Ion Transport in Energy Materials

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$\langle AP|\hat{h}|MS\rangle$
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- Past Experiments (may continue with Xiaolin Xu)
- Polaron-related studies using nuclear resonant inelastic x-ray scattering

- New Experiments with Neutrons and Pressure
- QENS studies of activation volumes of hydrogen
- VISION measurements of phonon DOS under *P,T*, in highly anharmonic material

Activation Volume for Hydrogen Diffusion

1. ***GOAL*** – Use pressure and temperature to characterize the mechanism of hydrogen diffusion in hydrogen storage materials
   - Obtain i) activation energy, and ii) activation volume, of hydrogen jumps in $YFe_2H_{2.6}$ using quasielastic neutron scattering
   - Develop techniques for inelastic neutron scattering measurements at high pressures
2. ***RESOURCES***
   - Techniques: Quasielastic inelastic neutron scattering (QENS), hydrogenation, pressure and temperature control
   - Partners/Personnel: Caltech: Brent Fultz (lead), Fred Yang, Hillary Smith. Carnegie (and SNS): Rus Hemley, Chen Li, Reini Boehler
3. ***MILESTONES***
   - Measure activation volume for hydrogen jumps in $YFe_2H_{2.6}$. Use it to interpret atom displacements around the jump of a hydrogen atom. (Year 1).
   - Study more challenging hydrides of practical interest. Further develop techniques to perform high pressure inelastic neutron scattering experiments. (Years 2-4).
4. ***IMPACTS***
   - Develop a new experimental technique for neutron scattering at pressure. Obtain new information about on local atom displacements during jumps of hydrogen atoms.
   - Understand hydrogen diffusion in materials at the level of individual movements of hydrogen atoms, and the distortions of its surrounding atoms.

Quasielastic Scattering and Pressure

Bove, et al, "Translational and Rotational Diffusion in Water in the Gigapascal Range," PRL 111, 185901 (2013).

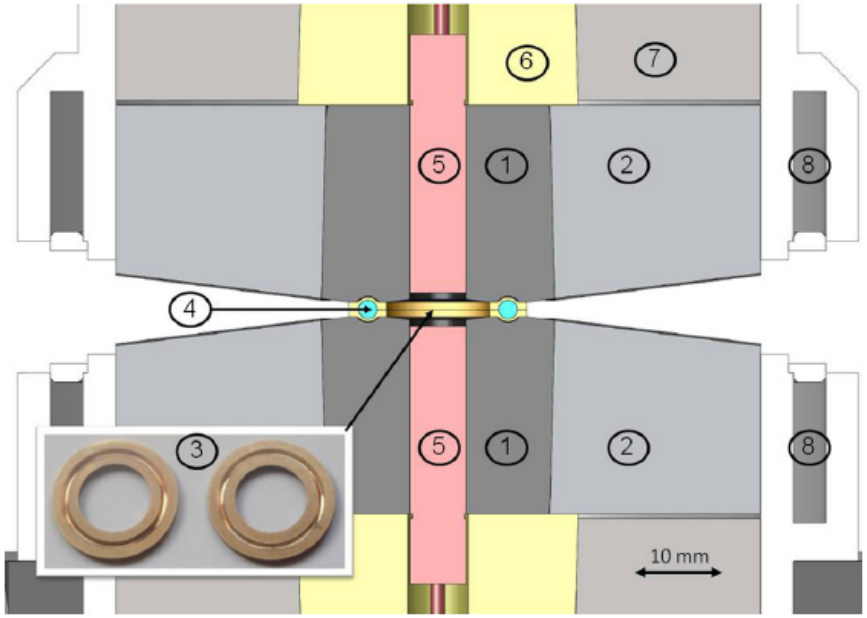


FIG. 1. Gasket-anvil assembly for high pressure QENS measurements. (1) and (2) anvil made of sintered cBN die supported by steel binding ring; (3) split CuBe gasket; (4) high pressure sample chamber; (5) cartridge heater; (6) and (7) anvil backing seat made of zirconia die and steel supporting ring; (8) cooling rings. Conical anvil faces (thick lines) are covered with gadolinium film.

