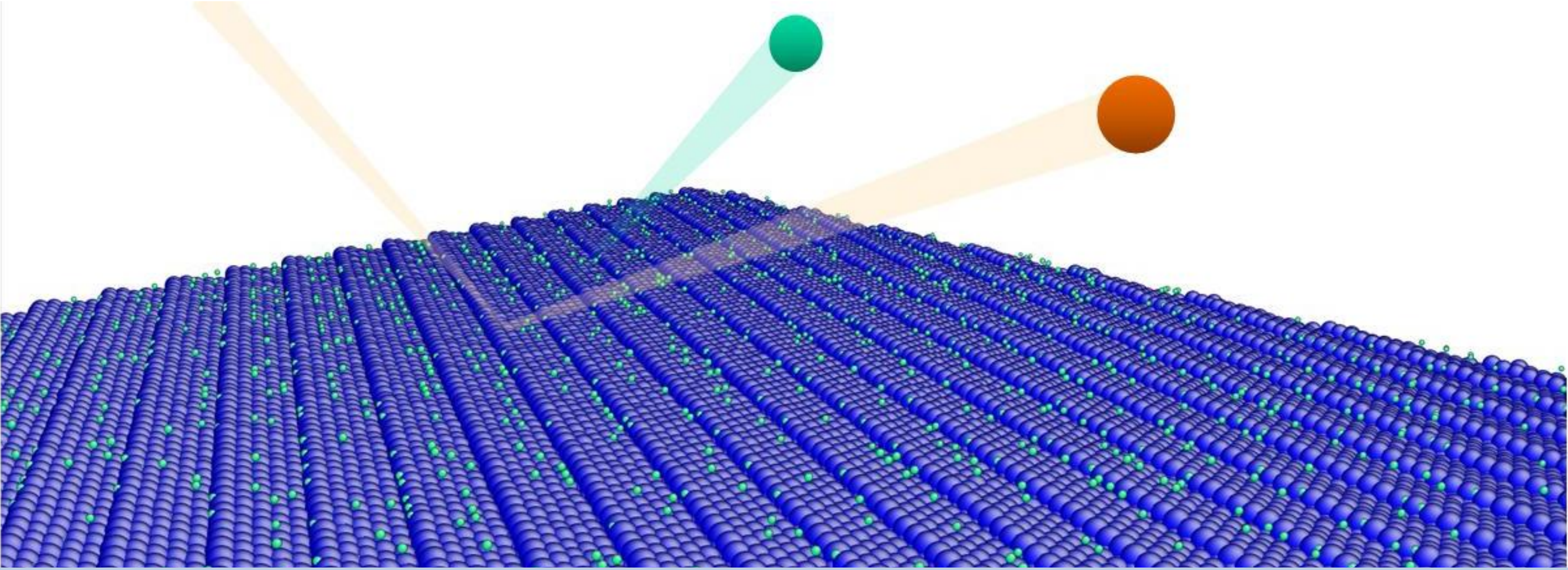
Hydrogen binding configuration and desorption kinetics on beryllium and tungsten surfaces

SAND2014-0013C



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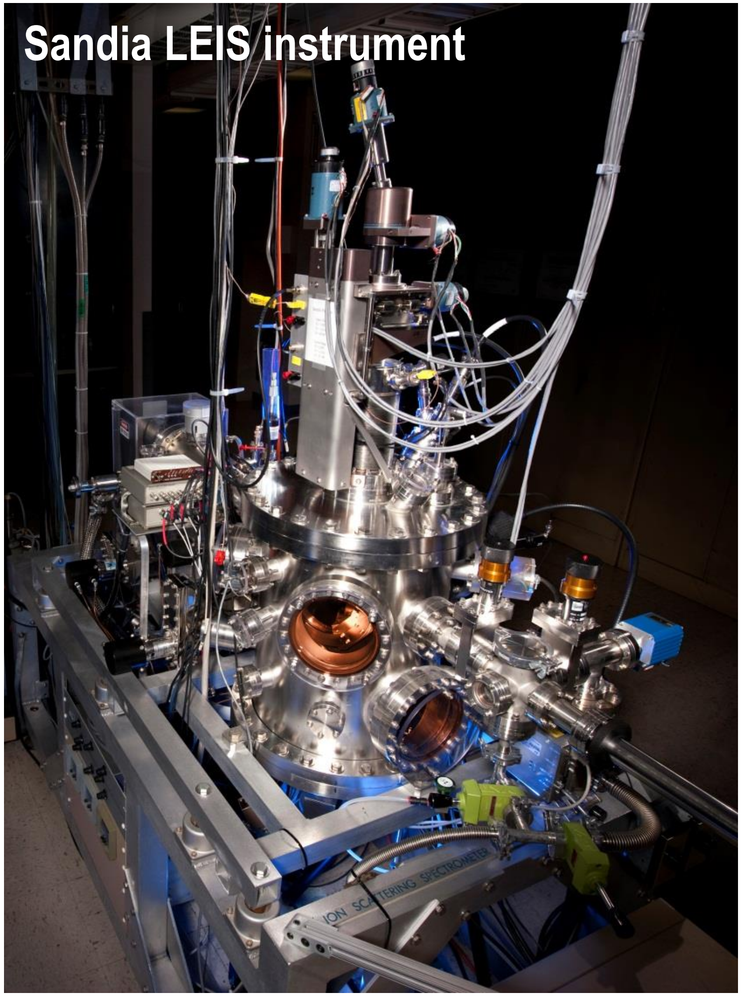
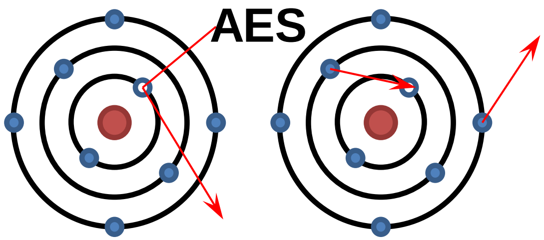
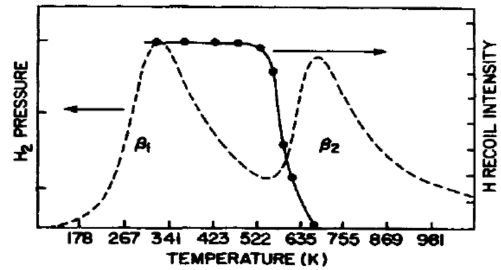
Outline: Using low energy ion scattering (LEIS) to detect surface hydrogen

- **Part 1**: Scattering maps as a means to determine atomic structure
- **Part 2**: Detecting adsorbed hydrogen using grazing-angle ion scattering
- **Part 3**: ICISS and large scale MD scattering simulations



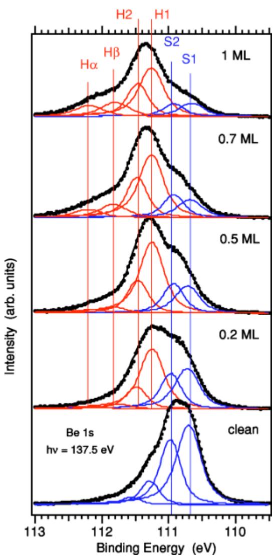
Challenges detecting adsorbed H with conventional surface techniques





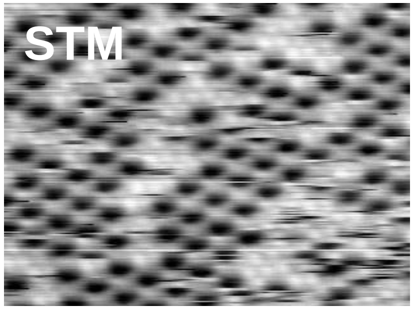
TDS

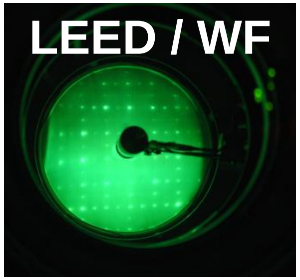
XPS

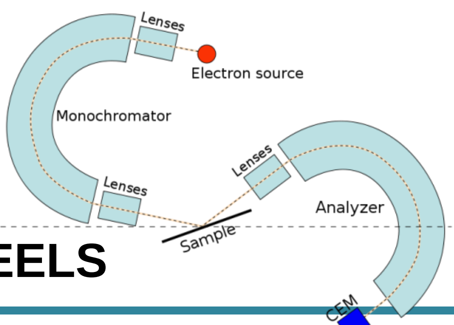


Detecting H poses unique challenges:

- Direct detection impossible with most surface techniques (AES, XPS)
- Detectable signal overwhelmed by substrate (LEED, STM, HREELS)
- Ambiguous/difficult to interpret. (TDS)



