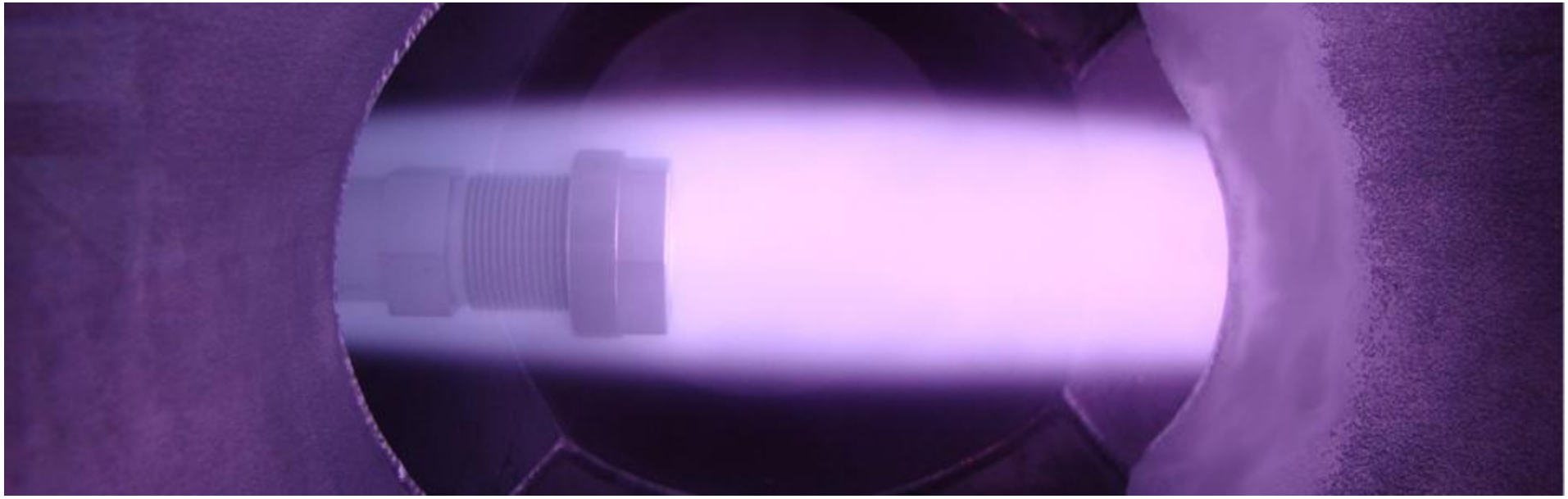
# Hydrogen behavior in materials and on surfaces: PMI research at Sandia



Sandia National Laboratories

Idaho National Laboratory

LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT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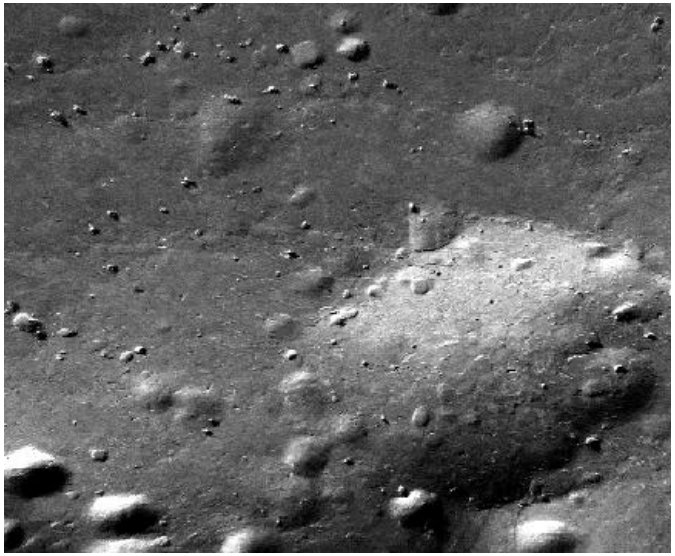
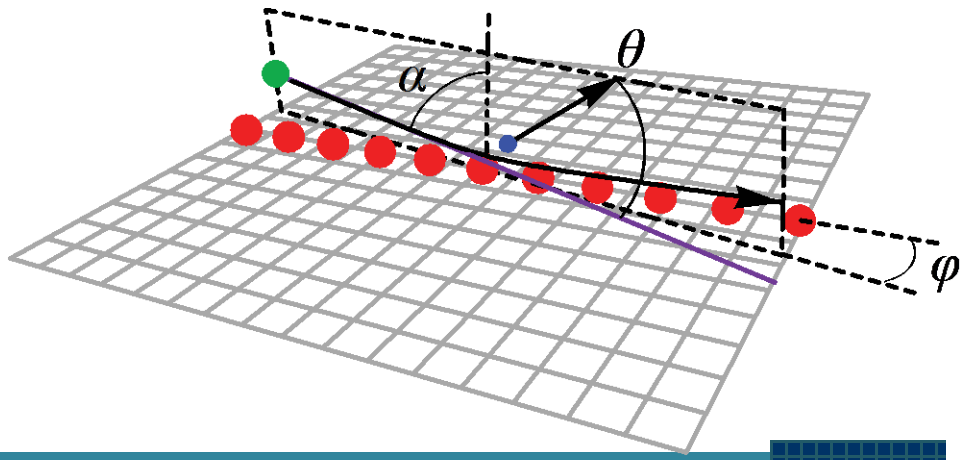
# Overview: Studying hydrogen from both continuum and atomic-scale perspectives

I will describe three ongoing activities:

- Collaboration with Tritium Plasma Experiment (TPE): bubble/blister formation studies.
- Continuum-scale bubble model development.
- Atomic-scale behavior of hydrogen on Be surfaces





# Part 1: Tritium Plasma Experiment

# TPE overview: Tritium retention in plasma-facing materials

Collaboration: INL and Sandia/CA:

- Tritium retention in materials
- Precipitation in tungsten
- Plasma-driven permeation
- INL collaborator: M. Shimada [PI, STAR facility]

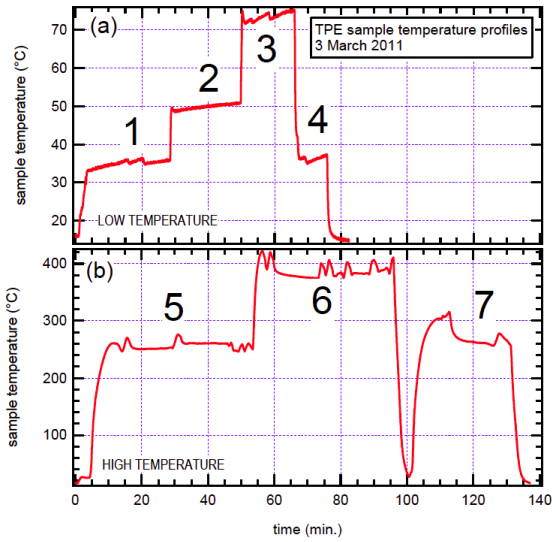
Experiment History:

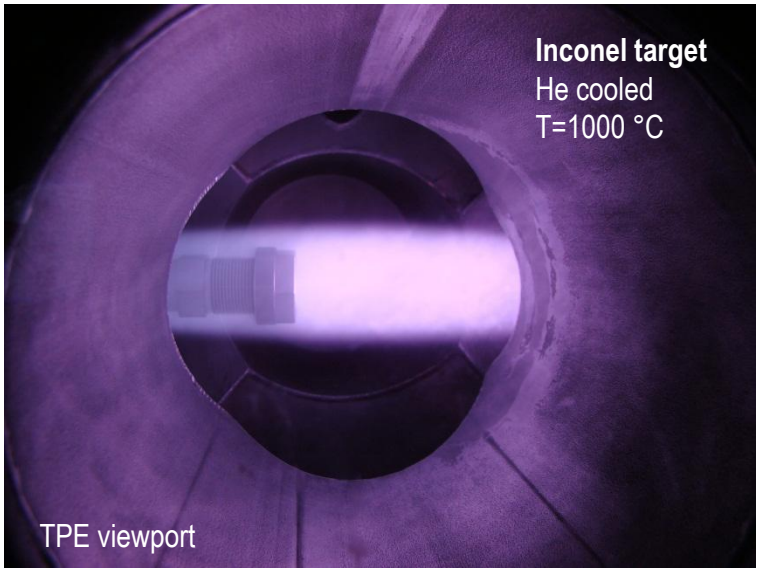
- Developed at SNL as TPX (1982), moved to LANL (1993) and INL (2002)
- Located at the Safety and Tritium Applied Research (STAR) facility
- Restarted plasma operations in August 2007
- Tritium work restarted in Feb. 2009
- n-irradiated studies in 2010-2011(INL/TITAN collaboration)

# Two new target designs for TPE tested

- Key challenge for plasma-driven permeation: stable operation at high temperature.
- Developed two retention stages (Cu and Inconel) to test new design concept.
- Leveraged concentric cooling channel design from PISCES.
- Successful testing Inconel target to T=1000 °C using He cooling.

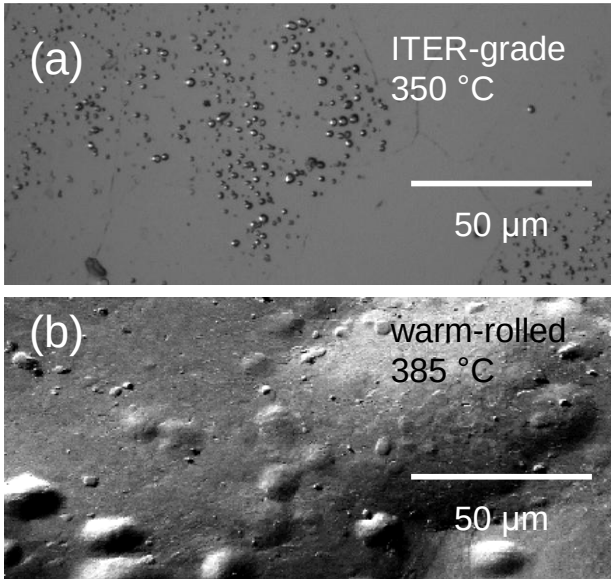
**Cu target**
Water cooled
T<500 °C



# Recent work focuses on bubble growth in ITER-grade tungsten

- Precipitation affects H migration, trapping in W [Wampler & Doerner, *Nucl. Fusion* (2009).]
- Warm-rolled and ITER-grade tungsten have much different grain structure.
- Exposed both materials in TPE. (ITER-grade to serve as database for comparison with tungsten.)
- For similar exposure conditions, bubble growth differs dramatically, suggesting drastically different growth mechanisms.
- How much H can be trapped within the bubbles?




Surface morphology of (a) ITER-grade and (b) warm-rolled tungsten samples exposed to 100 eV $D_2^+$. [Irradiation conditions: (a) $T_{surf}$=350 °C; $\Phi$=1.5×10$^{22}$ m$^{-2}$s$^{-1}$; $F$=1.1×10$^{26}$ m$^{-2}$; (b) $T_{surf}$=385 °C; $\Phi$=1.1×10$^{22}$ m$^{-2}$s$^{-1}$; $F$=0.8×10$^{26}$ m$^{-2}$]

# Part 2: Continuum-Scale Bubble Model

# Continuum-scale bubble model: underlying physical assumptions

**Basic model**: 1-D diffusion (sink terms for traps and bubbles):

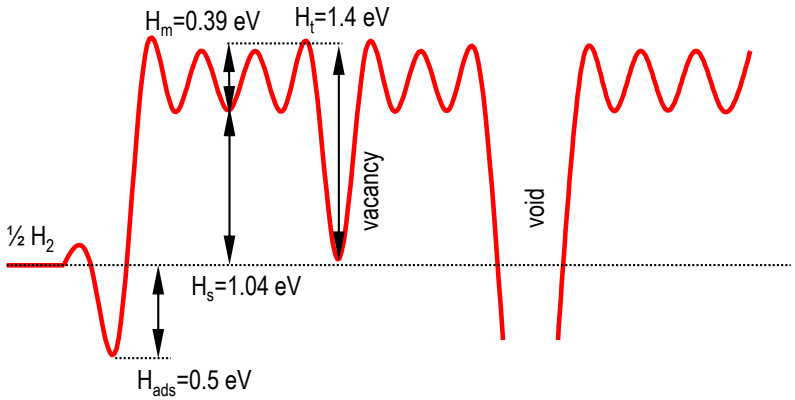
$$\partial u(x,t)/\partial t = D(t)\,\partial^2 u(x,t)/\partial x^2 - q_T(x,t) - q_B(x,t)$$

**Flow out of the bubbles**: F.S. Ham [*J. Phys. Chem. Solids* (1958)]:

$$q_B = \partial u_B(x,t)/\partial t = 4\pi D(t) r_B(x,t) N_B(x)\left[u(x,t) - u_{eq}(x,t)\right]$$

**Assume**:

1. Array of evenly spaced precipitates.
2. Concentration at the bubble surface is dictated by Sievert's law
3. Flow between individual cells containing bubbles is negligible.
4. Bubble spacing much larger than diameter
5. Thermal ramp slow; satisfies quasi-equilibrium




Energy diagram for H migrating through tungsten.

