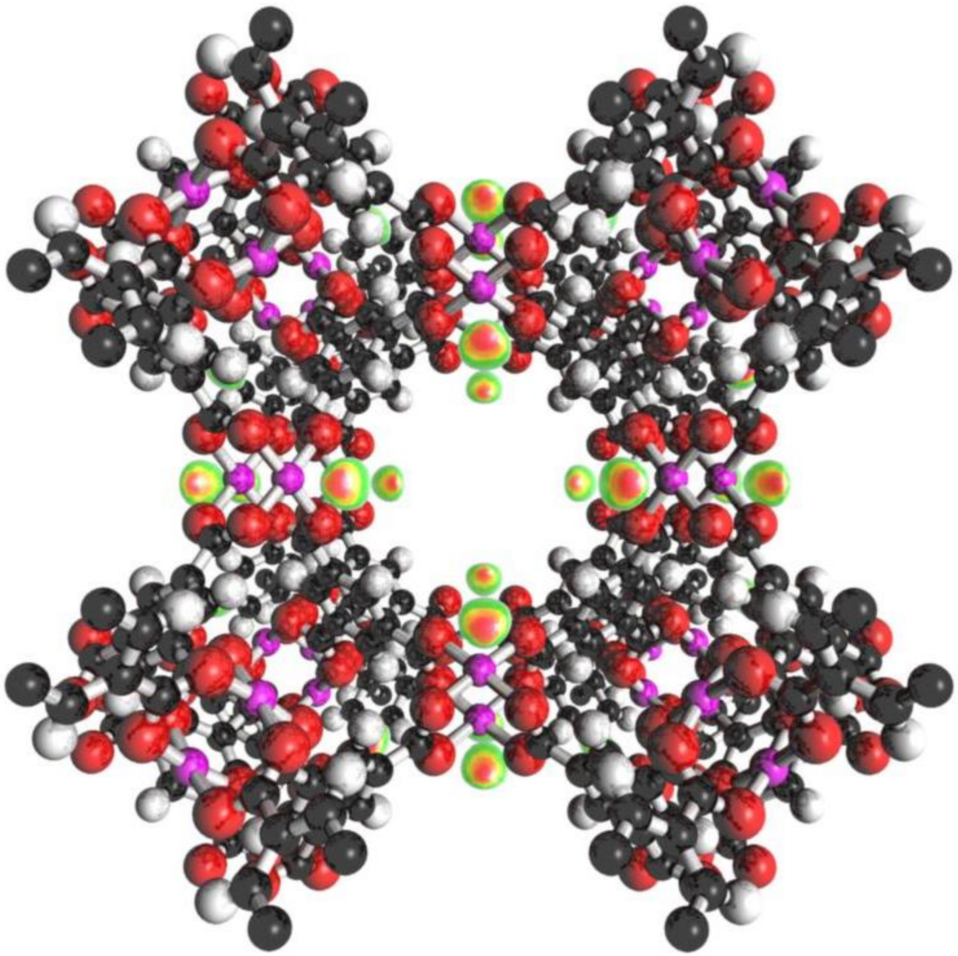
Difference Fourier techniques were utilized to determine four hydrogen adsorption sites within the MOF-5 material

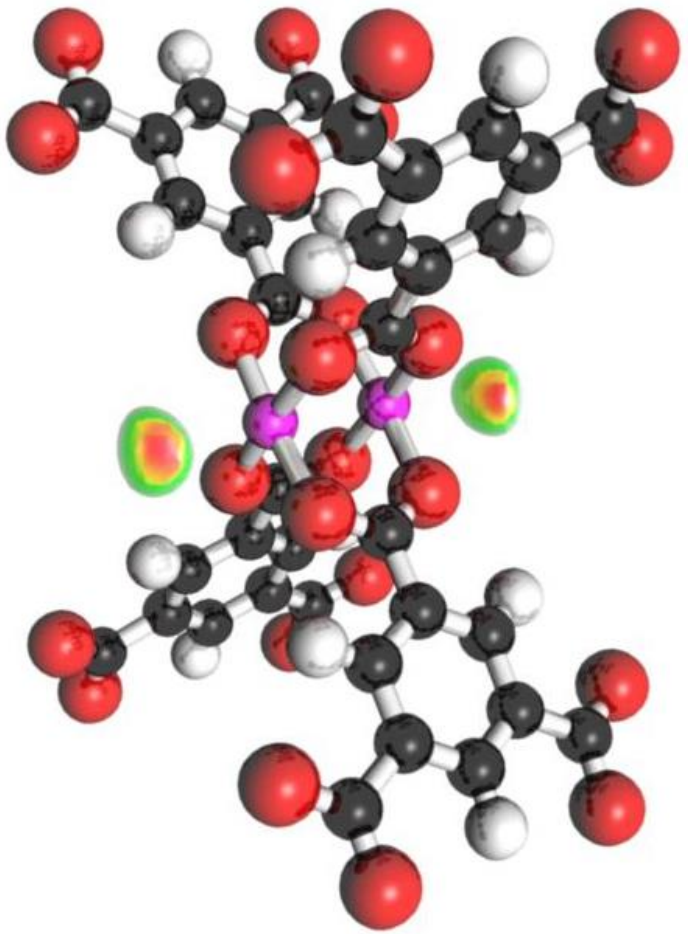




T. Yildirim & M.R. Hartman, PRL **95**, 215504 (2005).

H_2 in Cu HKUST-1





VPeterson, *et al.*, JACS **128**, 15578 (2006).

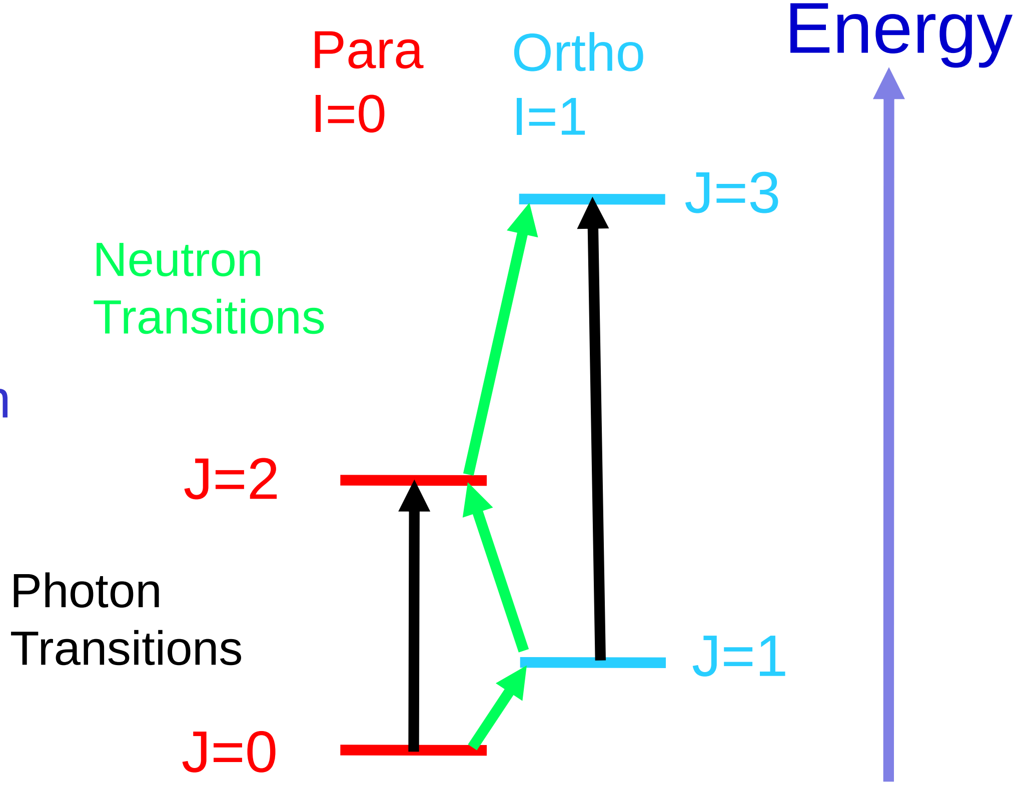
Hydrogen Rotational Transitions

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

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

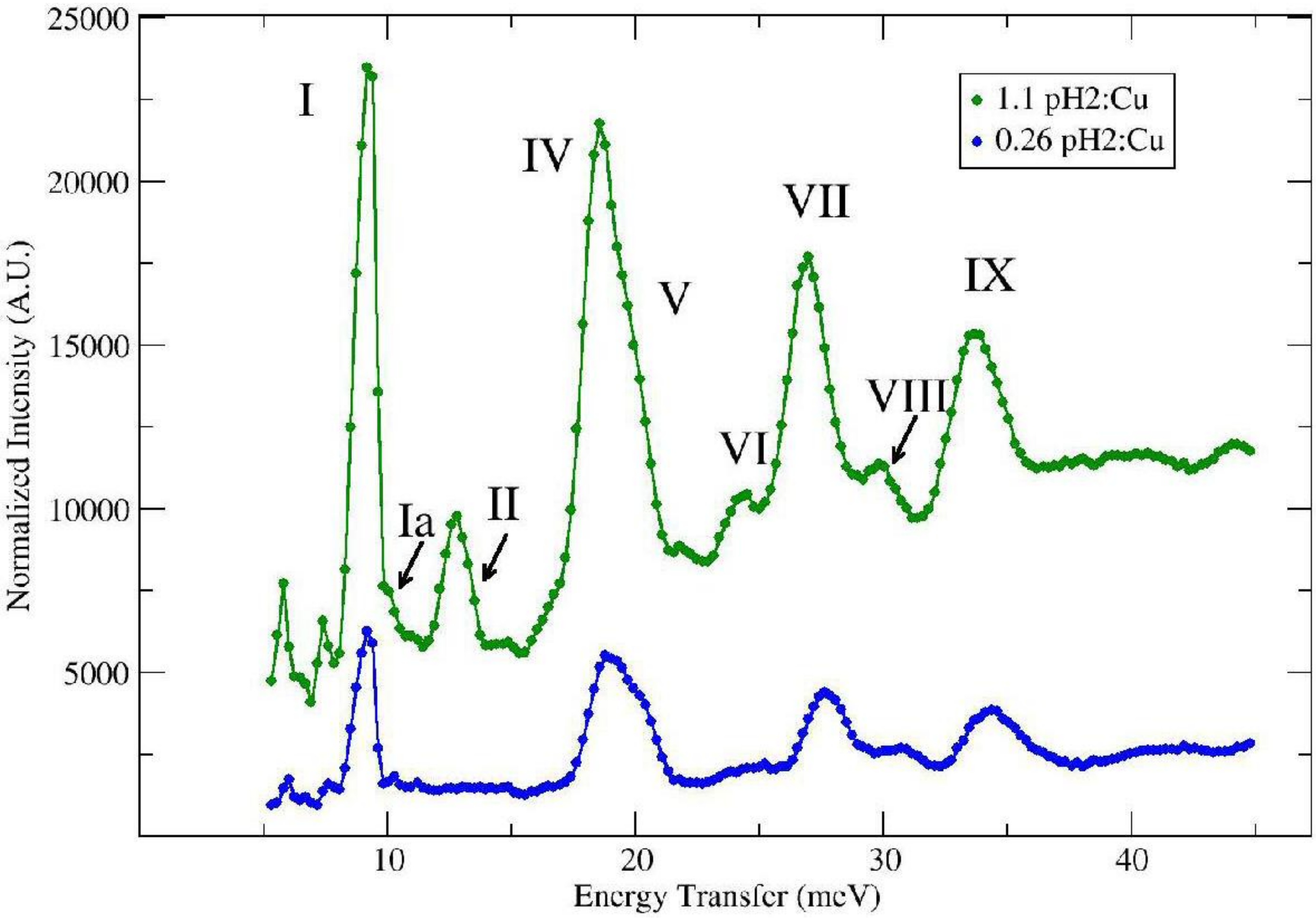
Ortho has a nuclear spin I=1.
This constrains J to be odd.

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



(Neutron energy loss)

p-H_2 in HKUST-1



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

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

Two dimensional free rotor: $E=BJ^2$ — J:0→1, ΔE=7.35 meV

Three dimensional free rotor: $E=BJ(J+1)$ — J:0→1, ΔE=14.7 meV

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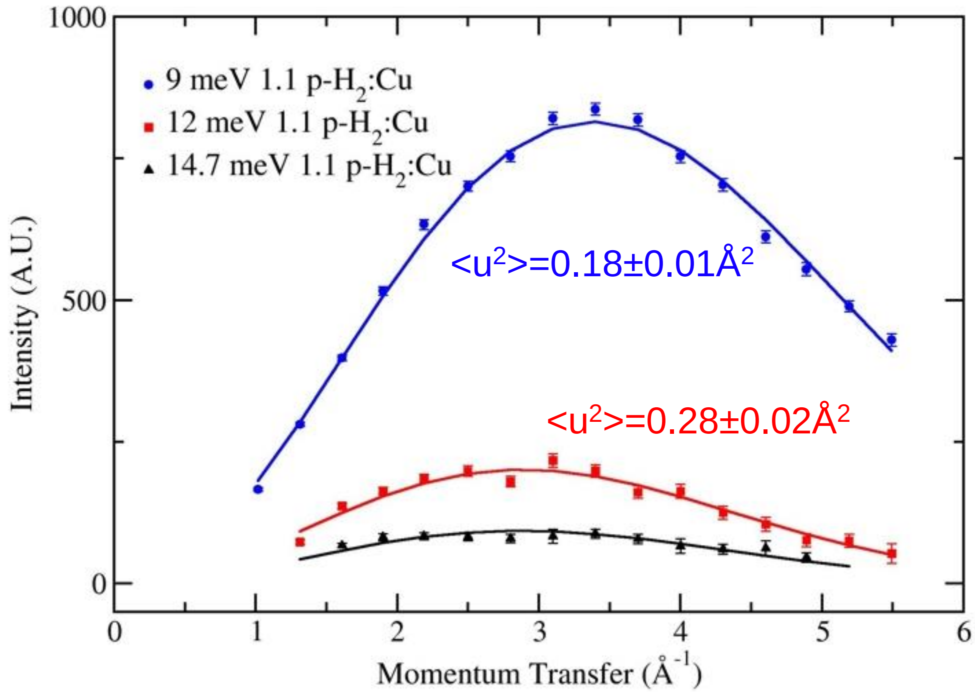
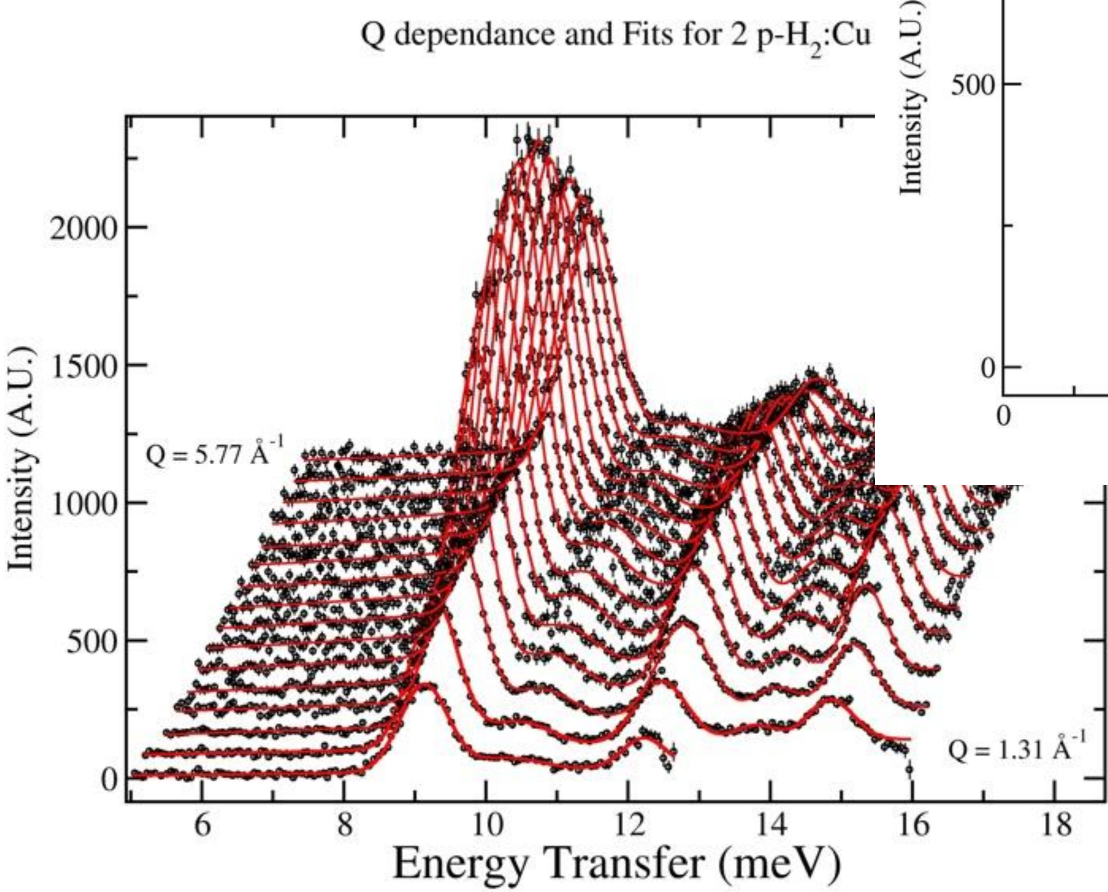
p-H₂ in HKUST-1

