Determination of hydrogen in niobium by cold neutron prompt gamma-ray activation analysis and neutron incoherent scattering

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Phy 224B
Chapter 20: Applications of Nuclear Physics
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(unused)

Intro

- small interstitial hydrogen atoms cause “vacancies” in Nb crystal which lead to embrittlement and diminish superconducting abilities in Nb

- Two techniques for measuring H:

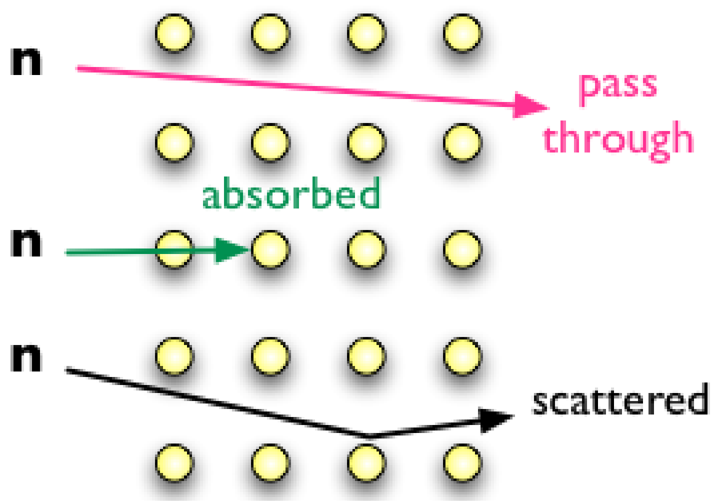
  - cold n prompt γ activation analysis (PGAA) - (n, γ) process - non-destructive, chemical form/shape not important, matrix independent, entire sample analyzed, fast, simultaneous for different isotopes

  - n incoherent scattering (NIS) - incoherent scattering cross section of hydrogen >> absorption cross section - higher sensitivity and faster detection of H than PGAA - but signal is not specific to H, hence a H-less sample is needed to account for n scattering by other elements

Questions to Answer

- Does the acid treatment of the niobium introduce a measurable amount of hydrogen?
- Can vacuum heating remove hydrogen?

Neutron and Material



scattering vector: $\vec{Q} = \vec{k}_f - \vec{k}_i$

$$\psi_i = e^{-ikz} \qquad \psi_f = -\frac{b}{r}e^{-ikr}$$

$$\frac{d\sigma}{d\Omega} = \frac{(\bar{b})^2}{N}\left|\sum_i^N e^{i\vec{Q}\cdot\vec{r}}\right|^2 + (\bar{b^2} - (\bar{b})^2)$$

- coherent scattering:
  - neutron interacts with sample as a whole
  - scattering depends on Q direction
- incoherent scattering:
  - neutron interacts with each nucleus independently
  - scattering is uniform in all Q directions

hydrogen incoherent scattering cross section is very high (80 b)

Niobium

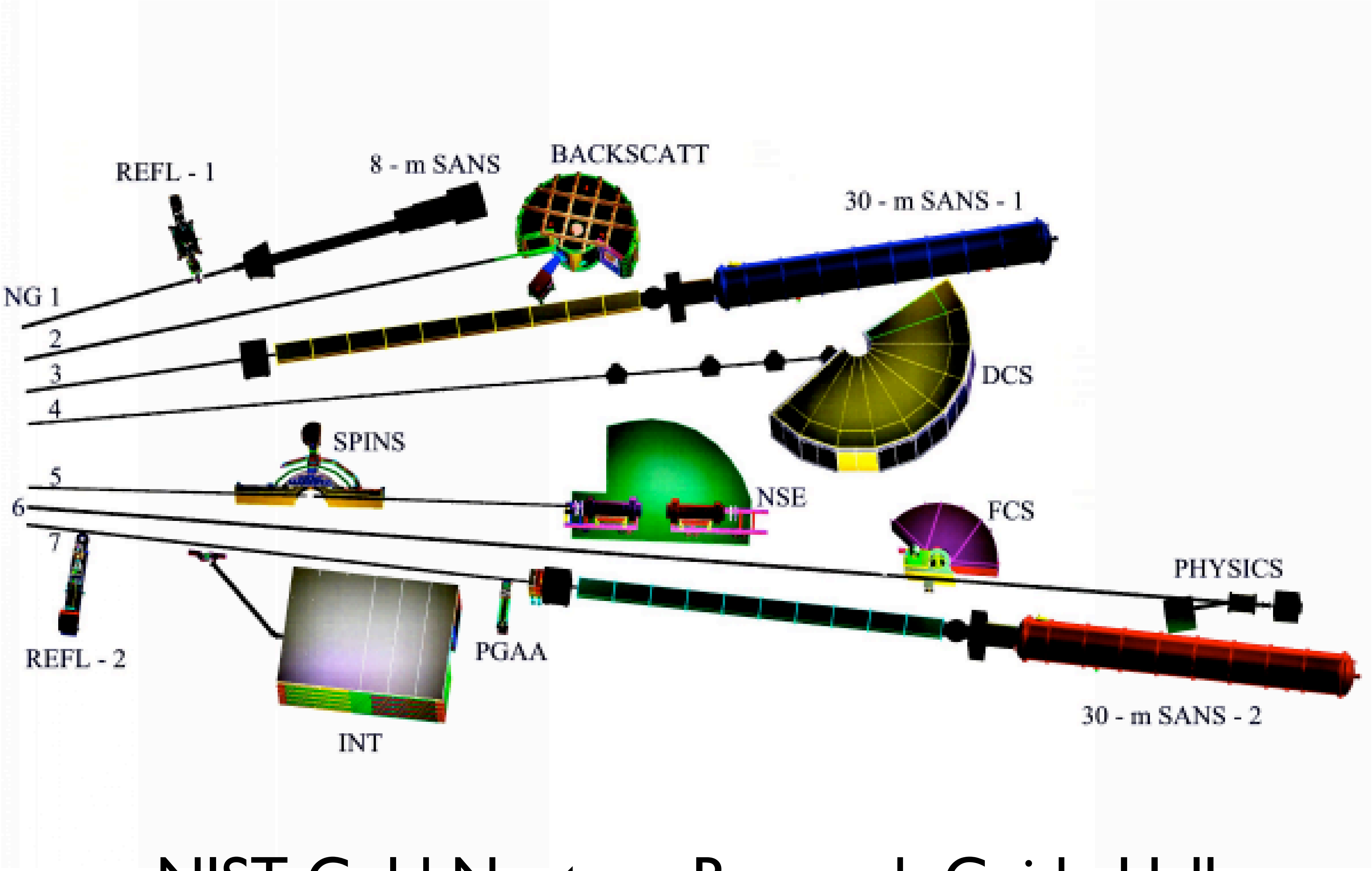
- $_{41}$Nb, atomic weight = 92.906
- soft, easily shaped
- low thermal neutron capture cross section
- At 1 atm, Nb has the highest critical temperature of the elemental superconductors, 9.3 K
- remains a superconductor even when inside high B field