# Precipitation depends on conditions necessary for chemical equilibrium

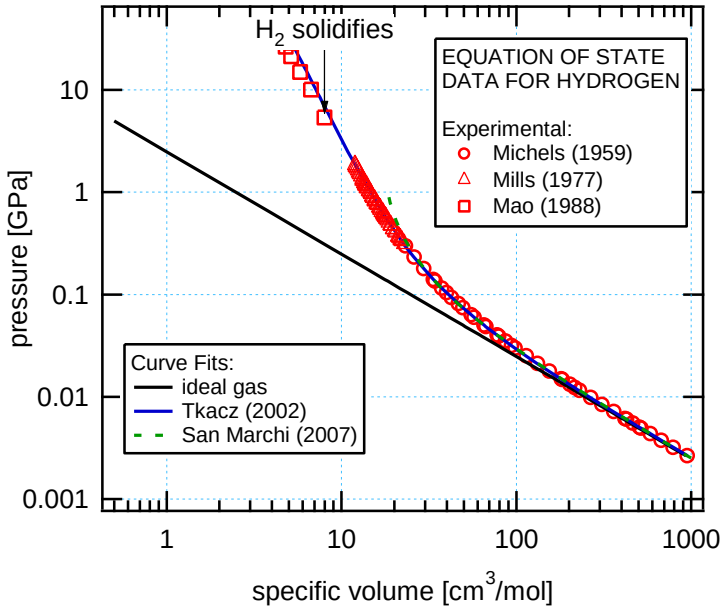
We assume bubbles grow by dislocation loop punching, where the pressure to expand a bubble is given by (with γ, μ, and b as materials constants):

$$p_{LP} \geq 2\gamma/r_b + \mu b/r_b$$

Filling of the bubbles is governed by chemical equilibrium:

$$u_{eq}(x,t) = \sqrt{f} S_0 \exp(-E_s/RT)$$

$$\ln(f/p) = \int_0^p (v(p,T)/RT - 1/p)dp$$




H equation of state at RT

# Suitable model system identified (characterized with PAS)

**Validation case**: Positron annihilation (PAS) by Van Veen et al. [*J. Nucl. Mater.* (1988)].

**Experimental conditions**:

- W(100) crystals damaged w/ 6 MeV protons.
- Annealed at 1200 K for 15 min.
- Void conc.: $10^{-6}$ /W to depth 35 μm.
- Void diameter: 1 nm (~30 – 50 vacancies.)
- Exposure to 2 keV $H_2^+$ [$\Phi$=1.25×$10^{18}$ $m^{-2}s^{-1}$; doses of $F$=$10^{22}$ $m^{-2}$ and $10^{23}$ $m^{-2}$ considered.]
- $T_{surf}$=350 K

# Predicted trap concentrations compare favorably with experimental results

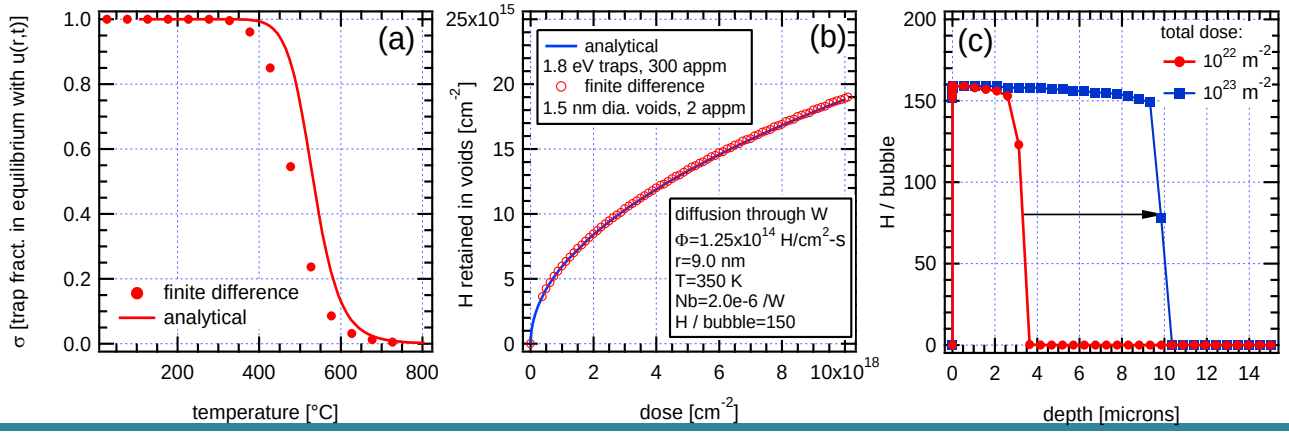
Simulations:

2 keV $H_2^+$ (or 1 keV $H^+$) ion bombardment

Populated a surface region with voids to a depth of 35 μm (1 nm dia.)

Results:

1. Consistent with Van Veen, no expansion of 1 nm dia. voids by loop punching.
2. Bubbles saturated at 40 H/bubble. Slight adjustment to void diameter (to 1.5 nm) increases this to 150 H/bubble, in accord with their Van Veen's meas.
3. Retention calculation also in agreement with TDS results.

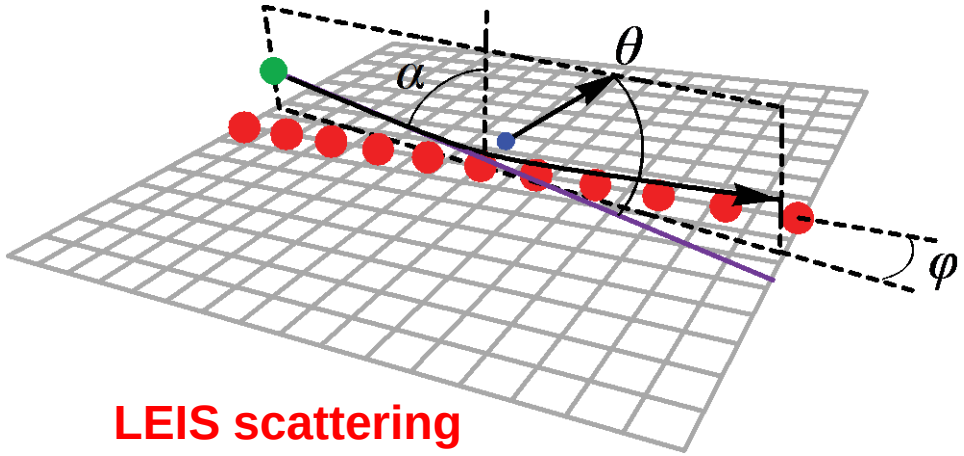



Comparison of bubble model results with analytical calculations: (a) temperature variation of fraction of traps filled, (b) total retention as a function of fluence, (c) simulation of void filling (behavior similar to saturable traps.)

