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Sandia National Laboratories

Microscopy and Modeling of Helium Nanobubbles in a Palladium Alloy

PRESENTED BY

David B. Robinson

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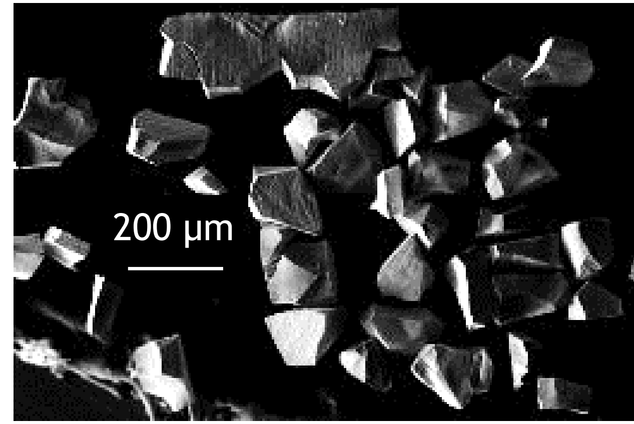
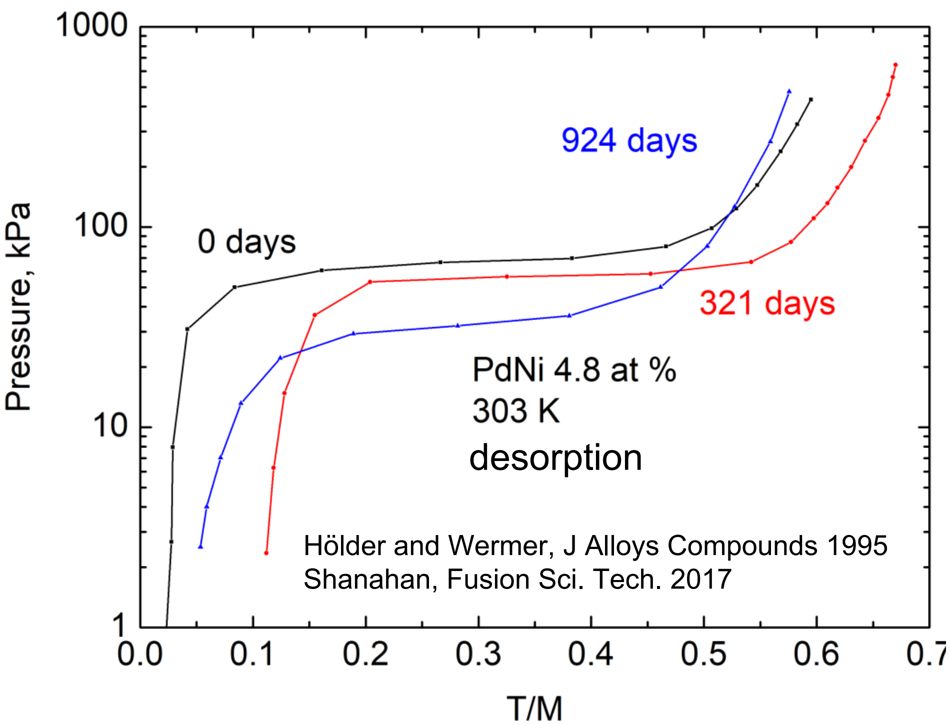
Macroscopic effects of helium in Pd alloy

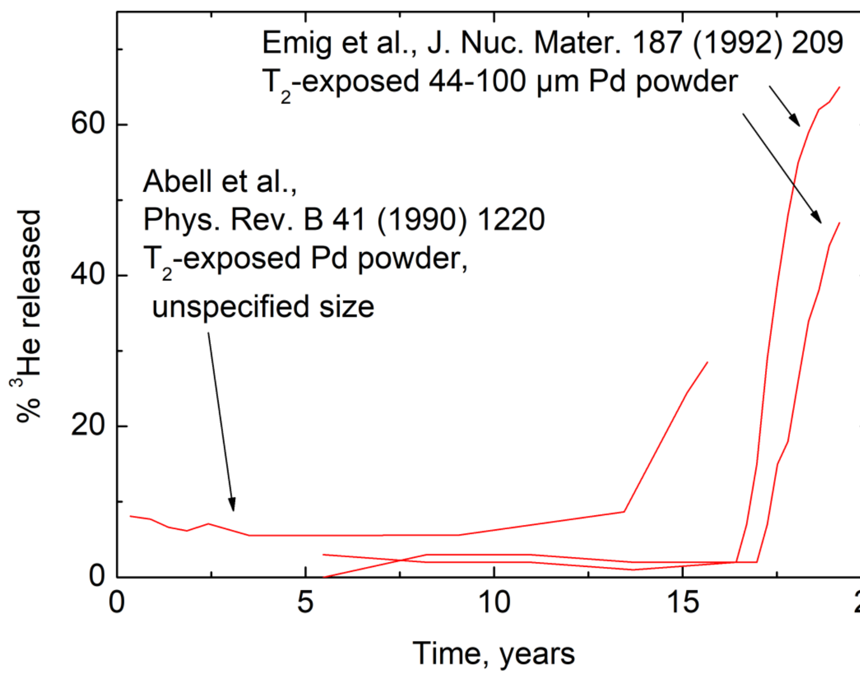
Helium decay product in Pd tritide changes:

- Tritium absorption properties
- Mechanical properties
- He release rate



Crumbled Pd-5 at. % Ni foil aged 3.8 years
Shanahan, Fusion Sci. Tech. 71 (2017) 555





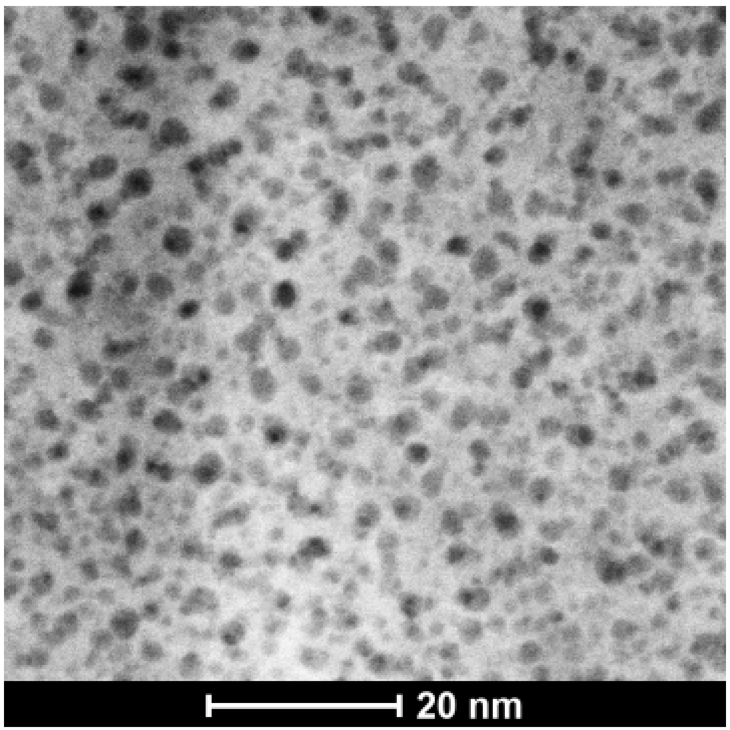
Microscopic helium effects likely dictate macroscopic properties