Niobium

- treated with acid to remove surface impurities
- operating temperatures 2 K <= T <= 4.2 K
- drop in superconductor's Q-value observed at 75 K <= T <= 130 K; attributed to hydride precipitation

Q (quality) factor
= reactance/resistance
= stored energy/energy loss rate

NCNR



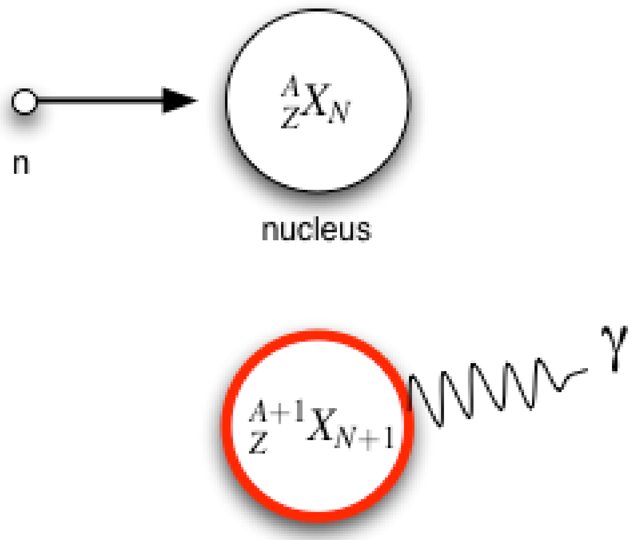
neutron
guides

NIST Cold Neutron Research Guide Hall

http://www.ncnr.nist.gov/instruments/coldinstr.html

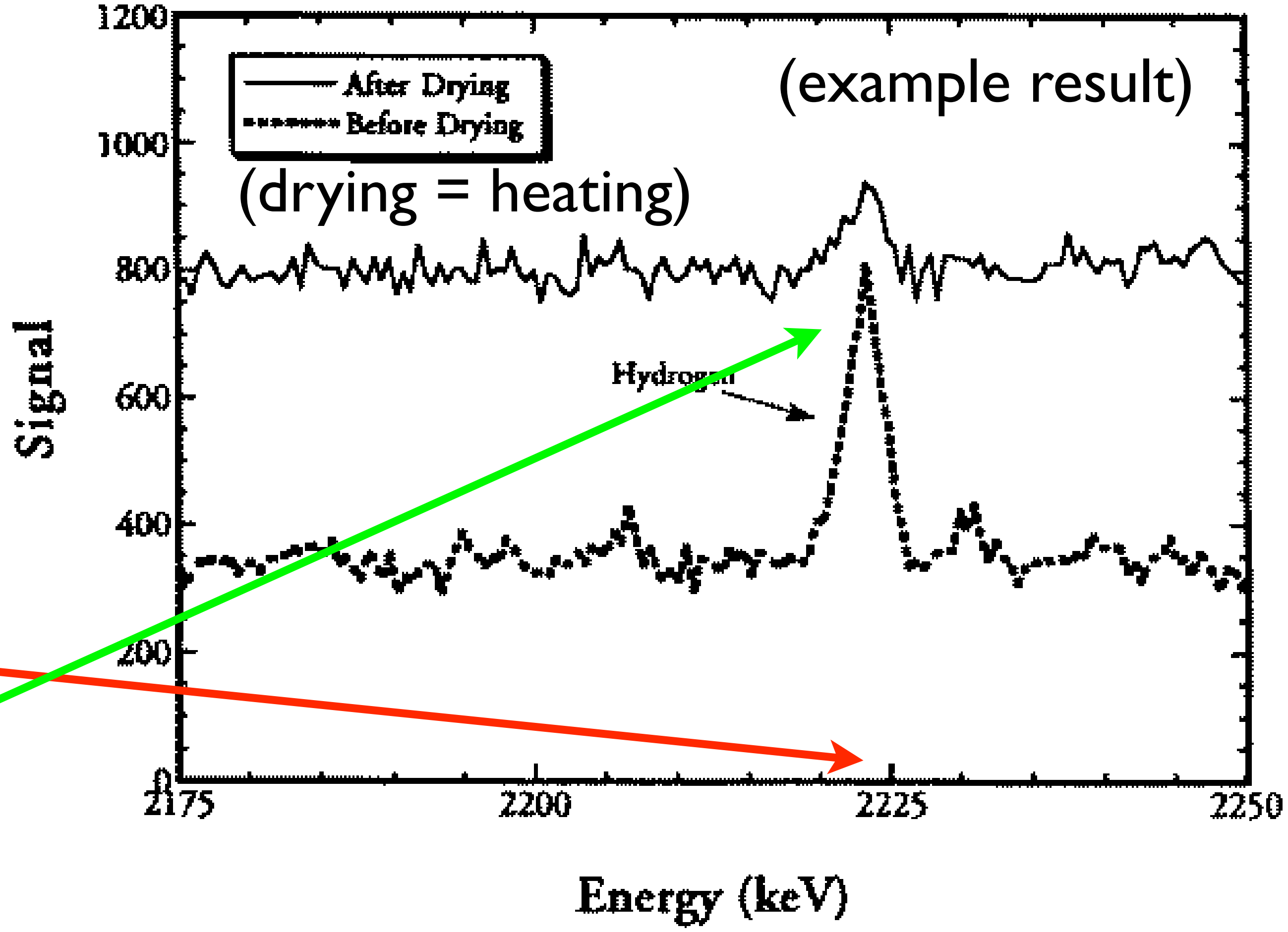
PGAA

neutron is captured, photon is promptly emitted with energy related to binding energy of added neutron