# Part 3: Surface Ion Scattering Studies

# Motivation: Detecting adsorbed hydrogen

- Predicting material behavior in ITER requires sophisticated models (DFT, MD, Kinetic Monte Carlo.)
- Need complementary experiments to validate model assumptions.
- Atomic-scale behavior of hydrogen is difficult to observe.




**LEIS scattering geometry**

Our approach: Low energy ion scattering (LEIS).

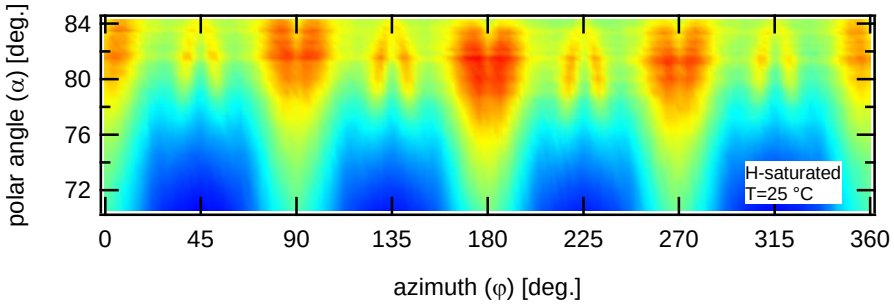
# Inconclusive experimental database for Be(0001)

- Experimental probes / DFT models of Be(0001) have not yielded a self-consistent atomistic picture.
  - DFT calculations: Be forms networks of surface vacancies [Stumpf & Feibelman, *Phys. Rev. B* (1995).]
  - Numerous configurations separated by 10's of meV.
- No clear experimental picture of temperature or coverage dependence of adsorption.
  - DFT calculations by A. Allouche [*Phys. Rev. B* (2008)] explore coverage dependence of H-binding.
- Can equilibrium vacancy structures predicted by DFT be reached?

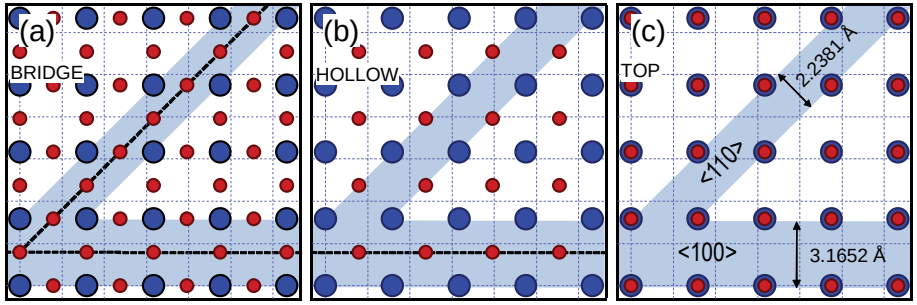
# Prior work: Detecting hydrogen adsorbed on tungsten

- Measurements of D location in bulk useful for continuum models of H diffusion.
- Similar approach for the surface?