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





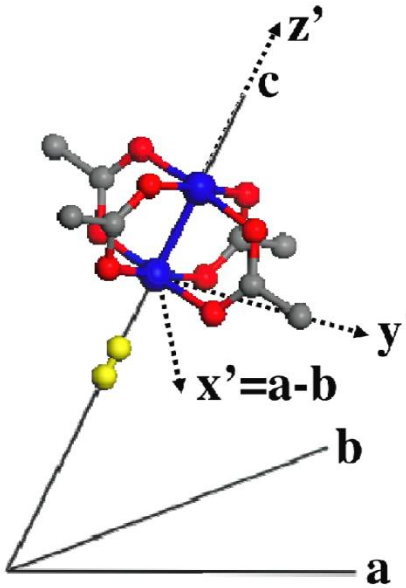
d_{HH}=0.74 Å

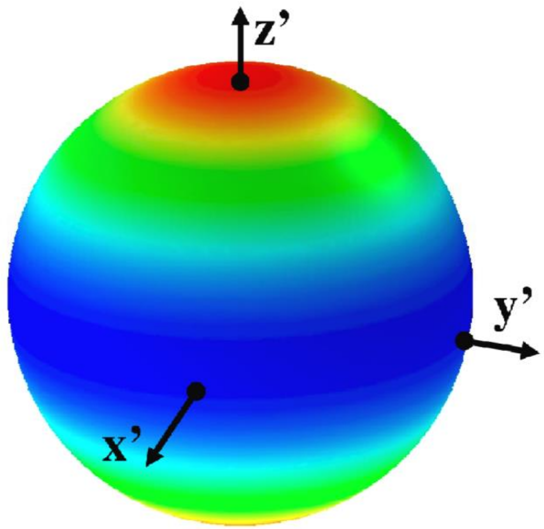
At ~5K, $<u^2>$ of p-H_2 =0.48 $Å^2$

(M. Nielsen PRB 1972)

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

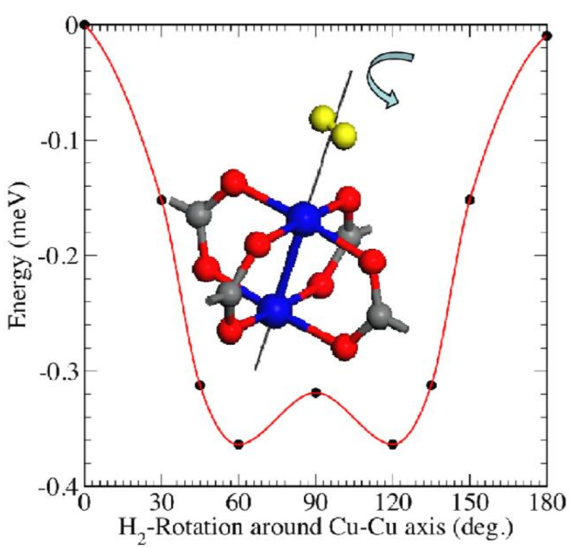
In-plane phonons

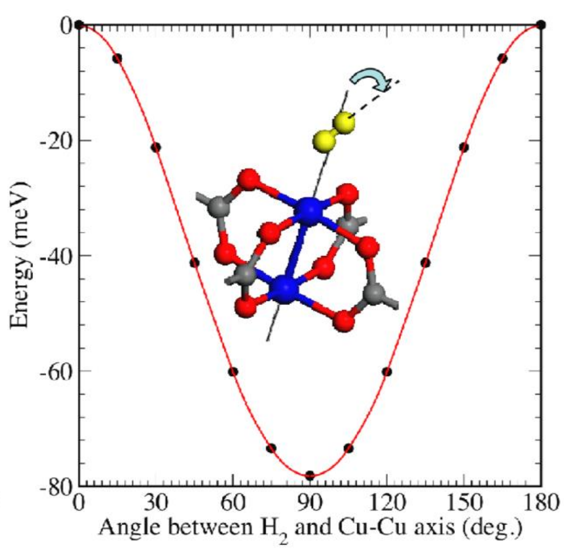
$\hbar\omega_{x'}$= 9.6 meV

$\hbar\omega_{y'}$= 13.4 meV

Out-of--plane phonons

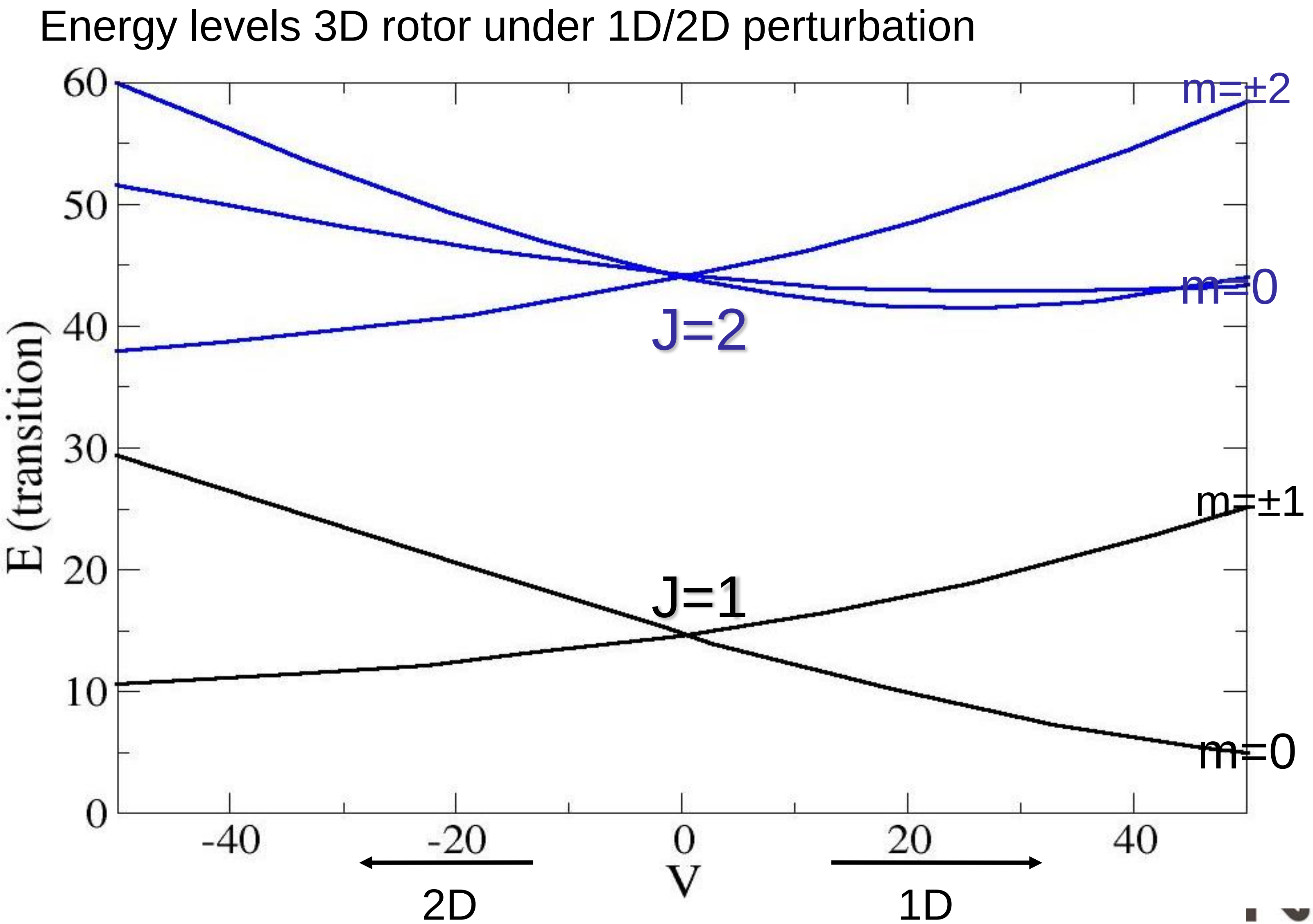
$\hbar\omega_{z'}$= 22.9 meV



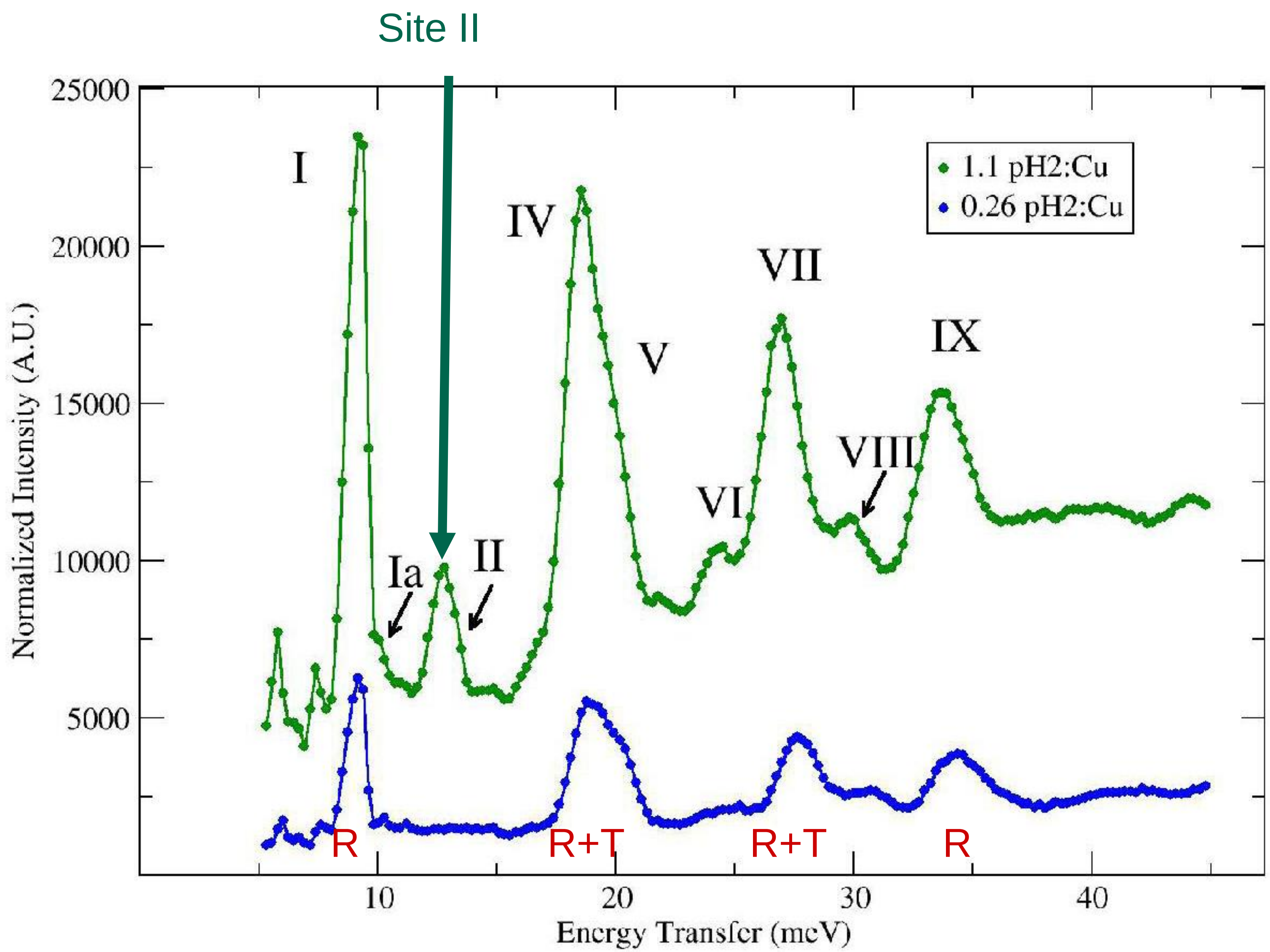


C.M. Brown *et al.*, Nanotechnology **20**, 204025 (2009).

The transition tells us about the symmetry and strength of the local potential. A larger rotational barrier *implies* a stronger binding.



p-H_2 in HKUST-1



Rotations are "pseudo" 2-D

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

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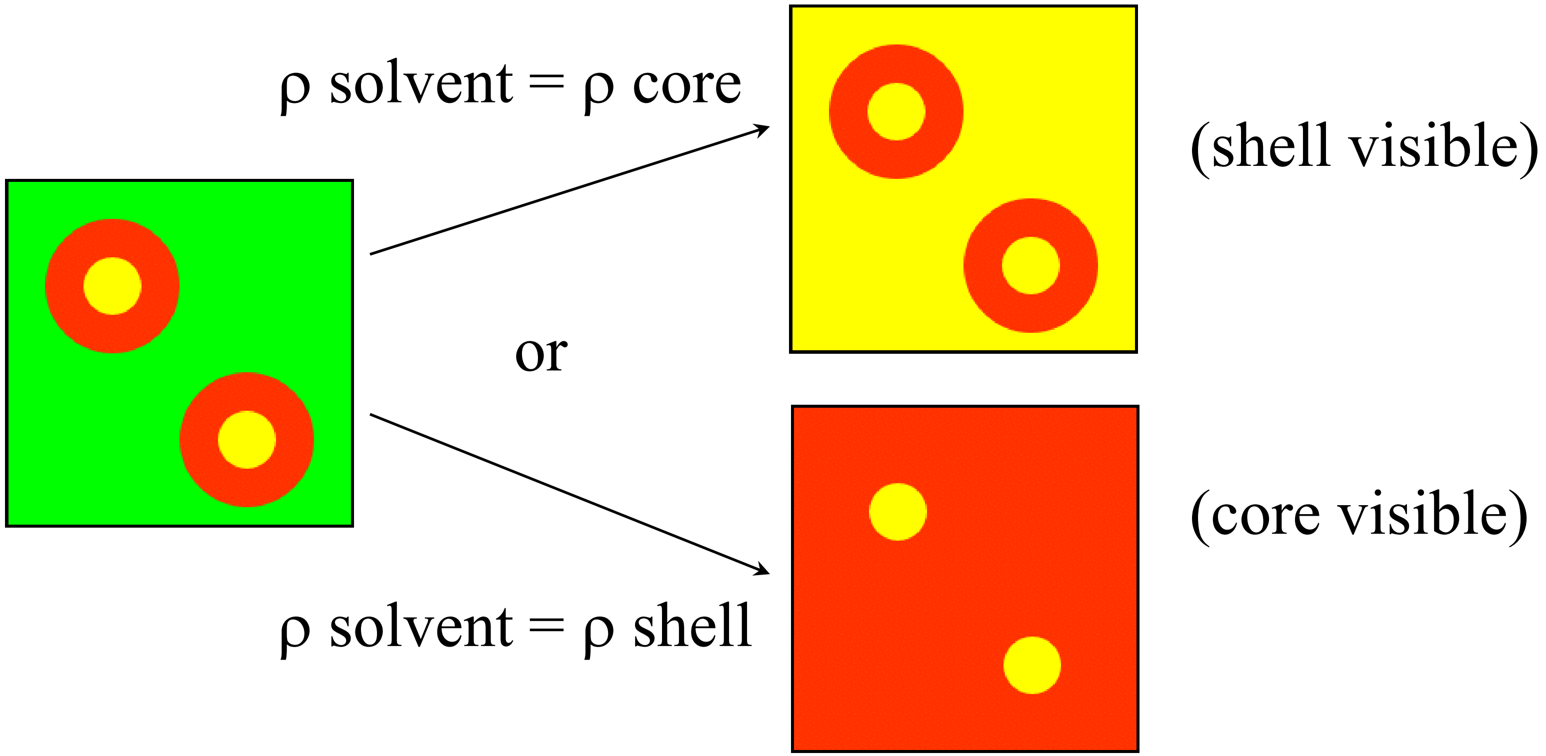
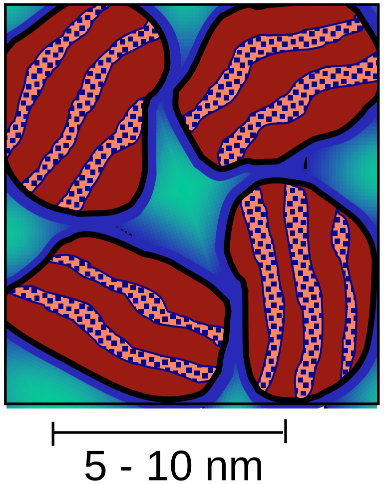
Solving Multi-Phase Structures