γ energies ID element species

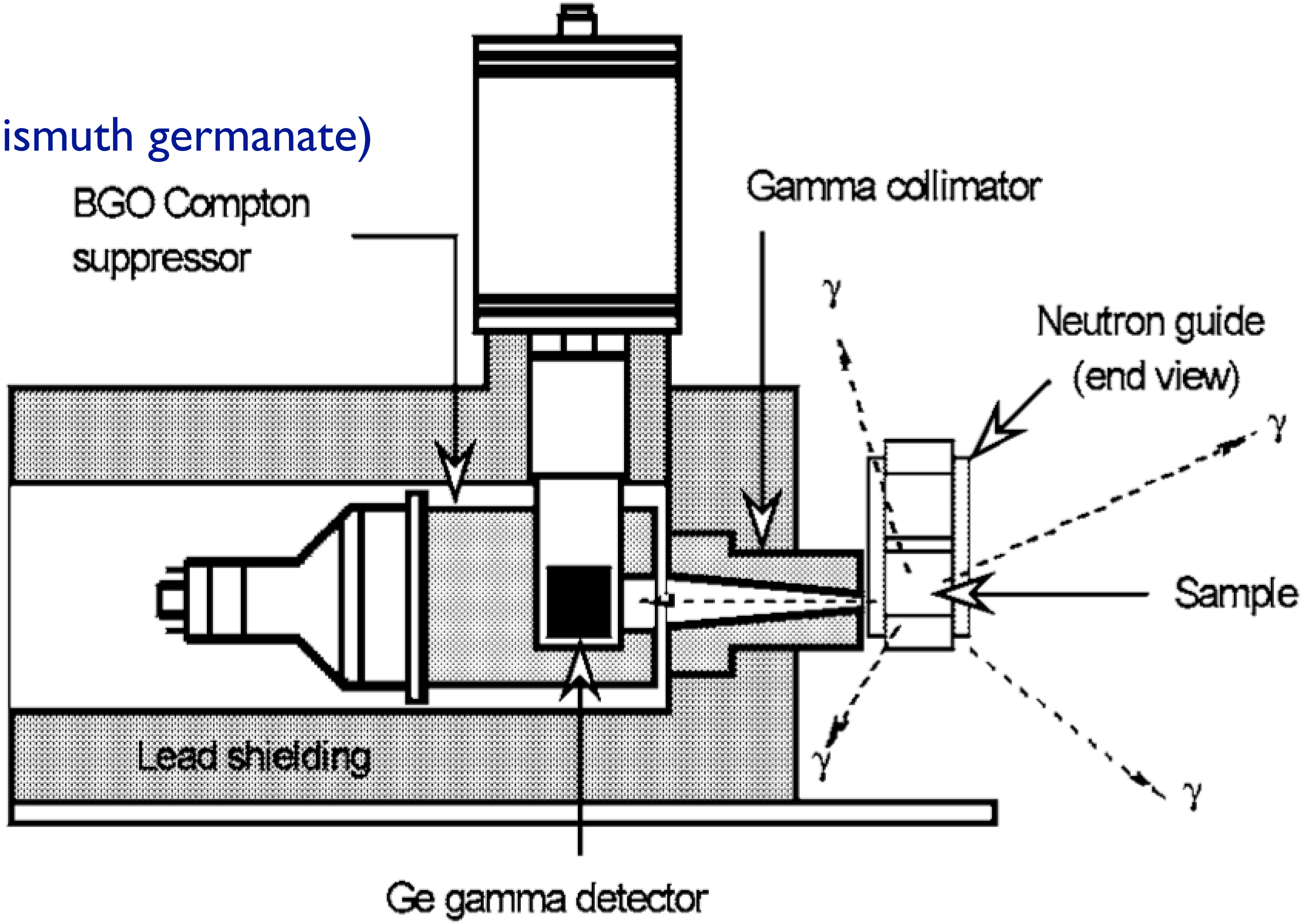
γ intensities gives concentrations



(example result)

(drying = heating)

PGAA



(bismuth germanate)

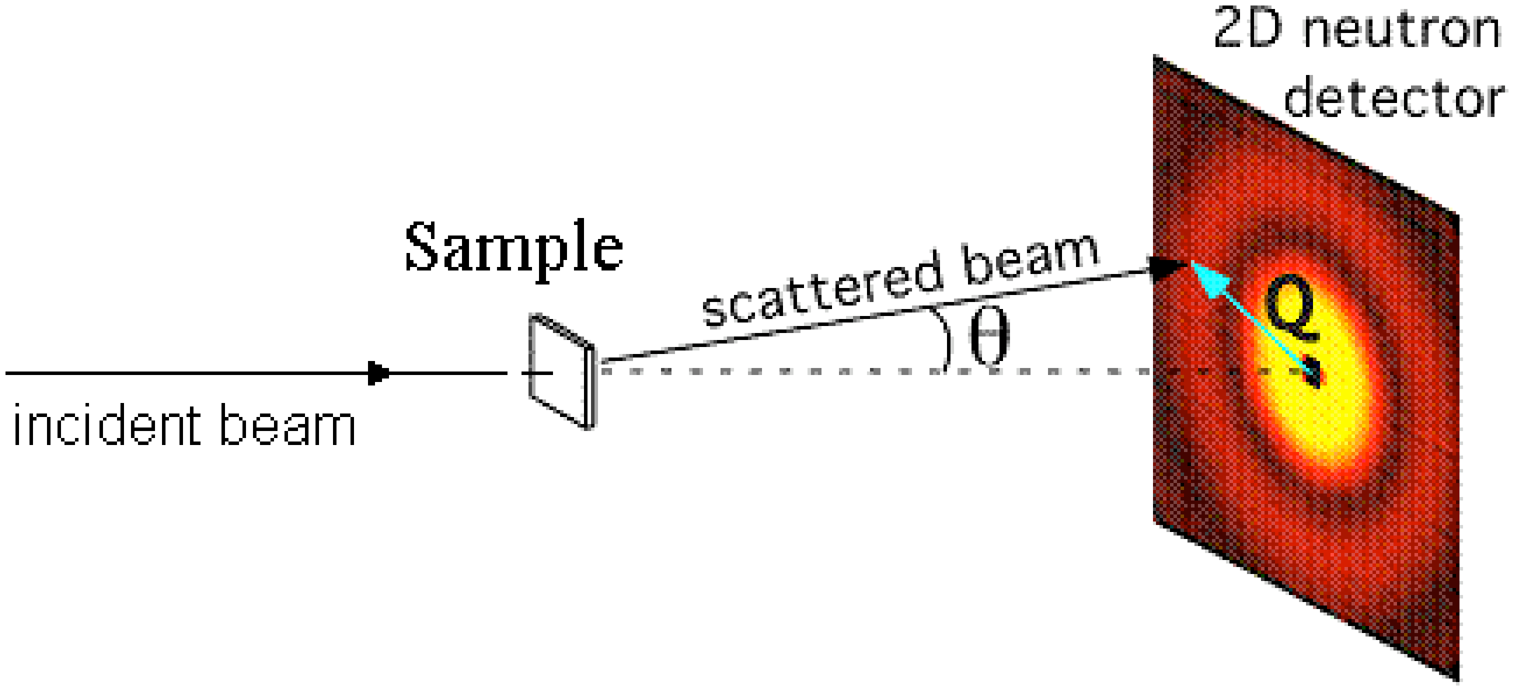
Fig. 1: cold neutron PGAA spectrometer

PGAA uses

- aircraft industry:
  - hydrogen embrittlement of titanium alloy jet engine turbine blades
  - hydrogen mass fraction of hydrogen-doped titanium alloy standard reference mateiral
- hydrogen in semiconductors and related materials (quartz, germanium, thin films on silicon wafers)
- hydrogen in fullerenes
- PGAA + small angle neutron scattering (SANS) is used to study hydrogen impurity and pore size in nanocrystalline metals

Fullerenes are molecules composed entirely of carbon, taking the form of a hollow sphere, ellipsoid, or tube.

