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Characterizing nano-scale helium bubbles within metals by electron energy loss spectroscopy

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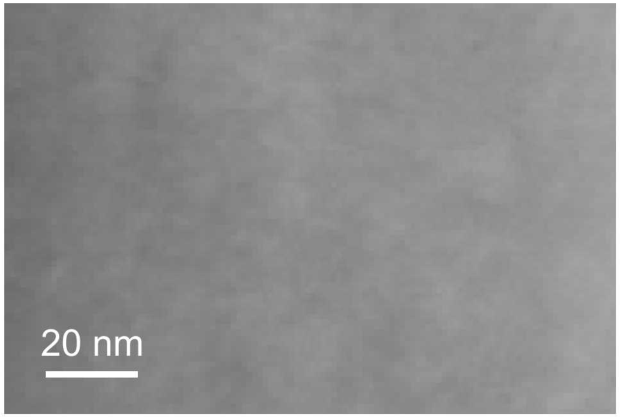
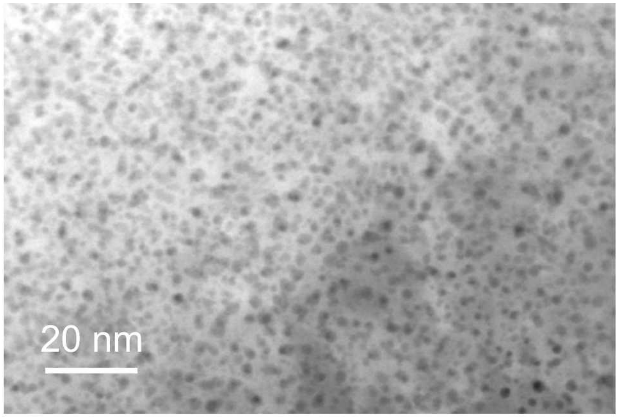
Tritium decays within metals to form nanobubbles of helium-3



Pd-Ni never exposed to tritium

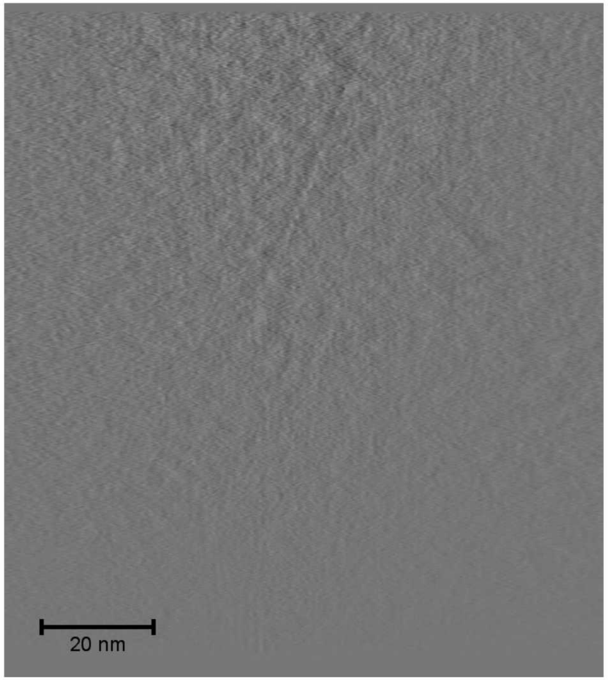


Pd-Ni stored under tritium for 4 years

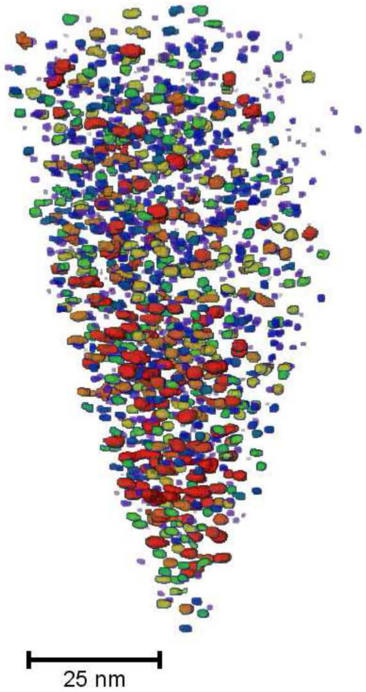
Helium bubble formation in tritium-exposed metals:

1. Tritium radioactively decays to helium-3
2. The insoluble helium precipitates into bubbles
3. Growth of helium bubbles causes blistering and fracture of metals
4. Metal degradation leads to helium release and loss of structural integrity

High resolution STEM and tomography have improved imaging of bubbles



Tomographic reconstruction of Pd-Ni



He bubbles in Pd-Ni

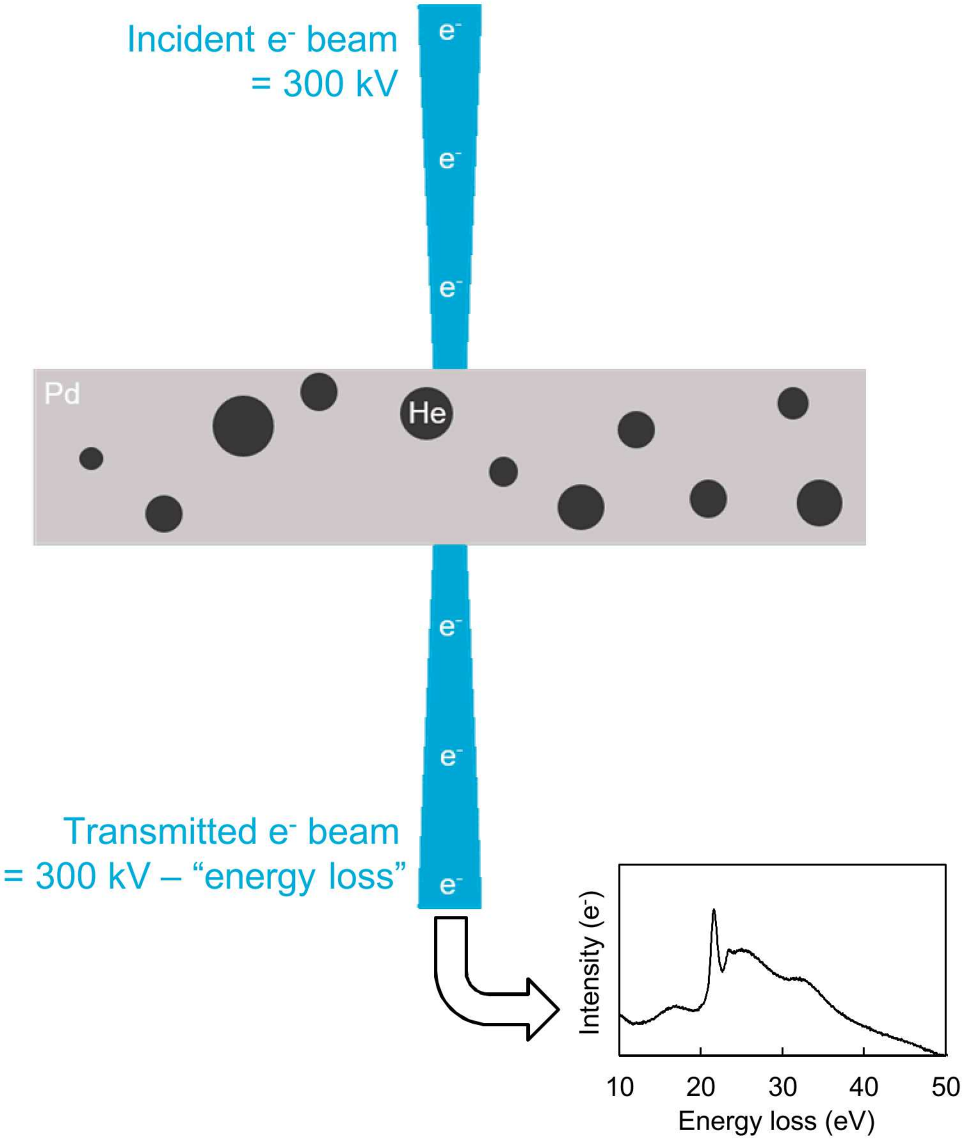
HR-STEM and electron tomography reveal:

- Total number of bubbles
- Bubble spatial distribution in 3D
- Bubble volumes, but…

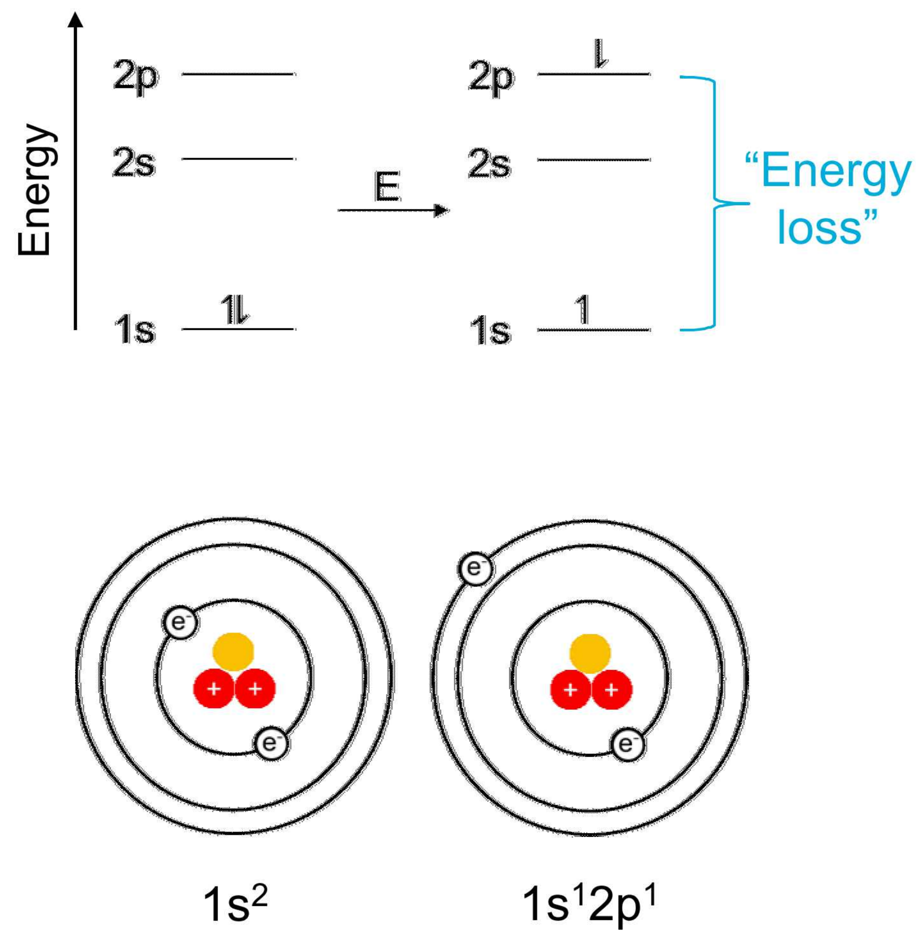
How much helium is in the bubbles? What is the internal bubble pressure?

Electron energy loss spectroscopy provides elemental composition

EELS measurement in a TEM



^{3}He 1s → 2p electronic transition

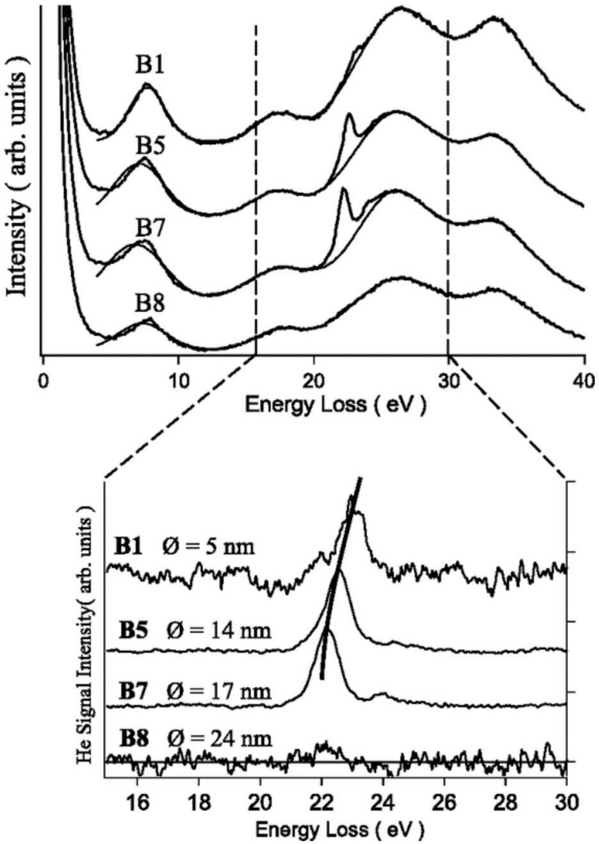


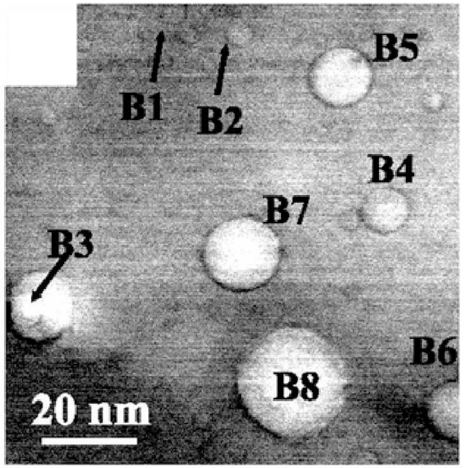
Helium detection by EELS can be achieved for bubbles >10 nm