Contrast Matching - reduce the number of phases "visible"



The two distinct 2-phase systems can be easily understood

Nanoscale Structure of Concrete



Calcium silicate sheets with OH^- groups

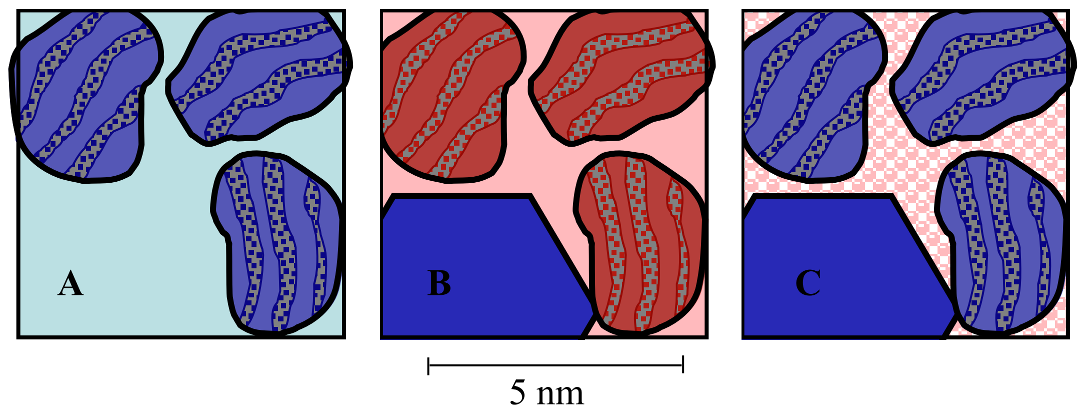
Interlayer space with physically bound H_2O

Adsorbed H_2O

Liquid H_2O in nanopores

The strength of cement comes from an amorphous phase called CSH

Use CD_3OH and uSAX in addition to D_2O for contrast variation



1) CSH is $(CaO)_{1.7}SiO_2(H_2O)_{1.80(3)}$ with mass density 2.604(22) g cm^{-3}
2) amounts of chemically-bound, adsorbed, and free H_2O contents
3) amounts of nanoscale CH phase in various cements

A.J. Allen, J.J. Thomas and H.M. Jennings; Nature Mater. **6**, 311 (2007)

NIST

SANS from Paint

Paints are typically mixtures of inorganic pigments and latex emulsions. The rheology of such mixtures is strongly shear dependent.

Researchers from Dow have studied polymer-colloid structure and interactions under shear using SANS and uSANS.

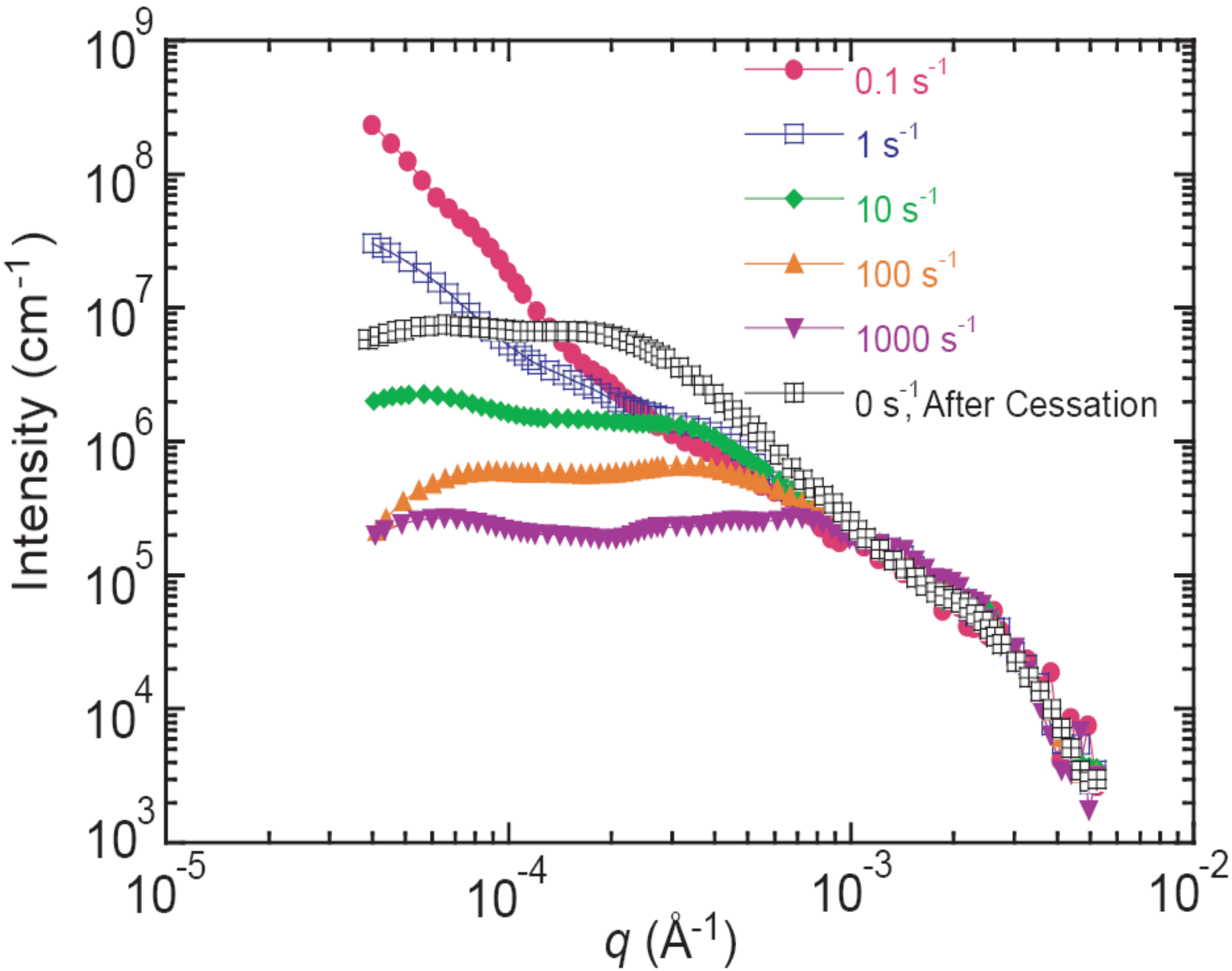
Solvent compositions were adjusted to the contrast match point of each dispersant to isolate the behavior of the 400 nm TiO_2 inorganic particles.

Antony Van Dyk and Alan Nakatani of Dow Coatings Materials won the American Coatings Award for 2012

Alan Nakatani

NIST

SANS from Paint



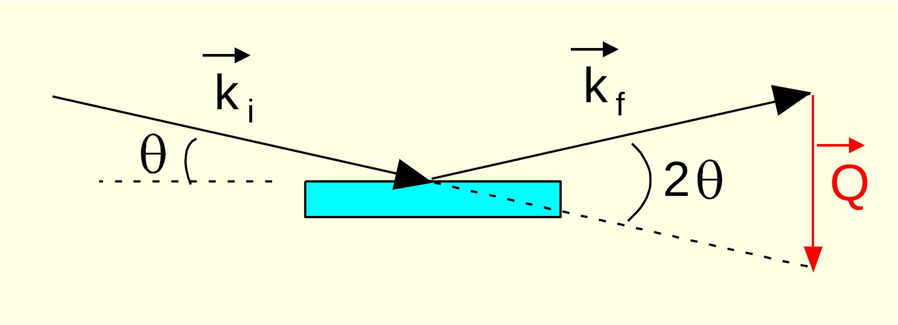
For high MW polyacid dispersants, applied shear breaks up aggregates of the TiO_2 particles.

After cessation of shear, the low angle scattering intensity increases, indicating reaggregation.

Diffraction Probes Structure in the Direction of $\vec{Q}$

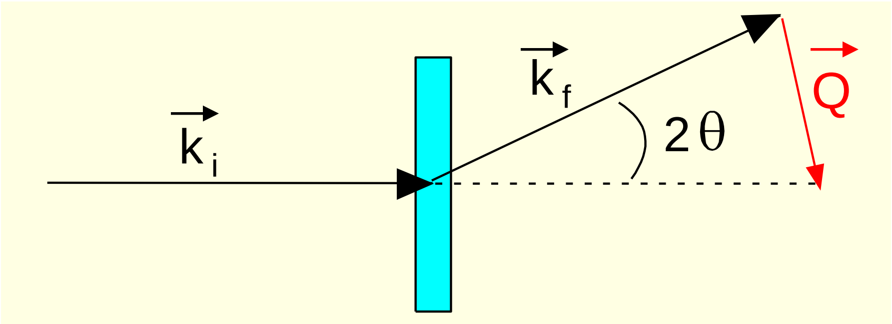
$$\vec{k}_i - \vec{k}_f = \vec{Q}$$

Specular Reflection Geometry



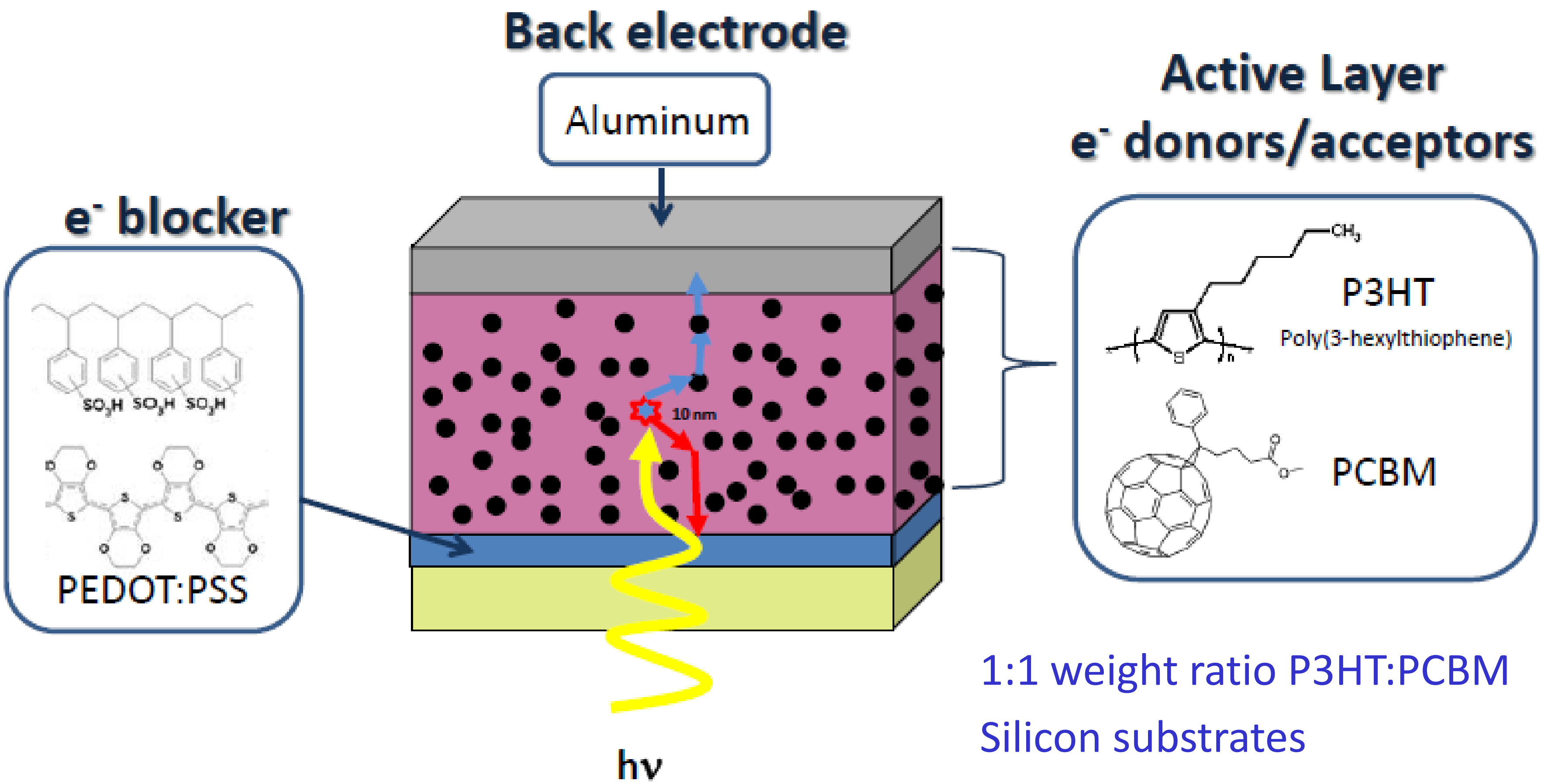
Reflectivity probes structure perpendicular to surface (parallel to Q), and *averages over structure in plane of sample*.

SANS Geometry



SANS probes structure in the plane (parallel to Q), and *averages over structure perpendicular to sample surface.*

Organic Photovoltaics



1:1 weight ratio P3HT:PCBM

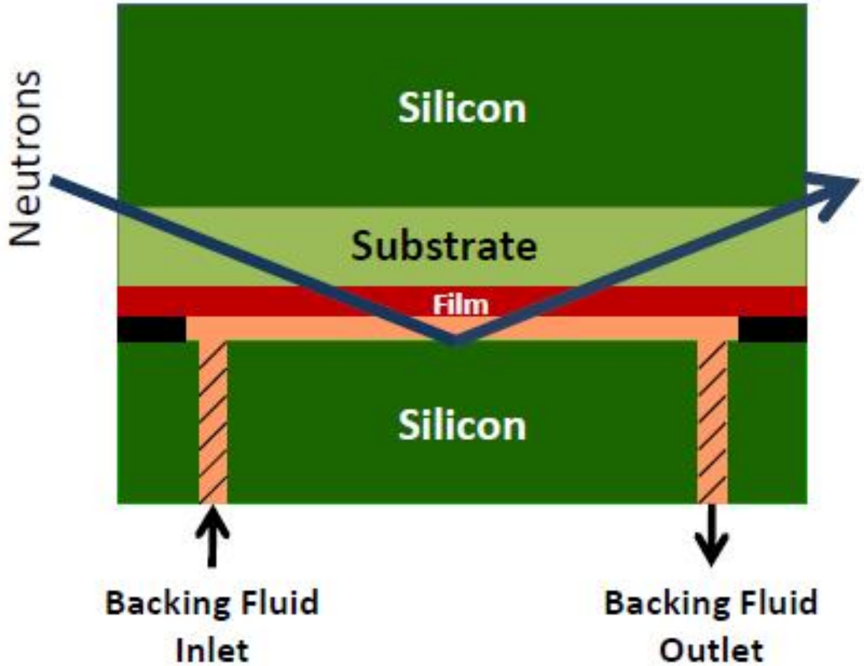
Silicon substrates

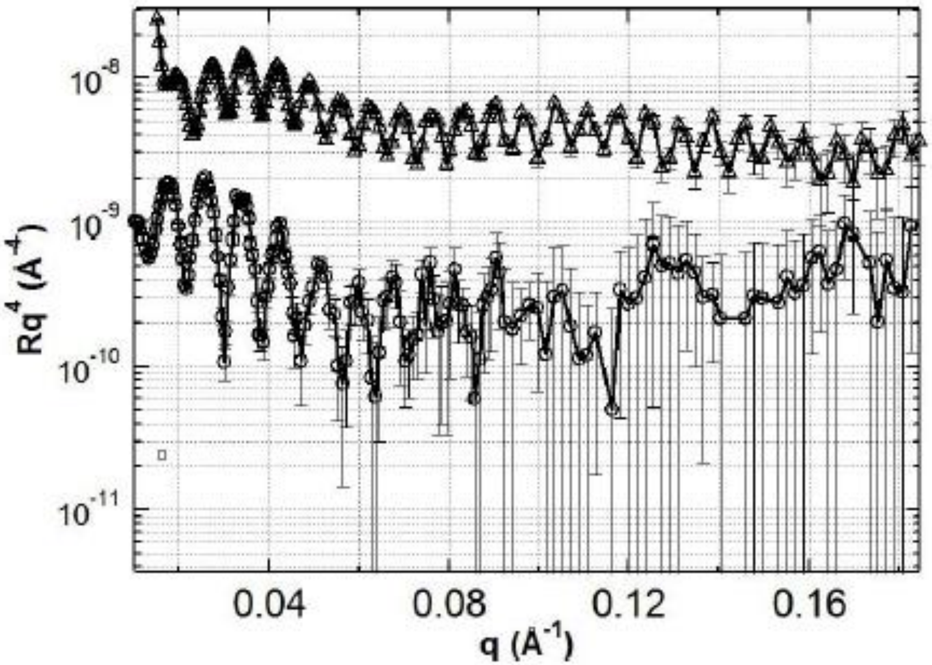
Annealing - 20 min at 140°C

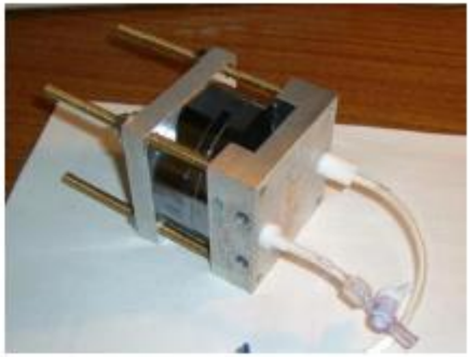
J. Kiel, B.J. Kirby, C. Majkrzak, B. Maranville, and M. Mackay, Soft Matter **6**, 641 (2010)