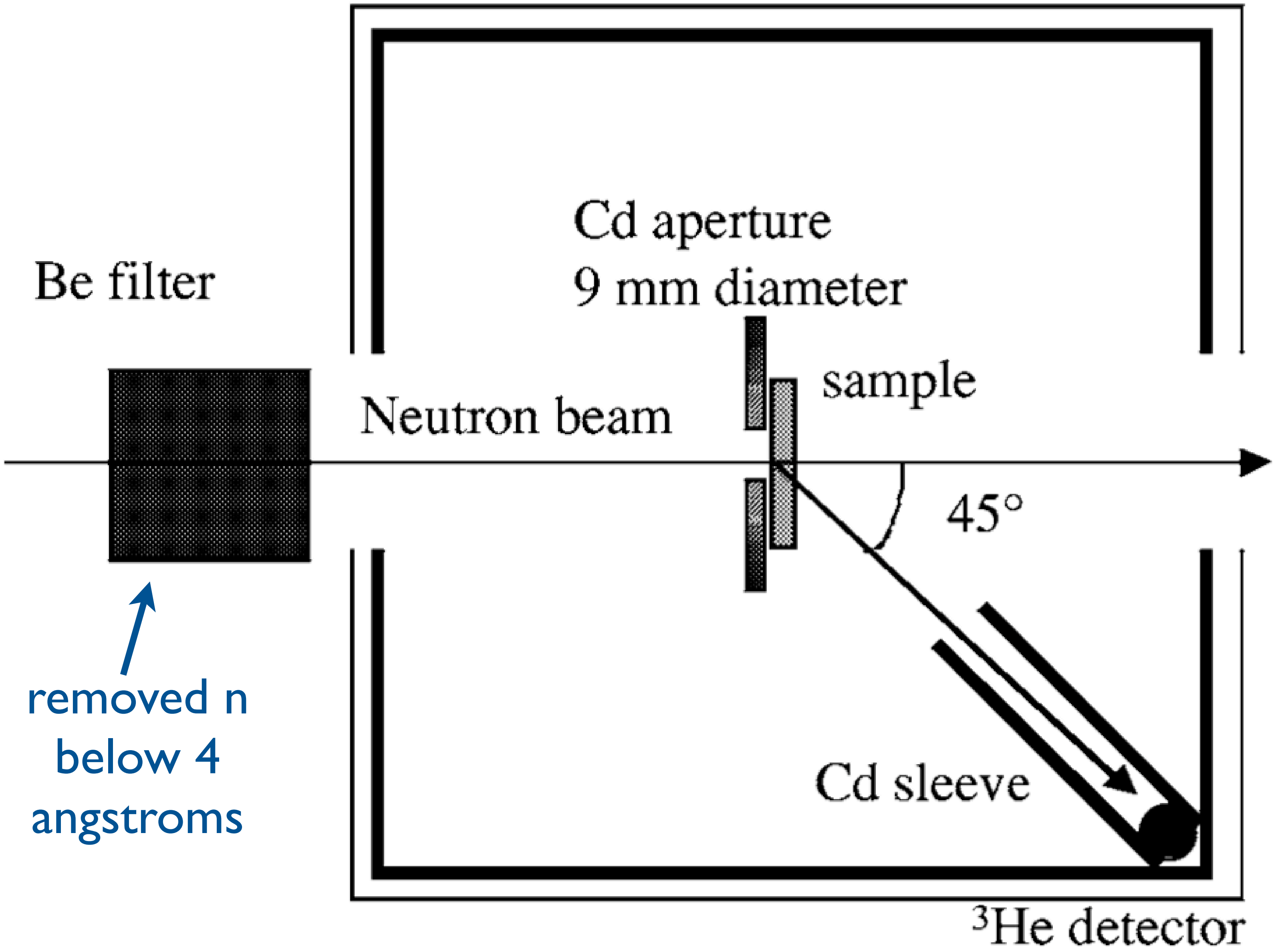
SANS



- measure large objects (1-10^3 μm)

SANS: http://www.ncnr.nist.gov/programs/sans/

NIS



removed n below 4 angstroms

Fig. 2: NIS measurement setup. Calibration using polypropylene films are done with this same setup.

information required:
(1) scattered neutron signal from sample
(2) blank measurement
(3) calibration of neutron signal vs. hydrogen concentration