Previous work by others indicates difficulty in detecting helium within nanobubbles:

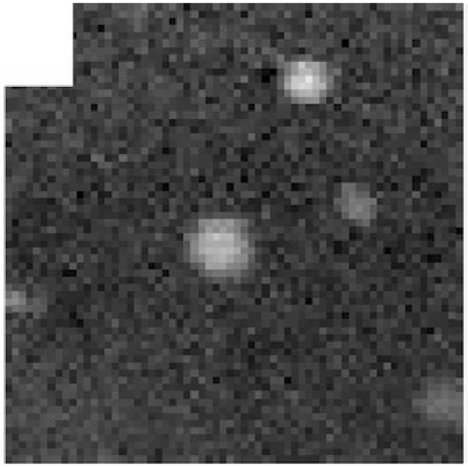
- Nano-scale bubble diameters → Low intensity He K-edge
- High internal bubble pressures → Overlap of He K-edge with metal plasmon peaks

Energy loss spectra of various bubbles





TEM image of He bubbles



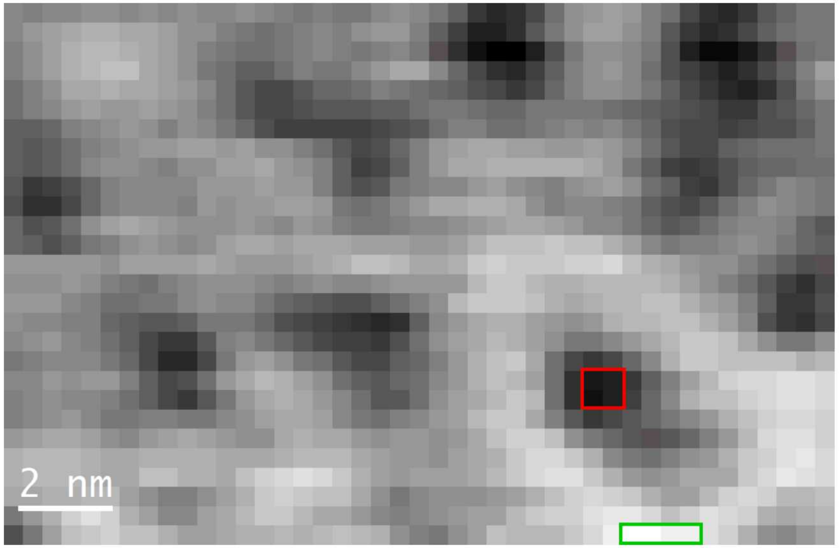
Map of He K-edge

Spectra after subtraction of metal plasmon peaks

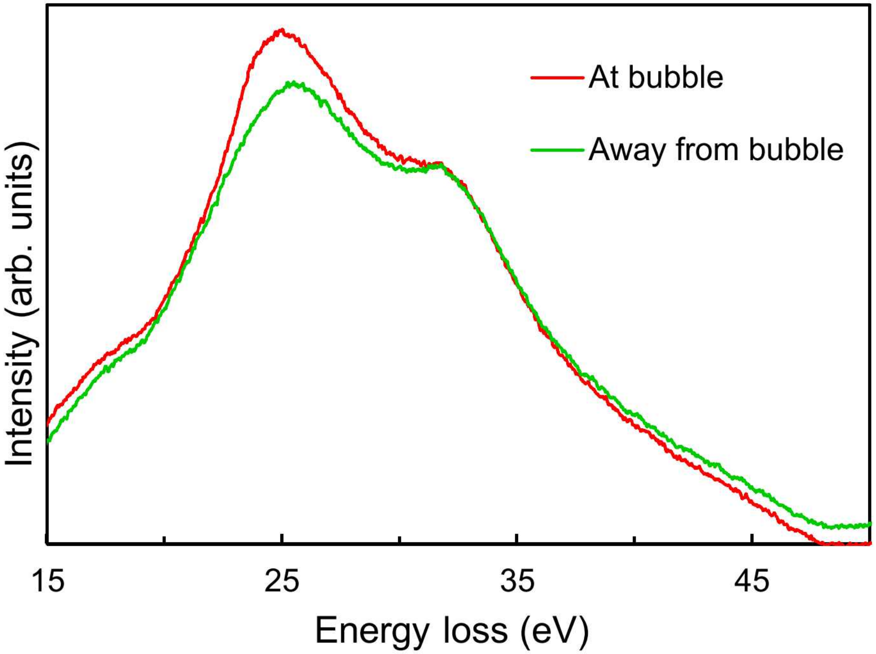
Taverna, D.; Kociak, M.; Stéphan, O.; Fabre, A.; Finot, E.; Décamps, B.; Colliex, C. *Phys. Rev. Lett.* **2008**, *100*, 035301.