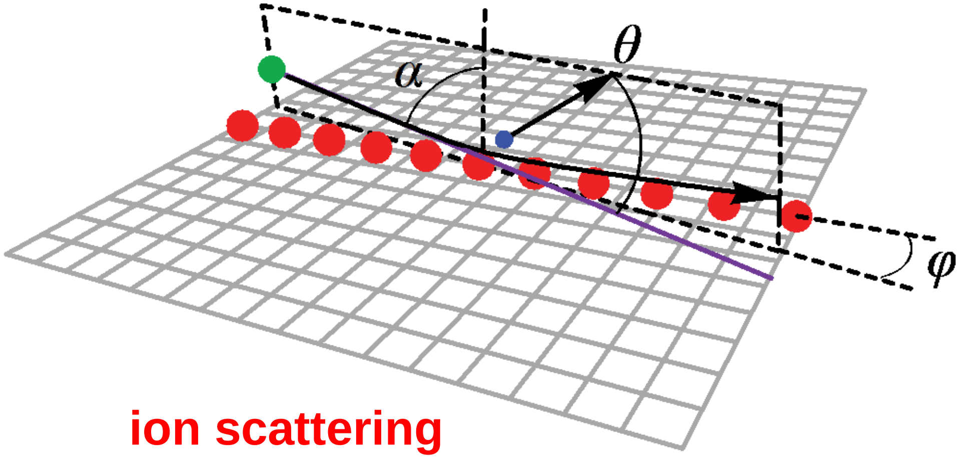




HREELS

Motivation: Understanding hydrogen behavior at an atomic scale

- Predicting material behavior in H environment requires sophisticated models
- Need complementary experiments to validate model assumptions
- Atomic-scale behavior of hydrogen is difficult to observe



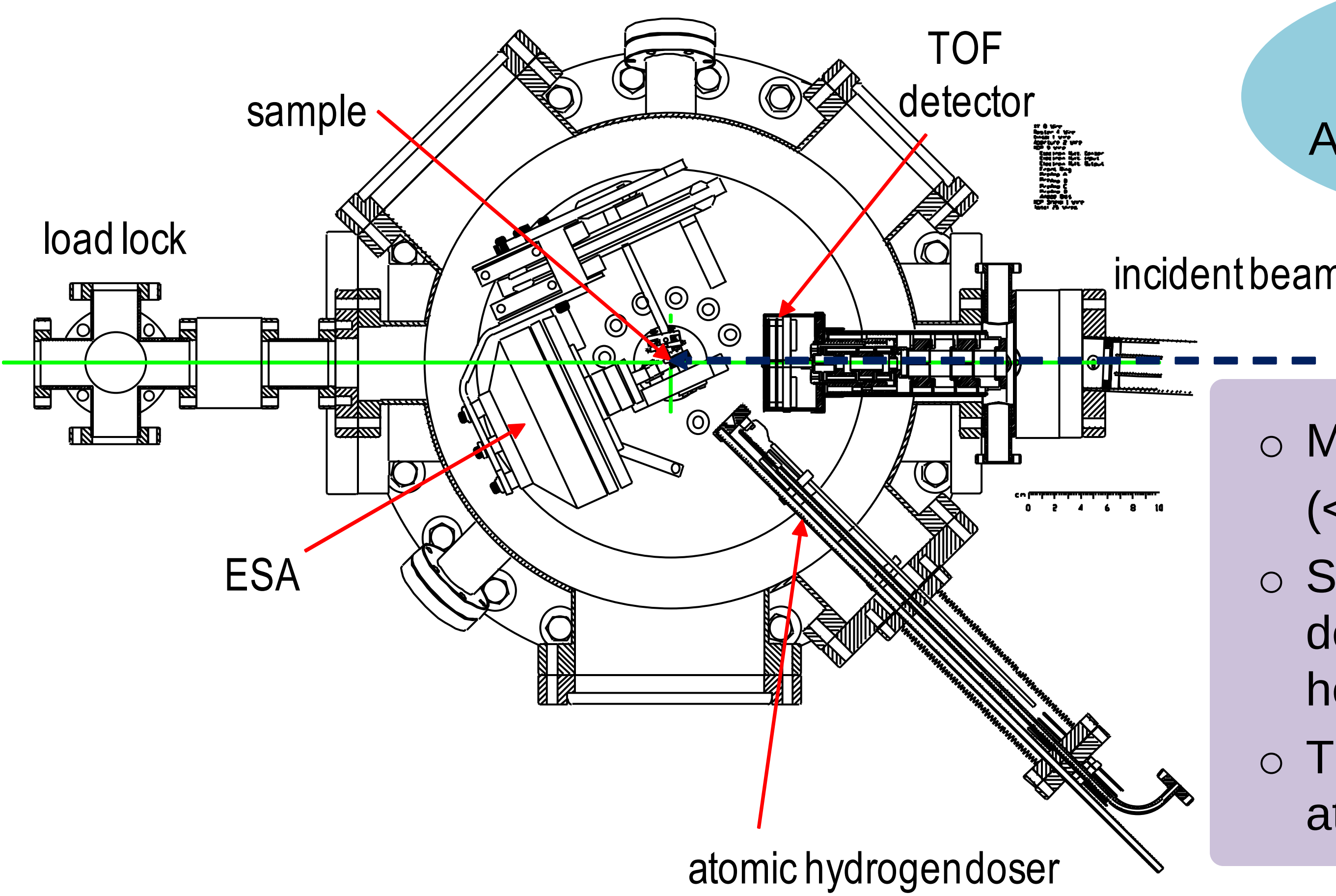
ion scattering geometry

Our approach: Low energy ion scattering

Many similarities to:
- TOF SIMS (Behrens)
- Molecular scattering (Chandler)

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.

Part 1: Using scattering to determine atomic positions

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?

Challenges associated with surface preparation

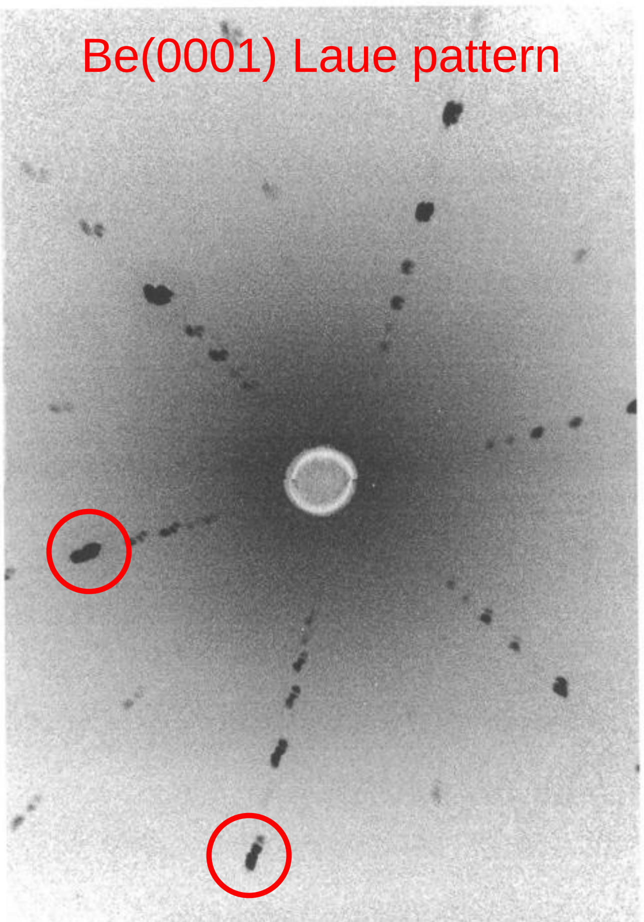
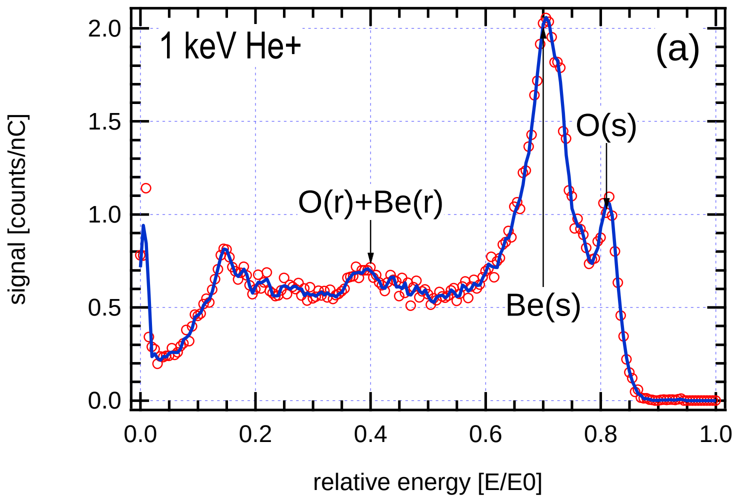


Image courtesy of Mr. René Koper, Surface Preparation Laboratory

- 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)