NIST

Neutron Reflectivity



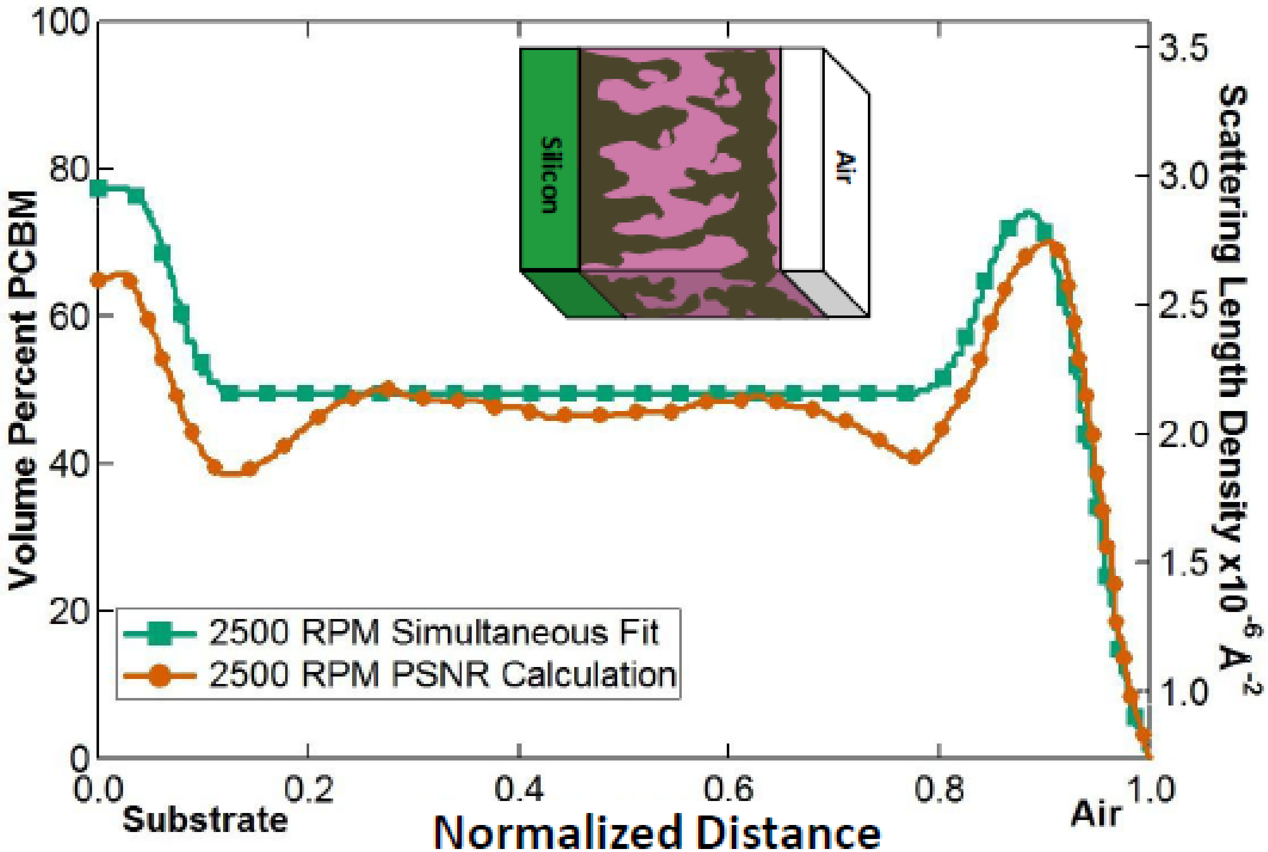




Addition of high SLD backing media greatly enhances scattering intensity and statistics

J. Kiel, B.J. Kirby, C. Majkrzak, B. Maranville, and M. Mackay, Soft Matter **6**, 641 (2010)

Dispersion of PCBM



- Simultaneous fitting and PSNR calculations show agreement
- High PCBM concentration at substrate
- High PCBM concentration near air interface

J. Kiel, B.J. Kirby, C. Majkrzak, B. Maranville, and M. Mackay, Soft Matter **6**, 641 (2010)

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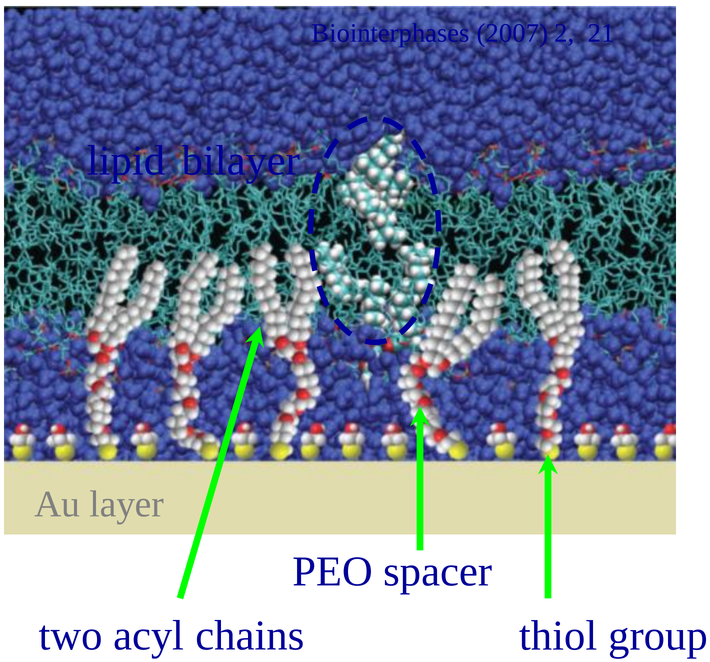
Tethered Bilayer Membranes (tBLM)

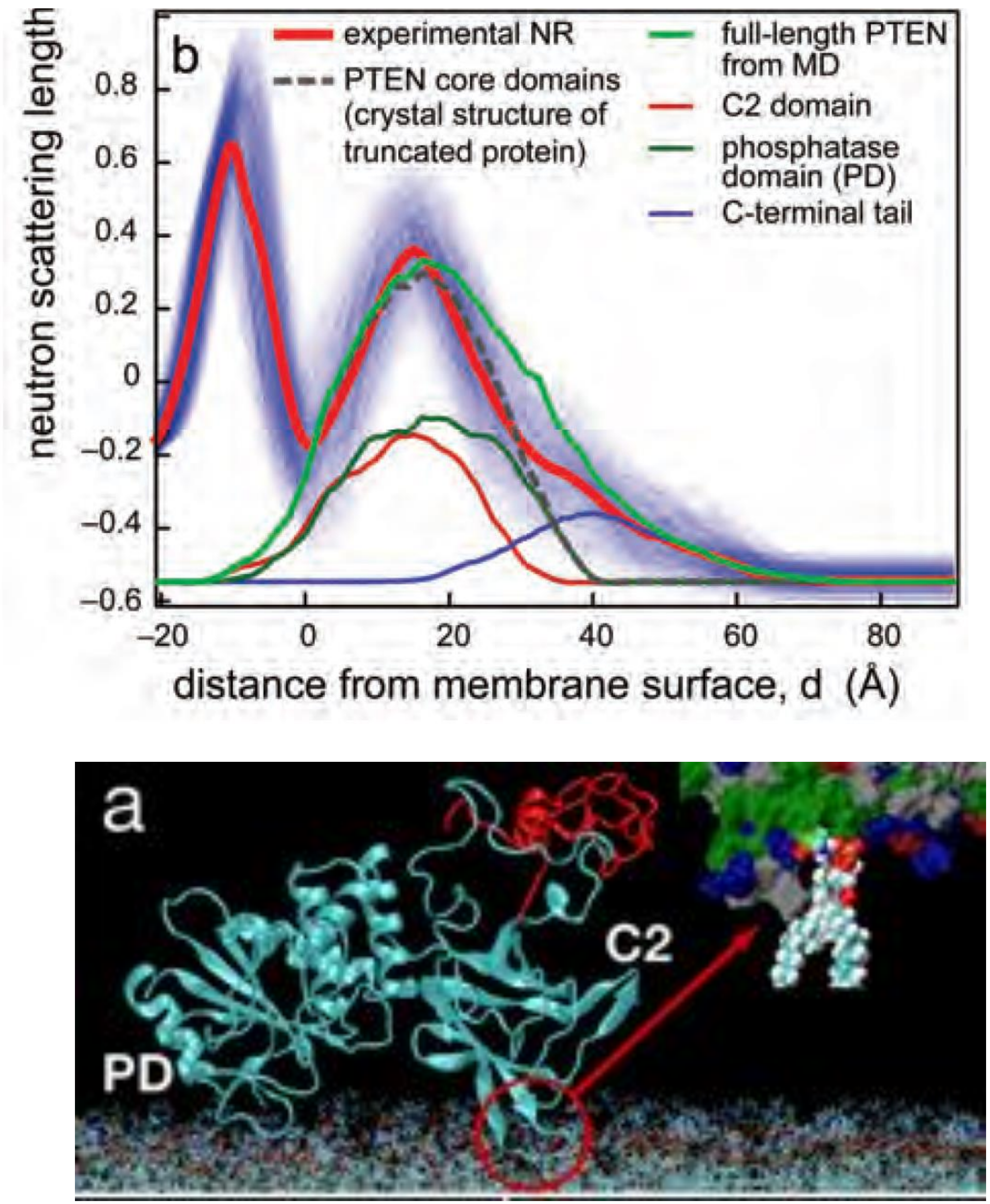
Bio-mimetic environment for studying protein-lipid interactions
(developed at NIST)



Tether partially decouples bilayer from substrate

Accommodate Proteins with sub-membrane domains

Fluid bilayer is highly stable
- Data acquisition times of several days
- Resilient to exchange of aqueous phase
- *In-situ* sample manipulation



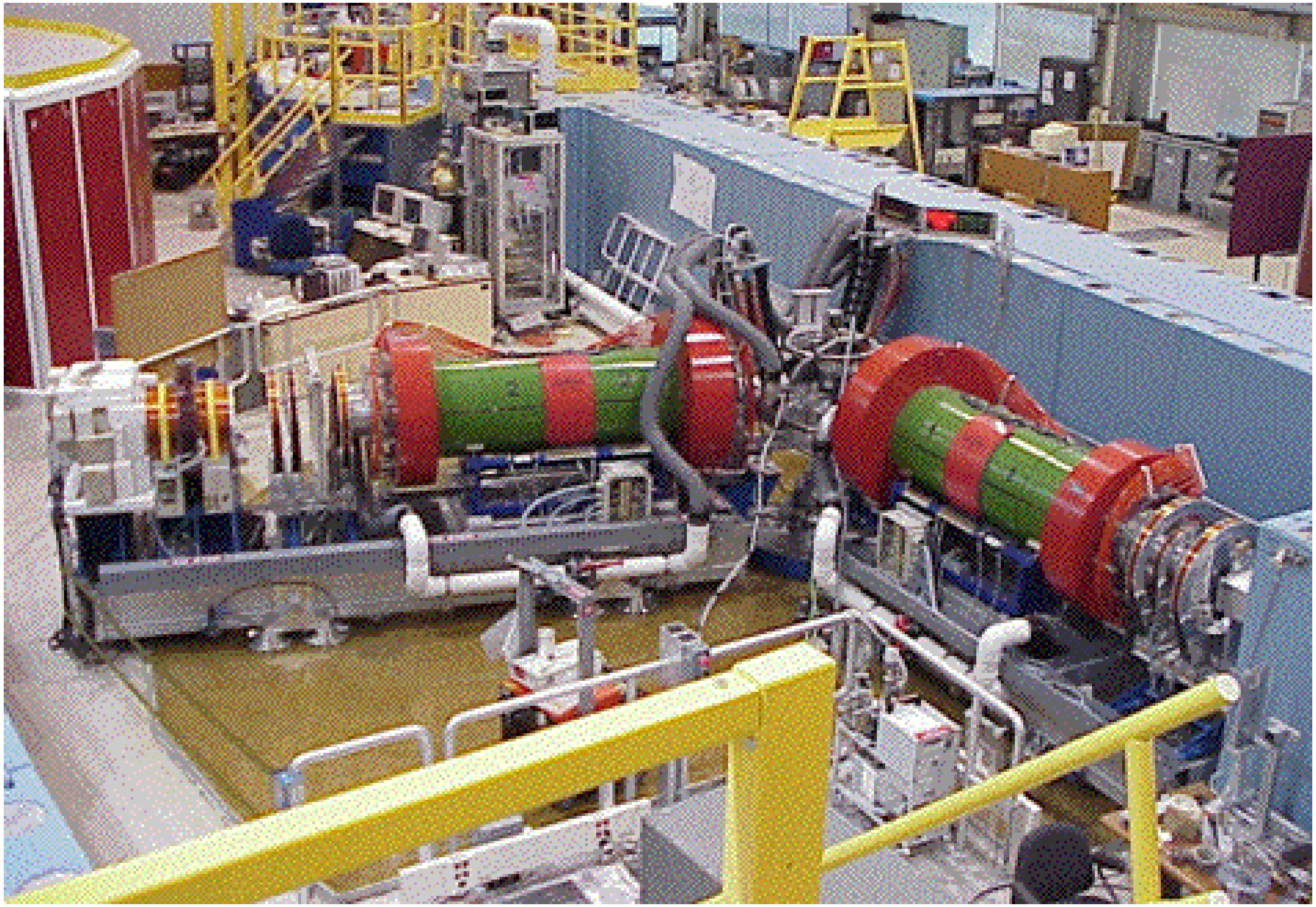
Neutron scattering and computation methods are natural partners

PTEN is a protein that regulates cell death

A crystal structure is available for the two core domains, but there is a disordered tail. NR reflectivity combined with MD simulations locate this section of PTEN and show that it different on the membrane than in solution.

S. Shenoy, *et al.*, PLoS ONE *7*, e32591 (2012).

Neutron Spin Echo Spectroscopy



Why precession?