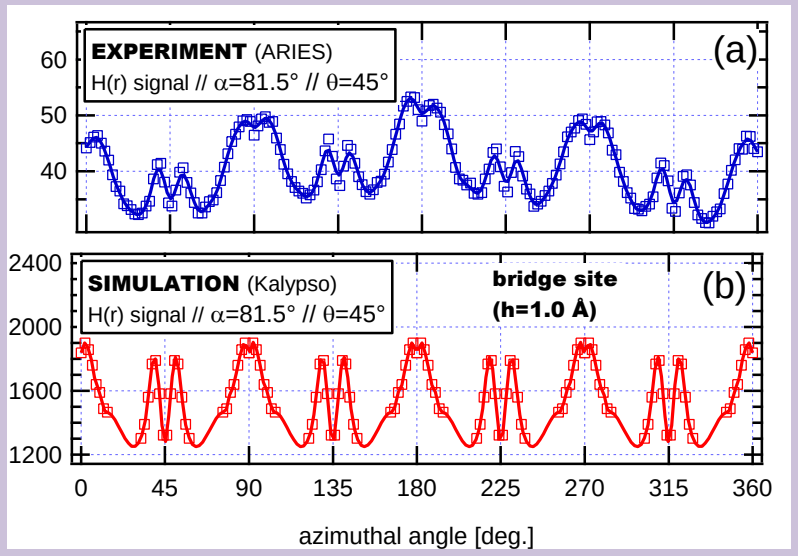
→YES – using surface channeling




Signal depends on where H resides



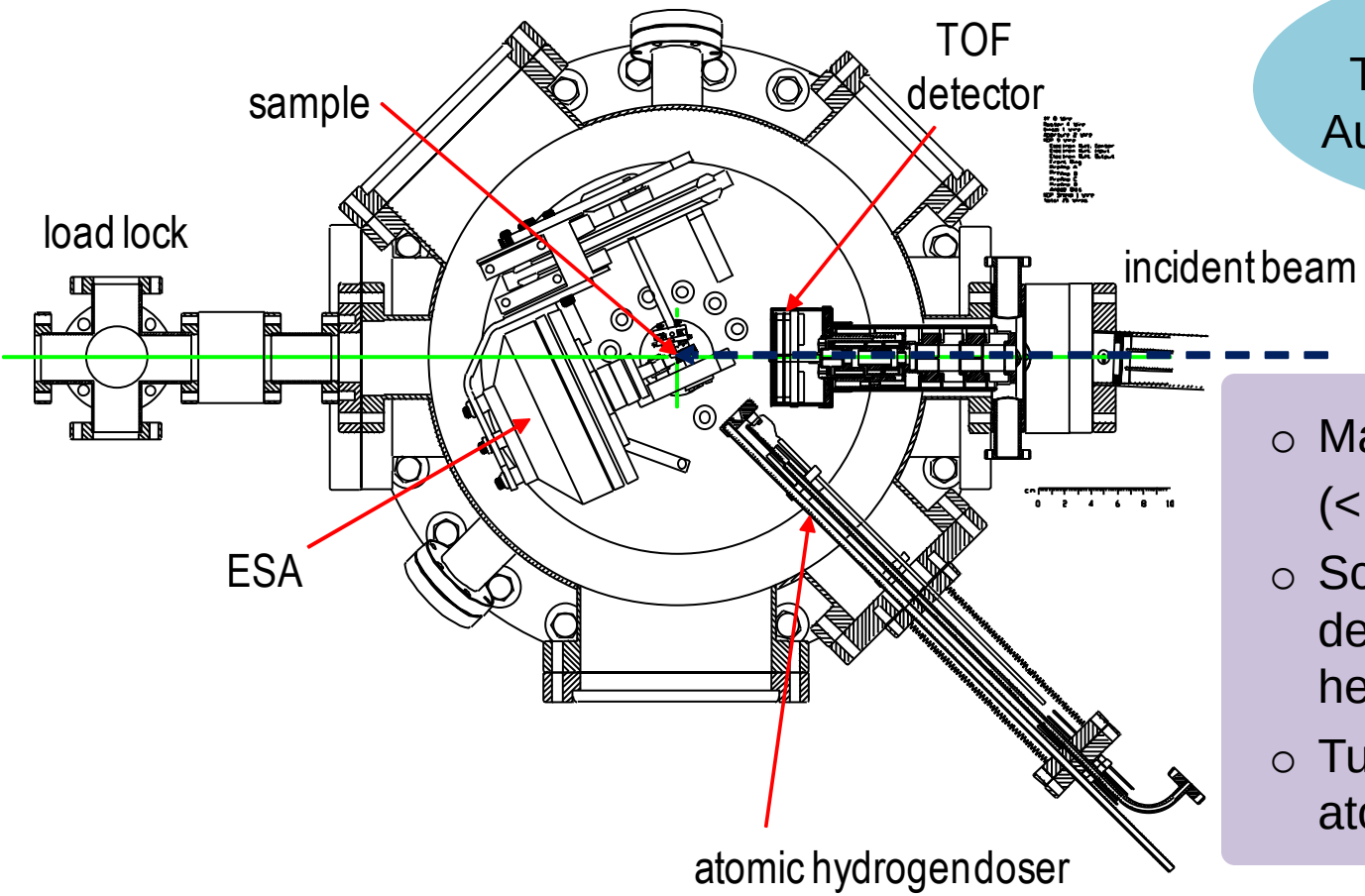

Simulated experimental results for different binding geometries:




Findings compare well with theoretical calculations. [Kolasinski et al., *Phys. Rev. B* (2012)].

# ARIES instrument is uniquely suited for hydrogen adsorption studies

Angle-resolved ion energy spectrometer (ARIES)




**Diagnostics:**
Time of flight and Auger spectroscopy

- Mass-separated beams (< 5 keV $He^+$, $Ne^+$)
- Scattered particles detected by rotatable hemispherical analyzer.
- Tungsten capillary for atomic H dosing.

# Challenges associated with surface preparation

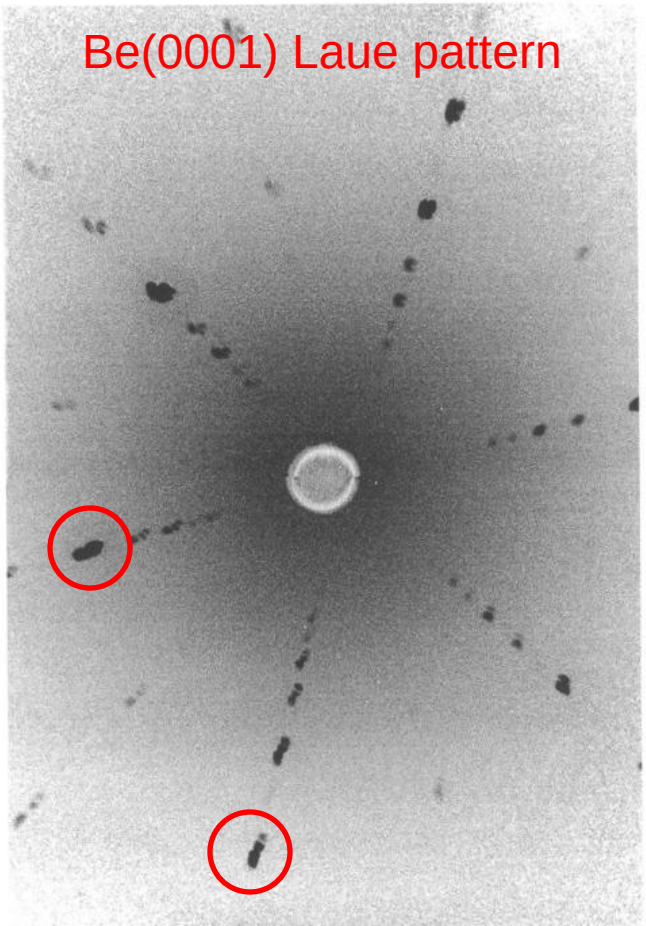
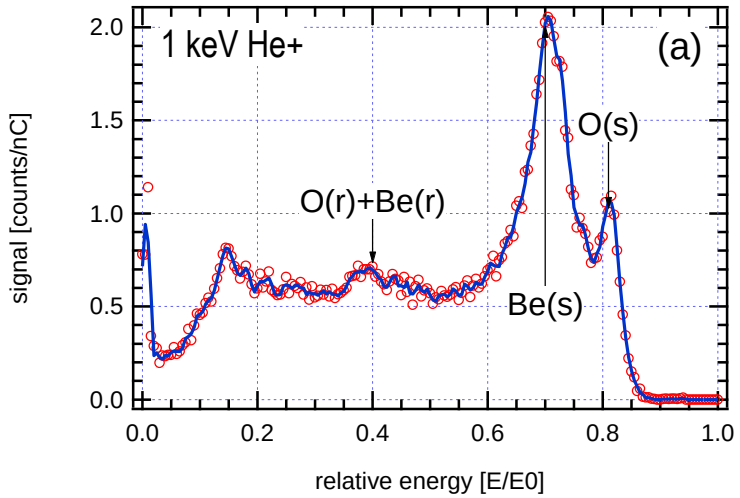



Image courtesy of Mr. René Koper, Surface Preparation Laboratory

- Be single crystals uncommon due to fabrication challenges
- Most contain defects (produce unusable LEED pattern)
- LEIS robust against surface defects
- Our sample:
  - Grown by Franklin Institute (Philadelphia)
  - Laue diffraction verifies orientation reveals slight mosaic structure
  - Crystal polished to within 0.5° of (0001) plane at Surface Preparation Laboratory (Amsterdam)