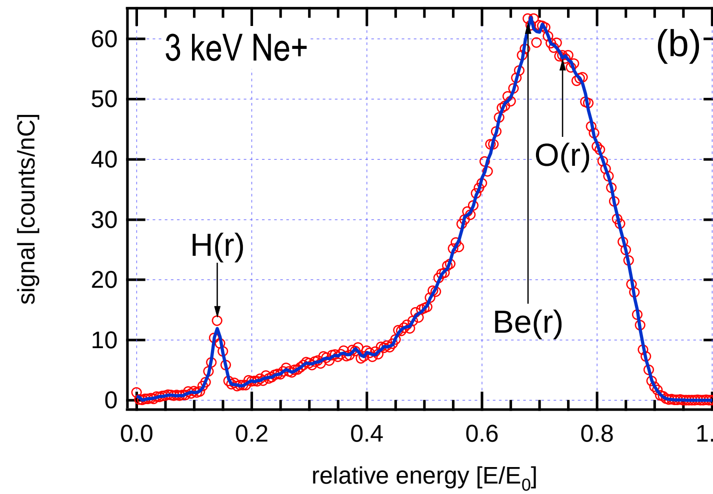
Separate analysis beams for substrate / adsorbate characterization

HELIUM



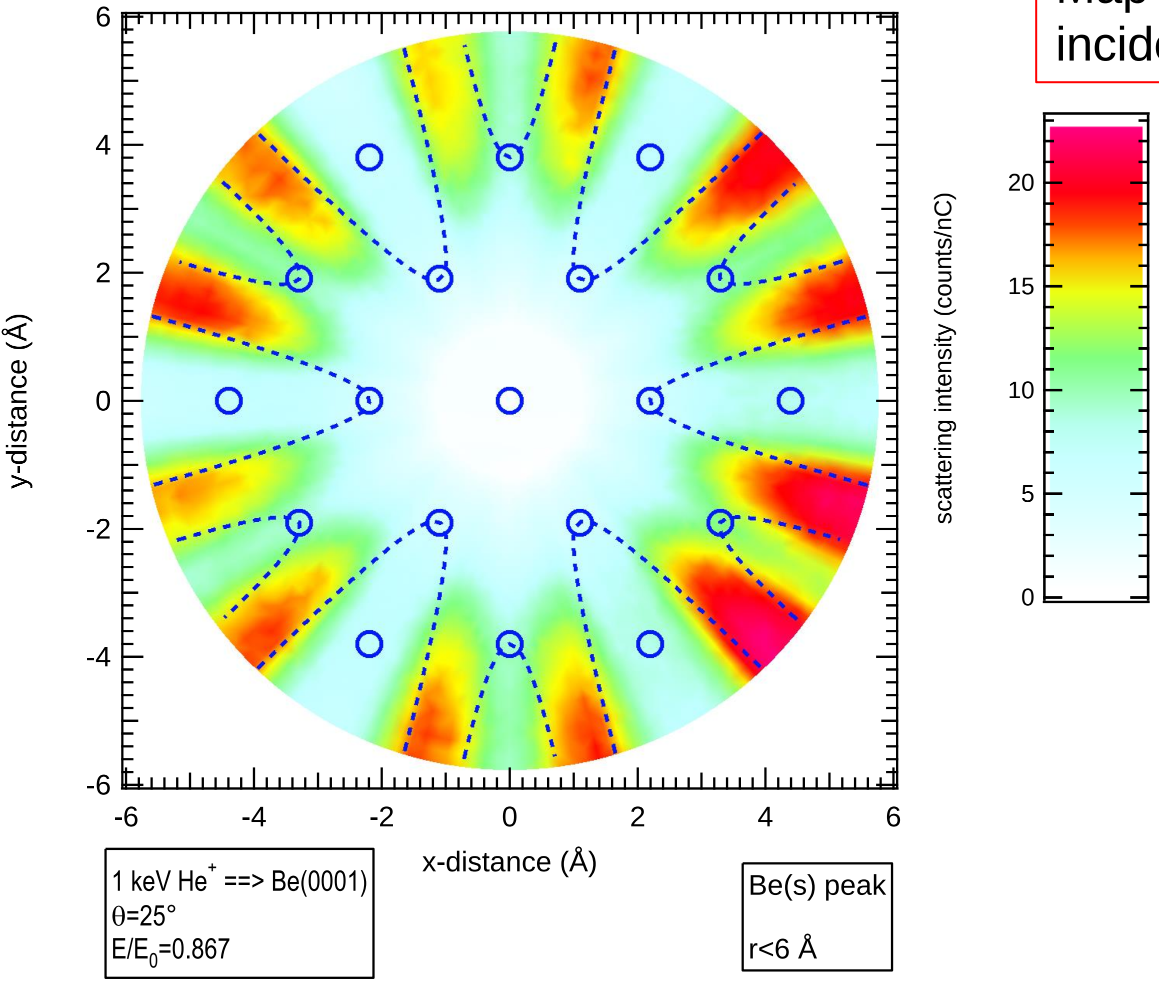
- He ions easily focused by Be surface atoms.
- Well-defined O signal.
- H recoil cross-section too small to be of use.

NEON



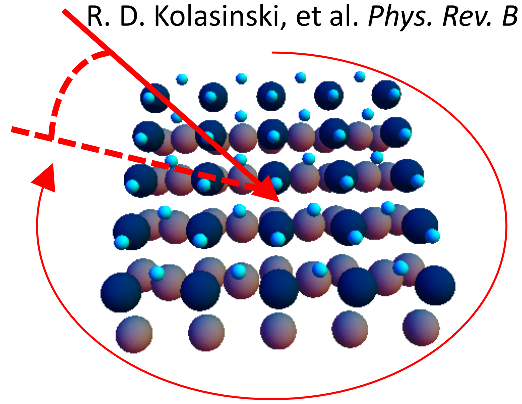
- Large cross-section for adsorbed H.
- Ne ions only weakly deflected by Be surface atoms.
- Need grazing incidence angle.

Scattering map verifies surface structure



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

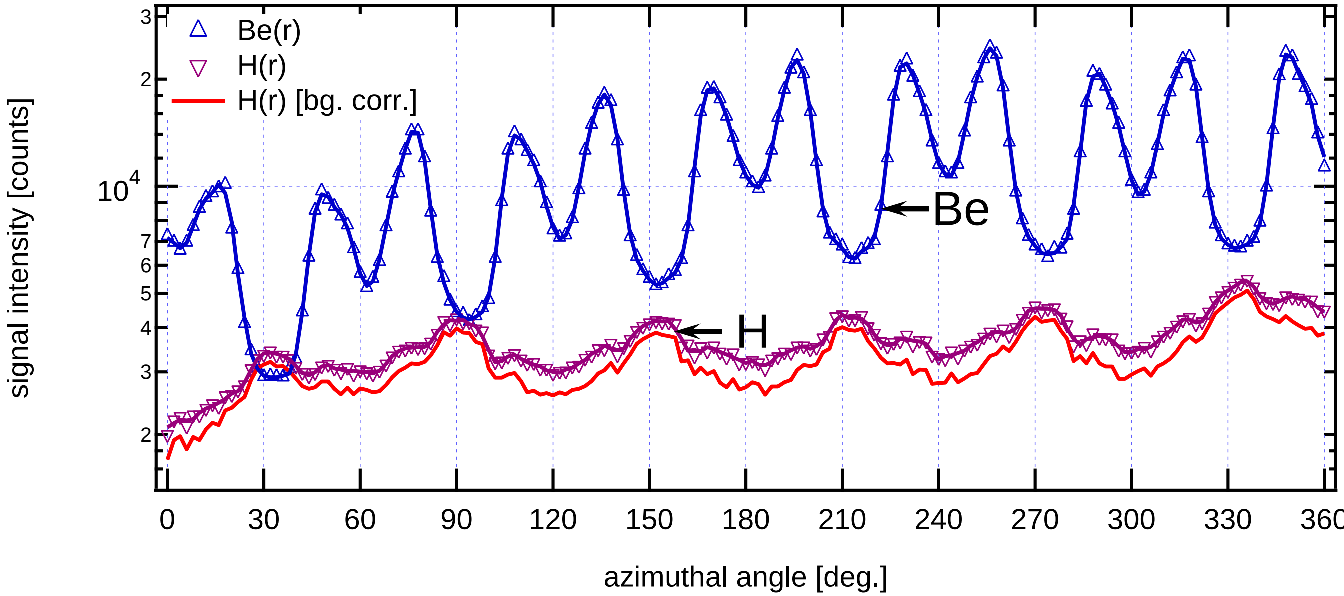
R. D. Kolasinski, et al. *Phys. Rev. B* (2009).



