DFT Analyses of Structures that Limit SRF Cavity Performance

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SRF Materials Workshop
July 16, 2012
Overview

- Background - Impurities in niobium SRF cavities
- Methods - Modeling crystal structures with DFT
- Hydrogen in Niobium
  - Niobium hydride phases
  - Interactions with the ideal and defective lattice
  - Application to SRF cavity performance and processing
- Other impurities (O, N, C) in Niobium
  - Niobium Oxide phases
  - Effect on hydride phase formation
  - Application to SRF cavity performance and processing
  - An additional concern
Superconducting Radio-Frequency (SRF) Cavities
Limitations Related to Impurities in Niobium

- **Impurities** can
  - be dissolved in the metal and cause reduction of $T_c$ and local heating
  - form precipitates with local magnetic moments or reduced $T_c$

- Resulting cavity behaviors include
  - **$Q$ – disease**, caused by large hydride precipitates?
  - **$Q$ – slope**, caused by smaller precipitates; dissolved oxygen, hydrogen, nitrogen, etc.; magnetic structures?
Impurity Absorption into Niobium Cavity Forming and Processing Procedure

- **Forming**
  - Complex – shape and ultra high purity – source of many lattice defects

- **Processing**
  - **Bulk electropolish** (~150 μm) of inner surface - remove damage layer from forming
  - Wash - remove chemical residues from EP
  - **800 °C bake** - outgas hydrogen absorbed during chemical processing
  - Tune - shape changes during processing
  - **Fine electropolish** - smooth surface
  - Wash - remove chemical residues from EP
  - Rinse - remove dust (prevent field emission)
  - Assemble
  - **120 °C bake** - it works (why?)
  - Test performance

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Density Functional Theory Modeling
Creating a Model

Properties of interest include:

- Energies – electronic, vibrational, strain
- Geometry
- Charge distribution
- Magnetic moments
- Phonons

Build a crystal structure
Infinitely expand structure with periodic boundary conditions

bcc Niobium

Compare properties of different structures with the same stoichiometry

NbH (β niobium hydride)

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Density Functional Theory Modeling Calculations

- Solve the electronic structure problem for the model system
- Hohenberg, Kohn, Sham – obtain properties from electron density instead of many-electron wavefunction: \( E = T(\rho) + V(\rho) + \text{Exc}(\rho) \)
  - \( T(\rho) \) – kinetic energy
  - \( V(\rho) \) – potential energy
  - \( \text{Exc}(\rho) \) – exchange-correlation energy - unknown form
    -> describe with parameterized ‘functionals’

- Parameters
  - Vienna Ab Initio Simulation Package (VASP)
  - Plane wave basis set w/400 eV cutoff
  - PAW pseudopotentials to describe atomic cores
  - PBE-GGA exchange-correlation functional
  - 0.25/Å gamma-centered Monkhorst-Pack \( k \)-point mesh

- Bader Method to assign local properties
Hydrogen in Niobium

- The niobium – hydrogen phase diagram is very complex
  - \( \alpha, \alpha' \) – interstitial hydrogen dispersed in bcc niobium
  - \( \beta, \epsilon \) – ordered hydrogen interstitials in fcc niobium
  - \( \delta \) – ordered hydrogen interstitials in fluorite structure
  - \( \lambda, \lambda_c \) – experimentally unconfirmed phases

- What do we have in SRF cavities and how is it affected by processing?

Hydrogen in Niobium Phase Models

\[ \alpha \quad \alpha' \quad \varepsilon \quad \beta \]

Energy difference between phase and isolated interstitial hydrogen (eV)

Unit cell deformation (\(\Delta a/a\))

- Disordered Interstitial H in bcc Nb
- Ordered Interstitial H in bcc Nb
- Epsilon Niobium Hydride
- Beta Niobium Hydride

\[ y = 0.0468x + 0.0024 \quad R^2 = 0.9994 \]

\[ y = 0.0565x - 0.0000 \quad R^2 = 0.9994 \]
Hydrogen in Niobium
How do Phases Form?