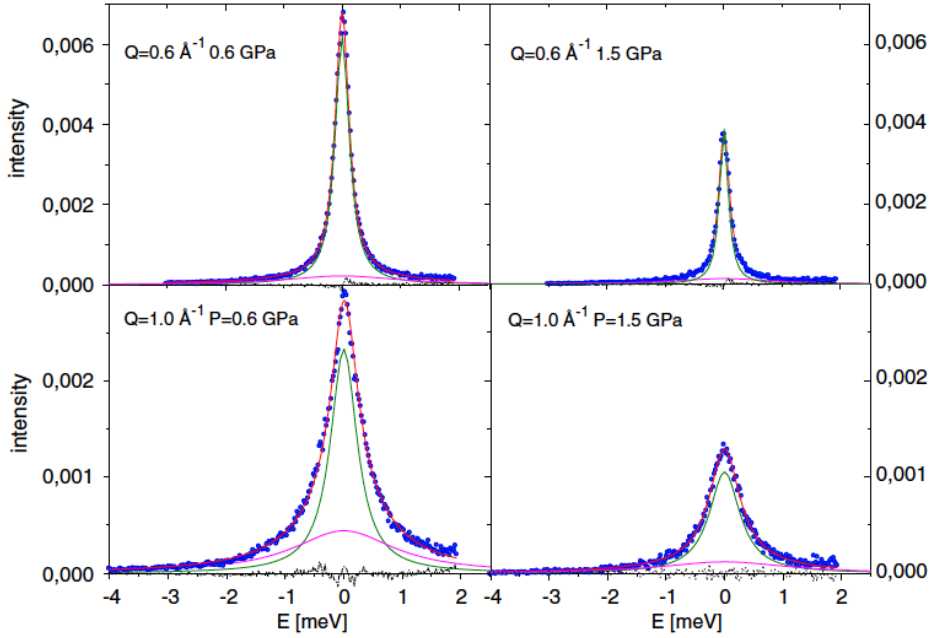


FIG. 3 (color online). Example of fit result (red line) compared to the measured intensity (blue dots) from water at 400 K at $P = 0.6$ and 1.5 GPa for Q-selected values. The translational

Quasielastic Scattering and Pressure

Klotz, et al., "Quasi-elastic neutron scattering in the multi-GPa range and its application to liquid water", APL 103, 193504 (2013).

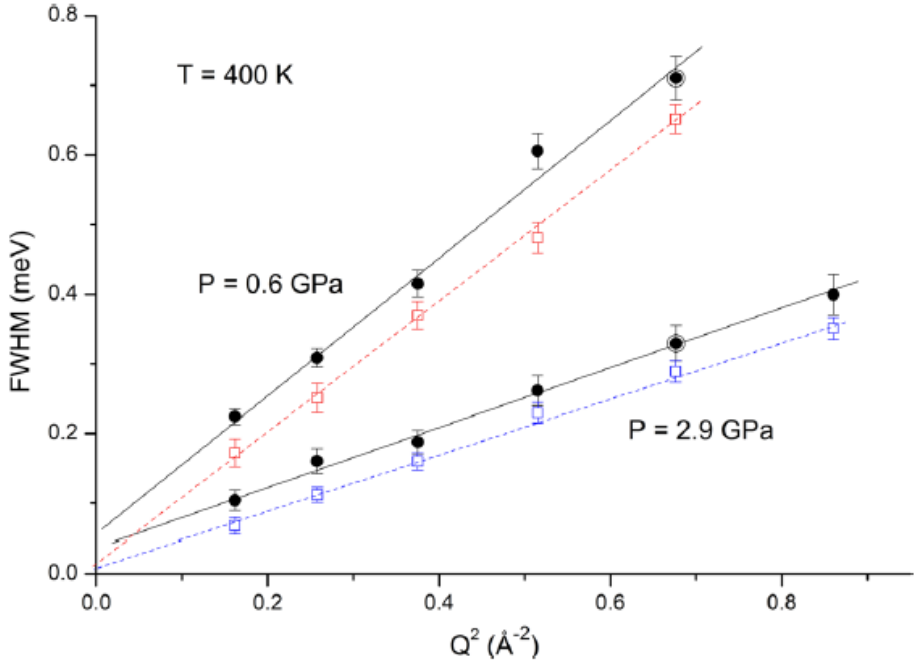


FIG. 3. Full width at half maximum (FWHM) of the fitted QENS signal plotted as a function of Q^2, at 0.6 GPa and 2.9 GPa. The marked dots (⊙) at 0.86 $Å^{-2}$ are those shown in Figure 2. Full symbols correspond to analysis

Activation volume:

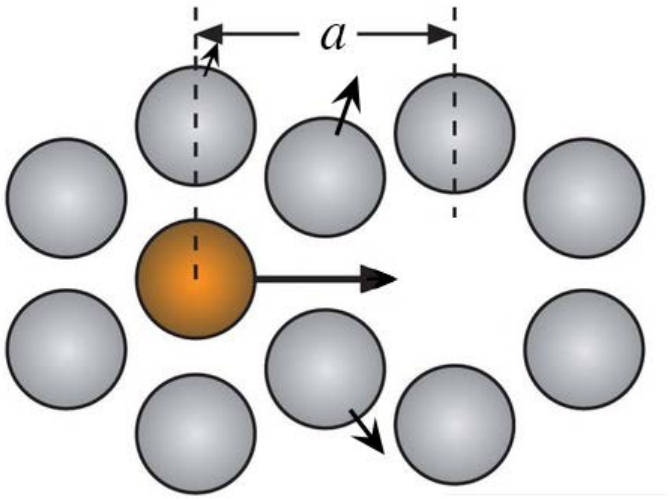
My estimate is +2 $Å^3$ for translational diffusion of water molecule in liquid.