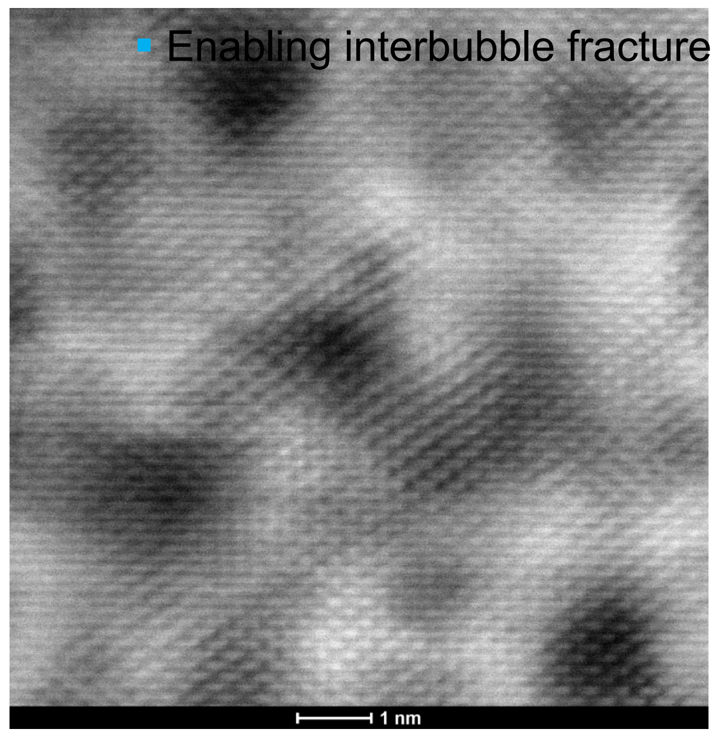
Helium evolves through several stages:

- Atomic transport, trapping, and clustering
- Bubble nucleation
- Bubble growth, migration, and coalescence

Bubbles may relate to macroscopic properties by:

- Storing and releasing the helium
- Straining the lattice, changing H absorption pressure
- Creating stable sites for H adsorption
- Enabling interbubble fracture





Dark patches are bubbles

Bright dots are columns of metal atoms

Scanning transmission electron microscopy (STEM) of He bubbles in Pd-5 at. % Ni foil aged 3.8 years

Rewind 4 decades

Experiment:

G.J. Thomas, J.M. Mintz, J Nuc. Mat. 116 (1983) 336 (Sandia authors)

- Pd tritide foil aged 66 days (6000 appm He):
  - 2 nm bubbles, 10^{24} bubbles/m^3
  - Uniformly distributed
- Pd tritide foil aged 20 days (1800 appm He):
  - Defects with strain contrast
  - Bubbles form after annealing to 600 K
  - Same observed for foil aged 7 days to 600 appm He

Interpretation:

- Nucleation by homogeneous He-He binding (self-trapping).
- Elemental impurities could also be trapping sites.
- Helium is mobile at room temperature.
- Minimal role of vacancies, grain boundaries, other extended defects.

Rewind 4 decades, continued

Theory:

W.D. Wilson, C.L. Bisson, M.I. Baskes, Phys. Rev. B 24 (1981) 5616 (Sandia authors)

- Molecular dynamics calculations for Ni:
- He atoms diffuse slowly (0.35 to 0.6 eV activation barrier; ~10^9 x slower than H)
- He atoms form clusters.
- 5+ He atoms can displace metal atoms, which themselves form nearby clusters.

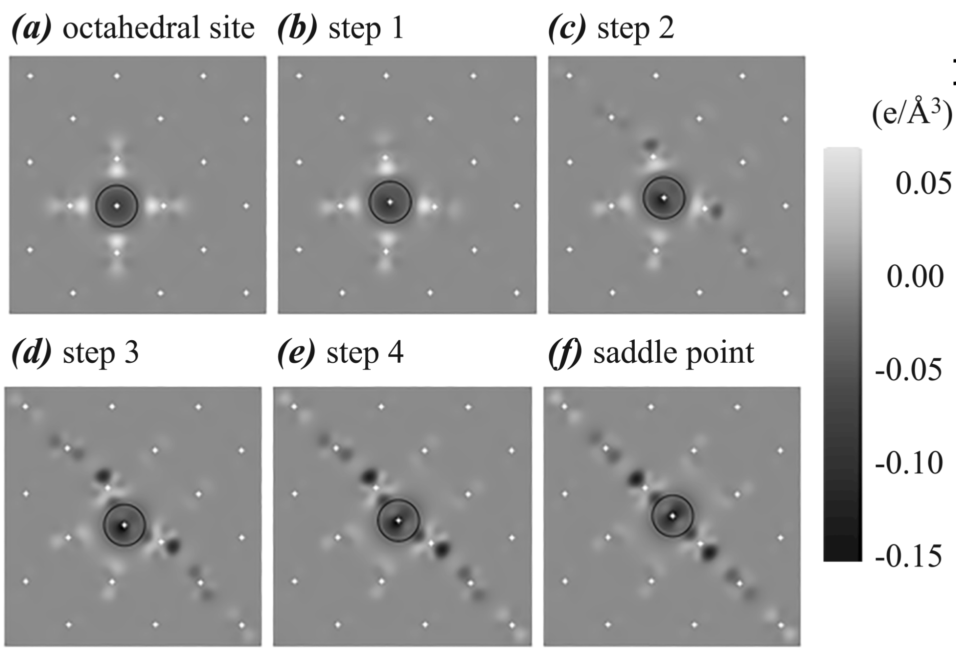
H. Trinkaus, W.G. Wolfer, J. Nuc. Mat. 122 (1984) 552-557

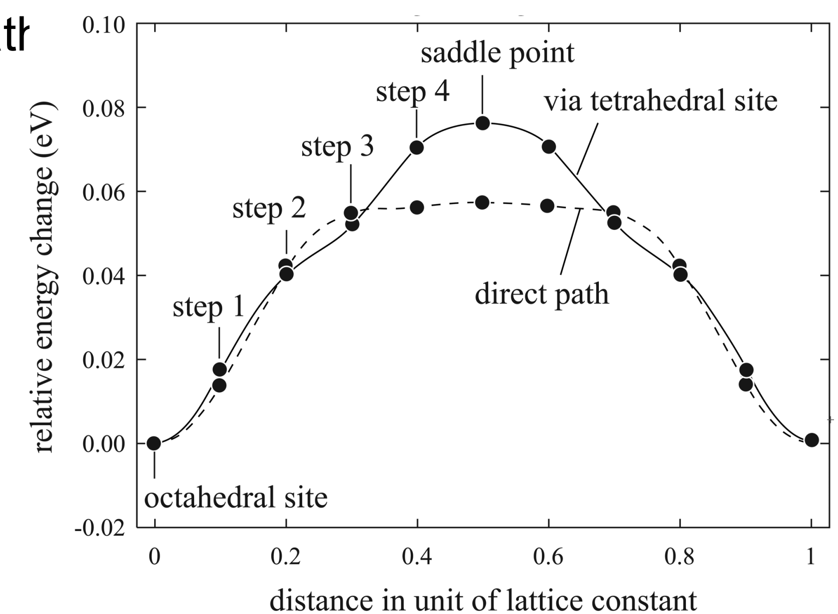
- Small bubbles emit self-interstitial atoms that form nearby clusters.
- Larger bubbles emit dislocation loops (pre-formed planar clusters).

2021: Helium diffusion is rapid.

X.W. Zhou, N.C. Bartelt, R.B. Sills, Phys. Rev. B 103 (2021) 014108 (Sandia authors)

- Helium diffusion is about as fast as H diffusion in a perfect Pd crystal.
- Density functional theory (DFT) identifies diffusion paths with low activation energy.
- Some agree: Cao and Geng, J. Nucl. Mater. 478 (2016) 13
- Some disagree: Segard et al., J. Nucl. Mater. 420 (2012) 388

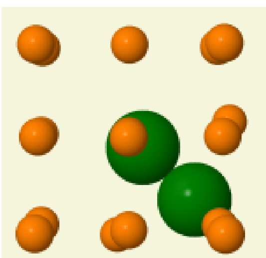




Even helium clusters diffuse rapidly.

- Helium clusters diffuse rapidly in a perfect crystal – until they create their own defects.
- Helium clusters displace metal atoms (and self-trap there) more easily in the hydride.
- Helium should still escape from many samples before it can self-trap.
- We still need an explanation for helium trapping!