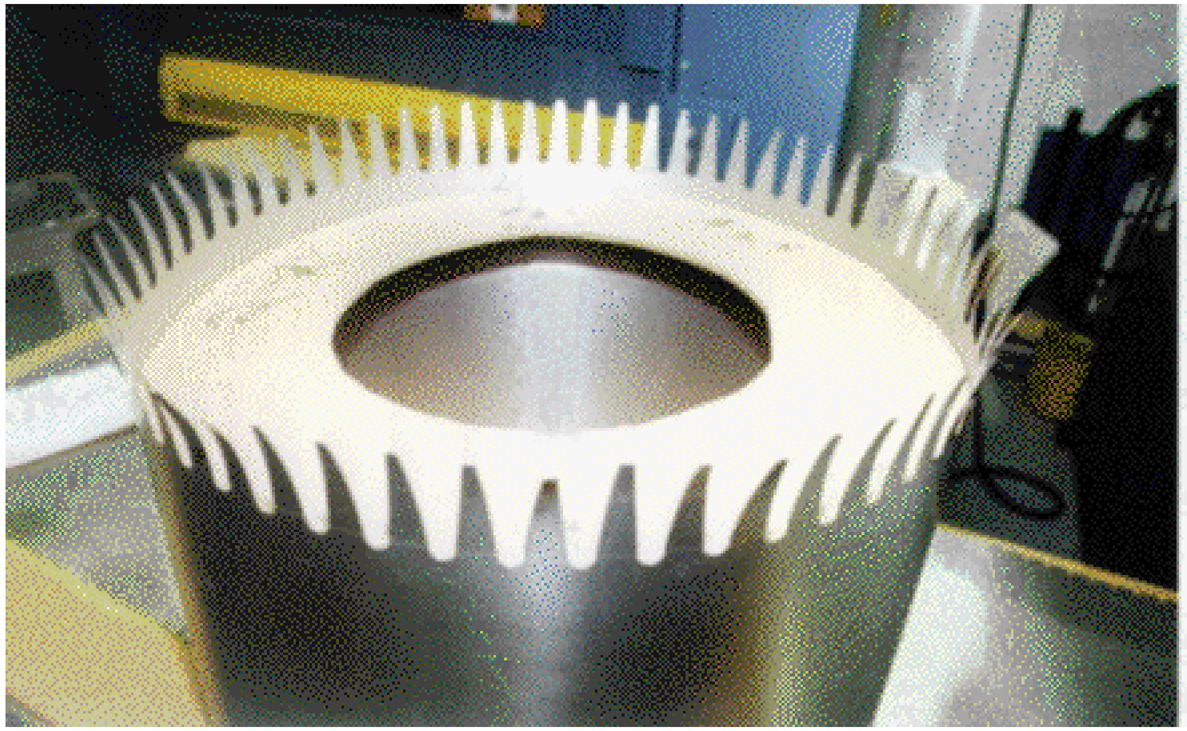
each sample measured for 6 mins

Method

- 5 slabs of ultra-pure niobium, each ~ 10 g
- degassed at Jefferson Lab by heating in hot vacuum furnace (for ~ 6 h) to remove hydrogen

Vacuum Heating (Degassing)

Jefferson Lab's vacuum furnace



designed to operate at 10^{-8} torr

extending from the top of each niobium insert are a series of notches which are bent over to seperate inserts together.