He detection by EELS of tritiated sample with 1-2 nm bubbles

Dark field image of tritiated $Pd_{95}Ni_5$



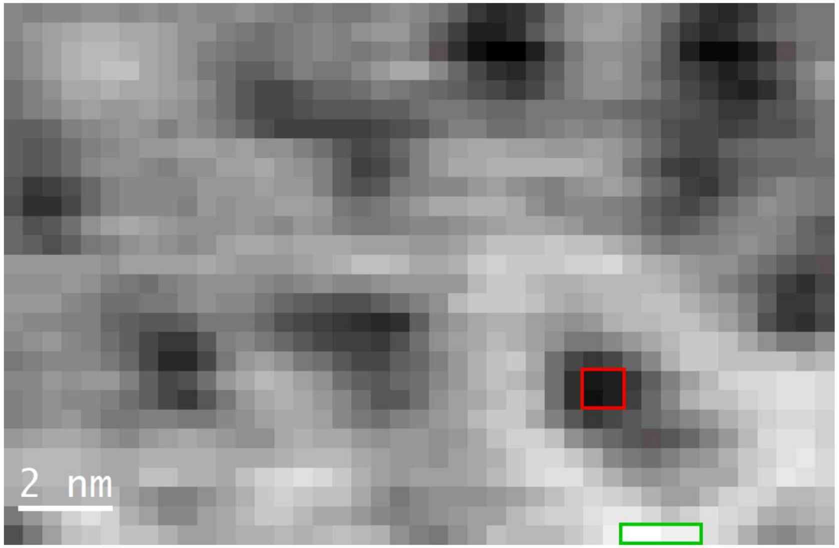
EELS of Tritiated Pd-Ni



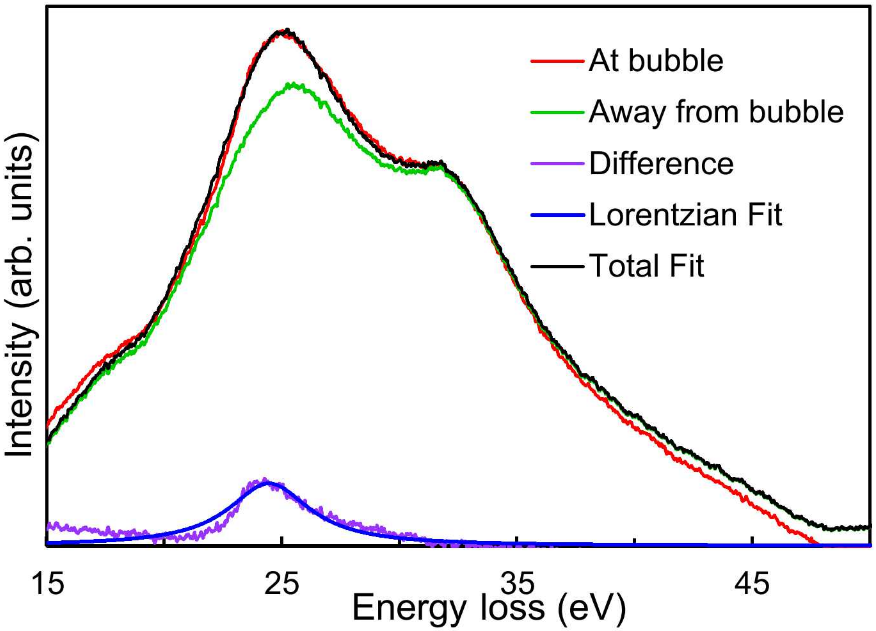
- $Pd_{95}Ni_5$ sample aged for 4 years under tritium contains bubbles roughly 2 nm in diameter
- Clear increase in intensity at 25 eV in bubble region compared to $Pd_{95}Ni_5$ background measured away from bubbles
- Helium K-edge may overlap with Pd plasmon

Difference in bubble and background spectra was fit by Lorentzian

Dark field image of tritiated $Pd_{95}Ni_5$



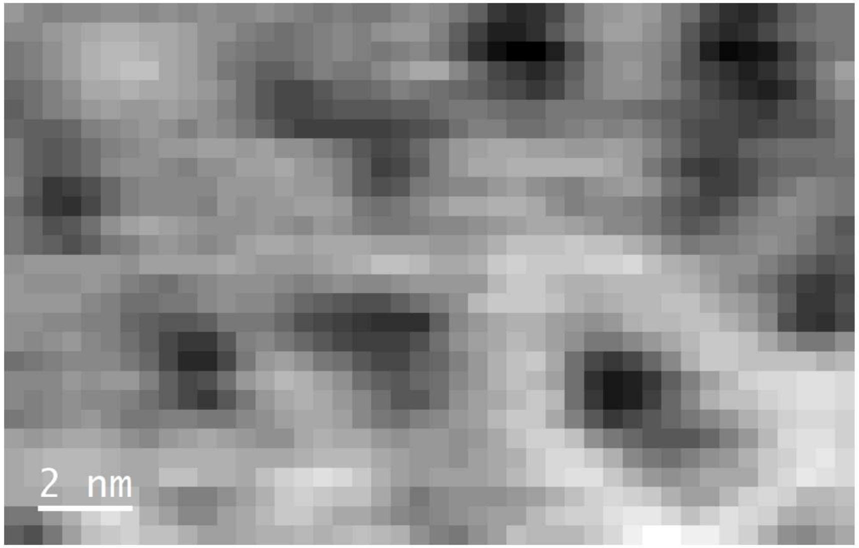
Least squares fit of bubble spectrum



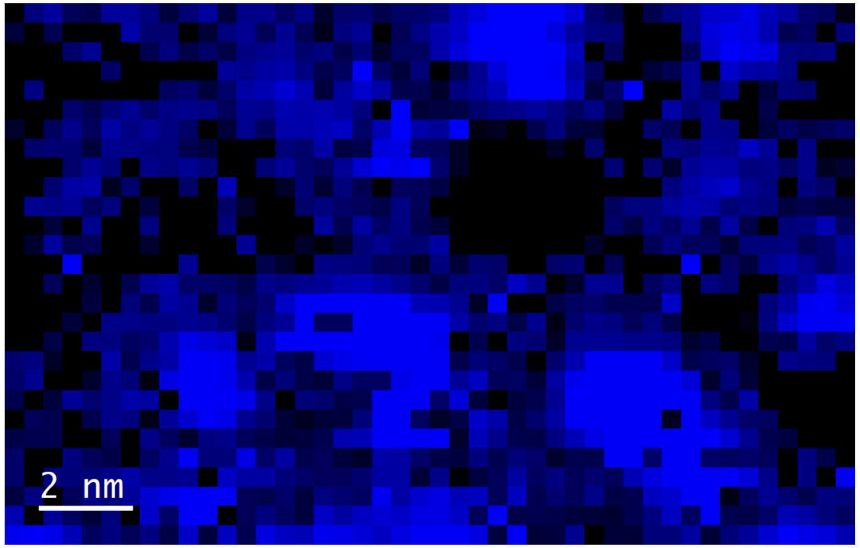
- Bubble spectrum after subtraction of Pd-Ni background was well fit by a Lorentzian function
- Non-linear least squares fit with Lorentzian function and Pd-Ni background matches spectrum measured at bubble
- Lorentzian function represents additional intensity due to helium

Lorentzian function represents helium and maps to bubble regions

Dark field image of tritiated $Pd_{95}Ni_5$



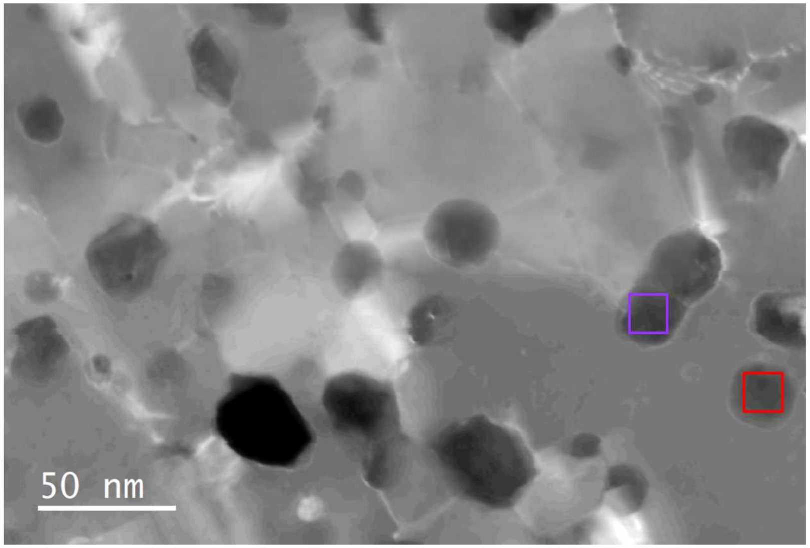
Lorentzian amplitude over background fit