We predict 10^{-6} He dimers per 1 µm sphere!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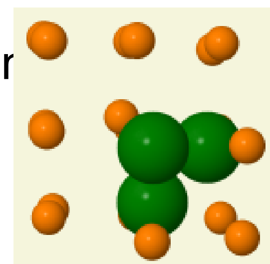
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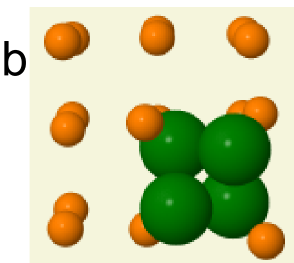
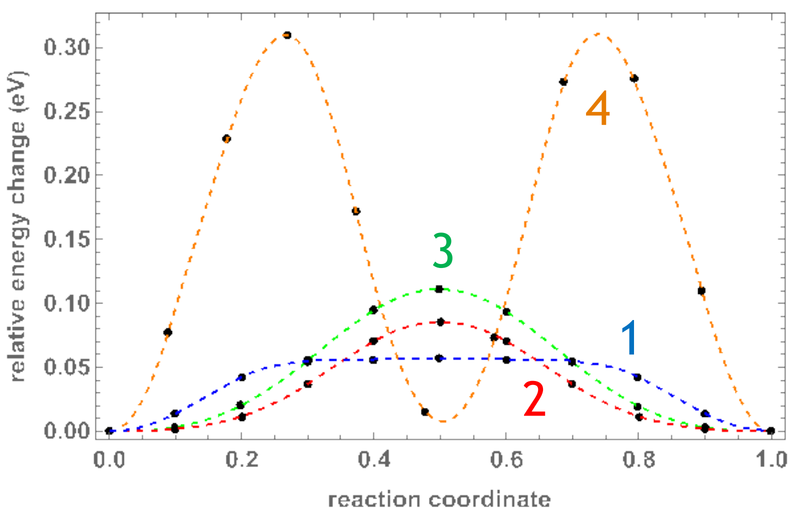
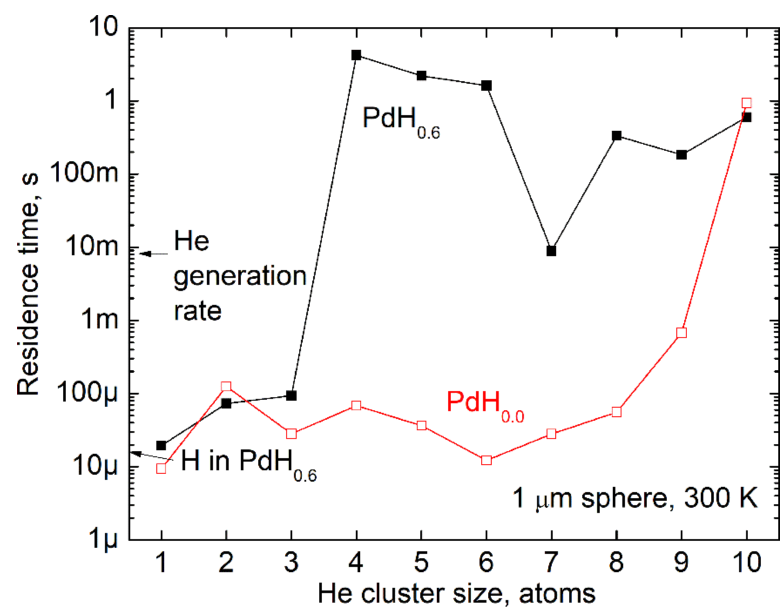

sters in Pd

residence time

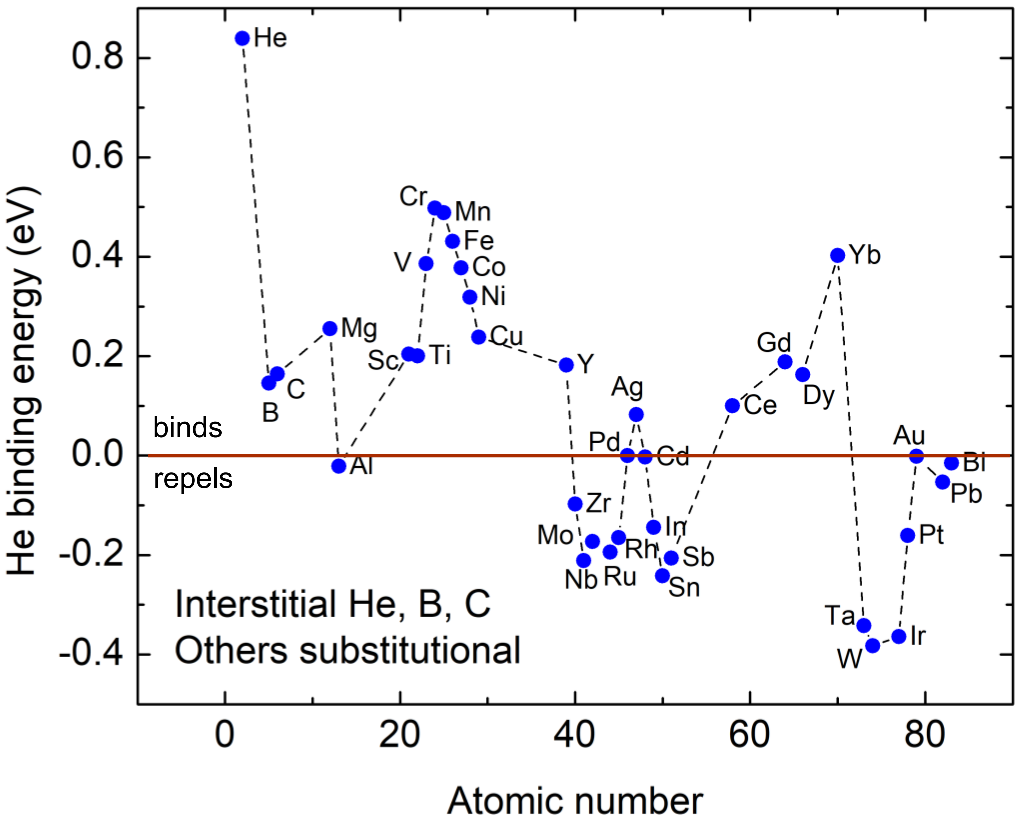




Can impurities trap helium?

Density functional theory by us (Bartelt) and others (P. Lin, GA Tech) suggests:

- Impurities in Pd can bind or repel He.
- Binding can slow diffusion, but not trap, atomic He at 25 °C.



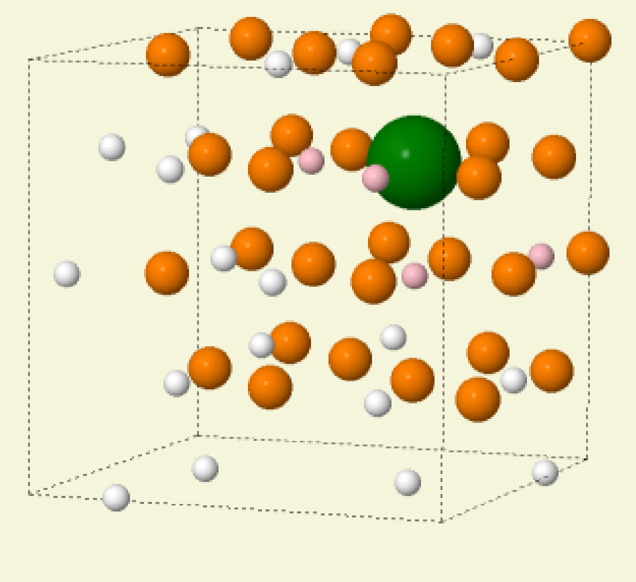
Vacancies; substitutional H and He

- Vacancies are Pd atoms missing from lattice sites.
- DFT predicts that vacancies strongly bind He (by several eV).
  - Bartelt, this work; Nazarov et al., Phys Rev B 2014; Das et al., Proc. Roy. Soc. A 2014
- Vacancy concentrations may be high in Pd hydride.
  - Positron lifetime measurements suggests 10 ppm concentrations – near that of bubbles; Cizek et al., J. Alloys Compounds 2015
- Vacancy mobility is low (0.9 eV activation barrier) and not affected much by H or He.