Results

both spectra show a peak at 2223 keV; similar magnitudes

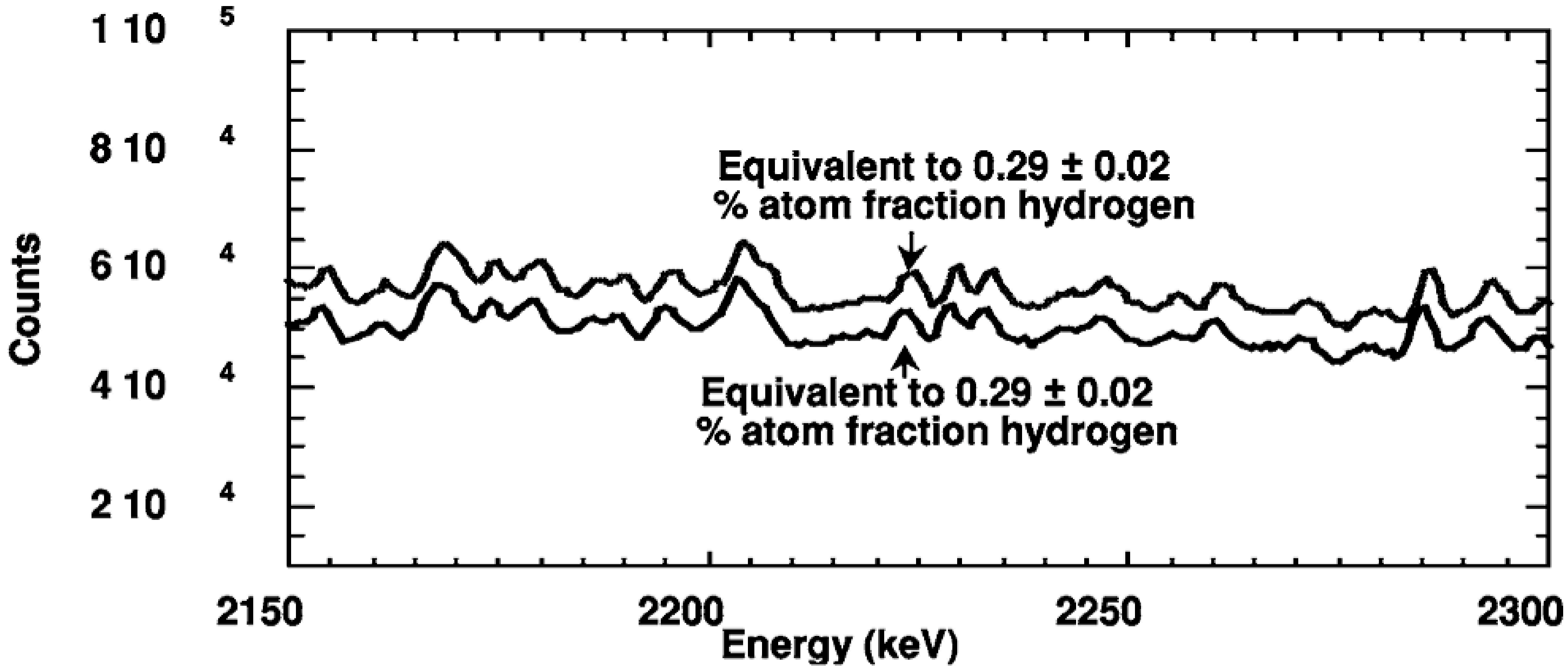
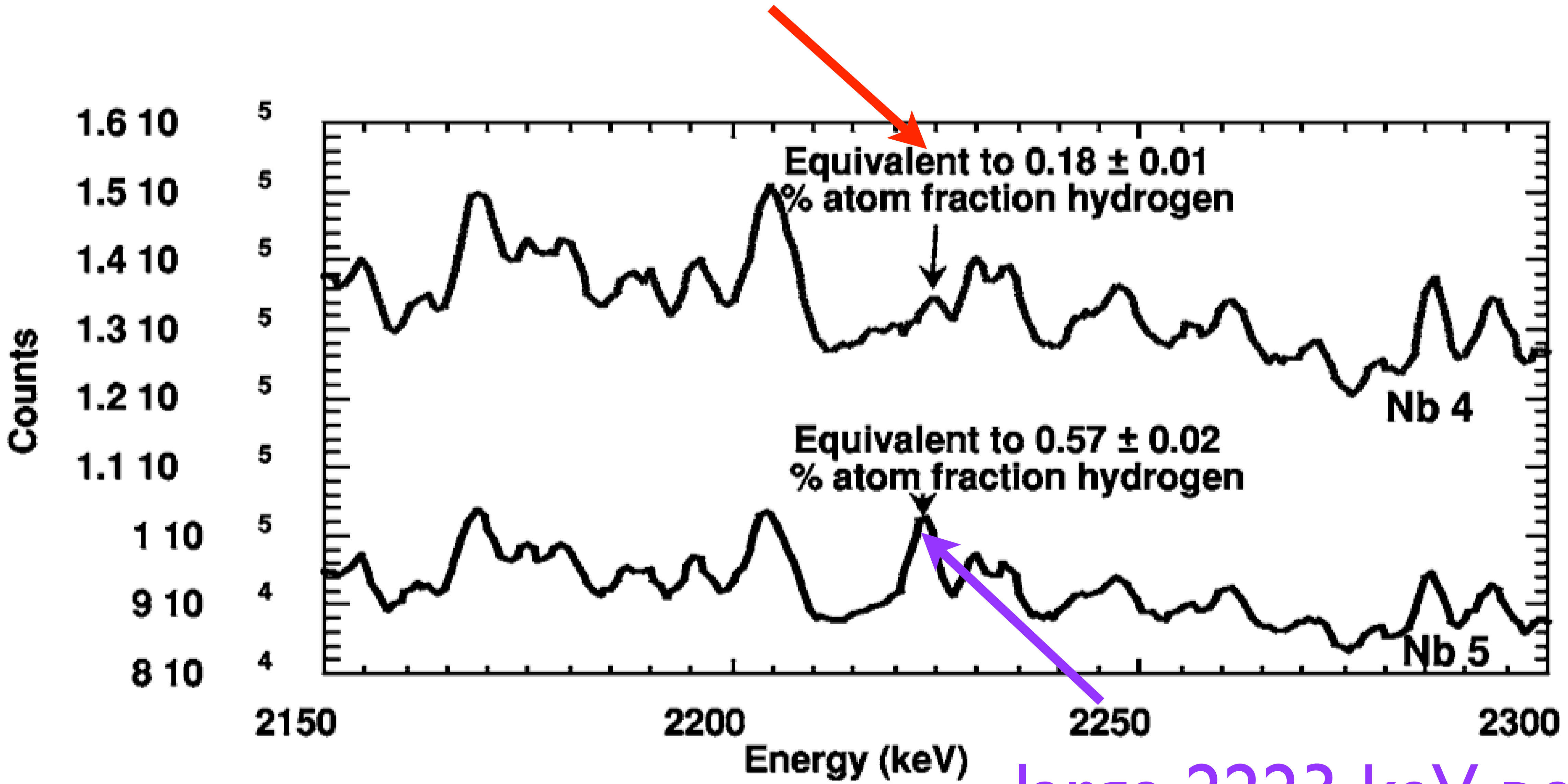


