First Principles Investigation of Hydrogen in Niobium

Denise C. Ford[1,2], Lance Cooley[1], David Seidman[2]

[1]*Fermi National Accelerator Laboratory, Batavia, IL, USA*

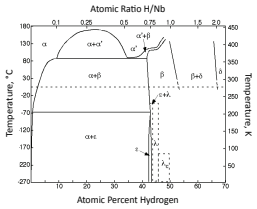
[2]*Northwestern University, Evanston, IL, USA*

Abstract

Niobium hydride is a contributor to degraded niobium SRF cavity performance by Q-slope and Q-disease. Hydrogen is easily absorbed into niobium when the protective oxide layer is disturbed, such as during electropolishing and other chemical treatments, and the structure and distribution of hydrogen in niobium is altered during other processing steps such as baking. To optimize cavity performance and production efficiency, it is fundamentally important to understand the structures of hydrogen in niobium, including the interactions of hydrogen with structural defects and other impurities such as oxygen. In this study density functional theory was used to evaluate these interactions. Hydrogen was examined as a dissolved interstitial impurity as well as in ordered niobium hydride phases; and the interactions between hydrogen, niobium, niobium site vacancies, and oxygen dissolved in niobium were evaluated. The results of this study yielded information about the thermodynamic, electronic, magnetic, and geometric properties of these systems, which lead to important implications about the mobility of impurities and vacancies in niobium and the precipitation of phases that are detrimental to cavity performance.

Hydrogen Absorption into Niobium

- Niobium is an active metal that easily absorbs hydrogen [1].
- Absorbed hydrogen becomes trapped in niobium when the oxide regrows after chemical processing.
- The niobium – hydrogen phase diagram is very complex [1].



- **α, α' – interstitial hydrogen dispersed in bcc niobium**
- **β, ε – ordered hydrogen interstitials in fco niobium**
- **δ – hydrogen in the tetrahedral sites of fcc niobium – fluorite structure**
- **λ, λ_c – experimentally unconfirmed phases**

- Diffusion of hydrogen in niobium is very rapid [2].

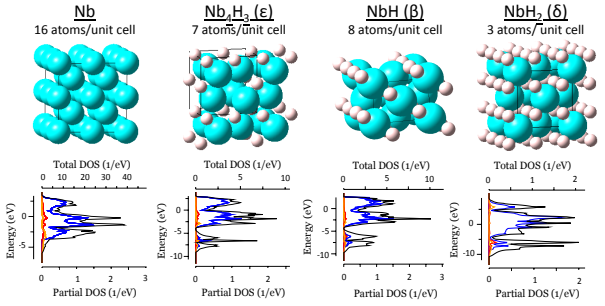
Scope of This Study

- Model plausible niobium hydride structures and evaluate their properties to help address the following questions:
  - **Which hydride phases are present in SRF cavities?**
  - **What are their properties?**

Methods of This Study

- **Density Functional Theory** implemented in VASP [3]
  - General parameters: PBE-GGA exchange-correlation, PAW pseudopotentials, 400 eV cutoff, Methfessel-Paxton smearing, 0.2 eV smearing width
  - Structure Optimizations: 0.25 Kpoints/Å mesh
  - Electronic Density of States (DOS): 0.15 Kpoints/Å mesh

Niobium Hydride Crystals

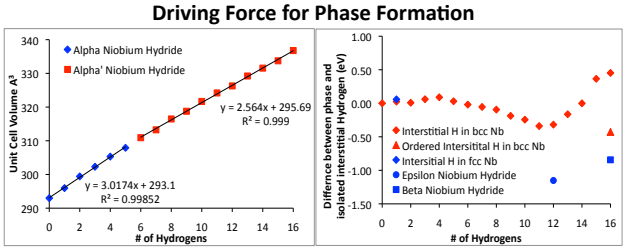


blue – d-states, red – p-states, yellow – s-states

- **Metallic character is preserved** as hydrogen content increases; but **superconducting character is lost**.
- Hydrides are **nonmagnetic.**

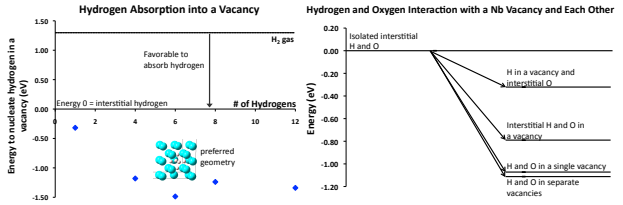
Niobium Hydride Phase Formation

Driving Force for Phase Formation



- α (gas-like) and α' (liquid-like) unit cells contain 16 niobium atoms in bcc arrangement with disordered hydrogen in tetrahedral sites.
- ε and β niobium hydrides are fco niobium with ordered hydrogen in tetrahedral sites.
- bcc –> fcc niobium requires 0.35 eV/atom.
- **The thermodynamic driving force to form ordered structures becomes apparent at ~ 43% hydrogen content.**

Phase Nucleation



- **Site vacancies in the Nb lattice attract chemical impurities.**
- **A single vacancy can hold up to 6 hydrogen atoms – one at each octahedral site.**
- **It is more energetically favorable to fill a vacancy with oxygen than with hydrogen.**

Conclusions

- **Conclusions**
  - Superconducting character is lost as the hydrogen content increases in the ordered phases -> substantial **precipitates can affect cavity performance -> Q-slope & Q-disease**.
  - There is a substantial thermodynamic driving force for hydrogen impurities to form ordered structures when the concentration exceeds ~ 43% **-> α' -> β or ε precipitate formation.**
  - Niobium lattice site vacancies attract impurities, and oxygen is preferred over hydrogen -> **dissolved oxygen hinders hydride formation**.
- **Implications for cavity processing**
  - **Chemical treatments:** hydrogen absorption -> hydride precipitation -> breakdown of superconductivity.
  - **120°C bake:** β and ε -> α' -> diffuse to **α (similar properties to Nb).**

Future Work

- What effects do dislocations have on impurity transportation?
- What effects do defects in the surface oxides have on hydrogen transportation?
- What are the properties and formation probabilities of oxy – hydride precipitates?

References

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Acknowledgements

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