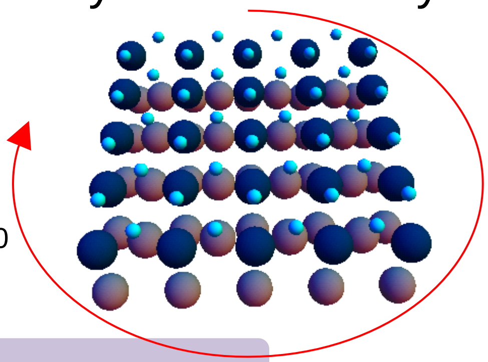
- Scattering pattern consistent with non-reconstructed, clean surface.
- Be atoms are effective at deflecting He^+ along open surface channels.

Part 2: Applying grazing-angle LEIS to detect adsorbed hydrogen

Dosing with atomic hydrogen produces a distinct recoil signal



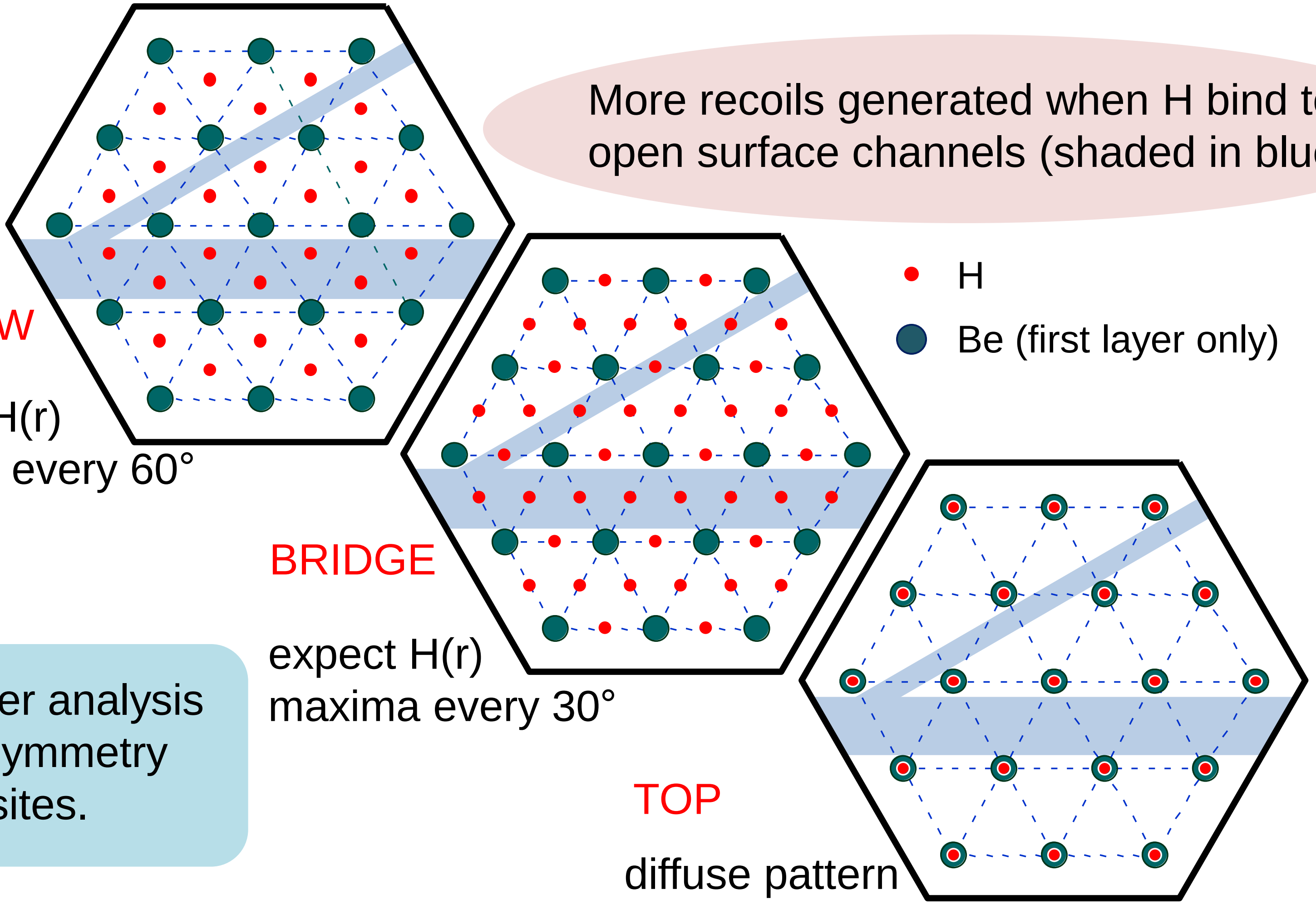
This plot depicts recoiled Be and H collected while rotating the Be crystal azimuthally.



- 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

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



HOLLOW

expect H(r) maxima every 60°

BRIDGE

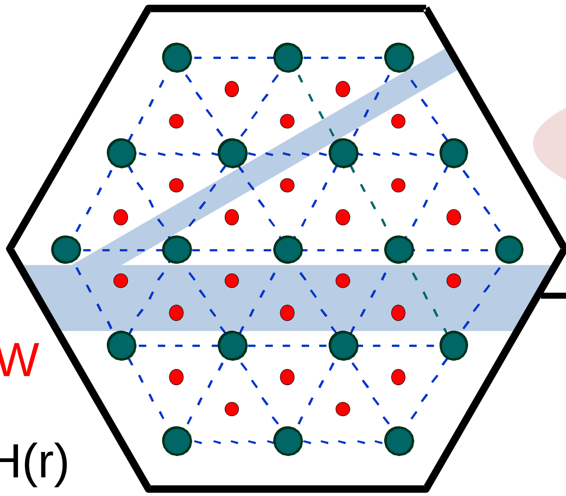
expect H(r) maxima every 30°

TOP

diffuse pattern lacking structure

First-order analysis of high-symmetry binding sites.

Our measurements are consistent with hollow site occupation



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

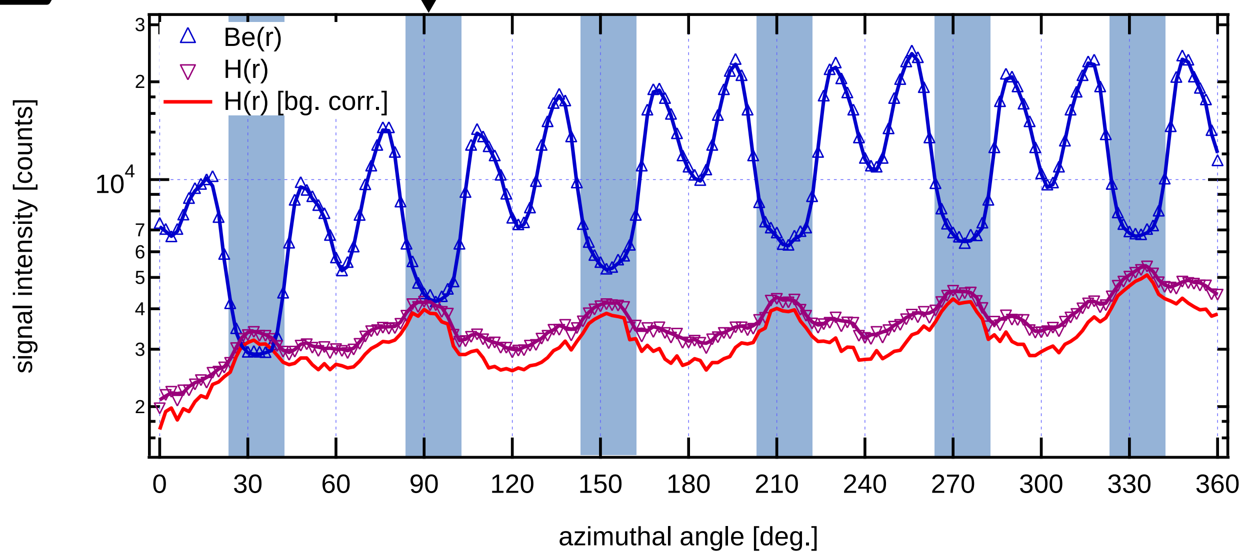
H

Be (first layer only)

HOLLOW

expect H(r) maxima every 60°

First-order analysis of high-symmetry binding sites.