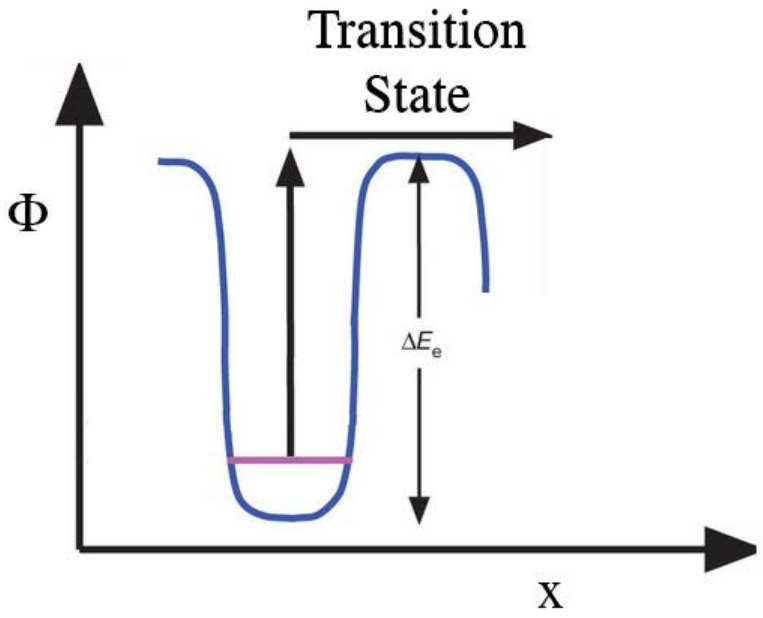
(*T*-Dependence?)

Hydrogen Storage Materials

- Chemisorption Materials
  - Metal hydrides: something new in bcc V-Ti-Ni-Cr (arpa-e)
- Physisorption Materials
  - Graphene derived from graphite oxide (EERE)
  - Nanostructured surfaces (Efree)
- What is the local atomic distortion as H atom moves through its activated state during a diffusive jump?

Activation States





Upcoming Beamtime at DCS at NCNR (early 2016)

Selected YFe_2/H for quasielastic scattering

- conveniently low activation energies
- opportunity to work at low temperatures (facilitating pressure studies)

Activation energies of 42 and 10 meV in the ranges of 295-390 K and 140-240 K.

Possible change from an adiabatic to a non-adiabatic mechanism at low temperatures (10 meV is very low).