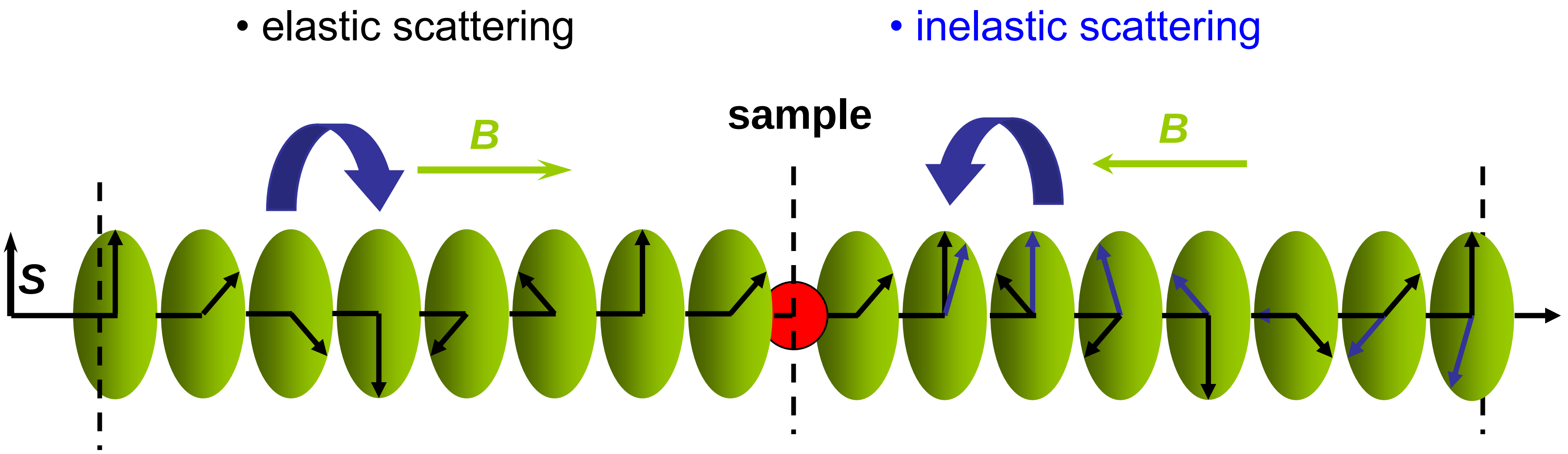
- **Goal:** **δE = 10^{-2} – 10 μeV** (very small !!!)

- We need low energy neutrons. Cold neutrons: λ = 5 – 12 Å, E = 0.5 – 3.3 meV

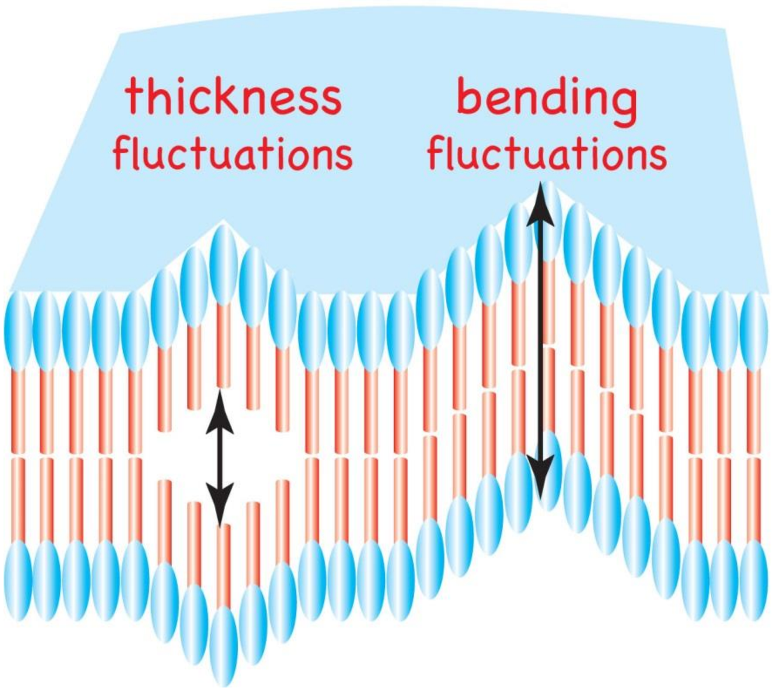
- **The problem:** neutron beam wavelength spread $\Delta\lambda/\lambda$ = 5 – 20%,
$\Delta E/E$ = 10 – 40%, **ΔE = 0.05 – 0.2 meV**

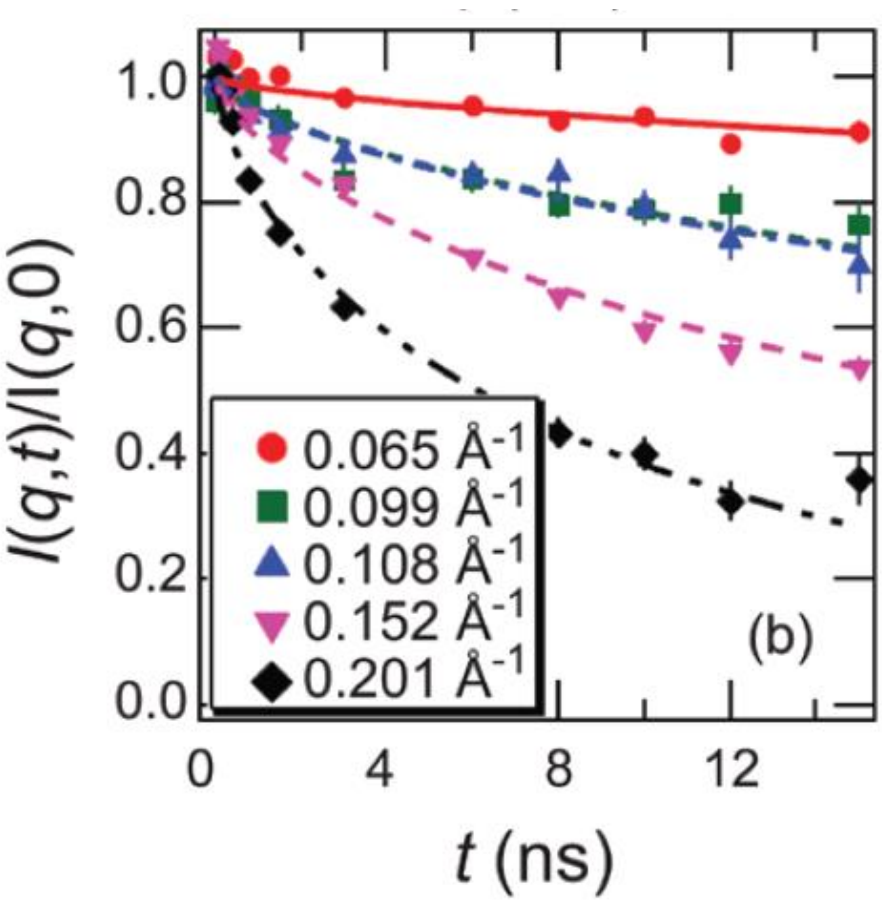
- **The solution**: Use neutron precession in magnetic field. Basically this allows us to attach an “internal” clock for each neutron. Thus, we can observe very small velocity changes of a neutron beam, regardless of the velocity spread

Scattering Event – Single Neutron



Thickness Fluctuations in Membranes





A.C. Woodka, P.D. Butler, L. Porcar, B. Farago, and M. Nagao, PRL **109**, 058102 (2012).

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Thickness Fluctuations in Membranes

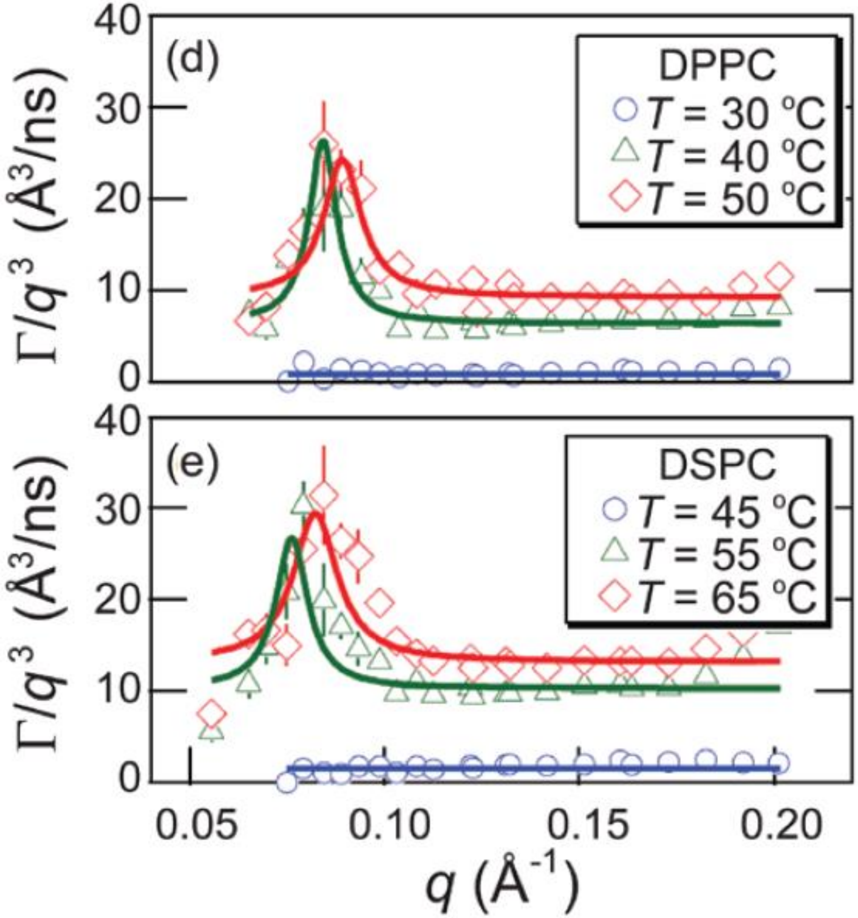
$$\frac{\Gamma}{q^3} = 0.0058 \frac{k_B T}{\eta_{D_2O}} \sqrt{\frac{k_B T}{\kappa}} + \frac{\Gamma_{TF}}{q_0^{\ 3}} \frac{1}{1+(q-q_0)^2 \xi^{-2}}$$

Relaxation time about 100 ns

(x100 that for surfactant membranes)

Amplitude (0.37±0.07) nm

≈ 8% of the membrane thickness

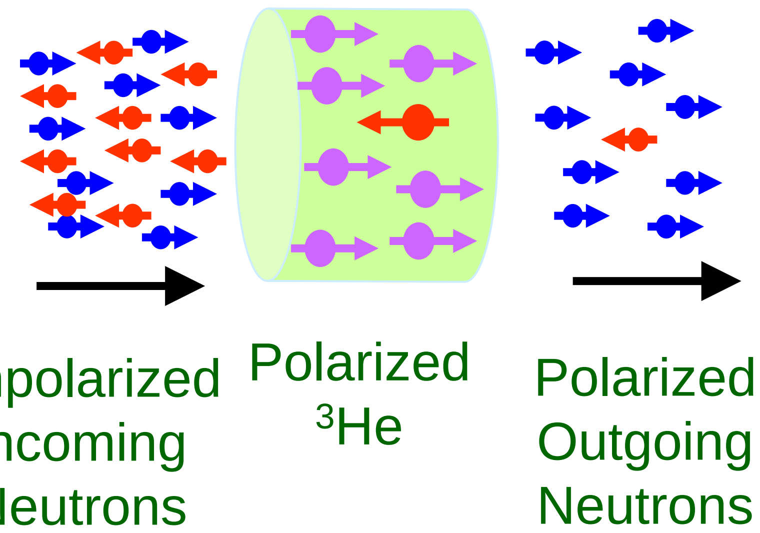


^{3}He Spin Filters

Spin Filters for Polarization

Polarized ^{3}He gas preferentially absorbs one neutron spin state

Tom Gentile PMML



Advantages of ^{3}He NSFs over SMs and Heusler crystals

- Large angular acceptance.
- Tunable transmission and polarization.
- Broadband.
- No added divergence.
- Single device for both polarizer and flipper (flipping spins using NMR).

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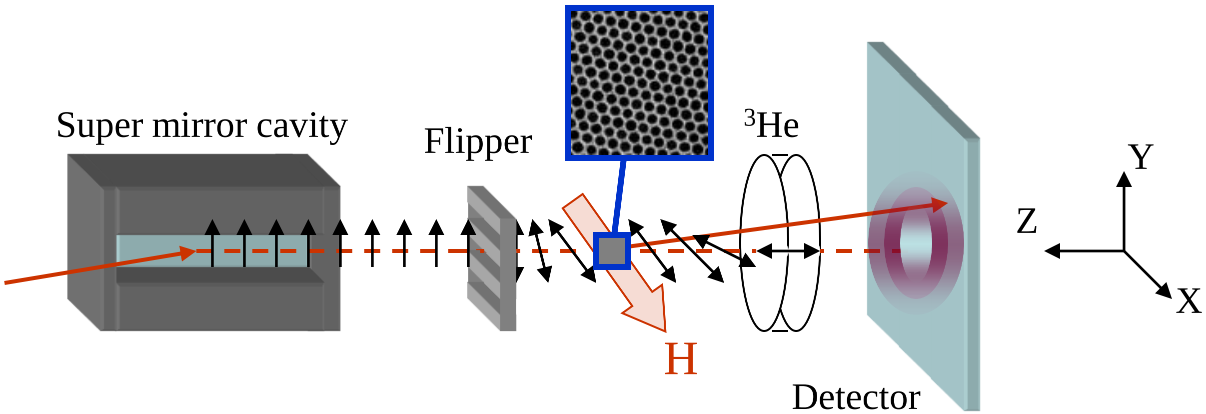
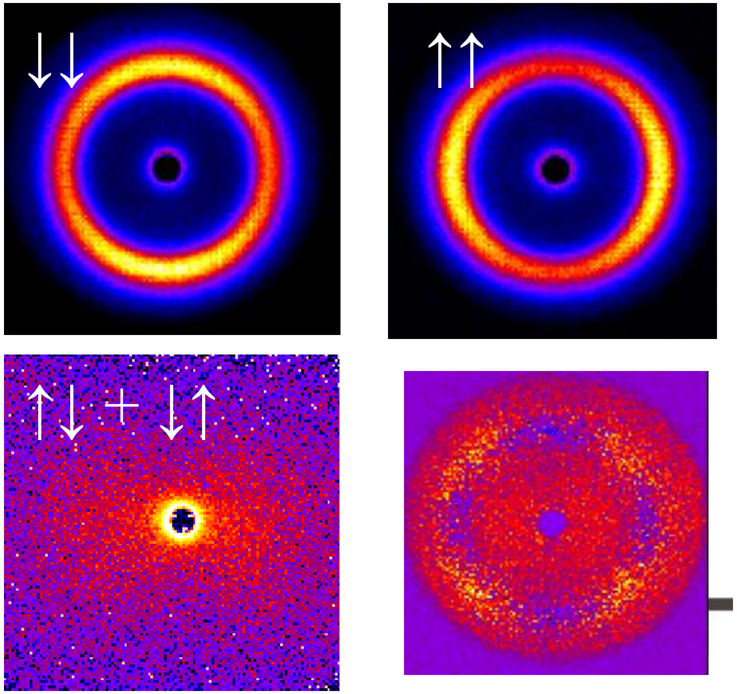
Magnetic Nanoparticles using SANS



$$I^{\uparrow\uparrow,\downarrow\downarrow}(horizontal) = N^2$$

$$I^{\uparrow\uparrow,\downarrow\downarrow}(vertical) = N^2 + M_X^2 \mp 2NM_X$$



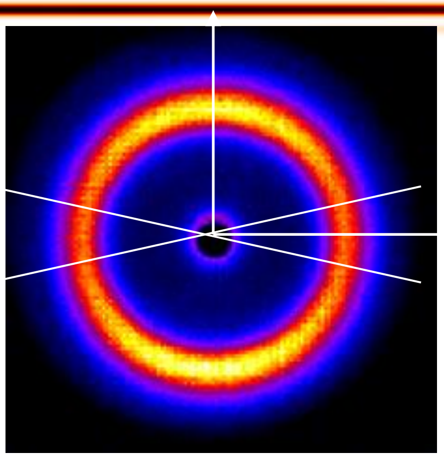
$$I^{\uparrow\downarrow,\downarrow\uparrow}(horizontal) = M_Y^2 + M_Z^2 = 2M_{PERP}^2$$

$$I^{\uparrow\downarrow,\downarrow\uparrow}(vertical) = M_Z^2$$

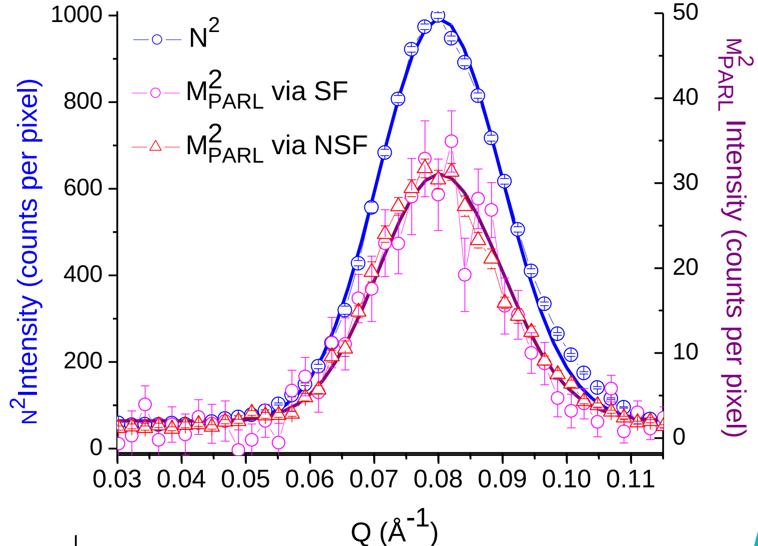
$$I^{\uparrow\downarrow,\downarrow\uparrow}(45^o) = 0.25M_X^2 - 1.25M_{PERP}^2$$