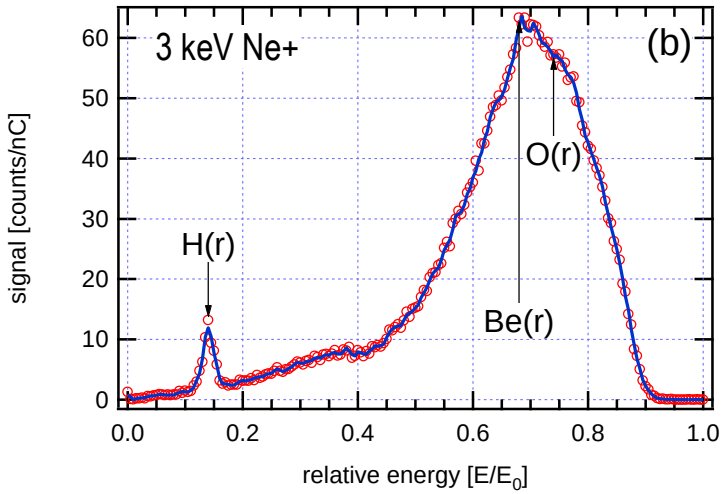
# Separate analysis beams for substrate / adsorbate characterization

## HELIUM



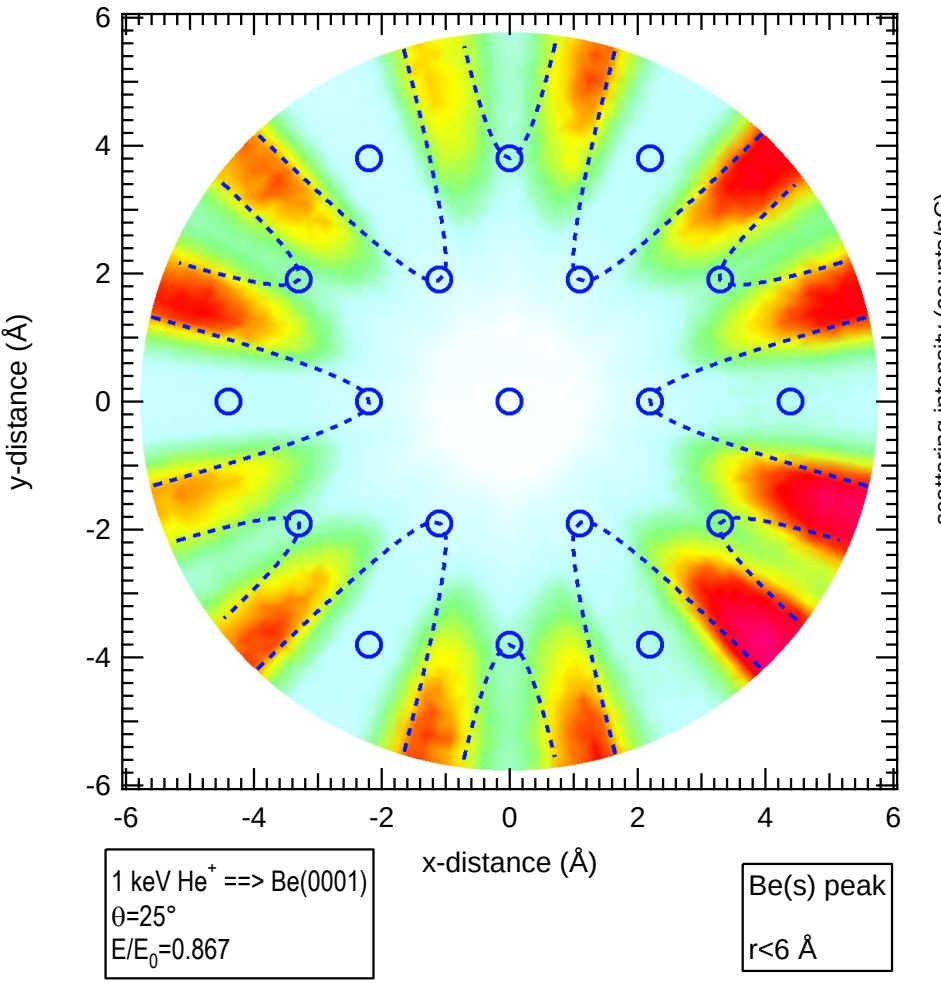

- He ions easily focused by Be surface atoms.
- Well-defined O signal.
- H recoil cross-section too small to be of use.

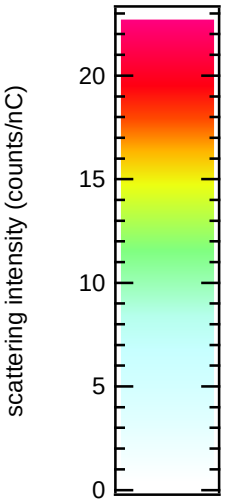
## NEON




- Large cross-section for adsorbed H.
- Ne ions only weakly deflected by Be surface atoms.
- Need grazing incidence angle.

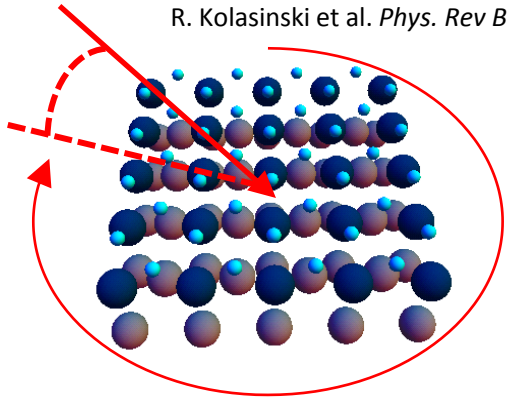
# Scattering map verifies surface structure