Can enough vacancies be formed?

- Vacancies can form during hydriding.
- Dislocations and surfaces can generate vacancies.
- Do easily displaced substitutional impurities exist?

DFT configuration of H, He at a vacancy (Bartelt)

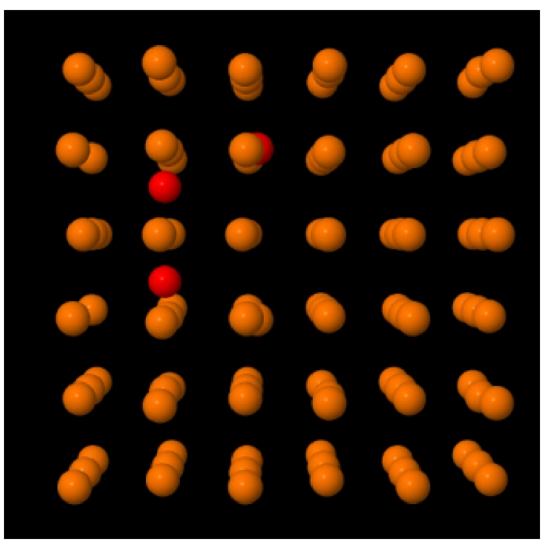


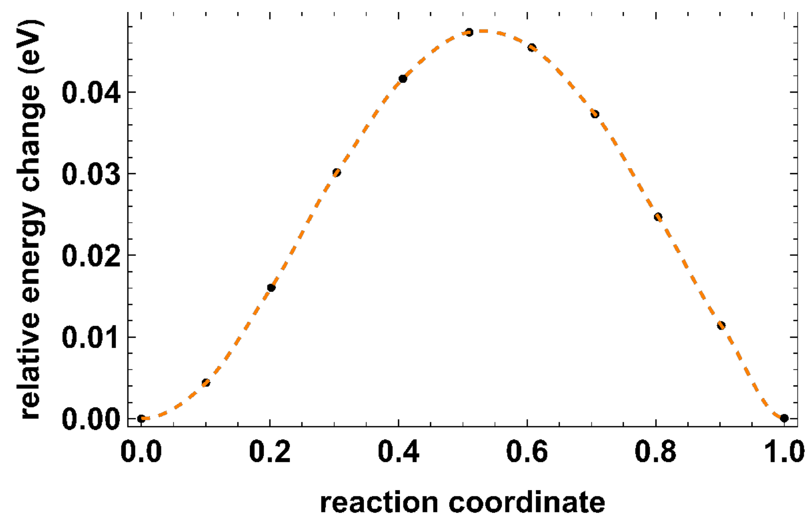
Pd
He in vacancy
T near vacancy
T

DFT predicts 0.55 eV vacancy formation energy in Pd hydride.

Where does displaced Pd go?

- Self interstitial atoms diffuse rapidly.
- Are they bound to the bubble?
- They can go to surfaces, trap at defects, and form clusters, which become dislocations.
- Dislocations and interstitial clusters are not regularly observed in experiments.
  - Unlike point defects, these are within reach of TEM observation.





40 years of progress

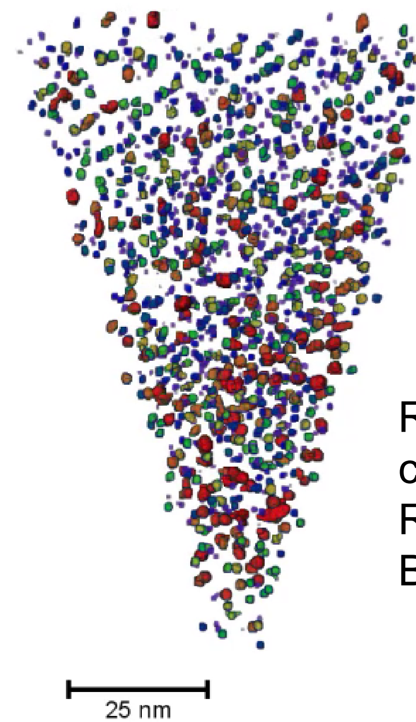
- We now believe that lattice helium is very mobile.
- We are less sure of what traps the helium.
  - Probably not just self trapping.
- We are still not sure where the displaced metal atoms go.

We believe that progress will accelerate!

- These topics are within reach of our modeling tools.
- We are advancing experimental methods to explore these topics.
  - Electron tomography – bubble size and spacing maps
  - Imaging of the smallest bubbles: optimizing imaging conditions
  - Automating acquisition and interpretation of data
- Experimental and data analysis methods are the topics of the remainder of the presentation.

Electron tomography

- In 2019 we published the first 3D map of helium bubbles formed in a metal tritide.
  - Catarineu et al., J. Phys. Chem. C 2019, 123, 19142
- Can we do it more than once?



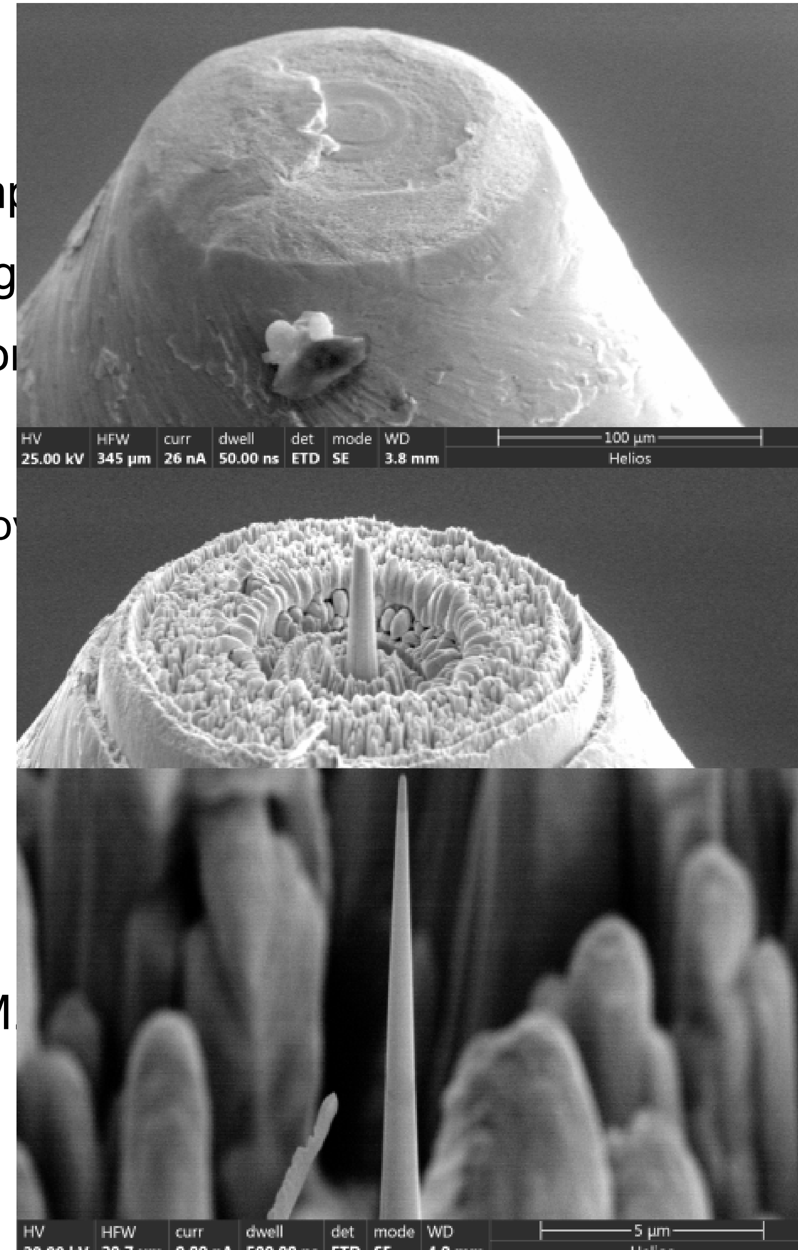
Rainbow color code:
Red = large
Blue = small

Tomography requires:

- Carefully sharpening a tip in the FIB-SEM
- Collecting TEM images at hundreds of angles
- Carefully aligning and reconstructing the images
- First time took us 3+ years

Tomography tip preparation

1. Mill a copper post to a few μm
2. Mill a triangular prism (“Toblerone”) from samp
3. Weld Toblerone to post (flat side up), trim edg
4. Mill rings around the sample, using edge of io beam to scrape atoms away.
   - Ion beam flux is roughly Gaussian.
   - Atoms farther from center are preferentially remo
   - Alignment of ring can be challenging.
5. Minimize ion beam damage with broad, low-voltage final step.
6. Clean off residual carbon in Ar/O_2 plasma just before use in the TEM.