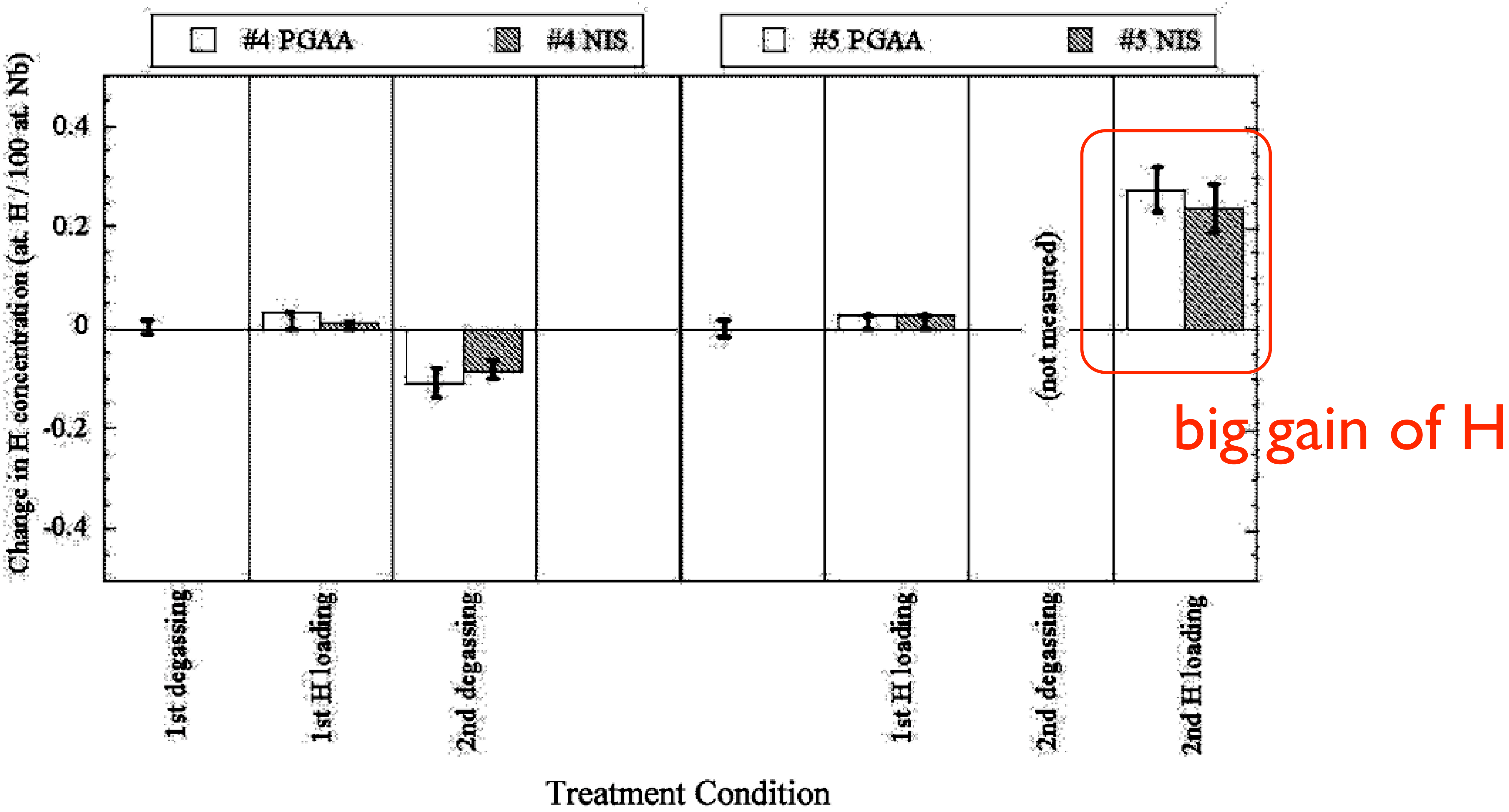
Fig. 3: PGAA spectrum (H energy region) of Nb sample 4 after 1st vacuum heating (top), and then after acid treatment (bottom).

smaller 2223 keV peak



large 2223 keV peak

Fig. 4: Top: PGAA spectrum (H energy region) of Nb sample 4 after the 2nd vacuum heating. Bottom: PGAA spectrum of Nb sample 5 after 2nd degassing and 2nd acid treatment



big gain of H

Fig. 5: The change in H concentration in Nb samples #4 (left) and #5 (right) relative to that after the 1st degassing as determined by PGAA. The results obtained after the 1st H loading are expressed as the "upper limit", since the changes observed are within the measurement uncertainty. The significant changes occurred only after the 2nd degassing for #4, and 2nd H loading for #5. PGAA uncertainties are 2s based on propagation of counting statistics and uncertainties in element sensitivities, NIS uncertainties are 2s based on the propagation of uncertainty in the polypropylene film thickness.

Conclusion

- amount of H did not show correlation with time or temperature of initial degassing
- H content was not correlated with duration of initial acid treatment
- significant gain of H in sample 5 (after 2nd vacuum heating and 2nd acid treatment)
    - 800 celsius heat removed strongly bound hydrogen, activating sites where H can be picked up by Nb upon subsequent acid treatment

Answers

1. Does acid treatment of Nb introduce a measurable amount of H?
2. Can vacuum heating remove H?

- answers:
  - NO for 1st cycle of treatment
  - YES for 2nd cycle

Resources

- http://www.ncnr.nist.gov/
- http://www.mrl.ucsb.edu/~pynn
- http://www.ansto.gov.au/ansto/bragg/