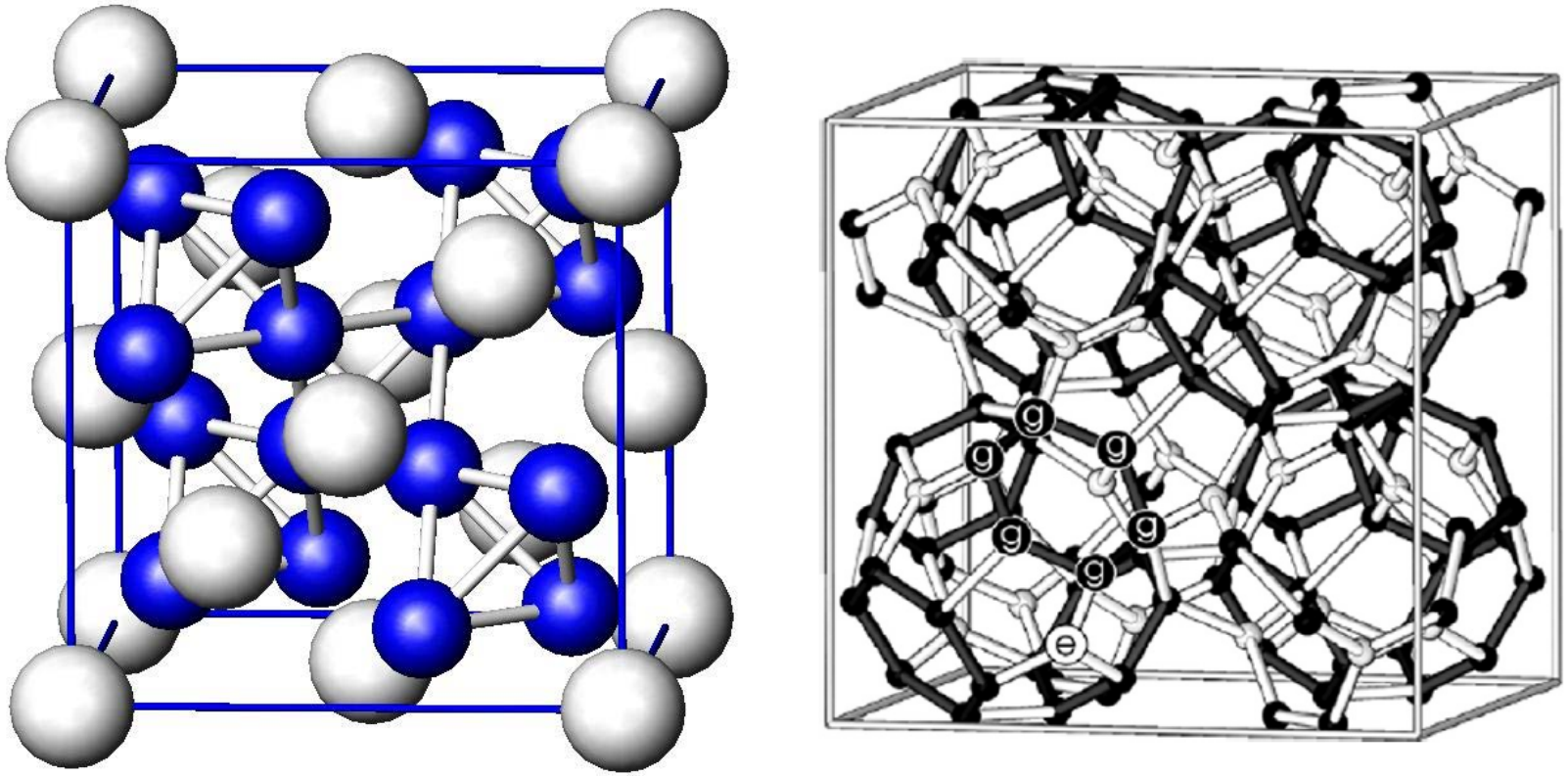


Fig. 1. The spatial arrangement of interstitial *g* sites (dark spheres) and *e* sites (light spheres) in the cubic C15-type AB_2 compound. Each *g* site has three *g*-site neighbors: two *g* sites on the same hexagon at a distance of r_1 (dark bars) and one *g* site on the adjacent hexagon at a distance of r_2 (light bars). Metal atoms are not shown. Each *g* site is coordinated by 2 *A* and 2 *B* atoms, and each *e* site is coordinated by 1 *A* and 3 *B* atoms.

A.V. Skripov, V. Paul-Boncour, T.J. Udovic, J.J. Rush, J. Alloy. Comp. 595, 28 (2014).

Upcoming Beamtime at DCS at NCNR (early 2016)

With jump frequency versus *T*, *P*, we can get activation energy and activation volume.

The jump frequency, $\Gamma(T)$, is proportional to the population of activated states:

$$\Gamma(T) = D_o \exp\left[\frac{-\Delta G}{k_B T}\right] = D_o \exp\left[\frac{-(E_a + P\Delta V - T\Delta S)}{k_B T}\right]$$

where T is temperature, E_a is the activation energy at ambient pressure, P is the applied pressure, ΔV is the activation volume, and ΔS is the entropy of activation.