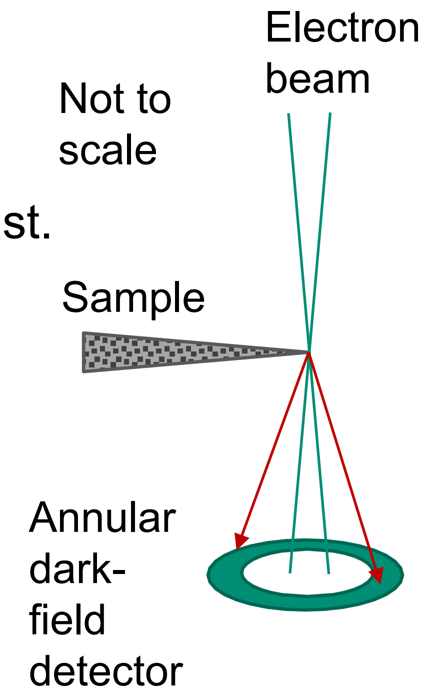
The final tip quality is hard to see in the FIB-SEM.

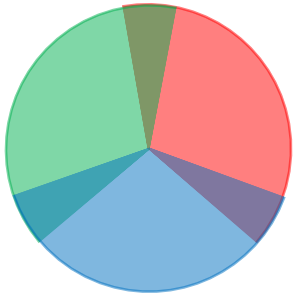
TEM operator may send it back for rework.

This takes some practice!

Data acquisition

- Imaging conditions must be optimized for tomography.
- Beam convergence angle balances resolution vs. depth of field.
- Detector angle balances intensity vs. undesired diffraction contrast.
- Sample rotates along tip axis.
- A good reconstruction requires 180° angle range.
  - A wider range aids alignment.
  - Our sample holder requires at least one manual offset.
- Tilt angle step balances image resolution vs. acquisition time.
  - Can be limited by mechanical precision of tilt stage.
  - We use 1°.
- Acquisition can be automated, but requires supervision.
  - Like a self-driving car…





Sample holder can tilt over 3 manually selected 142° ranges offset by 120°.

Acquired and filtered data

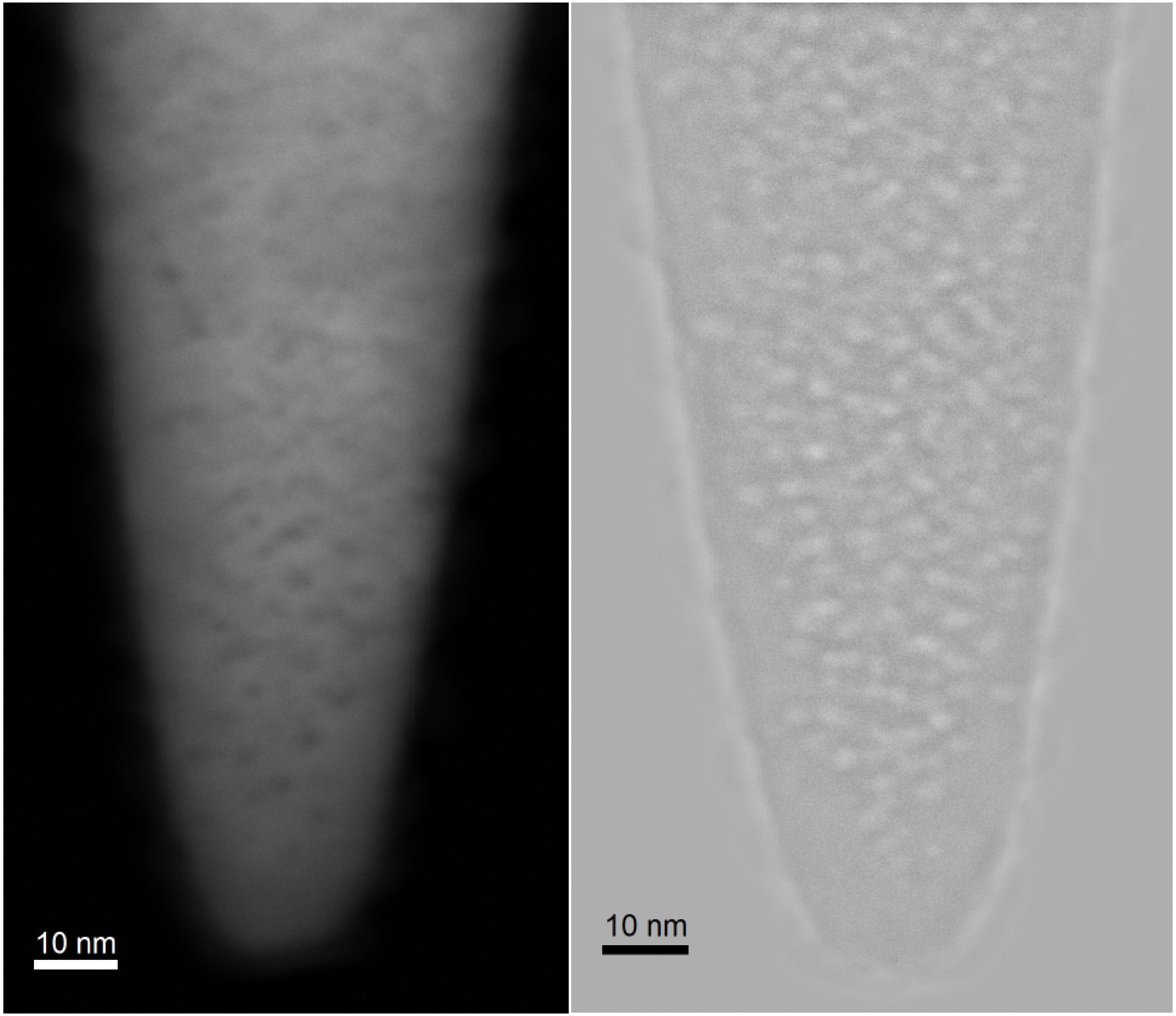
This is a new tip made from our Pd-5 at.% Ni exposed to tritium for 3.8 years.

263 angles collected

Dark-field STEM images (left) are first coarsely aligned by the tip position, and intensity is normalized.

Then digitally filtered (right) to retain mostly the small features of interest.

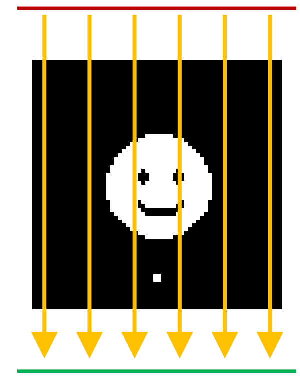
This aids fine alignment because



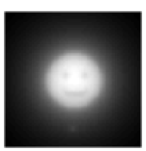
Reconstruction

Given 360 1D projections of a smiley image, how do we reconstruct it?