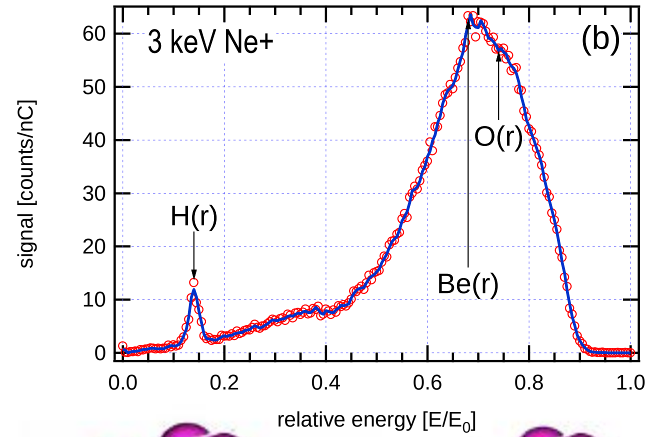
Our measurements correspond to low surface coverage case

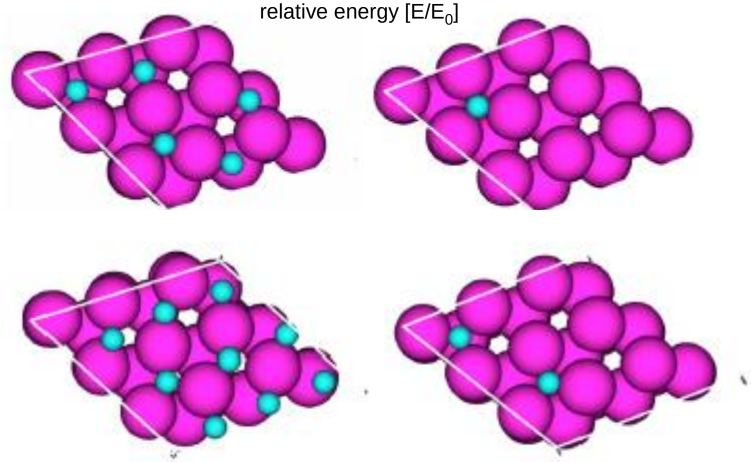
- **Analysis of our H-recoil peak height indicates a H surface coverage of <0.2.**
- Approaching 1 ML of adsorbed H requires T_{surf} < 200 K [1].
- High coverage required to cause reconstruction [2].
- For non-reconstructed surface, binding site is coverage dependent [3].
- **DFT predicts isolated H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



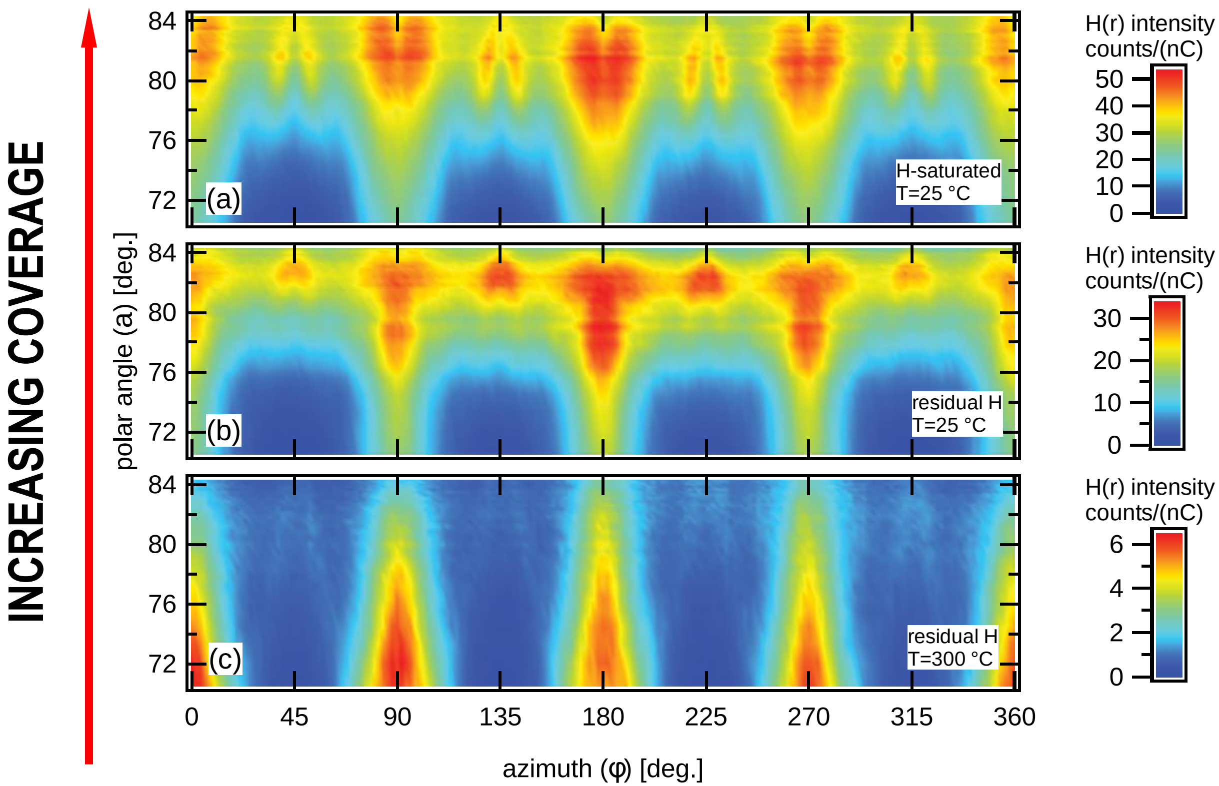


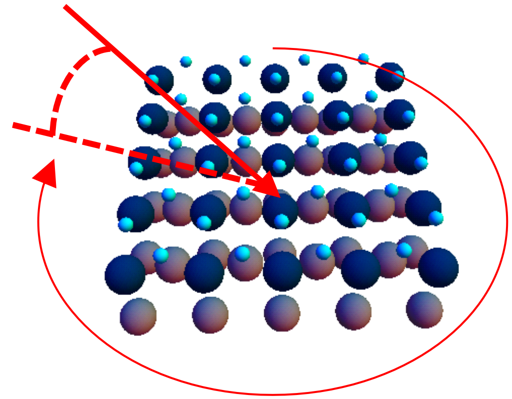
H binding site variation with surface coverage [image from Allouche, *Phys. Rev. B* (2008)].

H recoil maps reveal distinct structure on W(100) surface

- H recoils produced with 1 keV Ne+
- Dosed and heated sample to control H surface conc.

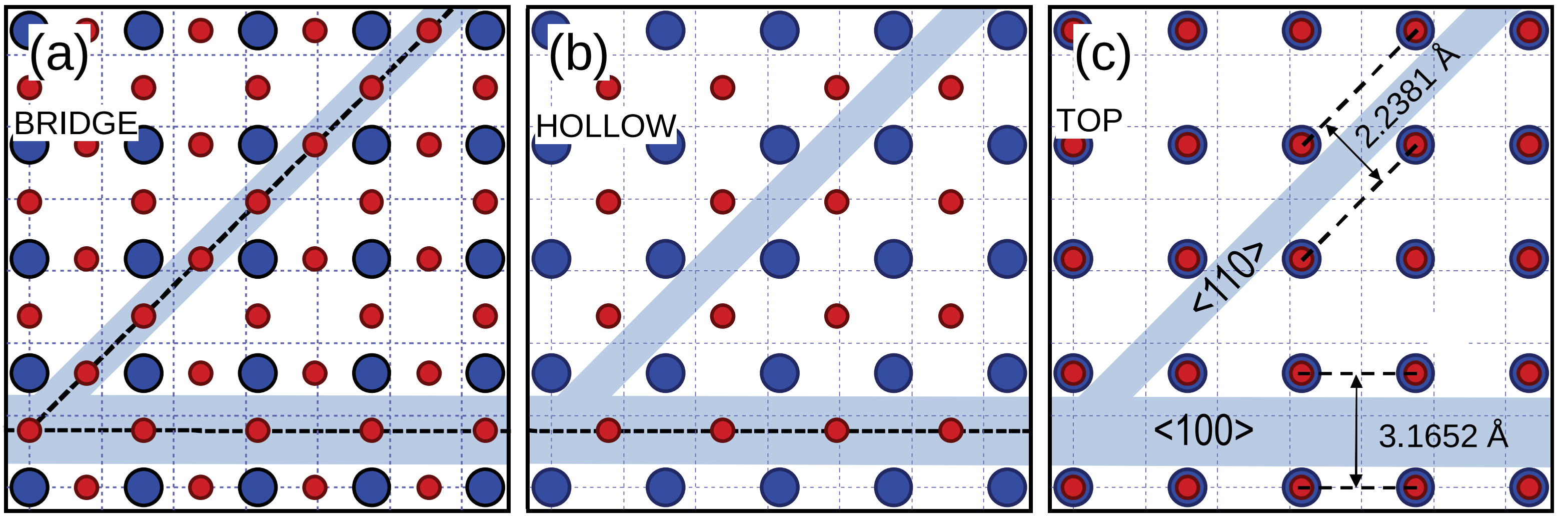
Map created by varying Ne^+ incidence angle and crystal azimuth.





Recoil pattern depends on surface coverage.