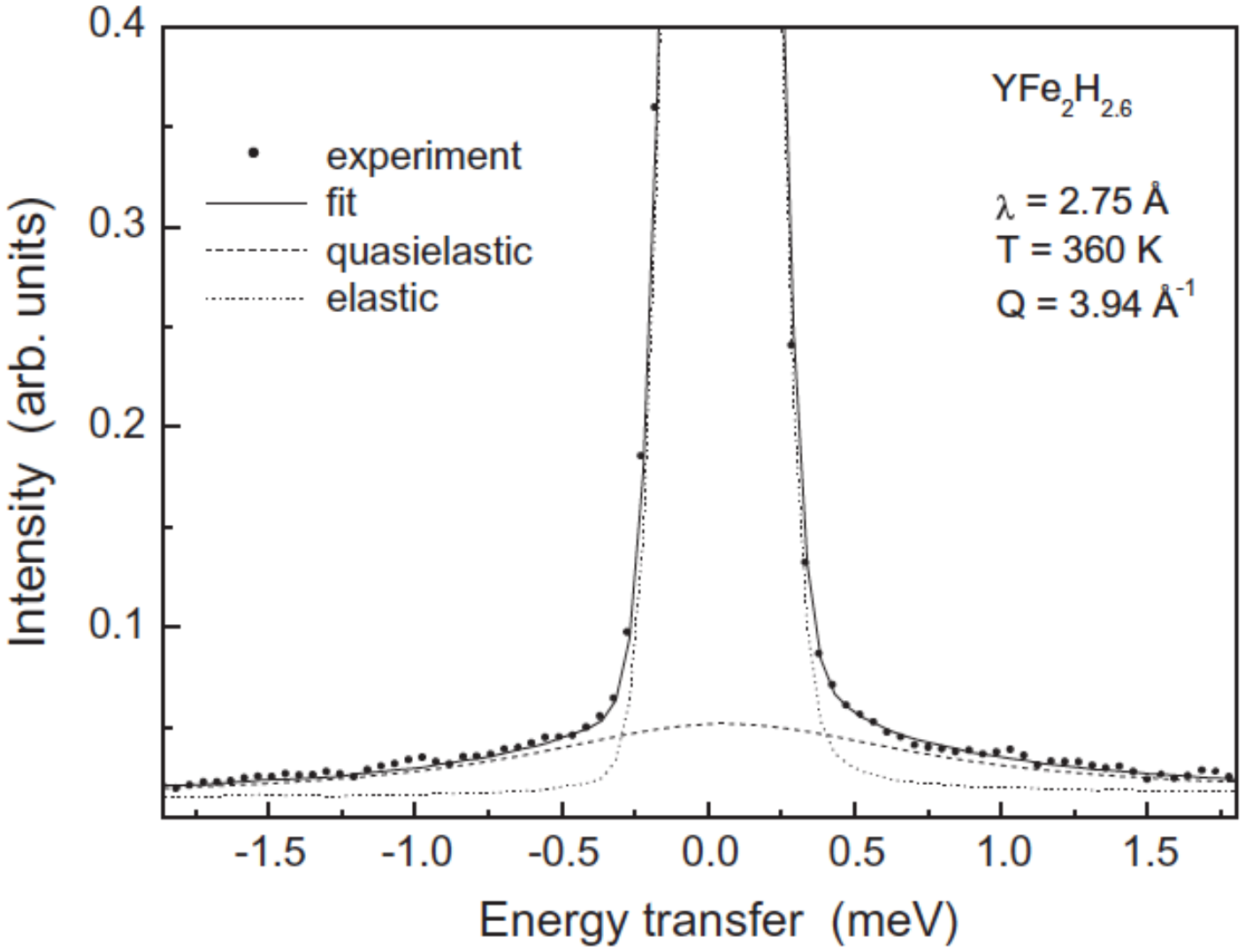


Fig. 3. The QENS spectrum for $YFe_2H_{2.6}$ measured on DCS at $\lambda = 2.75$ Å, $T = 360$ K and $Q = 3.94$ Å^{-1}. The full curve shows the fit of the two-component model (Eq. (1)) to the data. The dotted line represents the elastic component (the spectrometer resolution function), and the dashed line shows the Lorentzian quasielastic component.

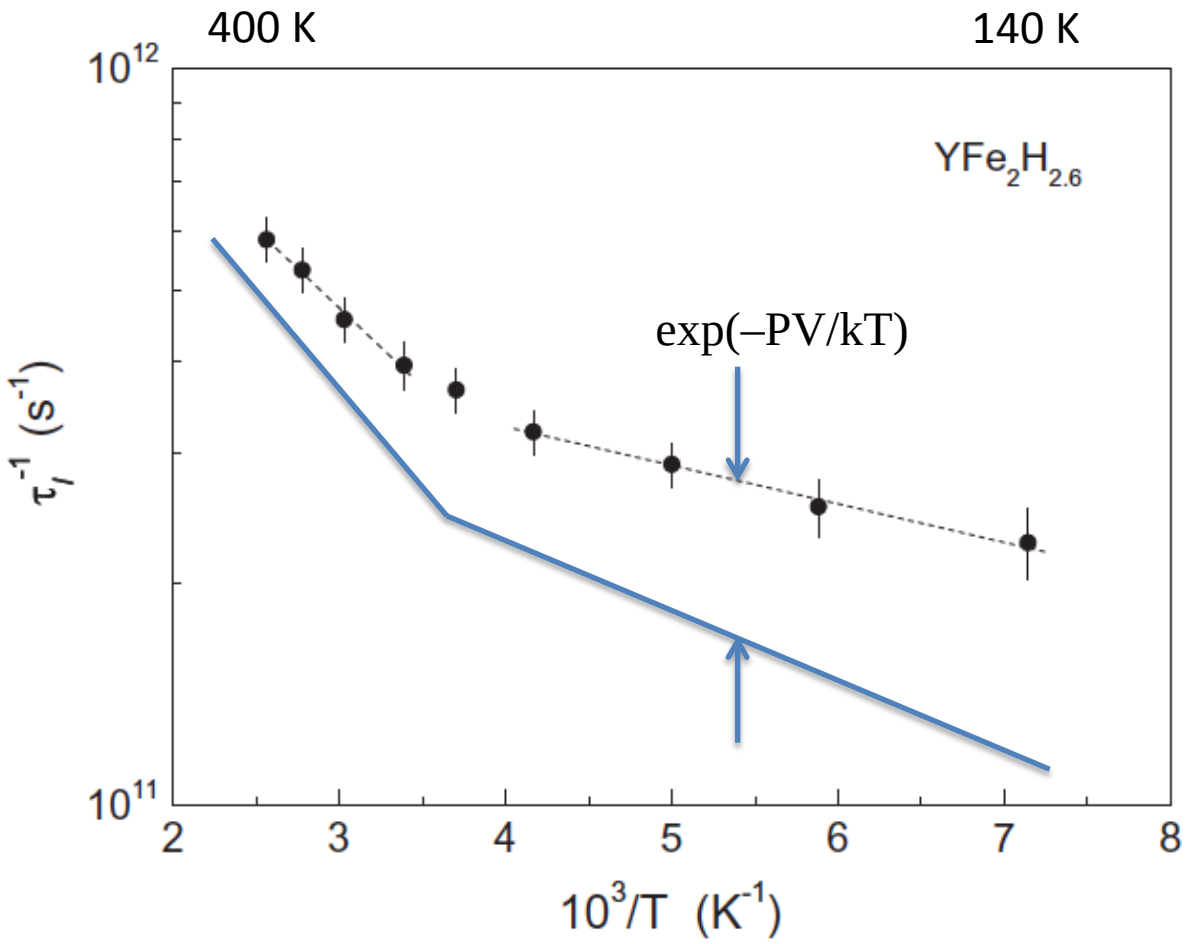


Fig. 5. The hydrogen jump rate derived from the width of the quasielastic component as a function of the inverse temperature. The dashed lines show the Arrhenius fits to the data in the ranges 295–390 K and 140–240 K.

Procedure

1) Add hydrogen to proper stoichiometry $YFE_2H_{2.6}$ at 300 K.
2) Cool to 77 K (immobilizing the hydrogen)
3) Acquire QENS spectrum
4) Add high pressure Ar, acquire another spectrum
5) Heat slightly, goto step 3.

Based on prior results from DCS on the same material:
For a pressure of 0.6 GPa the experiment should be sensitive to activation volumes ΔV as small as 0.1 $Å^3$ at 100 K
and 0.3 $Å^3$ at 300 K.