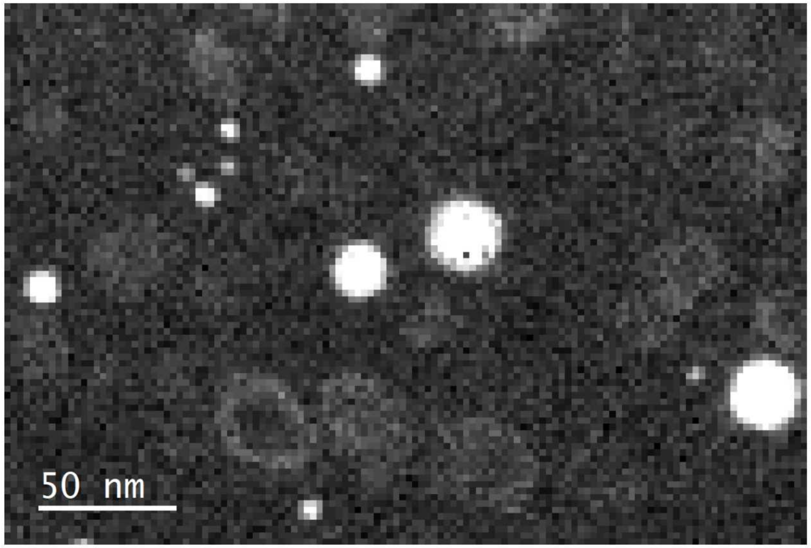
- Amplitude of Lorentzian function represents concentration of helium
- Positions of bubbles correspond with increase in amplitude of Lorentzian

He bubbles and voids have similar 25 eV Pd plasmon peaks

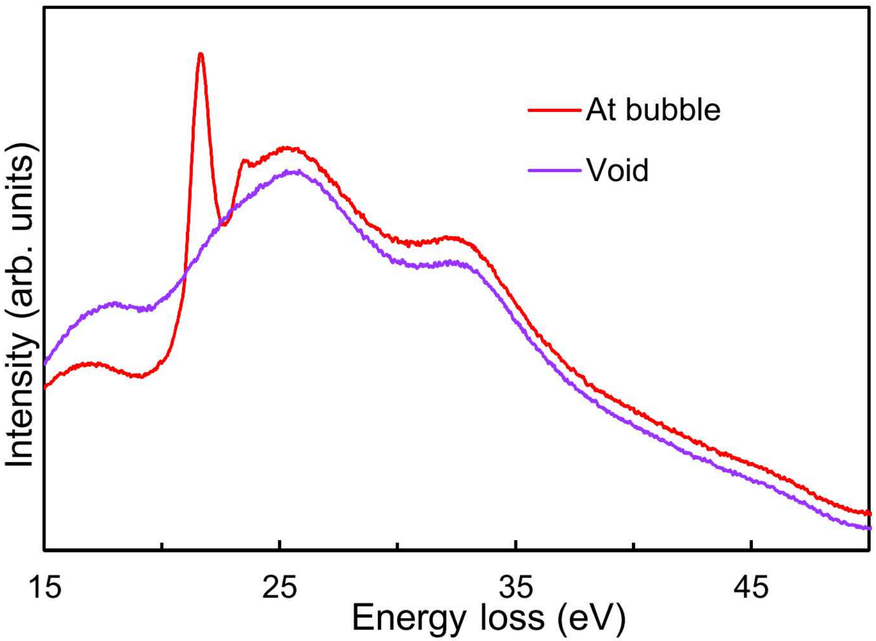
Dark field image of tritiated $Pd_{95}Ni_5$



Map of He K-edge



EELS of Pd implanted with He



- Pd foil was implanted with 1×10^{17} He^+/cm^2 and annealed at 600 °C for 2 hours
- Large bubbles formed with clear He K-edges
- Pd plasmon peaks at 25 eV are similar for He bubbles and voids

Helium bubbles coarsen significantly upon heating to 400 °C

In situ heating procedure:

1. Heated to 300 °C

   → No visible change

2. Heated to 400 °C

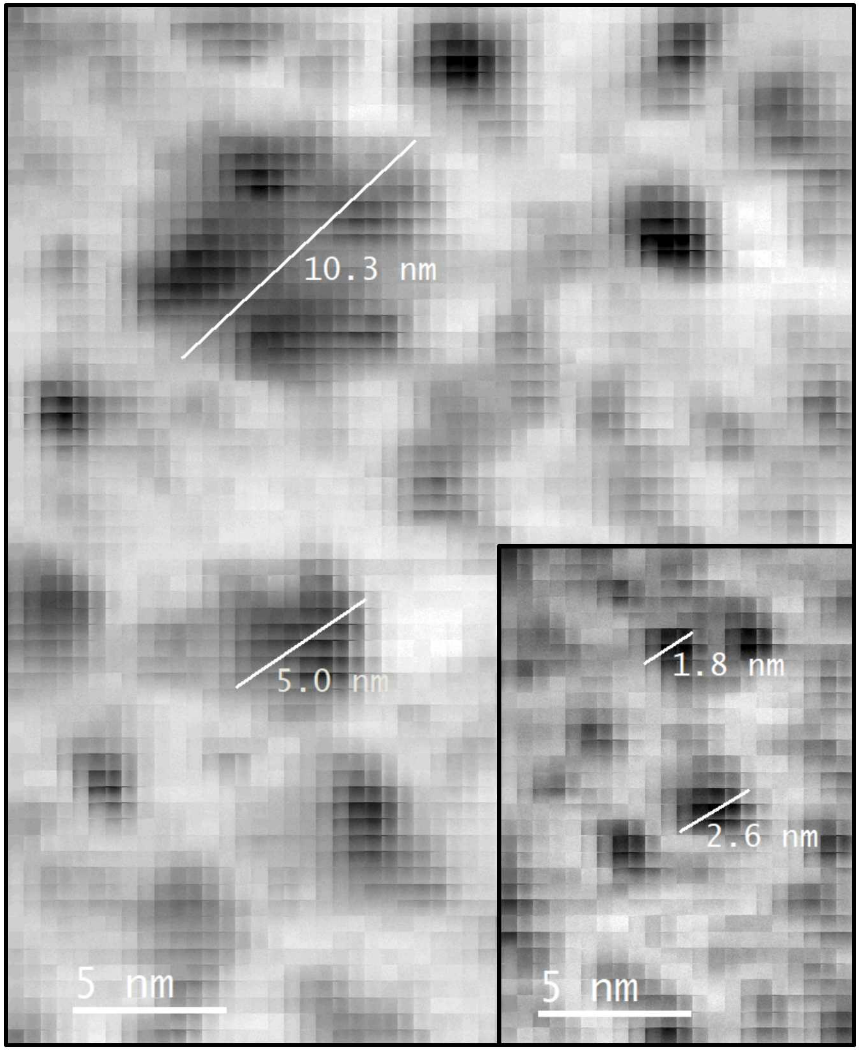
   → Stark increase in bubble size

   → Appearance of sharp EELS peaks at 22 to 24 eV

3. Cooled to 25 °C

   → No visible change

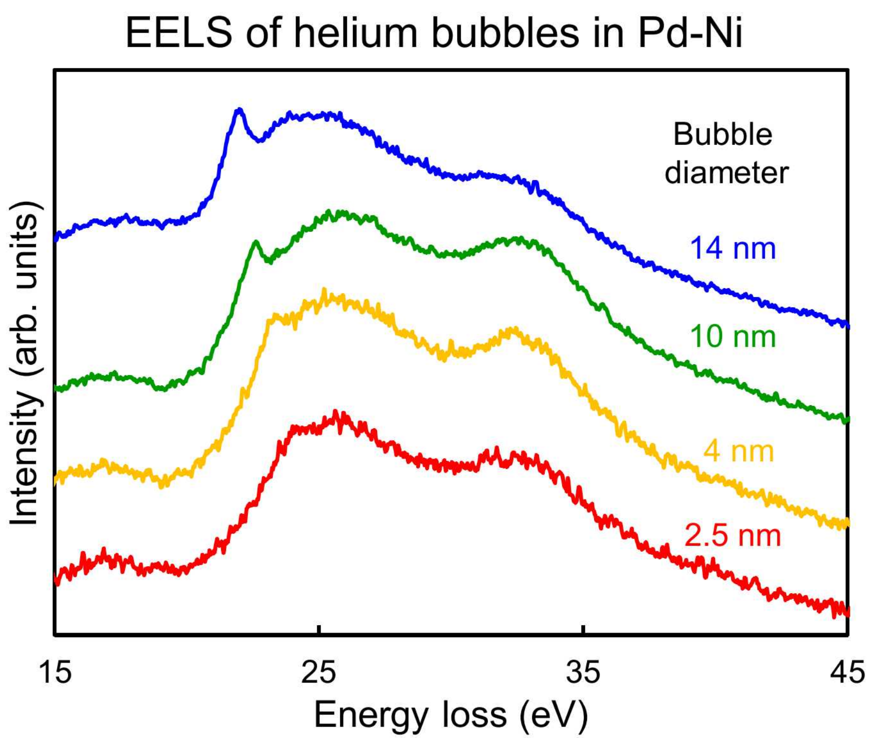
STEM dark field images

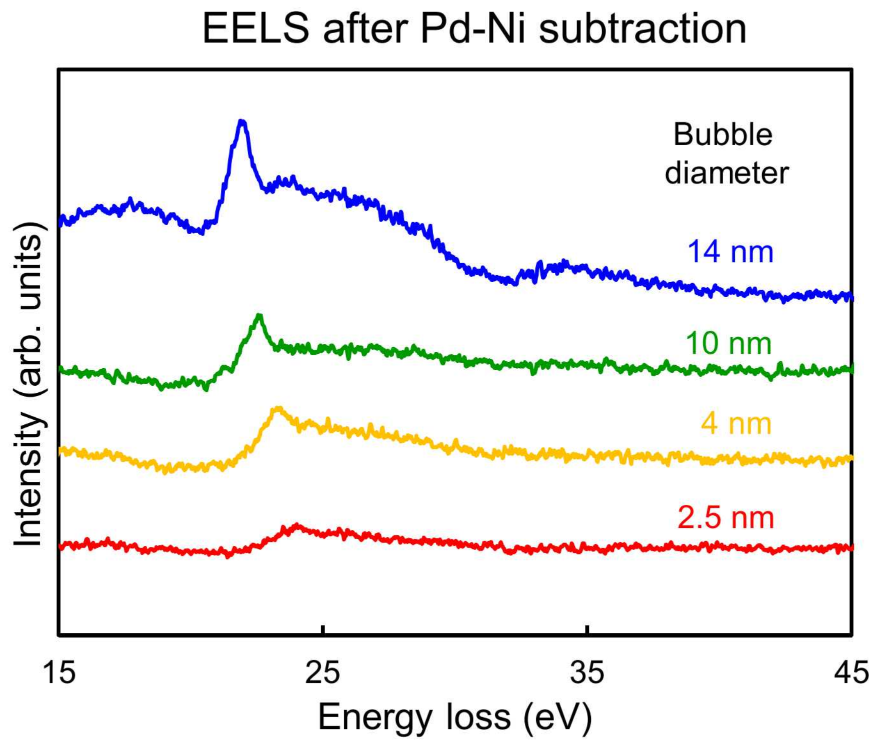


After heating to 400 °C

Inset: Before heating to 400 °C

Larger bubble size corresponds with more distinct He K-edge





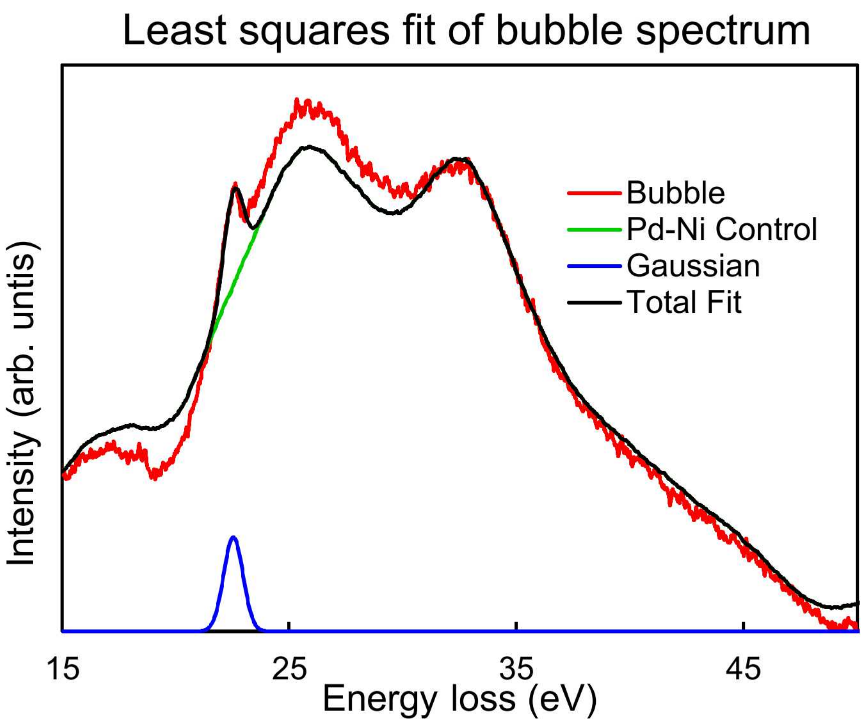
More helium atoms in electron beam path