Separating N^2, M^2_{PERP}, and M^2_{PARL}

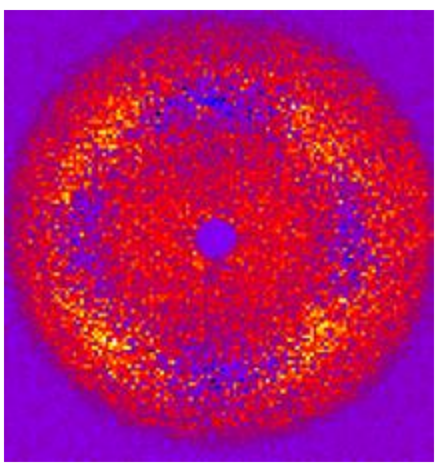
Krycka *et al.*, PRL (2010)

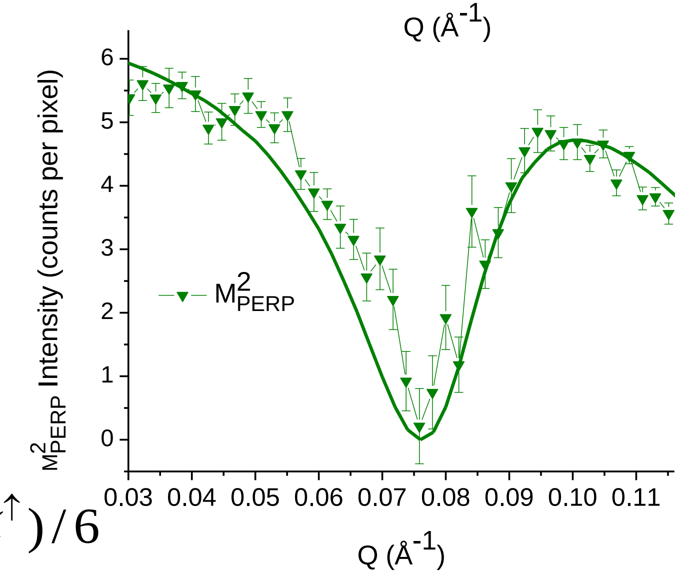


X, *H*

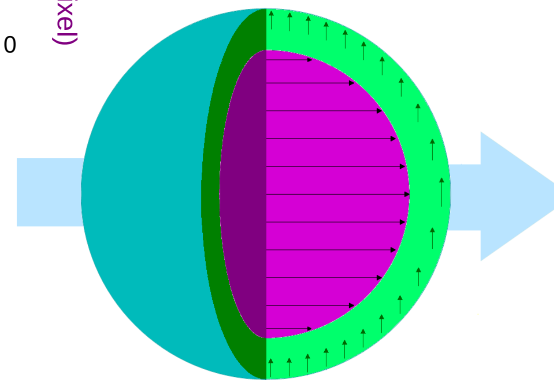


$$N^2 = (I_X^{\uparrow\uparrow} + I_X^{\downarrow\downarrow})/2$$





$$M_{PERP}^2 = (I_X^{\uparrow\downarrow} + I_X^{\downarrow\uparrow} + I_Y^{\uparrow\downarrow} + I_Y^{\downarrow\uparrow})/6$$



45 ± 2 Å Radius Sphere

10 ± 2 Thick Canted Shell

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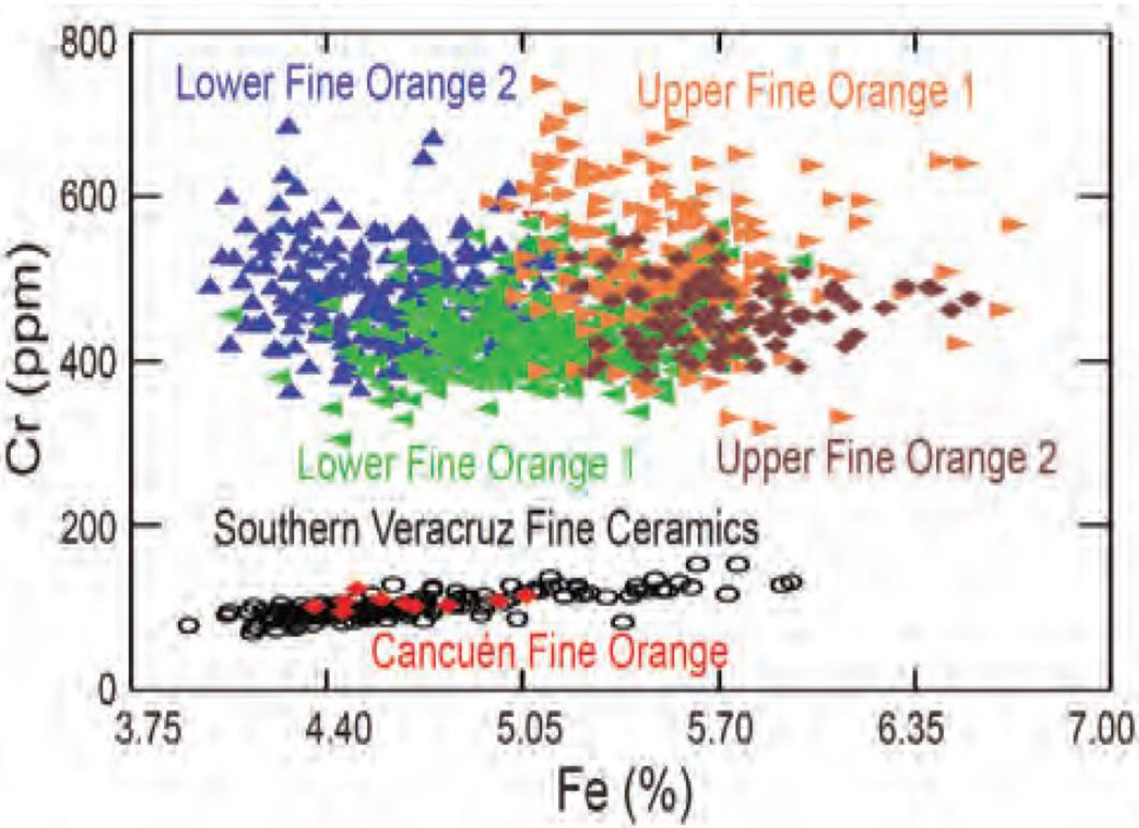
Smithsonian

Fine Orange Pottery

ubiquitous around the time of the collapse of the lowland Maya in the late 8th century



INAA showed the origin and spread of the manufacture of along the Usumacinta River.

A pot that was recently found in Guatamala (Cancuén) was reliably dated to 50 years earlier.

The INAA data revealed that it came from southern Veracruz in Mexico demonstrating contact in the mid 700's.

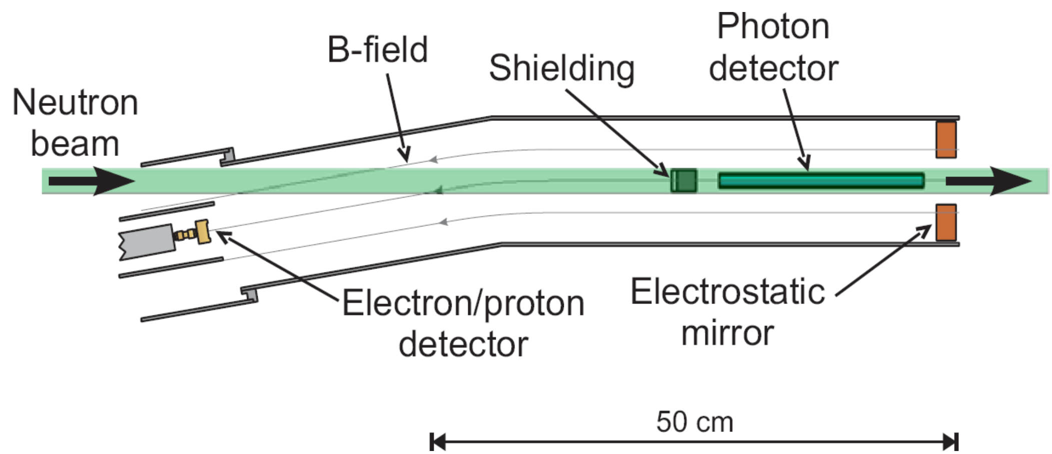
18 elemental compositions

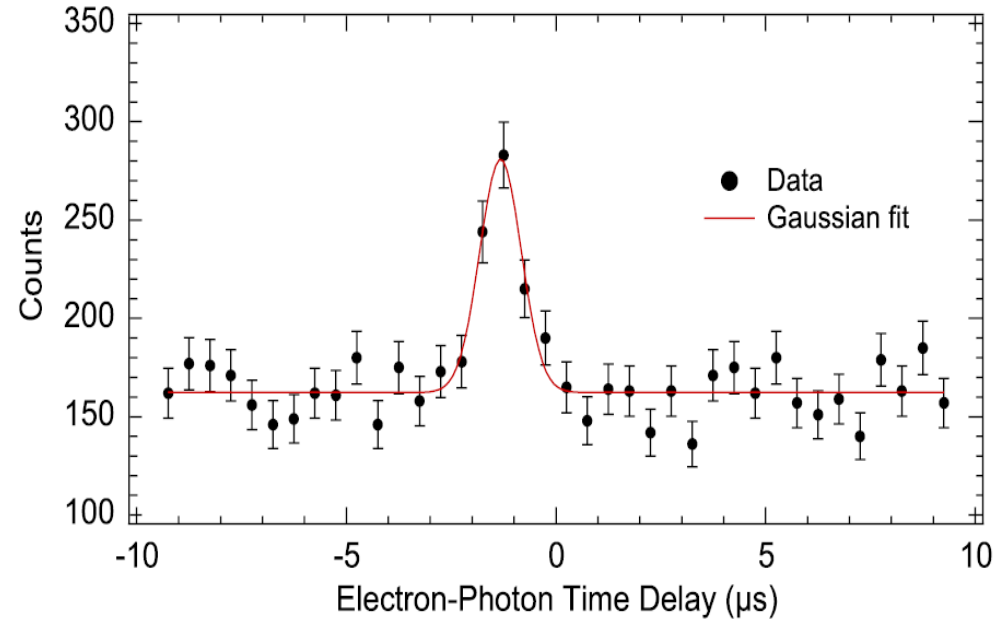
$$n \to p + e^- + \bar{\nu}_e + \gamma$$

Neutrons are composed of two down quarks and an up quark.

The weak interaction can convert a down quark into an up quark through the emission of the *W* gauge boson that subsequently decays into an electron and an antineutrino.

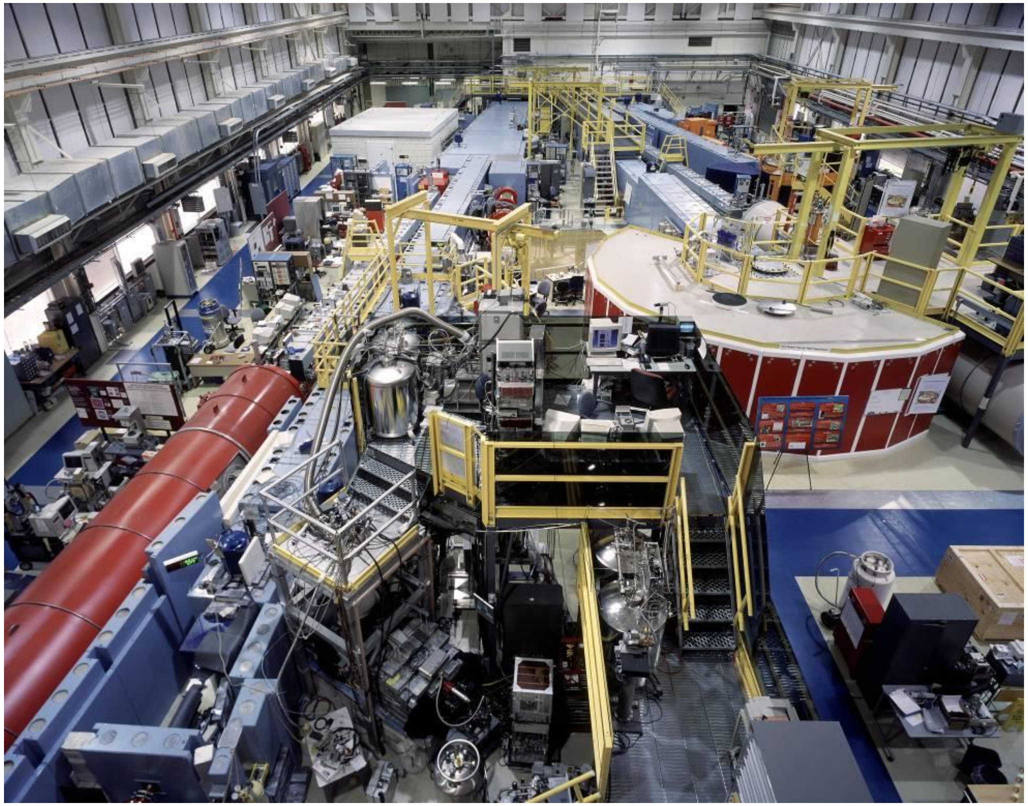
In a rare process, this decay is also accompanied by an inner-bremsstrahlung photon.





J.S. Nico *et al.*, Nature (2006)..

NCNR Expansion Project (2007)