Gibbs Free Energy

Partition Function for one mode, z:

$$z = \sum_{n=0}^{\infty} \mathrm{e}^{-n\hbar\omega/k_\mathrm{B}T} = \frac{1}{1 - \mathrm{e}^{-\hbar\omega/k_\mathrm{B}T}}$$

Partition Function for solid, Z:

$$Z = \prod_{j}^{3N} \frac{1}{1 - \mathrm{e}^{-\hbar\omega_j/k_\mathrm{B}T}}$$

Relate to density-of-states, $g(E)$, in m intervals of ΔE:

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for E,g_E in spectrum:
    Z *= one_osc(E,T) ** g_E
```

Fundamental Issue about the Origin of Entropy in Materials

$$S = S_{vib} + S_{conf} + S_{el} + S_{mag}$$

Simplify to non-magnetic insulators without chemical disorder

$$S = S_{vib} = S_{H} + \Delta S_{QH} + \Delta S_{AH}$$

Harmonic, Quasiharmonic, Anharmonic

T=0	T=0	T
P=0	P	P=0

Strategy for phonons that mostly works:

$\Delta\omega_{QH}(V)$ by DFT or DAC

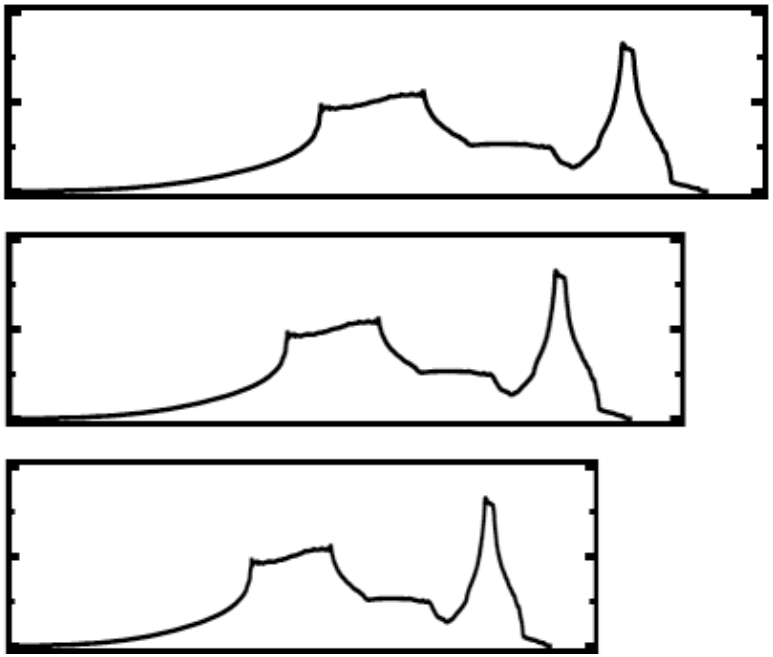
$\Delta\omega_{AH}(T)$ by AIMD or Furnace

Calculate $\Delta S_{QH}(\Delta\omega_{QH}(V))$ and $\Delta S_{AH}(\Delta\omega_{AH}(T))$
Add them together.

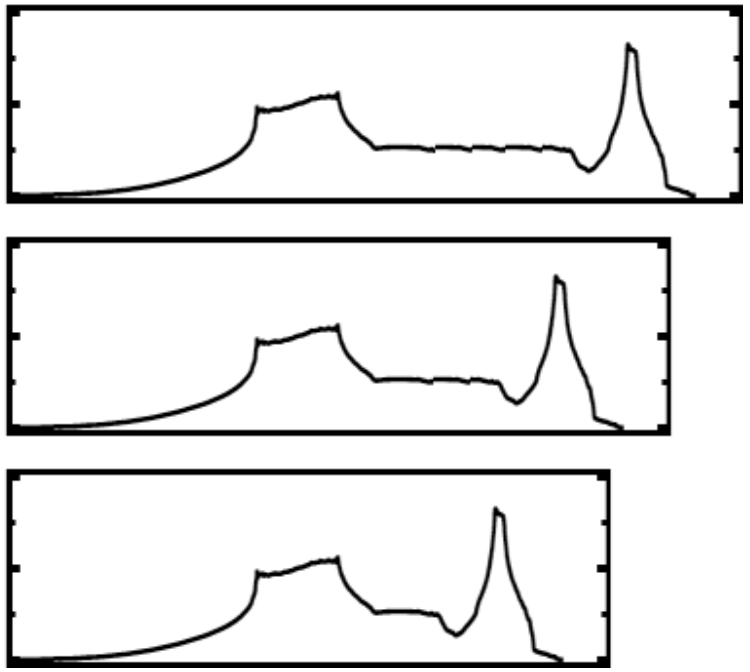
Doubts about Conventional Practice

If phonon DOS changes shape with pressure, thermal anharmonic effects will be altered.

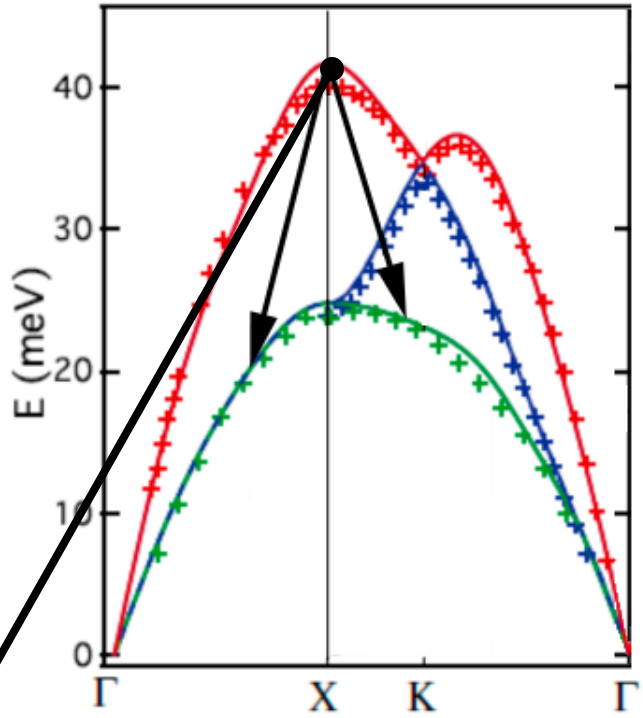
Equal mode Grüneisen parameters

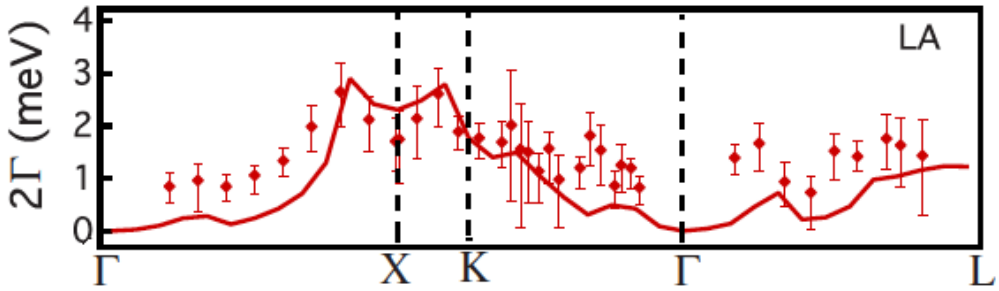


Unequal mode Grüneisen parameters



Kinematics (energy and momentum conservation)



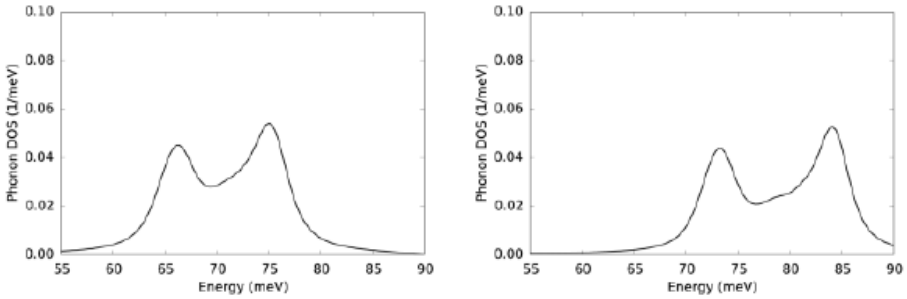