Ions focused along open surface channels undergo collisions with adsorbed H



expect H(r) maxima every 45°

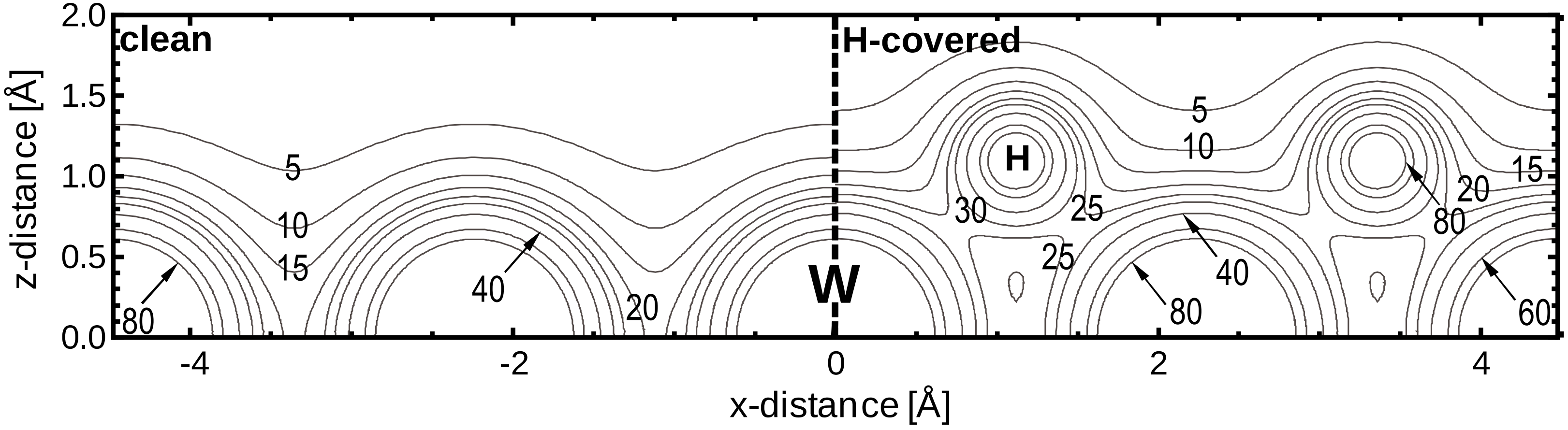
expect H(r) maxima every 90°

diffuse pattern lacking structure

First-order analysis of high-symmetry binding sites.

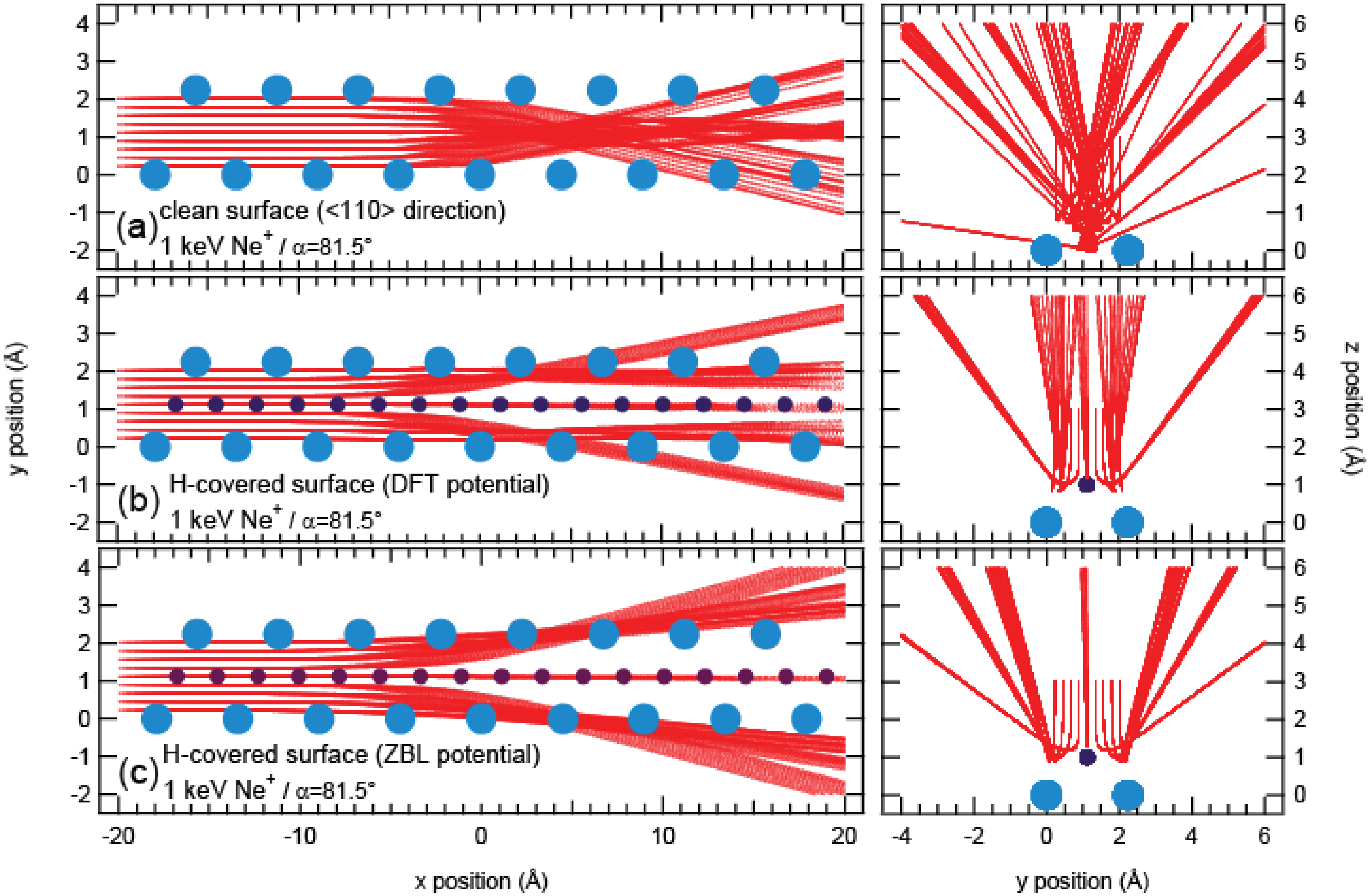
- H
- W (first layer only)

At grazing incidence, low energy ions interact with many surface atoms at once

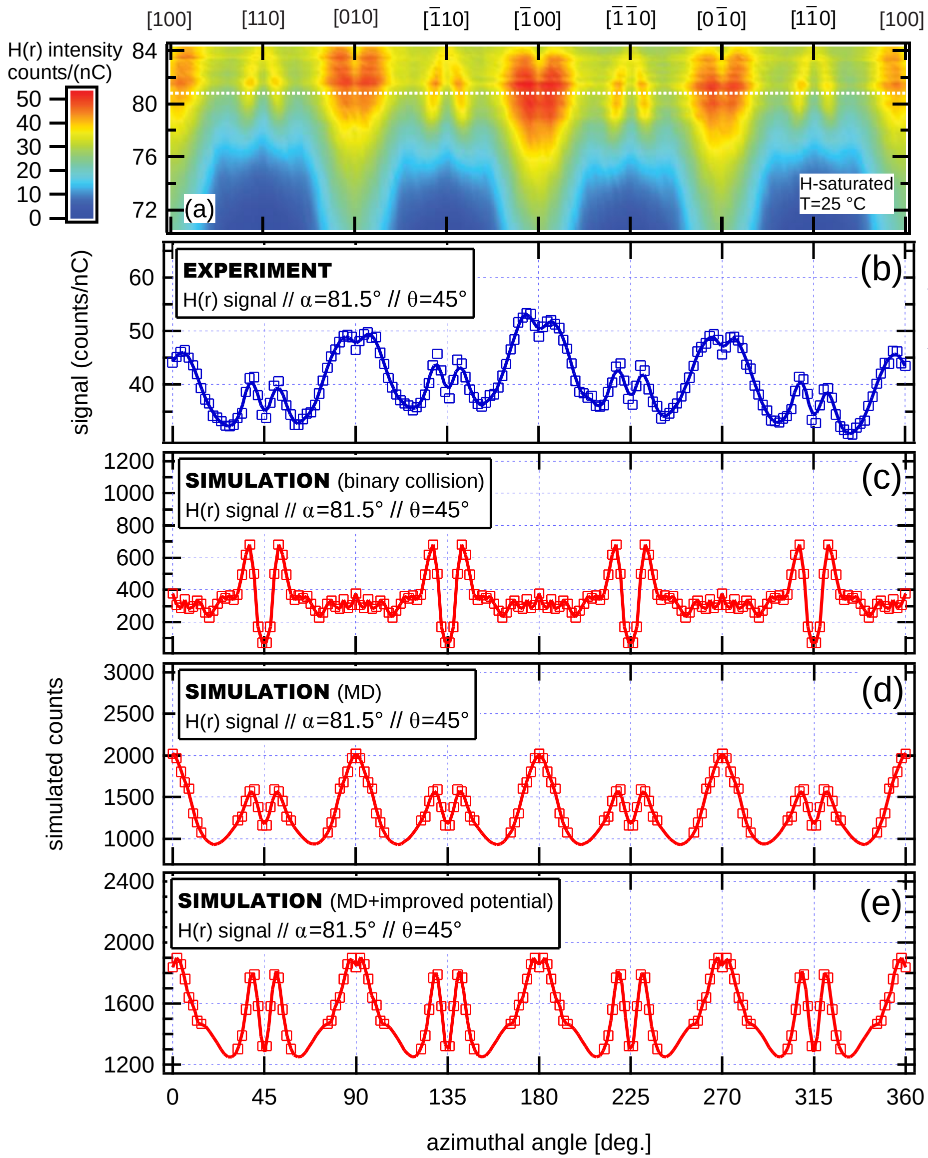


- ❑ Ion energy normal to surface small at grazing angles (< 10 eV.)
- ❑ Ions interact with many surface atoms at once.
- ❑ Distance of closest approach (estimated from equipotential contours) ~ 1 Å.
- ❑ Binary collision approx. fails: Need molecular dynamics (MD).
- ❑ Note: H in surface channels changes potentials near surface (affects ion trajectories.)