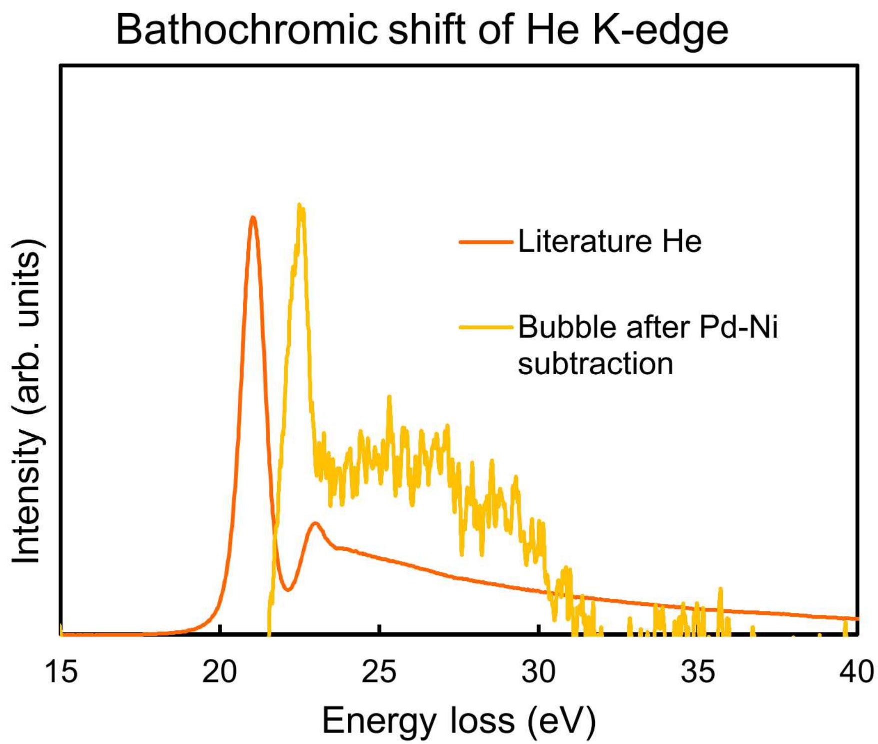
→ Increase in intensity of helium K-edge

Lower helium excitation energy at higher pressure

→ Less overlap with palladium plasmon peaks

Bubble spectra resemble a summation of Pd-Ni and helium K-edge





Bubble spectra are well-fit by:

1) Pd-Ni control never exposed to tritium

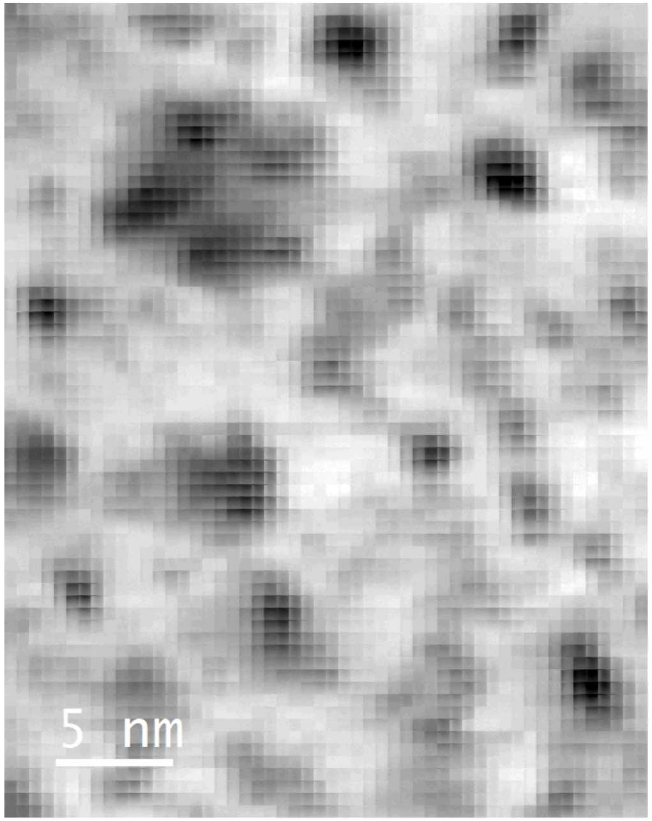
+

2) Gaussian function representing helium

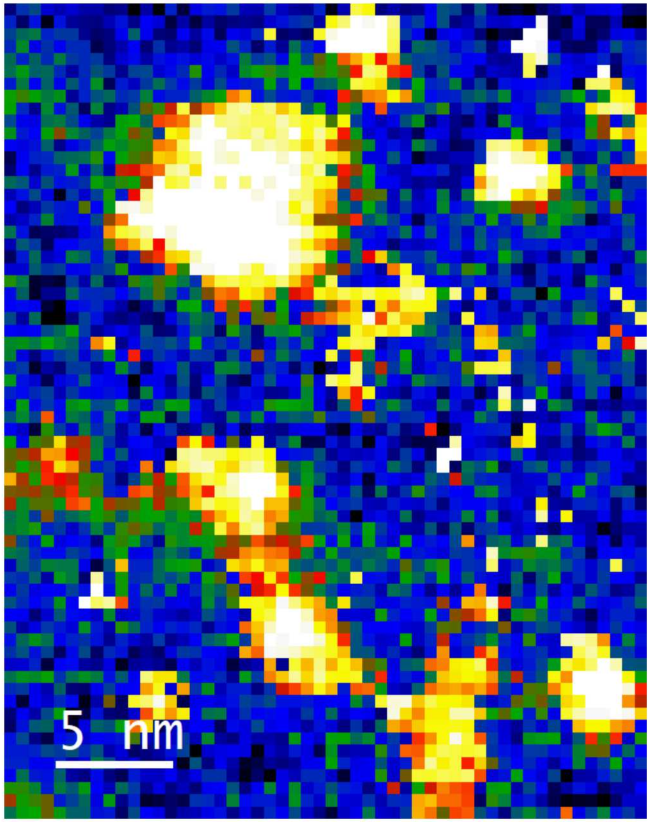
After subtraction of Pd-Ni, bubble spectrum resembles literature spectrum of helium