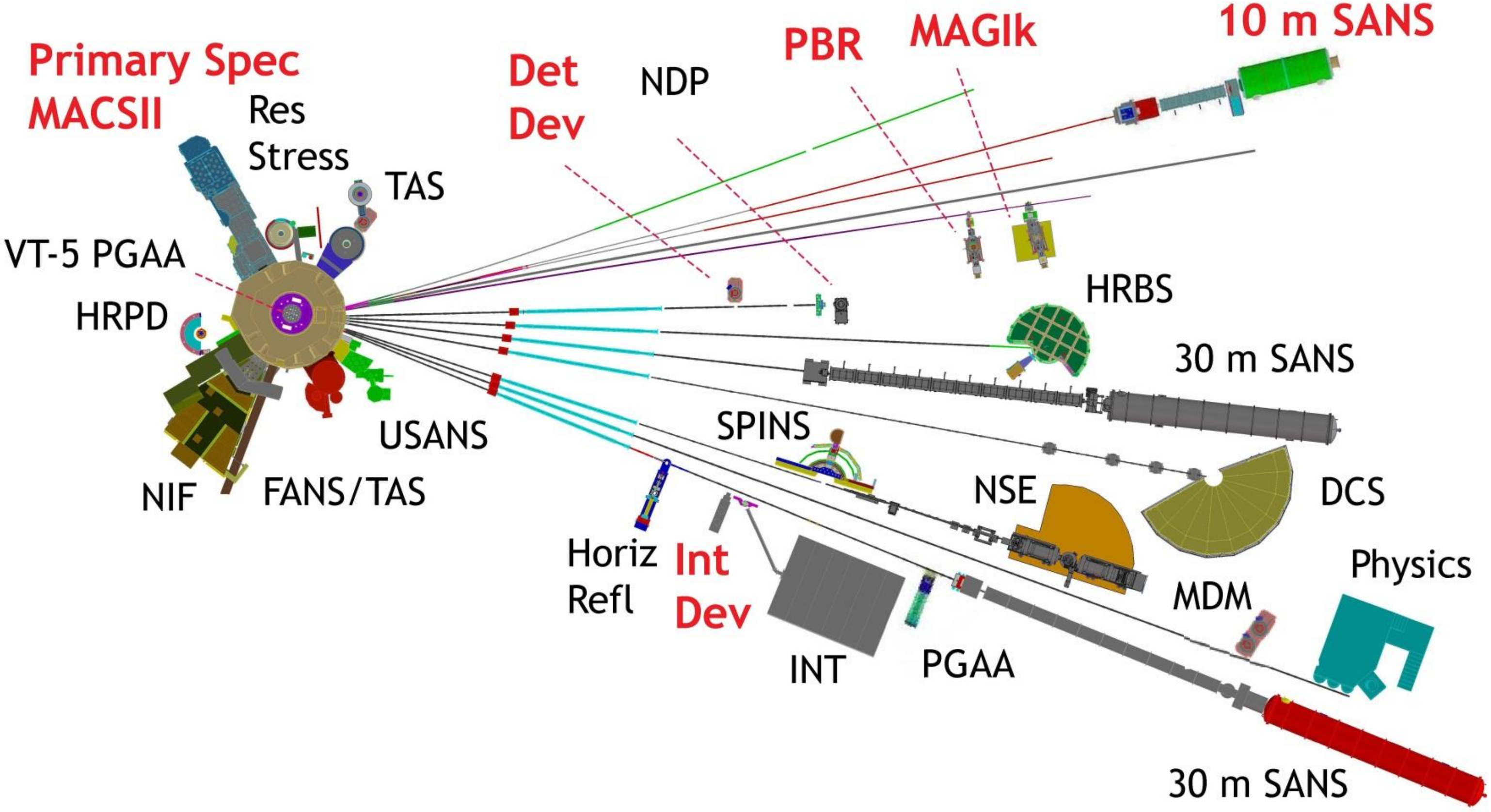


Project to increase cold neutron measurement capacity of NCNR

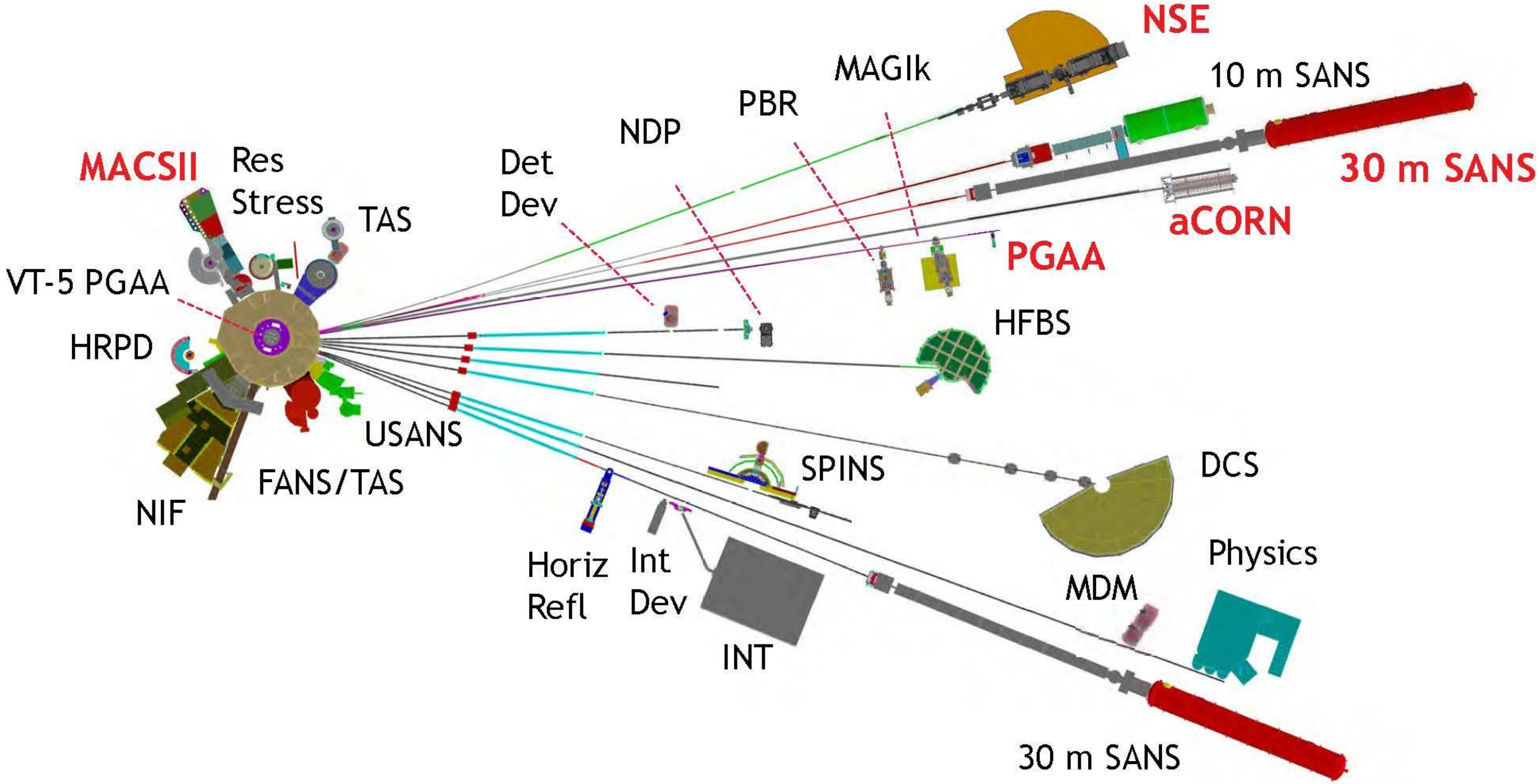
- New cold source & guide system
- Expanded guide hall
- New neutron instrumentation
- Support and office space


DESHAZO

NCNR Layout Dec. 2012



NCNR Layout July 2014



The NIST Center for Neutron Research

The NCNR a leading user facility for neutron research

≈ 250 operating days/year

> 98% reactor reliability

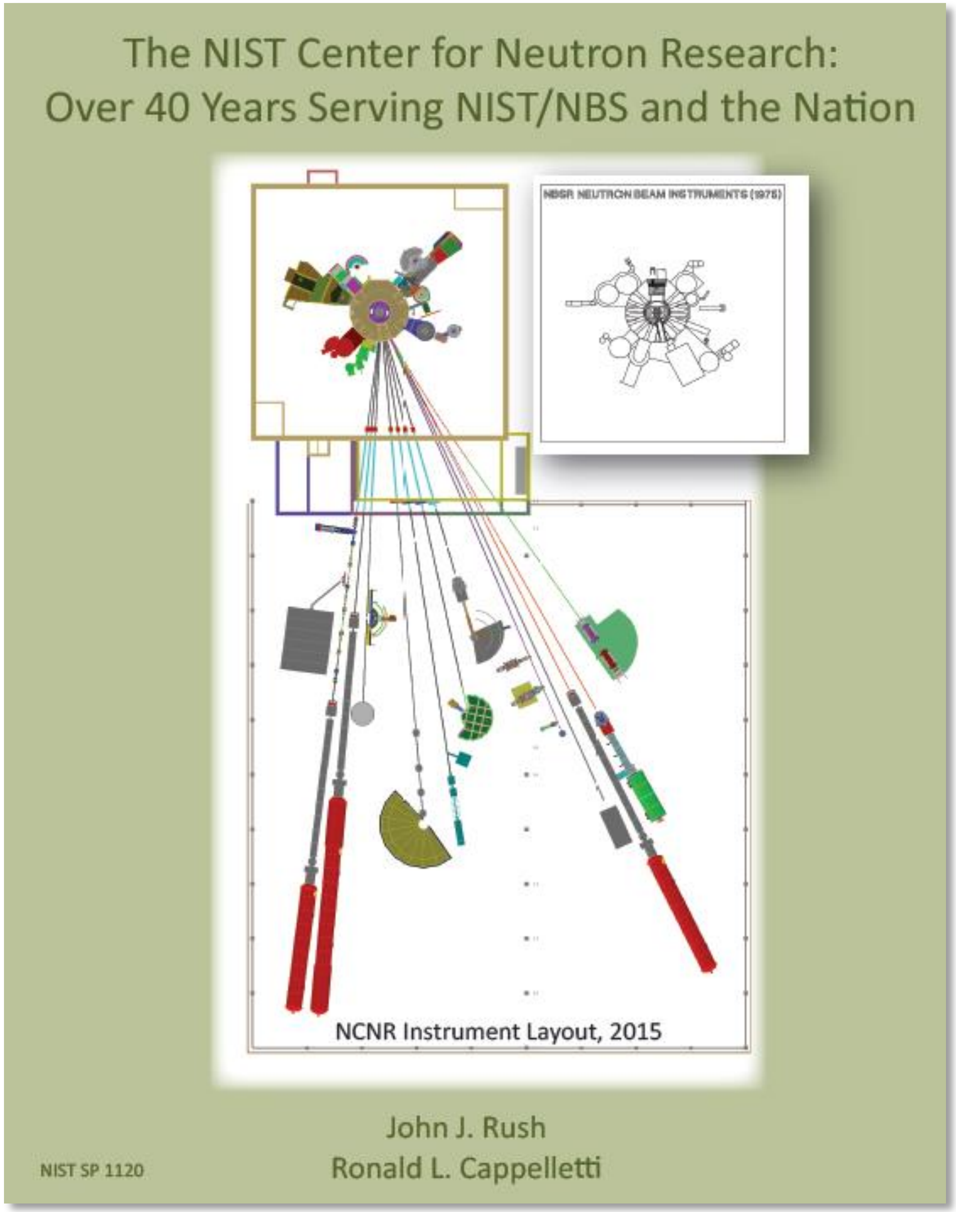
28 experimental beam instruments/experiments

> 2000 research participants/year

≈ 300 publications/year

NIST

The NCNR is an essential national user facility providing state-of-the-art neutron measurement capabilities to the US scientific and technical community.



To read more, download the history of the NCNR written by Jack Rush and Ron Cappelletti

http://www.ncnr.nist.gov/NCNRHistory_Rush_Cappelletti.pdf

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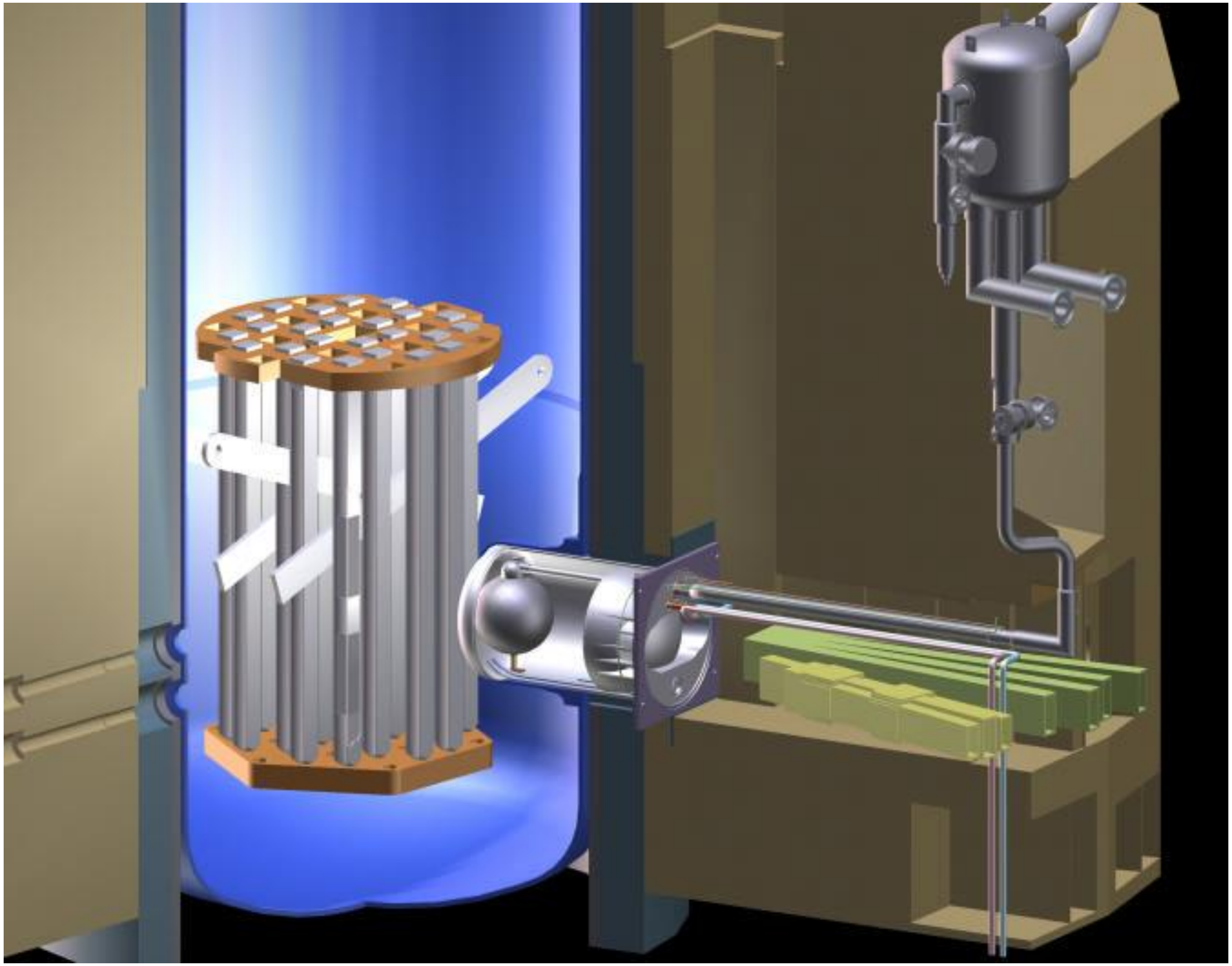
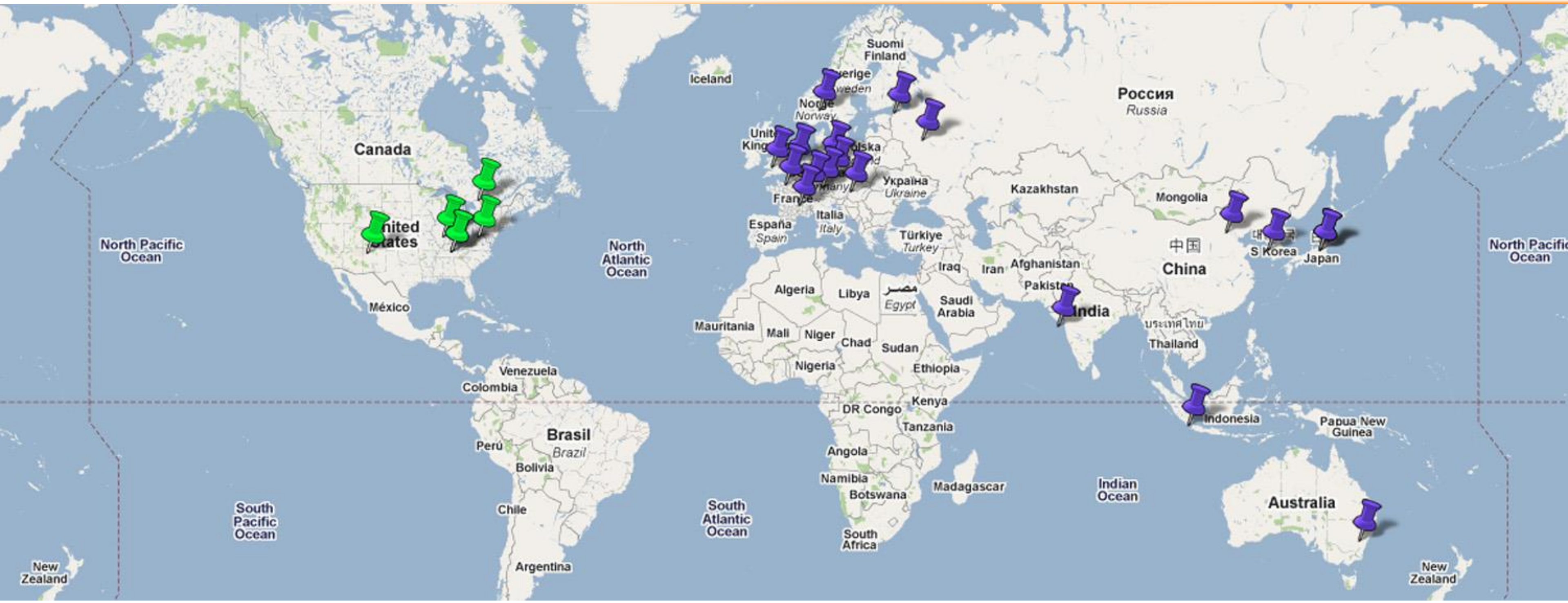
The Neutron Source



The NCNR operates on a 7 week (49 day) cycle = 38 days of normal operation followed by 11 days of maintenance.