Surface channeling strongly affected by the presence of hydrogen



Successive improvements to models provide better agreement with experiment



A H(r) map for W(100) at saturation coverage (experiment).

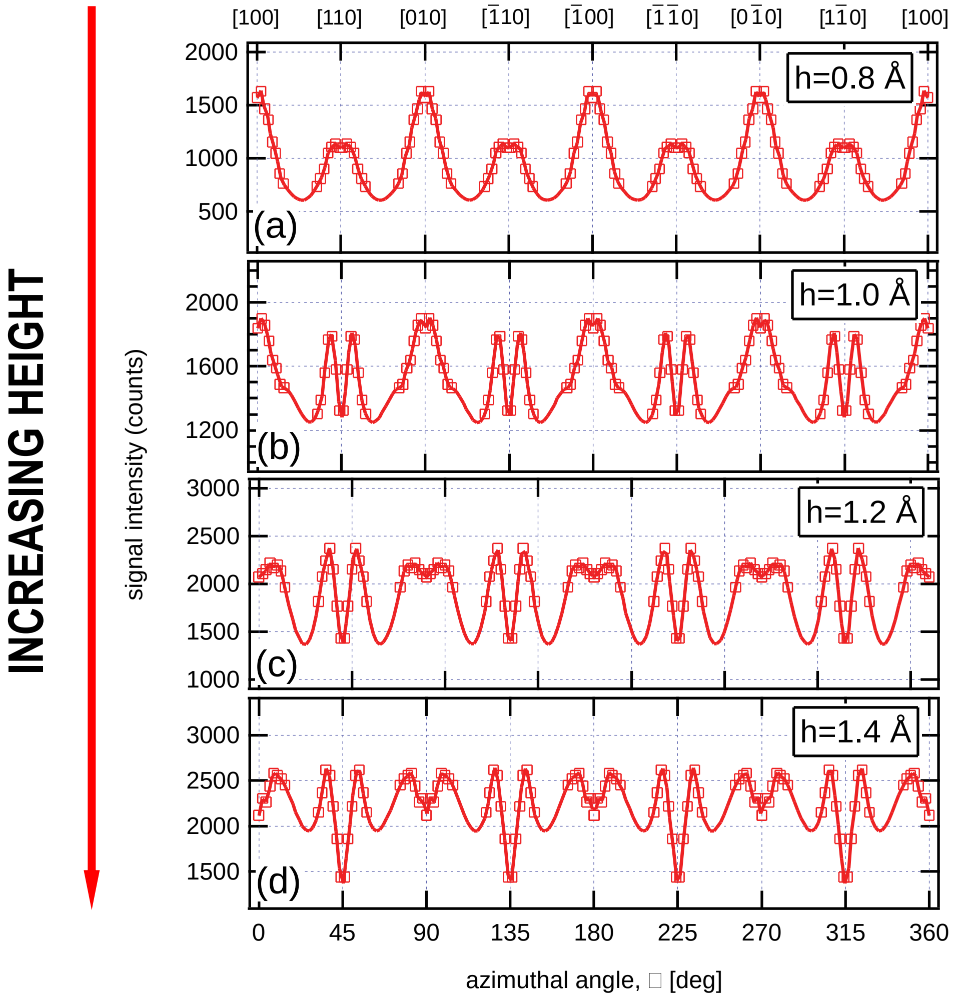
B Subset of data at single incidence angle (horizontal cut through map.)

C Simulation: Binary collision (MARLOWE)

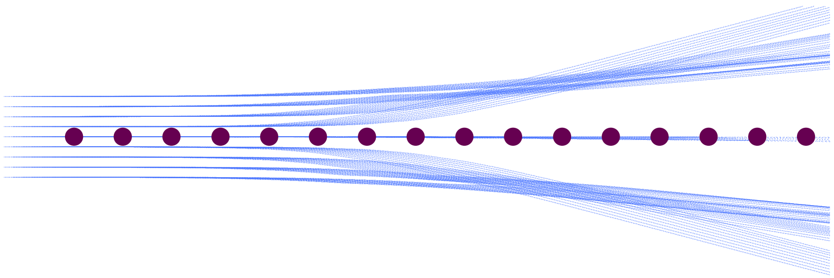
D Simulation: MD with ZBL potential

E Simulation: MD with improved potential

Perfect alignment along surface channel results in weak shadowing by H



1 keV Ne^{+} trajectories deflected around a row of H atoms

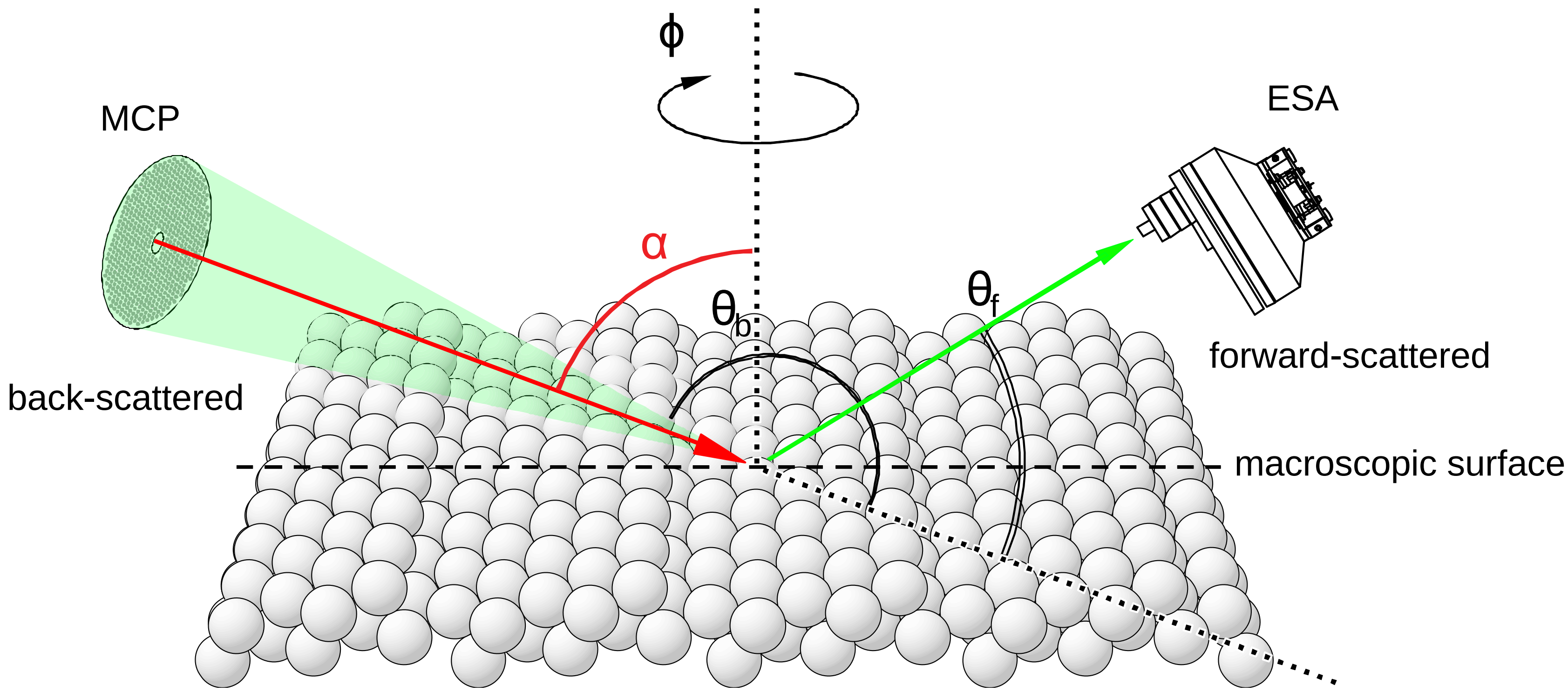


- Combined effect of adsorbed H in surface channels is very strong.
- Effect depends on height of H atoms above the surface.