$$D_{\downarrow}(i,\mathbf{q}) = \frac{1}{N}\sum_{\mathbf{q}_1,\mathbf{q}_2,j_1,j_2} \Delta(\mathbf{q}-\mathbf{q}_1-\mathbf{q}_2)\,\delta(\omega-\omega_1-\omega_2)$$

Statement of research (please stay within the available

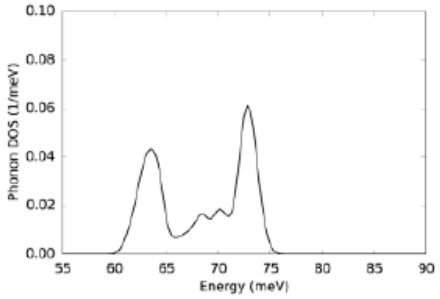
Effects of Simultaneous Pressure and Temperature on Phonons in Cu_2O

Fred Yang, Brent Fultz, Chen Li, Reini Boehler, Bianca Haberl, Yongqiang Cheng, Yang Shen, Olle Hellman, Hillary Smith, Tabitha Swan-Wood

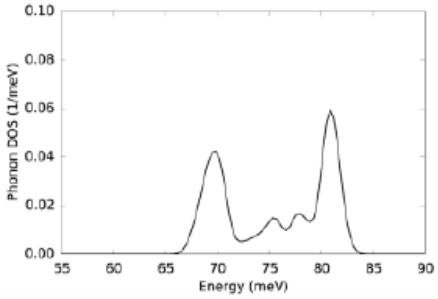


(a) 0 GPa, 300 K

(b) 10 GPa, 300 K



(c) 0 GPa, 0 K



(d) 10 GPa, 0 K

Figure 1. Calculated broadening and shifts of the phonon DOS for optical phonons in cuprite, dominated by oxygen atom motions [unpublished results].

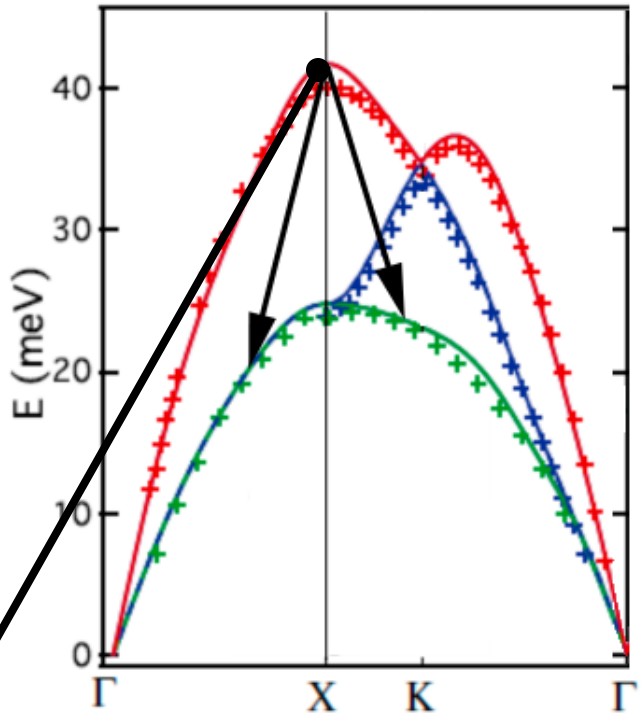
Background of VISION will make or break this experiment

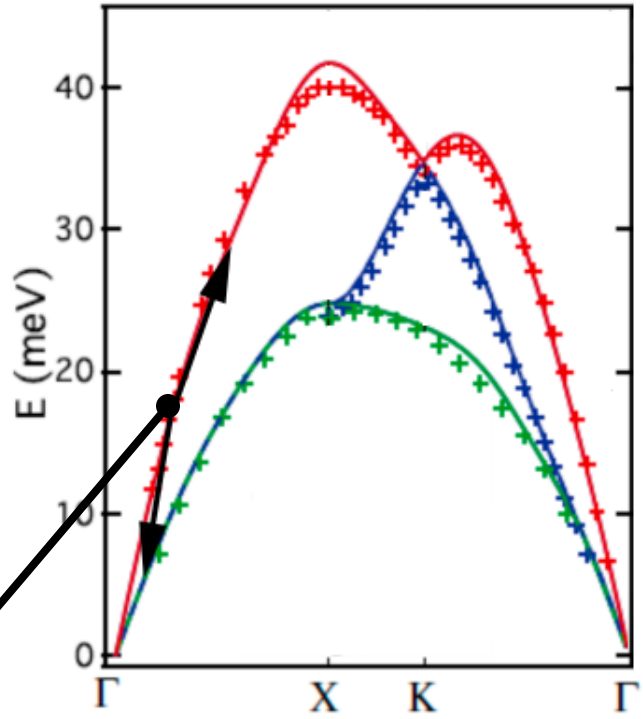
Fig. 2. Prototype of the collimator for the diffraction detector banks of VISION.

Proposal Declined, but Reviews were Encouraging…

- This seems to be an experimentally challenging, but really interesting, proposal.
- Loved the use of 3D printing to help plan the work.
- Fundamental and underpinning science that is essential to allow the development of new capabilities on the Vision instrument.
- The team has carefully chosen an excellent test material to both proof the capabilities of the Vision high pressure cell and also further the understanding of solid-state Gibbs free energy of materials.