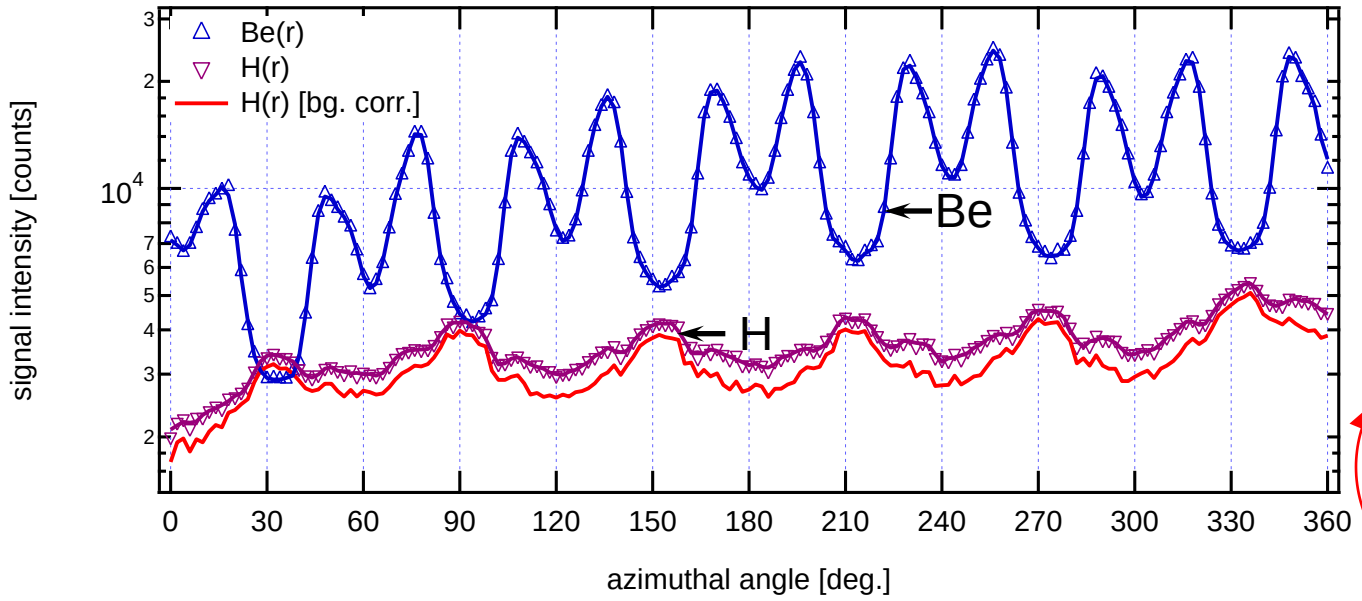

Map created by varying $He^+$ incidence angle and crystal azimuth.

R. Kolasinski et al. *Phys. Rev B* (2009).

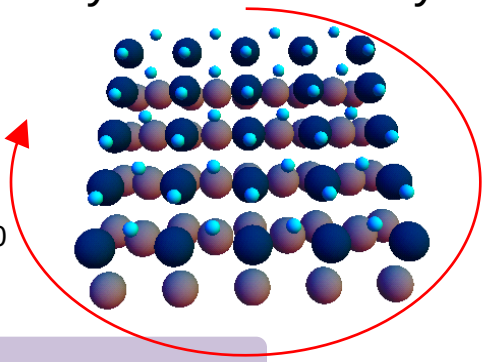


- Scattering pattern consistent with non-reconstructed, clean surface.
- Be atoms are effective at deflecting $He^+$ along open surface channels.

# Dosing with atomic hydrogen produces a distinct recoil signal

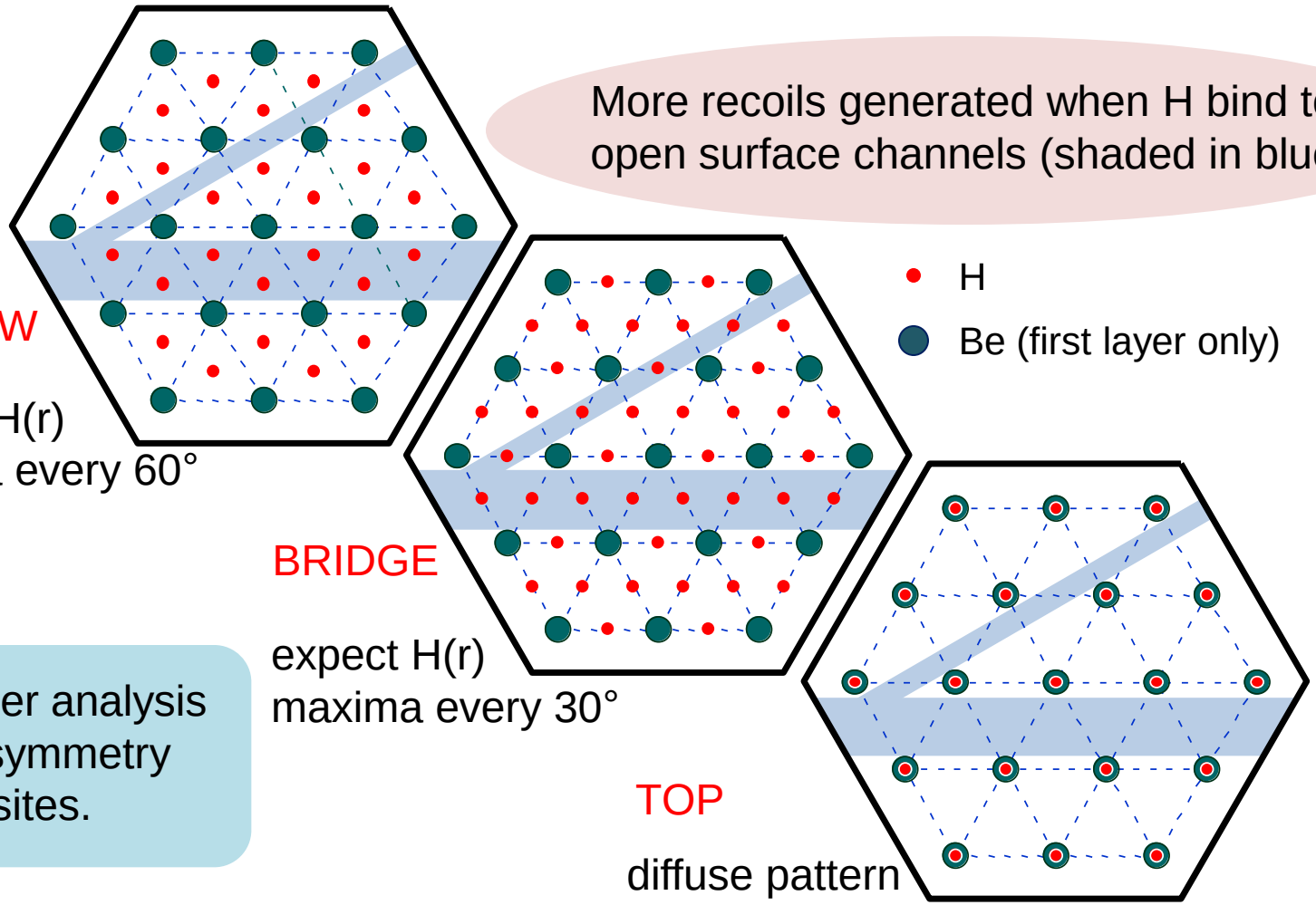



This plot depicts recoiled Be and H collected while rotating the Be crystal azimuthally.

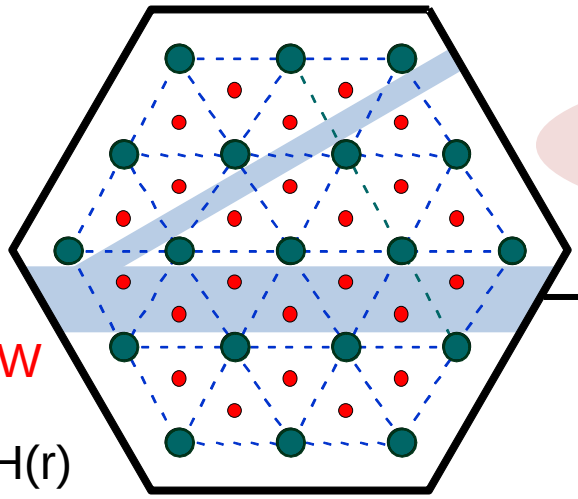


- Dissociative chemisorption not favorable for $H_2$(g).
- Tungsten doser heated to 1700 °C to provide a flux of atomic H (~$10^{14}$ H/cm$^2$s).
- Monitored O recoil signals to determine surface cleanliness.