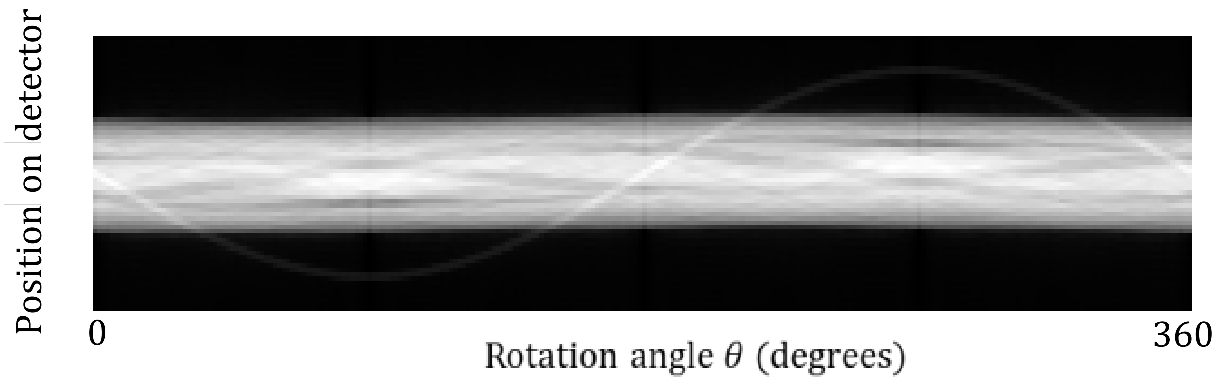
1. Project intensity at each point on line back onto the plane.
2. Sum each plane.
3. Apply a digital spatial filter to compensate for overrepresented low frequencies.

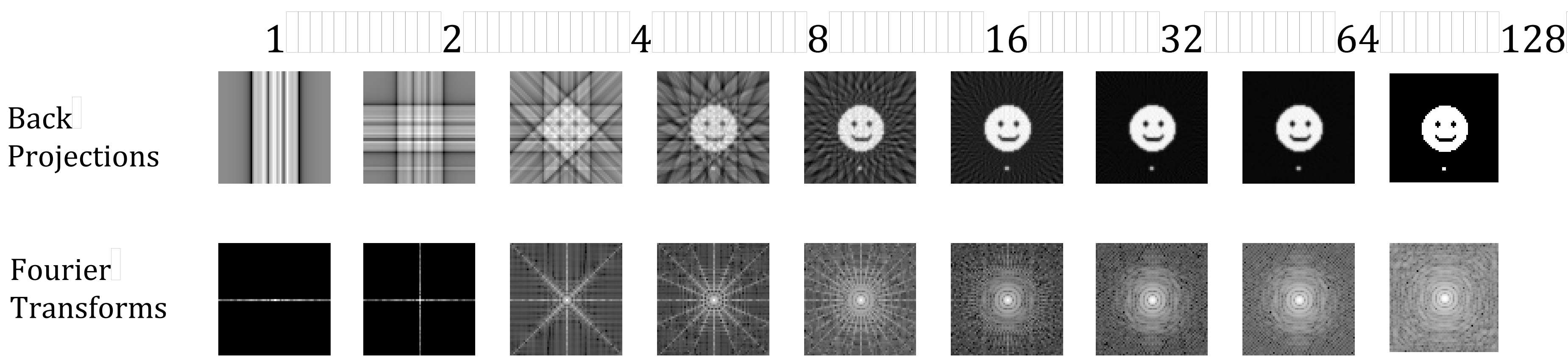


3D tomography is just many rows of 2D tomography.