International neutron scattering user facilities



Western Europe dominates in terms of…

- number of users
- capacity/throughput
- scientific productivity

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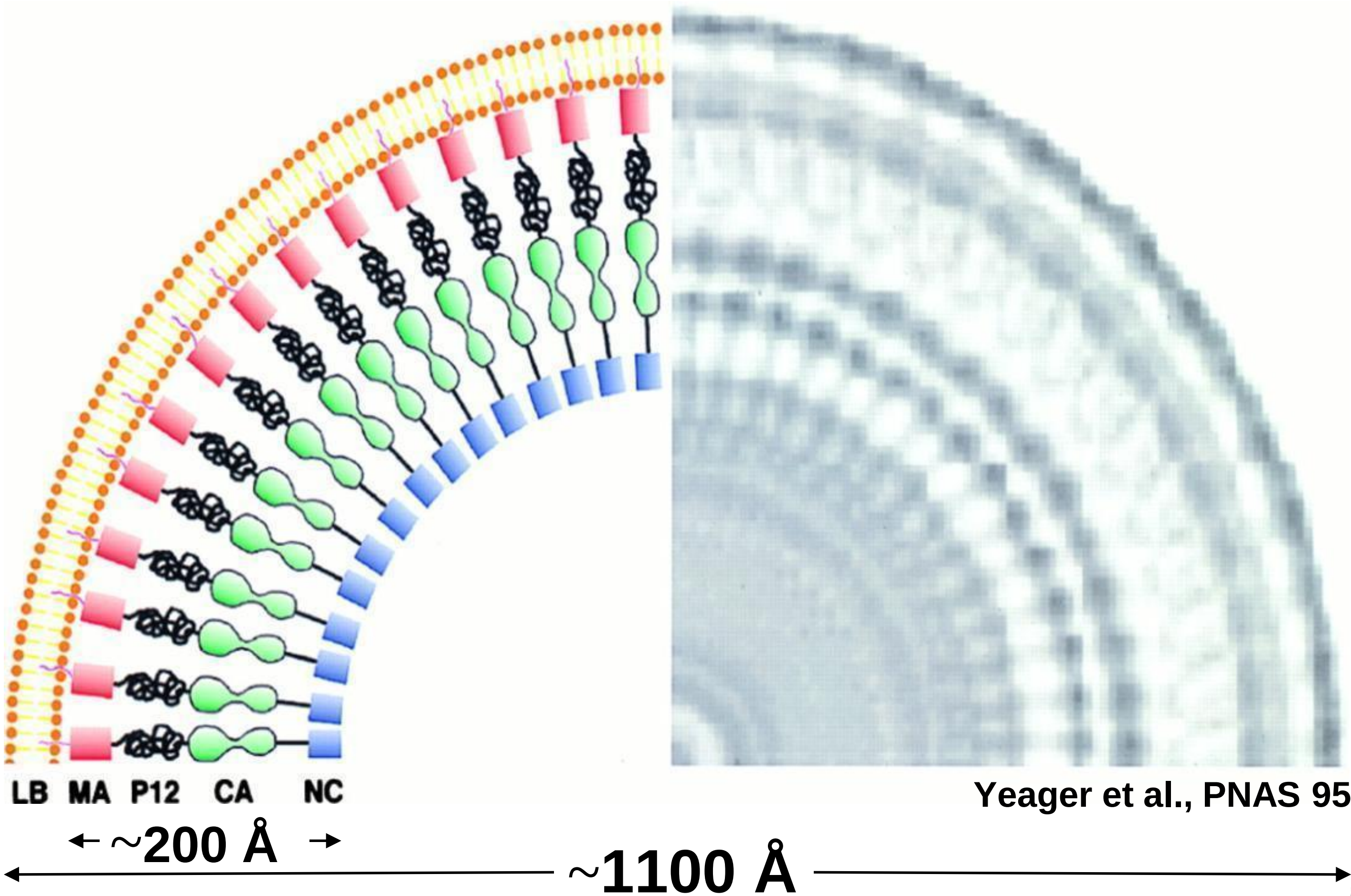
Basic Structure of an Immature Retrovirus

Biochemical evidence suggests that HIV-1 Gag is NOT extended in solution.



Yeager et al., PNAS 95: 7299, 1998

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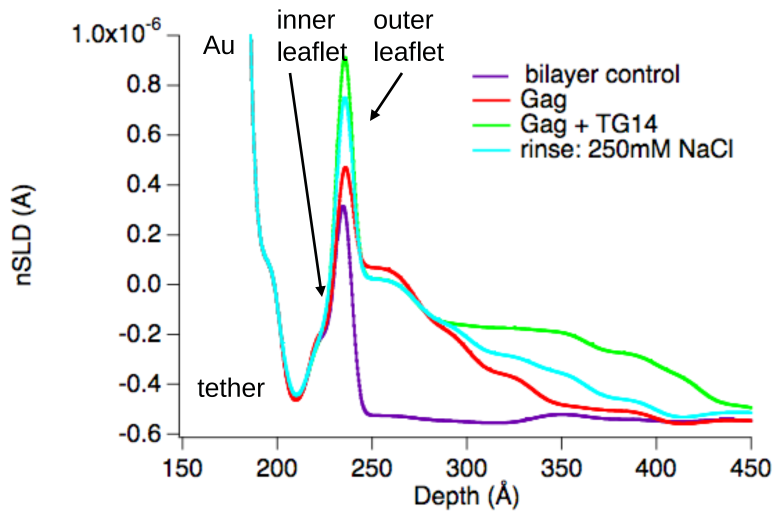
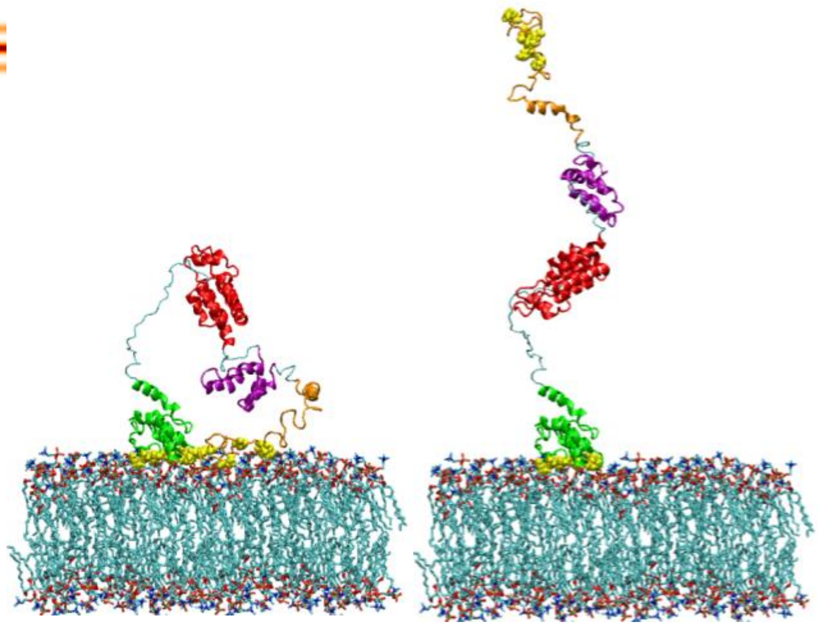
Gag Layer On Membrane Surface





nSLD increases for distances beyond the lipid bilayer surface.

nSLD increases at greater distances from the lipid bilayer surface.

High salt rinse removes DNA and original profile is recovered.

H. Nanda, *et al*., Biophys. J. (2010).

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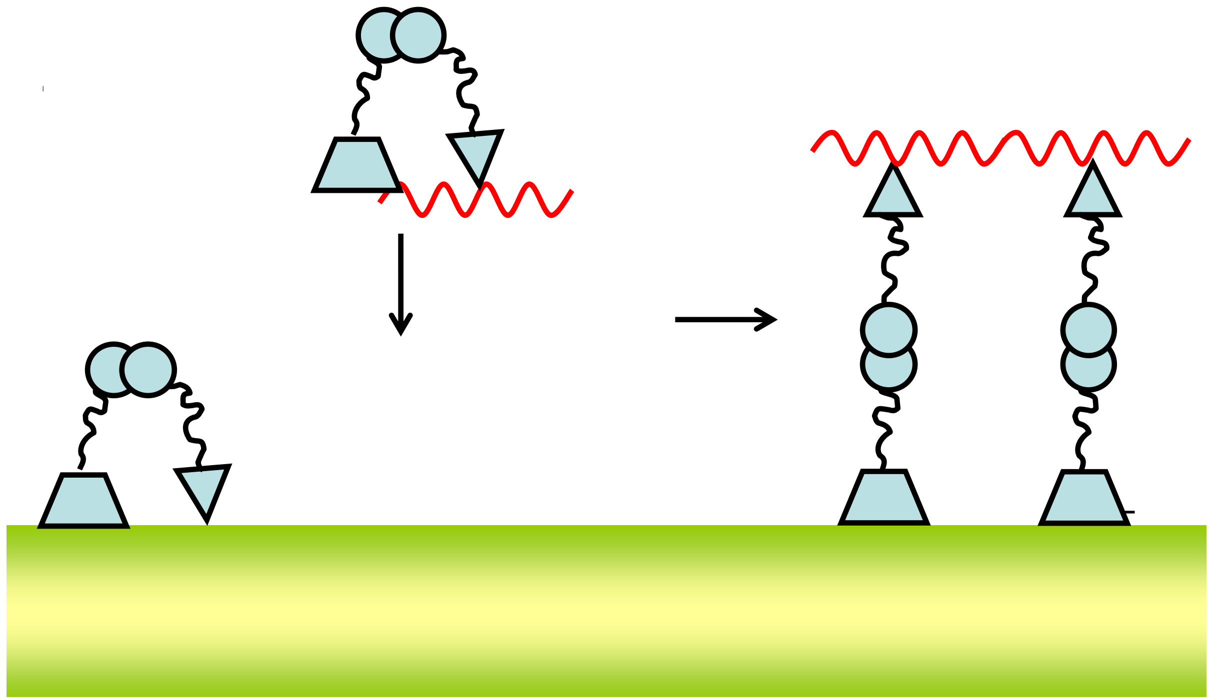
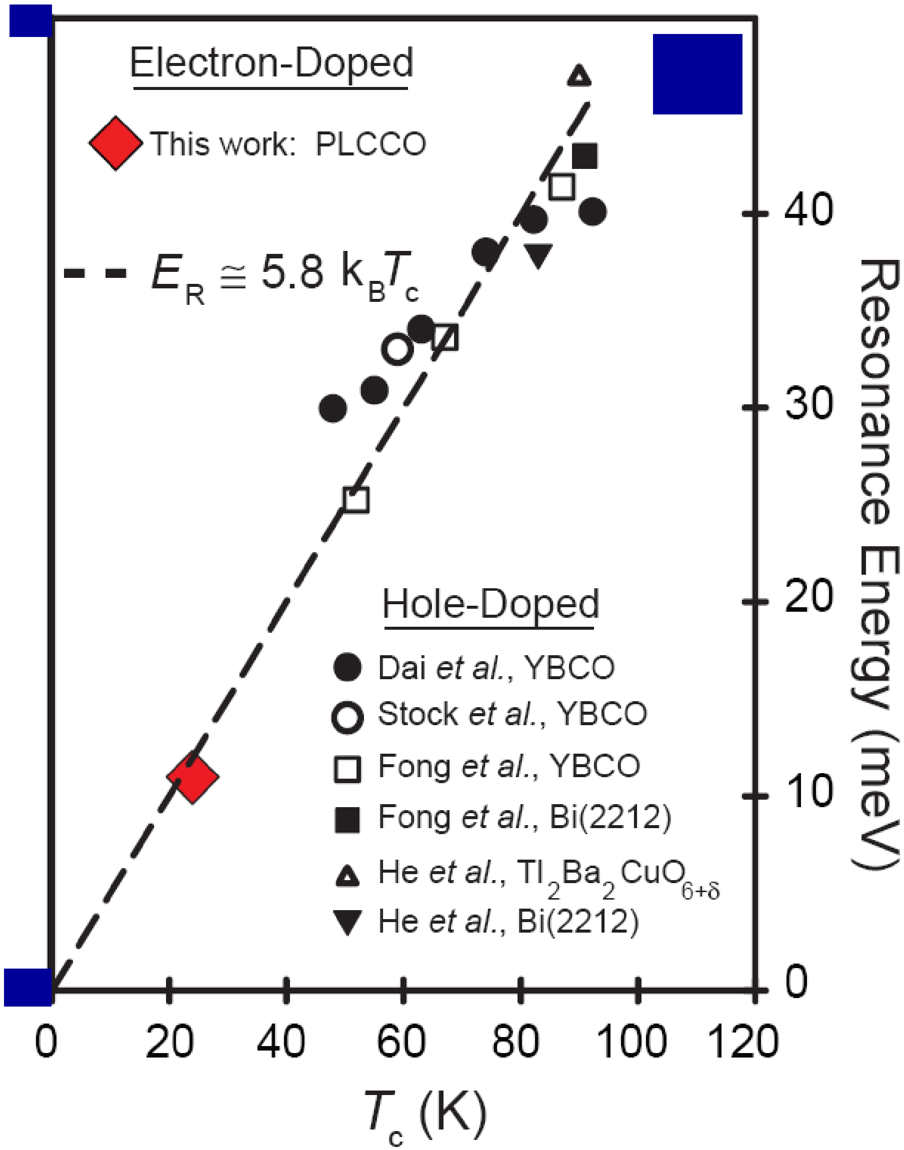
Model for Gag Assembly on Bilayer

Both nucleic acid and lipid binding
are needed for extension of Gag protein



H. Nanda, *et al.*, Biophys. J. (2010).

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)

vSANS – Detector

Hot, Thermal and Cold Neutrons

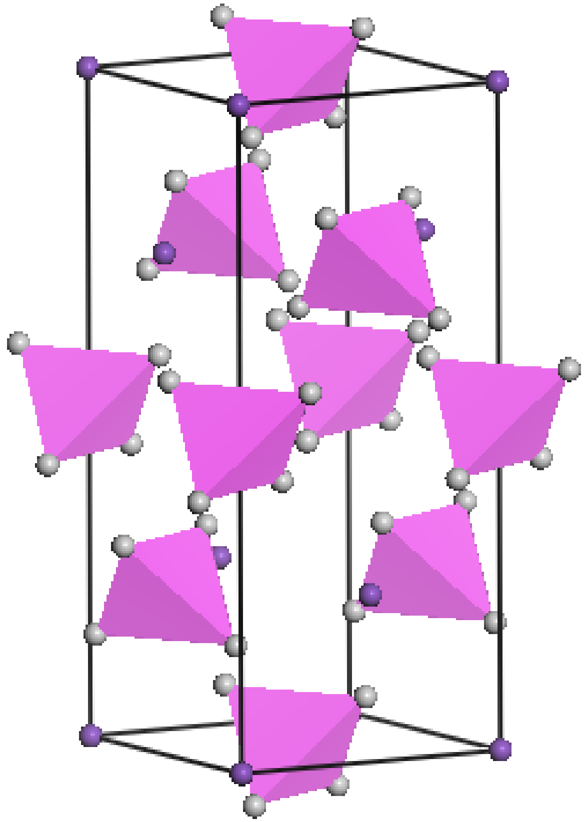
Hot neutrons – wavelengths ~ 0.07 nm (170 meV)

Thermal neutrons – wavelengths ~ 0.2 nm (20 meV)

Cold neutrons – wavelengths ~ 0.6 nm (2.3 meV)

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



$NaAlH_4$

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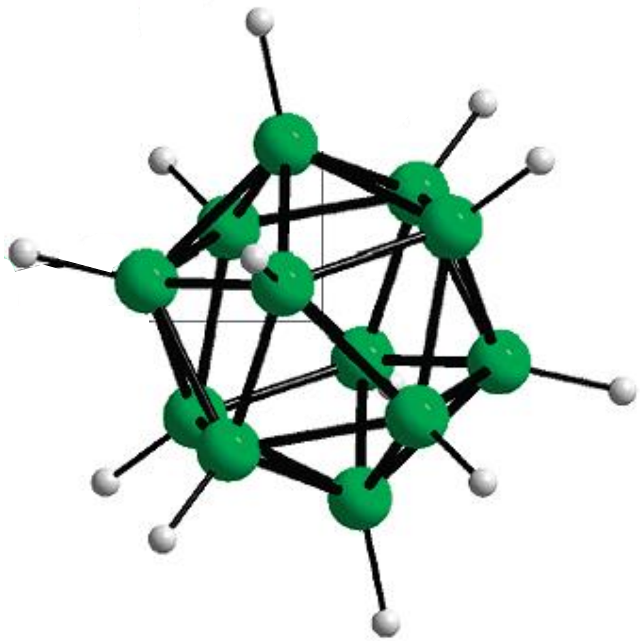
Li - Borohydride

$LiBH_4$ releases H during decomposition

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



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