# Recoil signals depend on how hydrogen is positioned on the surface



# Our measurements are consistent with hollow site occupation



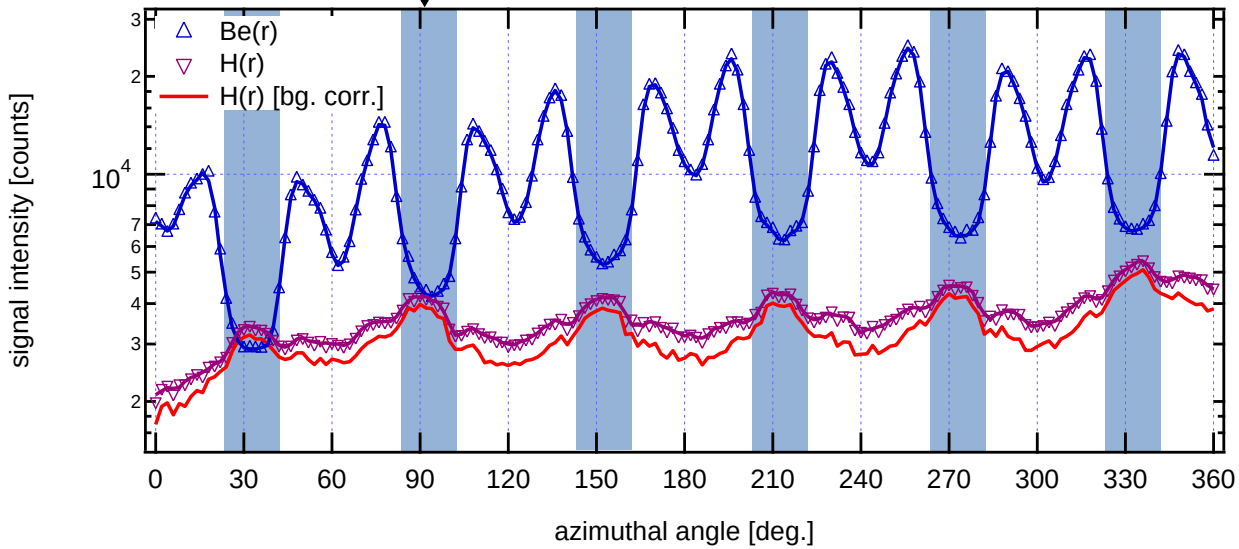
HOLLOW

expect H(r) maxima every 60°

More recoils generated when H bind to open surface channels (shaded in blue.)

H

Be (first layer only)

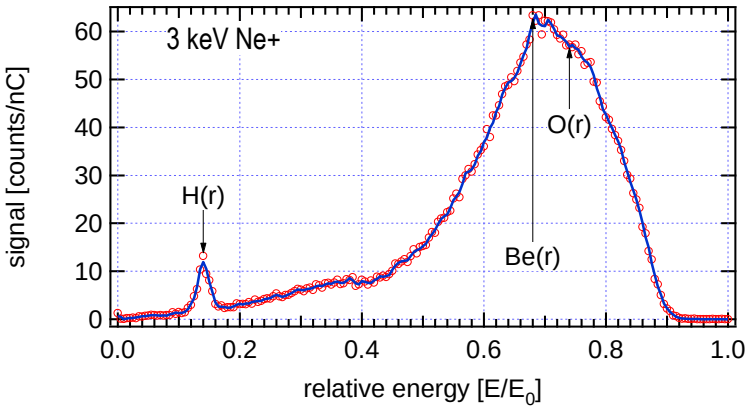


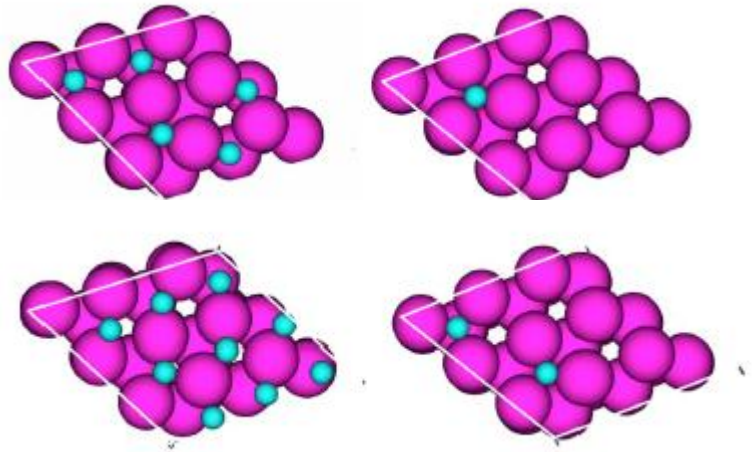

First-order analysis of high-symmetry binding sites.

# Our measurements correspond to low surface coverage case

- **Analysis of our H-recoil peak height indicates a H surface coverage of <0.2.**
- Approaching 1 ML of adsorbed H requires $T_{surf}$ < 200 K [1].
- High coverage required to cause reconstruction [2].
- For non-reconstructed surface, binding site is coverage dependent [3].
- **DFT predicts isolated H atom prefers hollow site [2,3], consistent with our findings.**


[1] Lossev and Küppers, *J. Nucl. Mater.* (1992).
[2] Stumpf and Feibelman, *Phys. Rev. B* (1995).
[3] Allouche, *Phys. Rev. B* (2008).

H binding site variation with surface coverage [image from Allouche, *Phys. Rev. B* (2008)].

# Concluding Remarks

- **TPE**: Developed new target system to test different aspects needed for plasma-driven permeation system.
- **Precipitation**: Successful modeling of prior PAS results; experimental studies with TPE underway.
- **Surface studies**: Clean Be(0001) surface prepared, scattering maps verify structure. Be surface dosed with atomic H, observed to adsorb in hollow sites at low coverage fractions (<0.2 H/Be), consistent with DFT calculations.

# Acknowledgements


- It is a pleasure to thank Robert Bastasz, Thomas Felter, Russ Doerner and Norm Bartelt for their helpful suggestions regarding this work.

- We express our appreciation to René Koper (Surface Preparation Laboratory) for the polishing of our Be(0001) sample.

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