Map of K-edge indicates bubbles are filled with helium

Dark field image of annealed $Pd_{95}Ni_5$



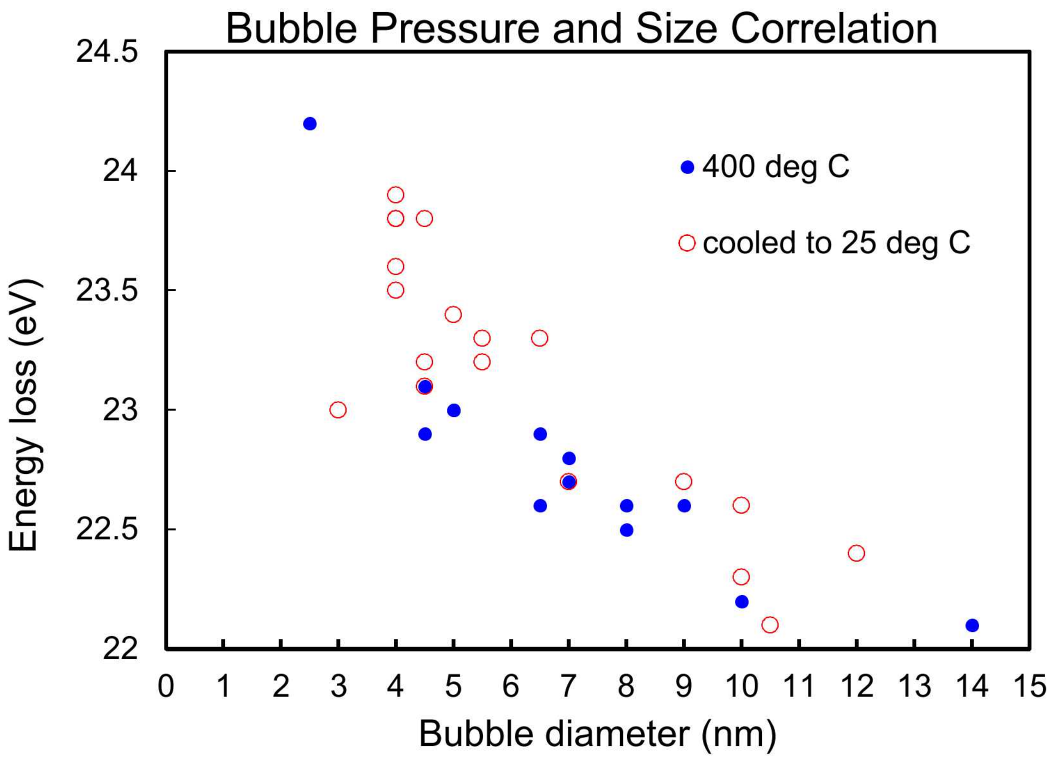
Amplitude of Gaussian corresponding to He



Map of helium K-edge reveals nearly all bubbles contain helium

In situ heating followed by EELS allowed detection of helium in a sample that grew bubbles only up to ~2 nm

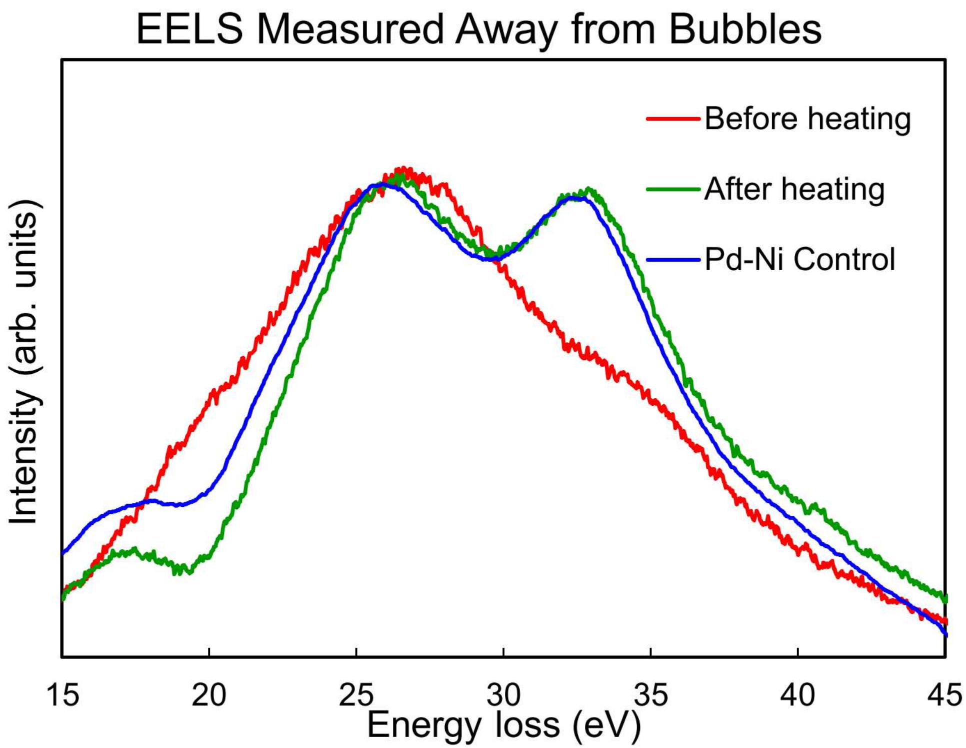
Bubble size and helium pressure are strongly correlated



He K-edge of larger bubbles is at lower energies indicating lower internal pressure

Overlap of atomic orbitals of neighboring He atoms under high pressure increases helium 1*s* → 2*p* excitation

Annealed Pd-Ni away from bubbles resembles Pd-Ni control



Post-heating spectra resemble Pd-Ni control; pre-heating spectra do not

Heating may liberate helium trapped in the bulk palladium lattice allowing it to migrate to bubbles

Conclusions

Does helium remain in tritiated metals after several years?

Yes, results indicate nearly all of the bubbles in tritiated $Pd_{95}Ni_5$ contain helium

How can we detect helium in <10 nm bubbles?

Annealing to induce bubble coarsening followed by electron energy loss spectroscopy reveals the helium K-edge

How can we measure the internal pressure and total helium content?

Bubble size is inversely correlated with pressure; degree of bathochromic shift of helium K-edge indicates internal bubble pressure

Is there helium in the metal lattice outside of bubbles?

Changes in EELS intensity at 25 eV measured away from bubbles may result from overlap of helium K-edge with metal plasmon peak

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Sandia National Lab, NM collaborators:

Caitlin Taylor, Brittany Muntifering, Clark Snow, Khalid Hattar

Savannah River National Lab collaborators:

Lynn Bouknight, Kirk Shanahan

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Figure Slide