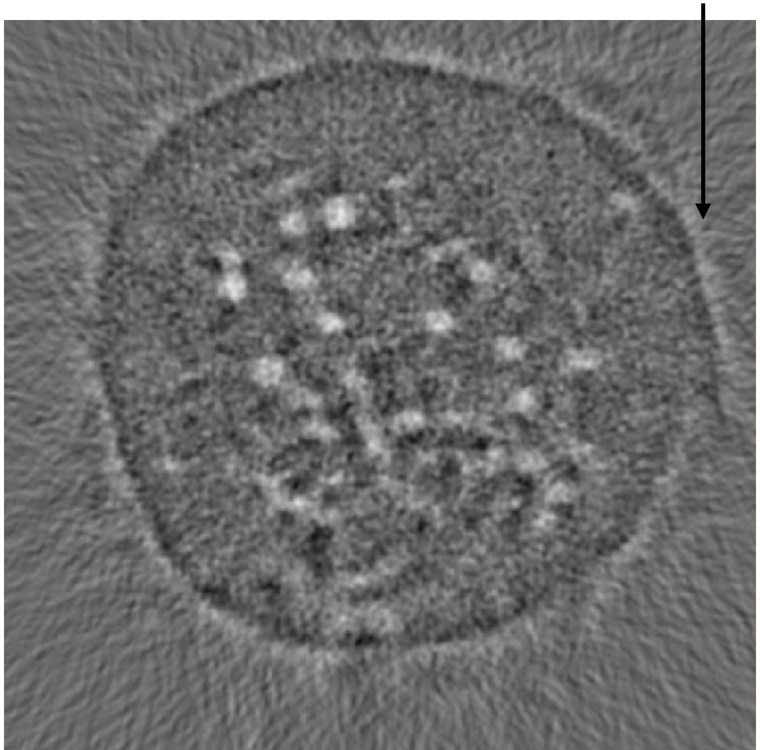
Result without spatial filter

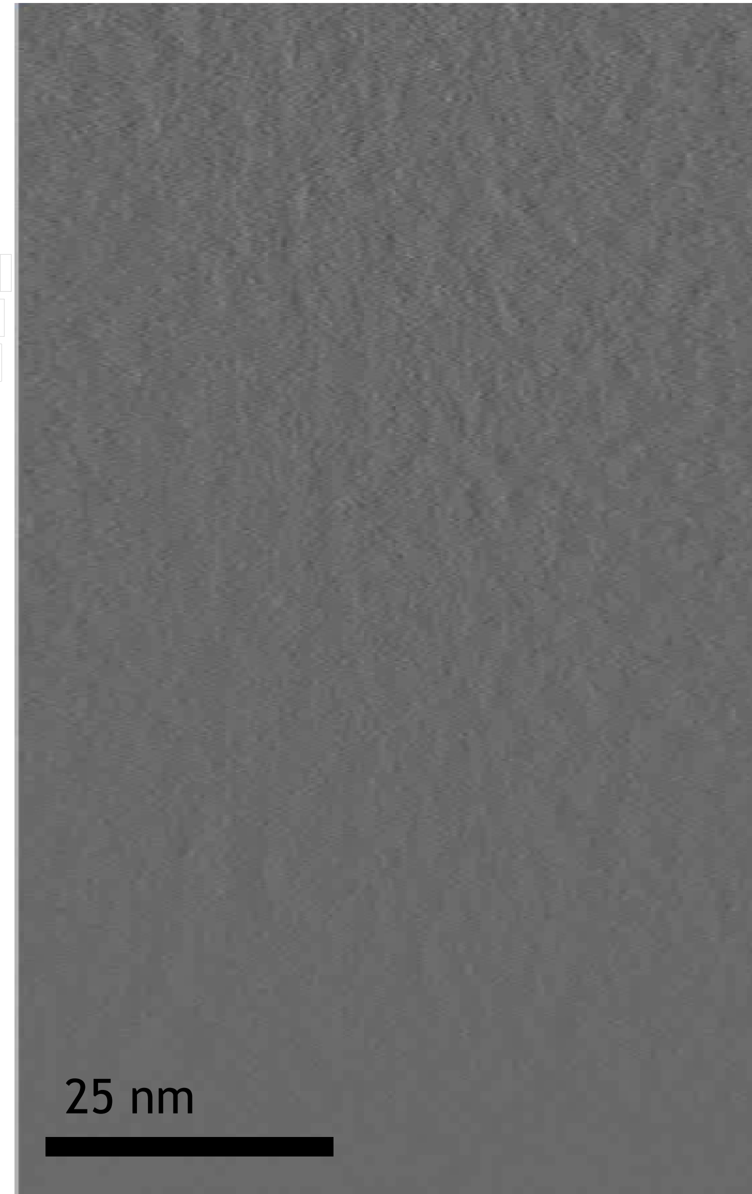




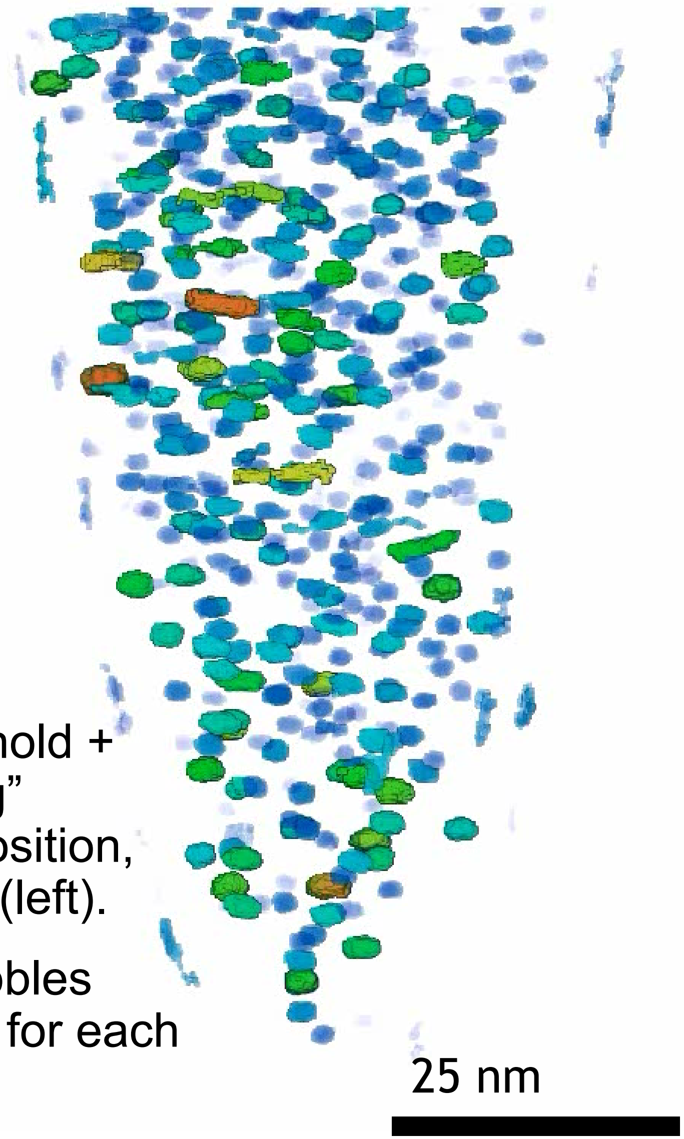
Reconstructed tip

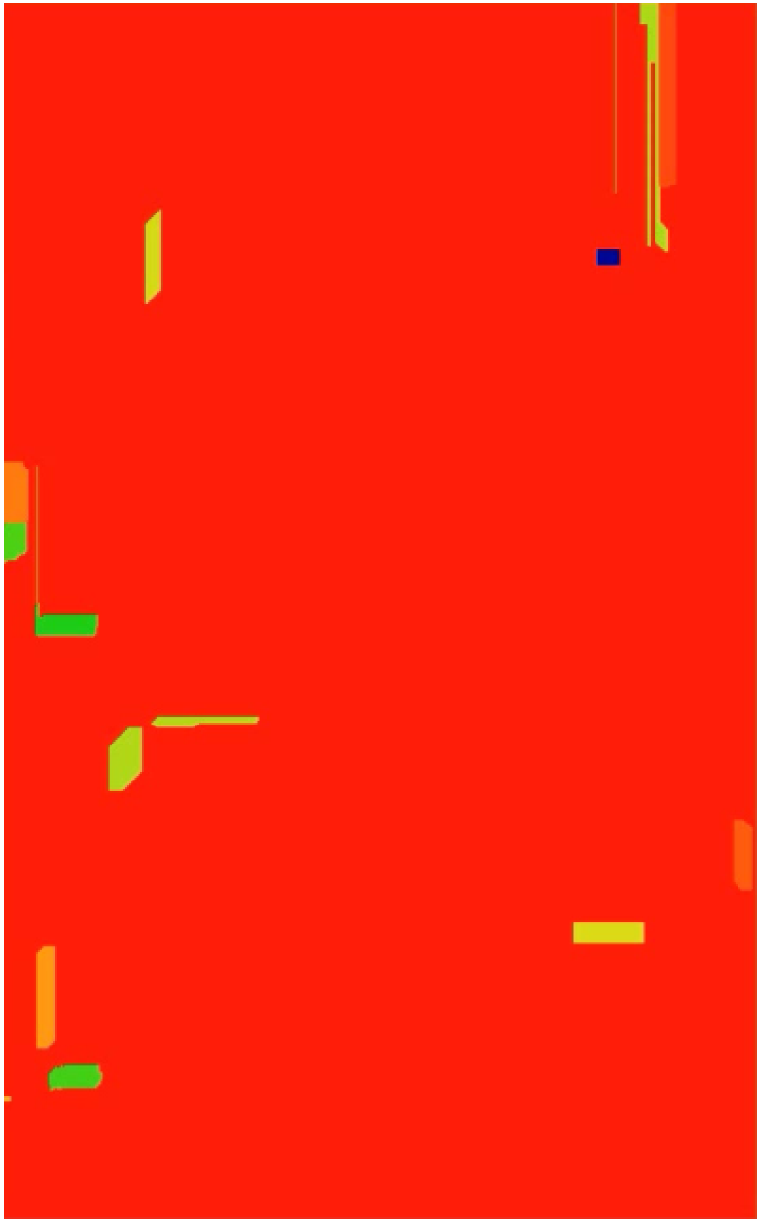
- Good bubble contrast vs. our 2019 work.
- More angles, imaging optimization helped.
- Automation results in some blurry or saturated images.
- Alignment improvements might be possible, aided by extra tilt angles.





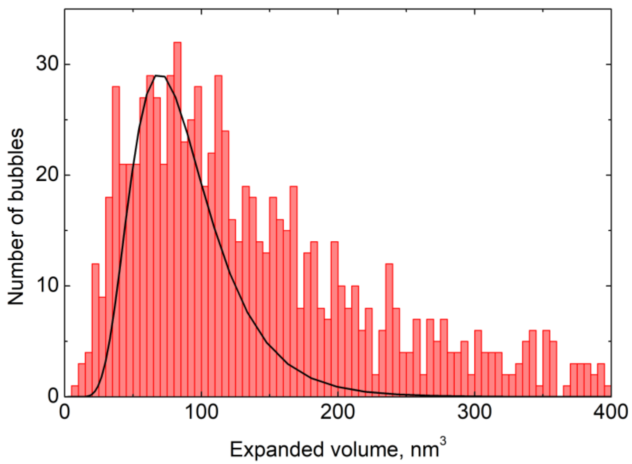
Identification of bubbles and bubble spacing



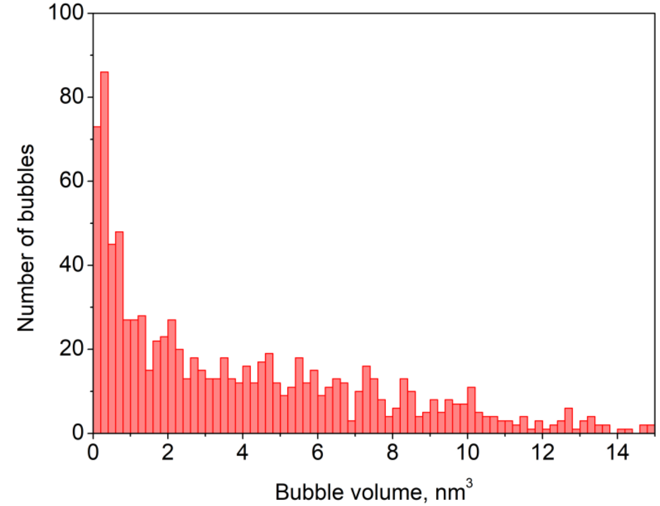


- Intensity threshold + digital "polishing" yields bubble position, size and shape (left).
- Expanding bubbles defines territory for each (right).