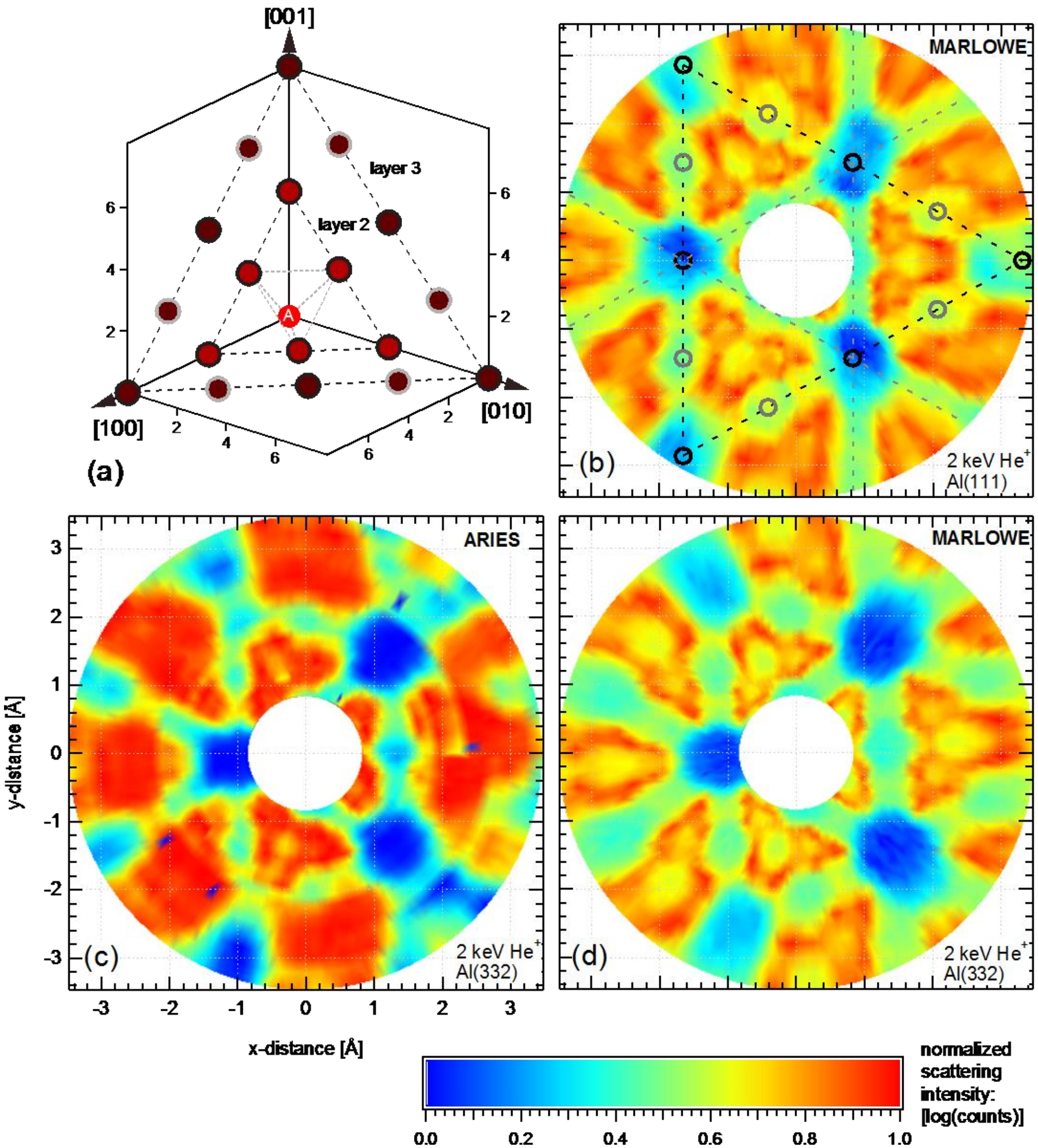
R. Kolasinski, N. Bartelt, J. Whaley, T. Felter, *Phys. Rev. B* (2012.)

Part 3: ICISS and extended MD simulations

Forward and backscattered geometries provide differing structural information

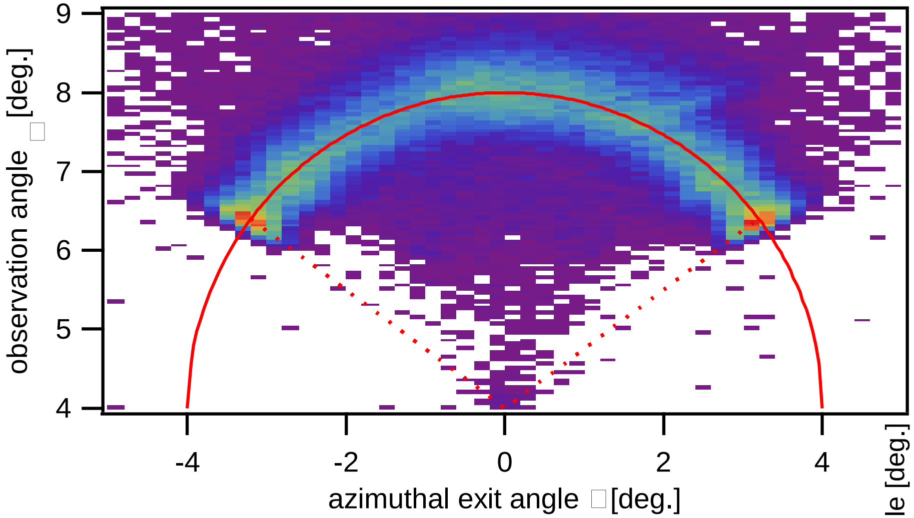


ICISS maps enable atom positions to be determined within a high level of accuracy

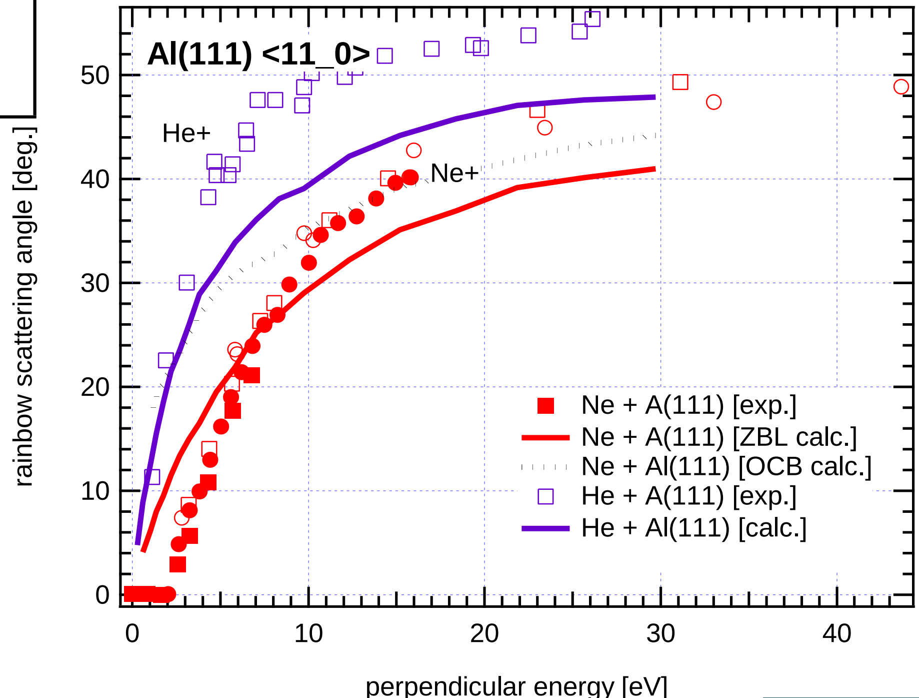


- Local minima correspond to directions where first layer atoms block atoms in deeper layers.
- Surface channels also readily evident.
- Al(332) surface map shows features offset from the Al(111) surface simulation.

We have developed a MD model based on LAMMPS



We developed an MD model capable of being executed on large computing clusters.



As a validation of our approach, we simulated rainbow scattering and compared with the results of Winter et al. [NIMB 2005].

Concluding Remarks

- Combined experimental / computational tool developed for characterization of adsorbed H.
- Clean Be(0001) surface prepared, scattering maps verify structure and illustrate focusing mechanisms along open surface channels.
- Be surface dosed with atomic H, distinct recoil signal observed along <0001> surface directions.
- Hydrogen observed to reside in hollow sites at low coverage fractions (<0.2 H/Be), consistent with DFT calculations.
- Experiments underway to characterize more complex systems [e.g. Al(332)].

Acknowledgements

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