- The experiments seem achievable and should produce results of high impact. Good science and good proposal, but premature.
- Tests of the DAC are only just starting on VISION.
- VISION will reconsider this proposal if tests progress sufficiently in early 2016.

Kinematics (energy and momentum conservation)





$$D_{\downarrow}(i,\mathbf{q}) = \frac{1}{N}\sum_{\mathbf{q}_1,\mathbf{q}_2,j_1,j_2} \Delta(\mathbf{q}-\mathbf{q}_1-\mathbf{q}_2)\,\delta(\omega-\omega_1-\omega_2)$$

$$D_{\uparrow}(i,\mathbf{q}) = \frac{1}{N}\sum_{\mathbf{q}_1,\mathbf{q}_2,j_1,j_2} \Delta(\mathbf{q}+\mathbf{q}_1-\mathbf{q}_2)\,\delta(\omega+\omega_1-\omega_2)$$

Phonon-Phonon Interactions in Aluminum: Lifetime Broadening of Phonon Linewidths

The phonon-phonon interaction is treated within second-order perturbation theory. The phonon linewidth contributed from the leading third order anharmonicity is

$$
\begin{aligned}
2\Gamma(\vec{q},j) = \frac{\pi\hbar}{8N} \sum_{\vec{q}_1,\vec{q}_2,j_1,j_2} & \frac{|\Phi(-\vec{q}j;\,\vec{q}_1 j_1;\,\vec{q}_2 j_2)|^2}{\omega(\vec{q}_1 j_1)\,\omega(\vec{q}_2 j_2)\,\omega(\vec{q}j)} \\
& \times \left[(n_1+n_2+1)\,\delta(\omega-\omega_1-\omega_2)\,\Delta(\vec{q}_1+\vec{q}_2-\vec{q})\right. \\
& \left. + 2(n_1-n_2)\,\delta(\omega+\omega_1-\omega_2)\,\Delta(\vec{q}_1+\vec{q}_2-\vec{q})\right]
\end{aligned}
$$