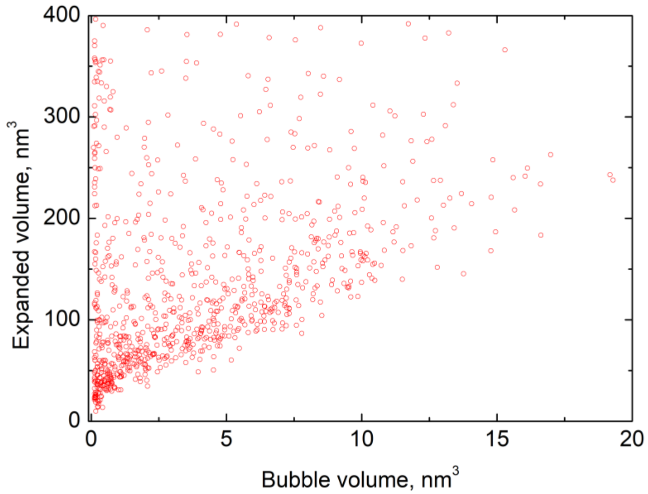
Bubble statistics confirm prior results



Expanded volume distribution is roughly log-normal.
Curve fit is from our 2019 work.



Bubble volume distribution is not log-normal.

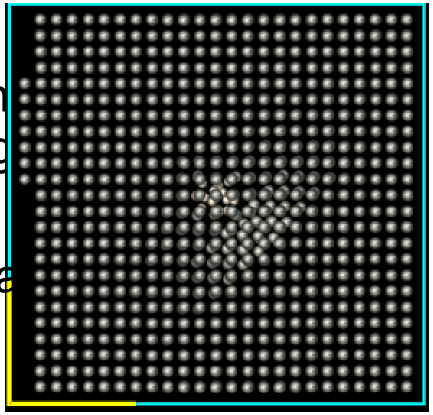


No correlation between bubble and expanded volumes.

- Qualitatively the same results as 2019 paper.
- A correlation would suggest that all bubbles nucleate at the same time, and all helium diffuses to the closest bubble. This is apparently not true.
- Quantities remain sensitive to choice of intensity threshold.
- If we are missing the smallest bubbles, this could also destroy the correlation.
- Can we overcome these concerns?

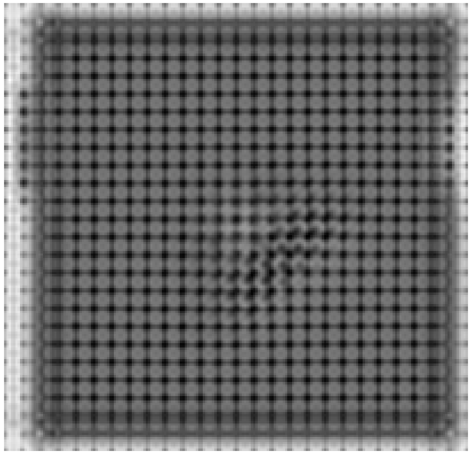
What are the smallest bubbles that can be imaged?

- We generated small bubbles using Molecular Dynamics simulations of Pd hydride starting with interstitial He.
- We then used multislice electron optics simulations to predict how they would look with different TEM imaging configurations.
- Detecting such small bubbles and distinguishing them from oth features would benefit from new 4D STEM technology that imag all scattered electrons.



MD result contains a tiny bubble plus distorted lattice.

Annular bright field 7.6 – 10.1 mrad



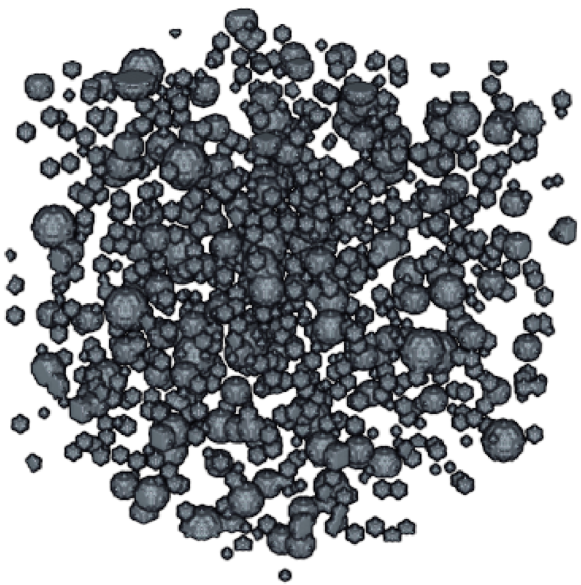
High-angle annular dark field 76 – 106 mrad

Pd [100] with 21 He
49Å thick
300 kV STEM
14 mrad probe semi-angle
9 nm overfocus

Prior work: Thiebaut et al., J. Nuc. Mat. 277 (2000) 217

What are the smallest bubbles that can be reconstructed?

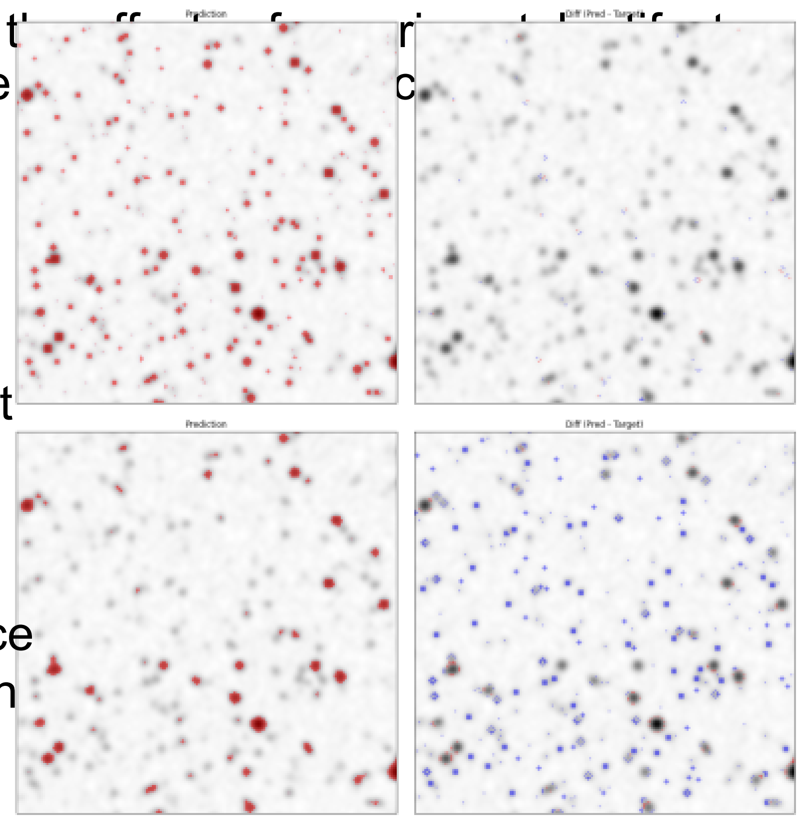
- We generated synthetic data: a 3D cube containing bubbles of known size and position.
- We then simulated tomography by calculating projections, adding artifacts, and reconstructing.
- We used the data to train a machine learning algorithm to find bubbles in other synthetic data and real experimental data.
- We are the ones who are learning – about t r
  and actual bubble c



Synthetic dataset

Top: machine learning result
Bottom: intensity threshold result

Left: identified bubbles
Right: difference vs. ground truth



Summary

Helium nanobubbles likely dictate macroscopic mechanical and chemical properties of metal tritides.

Progress on the theory of helium bubble formation and evolution continues:

- Helium diffuses rapidly, but is readily trapped by other point defects to form immobile clusters.
- Hydrogen-stabilized vacancies, formed during hydriding, are good candidates for the traps.
- Metal atoms displaced by bubbles are mobile.

This progress depends on the availability of experimental data enabled by modern methods:

- Electron tomography is helping us understand mechanisms of nucleation, and is maturing as a technique.
- TEM simulation may help us find the smallest bubbles, and effects of displaced atoms.
- Emerging data analysis methods like deep learning will help us generate more reliable measurements of bubble numbers, sizes and positions.

Acknowledgements

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Declan Mahaffey-Dowd (synthetic data)

Tyler Ganter (machine learning)