- 3 H₂ gas phase
- 6 H in bcc Nb interstices
- move one H into vacancy
- move four H into vacancy
- move six H into vacancy
- formation of β-phase
- formation of ε-phase

Energy (eV)

vacancy formation
Application to SRF Cavities

• Hydrogen in niobium could be a source of Q-slope and Q-disease.
  • Ordered hydride phases suffer from a greatly reduced superconducting $T_c$
  • Does the size of the precipitate matter? Large precipitates -> Q-disease; small precipitates, interstitial hydrogen -> Q-slope?

• Niobium hydride phase modeling showed
  • The driving forces for phase formation are evident in both lattice strain and energetic analyses of the presented models
  • Niobium lattice point defects can serve as nucleation centers for phase formation
Other Impurities in Niobium Oxide Layers

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb – cubic</td>
<td>Cubic</td>
<td>3.3 Å; 90°</td>
</tr>
<tr>
<td>NbO – cubic</td>
<td>Cubic</td>
<td>4.2 Å; 90°</td>
</tr>
<tr>
<td>NbO₂ – tetragonal</td>
<td>Tetragonal</td>
<td>9.7, 9.7, 6.0 Å; 90°</td>
</tr>
<tr>
<td>Nb₂O₅ – monoclinic</td>
<td>Monoclinic</td>
<td>20.7, 3.8, 19.6 Å; 90, 65, 90°</td>
</tr>
</tbody>
</table>

- Thermodynamic ordering of oxide layers on the niobium surface
- Strained and defective interfaces
- Surface layer can be highly defective or amorphous
- Interfaces can be trapping centers for other impurities such as H
Other Impurities in Niobium
Relation to Hydrogen

- Tetrahedral absorption (H)
- Octahedral absorption (C,N,O)
- Increased binding energy
- Reduced lattice strain

Graph showing the relationship between lattice strain energy and binding energy, with specific points for isolated interstitial H and O, interstitial O and H in a vacancy, and interstitial H and O in a vacancy.
Application to SRF Cavities

- The success of the 120 °C bake may be related to the interaction between impurities and lattice defects.

- Suggested mechanism:
  - Hydrogen is liberated from both the ordered hydride phases and the niobium site vacancies
  - Hydrogen diffuses into the niobium bulk
  - Some oxygen diffuses from the oxide phases or niobium interstitial sites and becomes trapped by the niobium vacancies in the near surface region
  - Hydrogen is prevented from returning to those phase nucleation centers
  - Hydrogen may also become trapped by sites in the niobium bulk
Oxygen in Niobium
An Additional Concern

Create a chain of oxygen vacancies (1.4%)
Summary

- **Hydrogen in Niobium**
  - Phase properties and driving forces for phase formation
  - Nucleation of phases by niobium lattice defects
    -> Removal of nucleation sites -> prevention of hydrides

- **Other impurities (O, N, C) in Niobium**
  - Oxide structures
  - Interactions between impurities and the niobium lattice during the 120 °C bake
    -> dissociation/prevention of hydrides
  - Magnetism in defective oxides
Acknowledgments

- Lance Cooley and Superconducting Materials Group members
- David Seidman and group members
- Computing resources at Fermilab
Hydrogen in Niobium
Electron and Phonon States

<table>
<thead>
<tr>
<th>Nb</th>
<th>$E_F$ (eV)</th>
<th>DOS @ $E_F$ (states/eV)</th>
<th>$&lt;\omega&gt;_{log}$ (MeV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>4.78</td>
<td>0.13</td>
<td>28.5</td>
</tr>
<tr>
<td>$\alpha'$</td>
<td>4.73</td>
<td>0.09</td>
<td>42.6</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>4.88</td>
<td>0.03</td>
<td>62.2</td>
</tr>
<tr>
<td>$\beta$</td>
<td>5.24</td>
<td>0.04</td>
<td>69.4</td>
</tr>
</tbody>
</table>

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The highest, lowest, and average charges are shown.

The charge on Nb atoms increases with increasing H concentration.

The charge on the H atoms slightly decreases with increasing H concentration and is the lowest for the ordered phases.

The charges on the Nb and H atoms are ~ constant for the ordered phases and equal and opposite for the beta phase.
Interaction energy and self-trapping energy decrease with increasing H concentration; self-trapping energy is zero for the ordered configurations.

Lattice strain energy increases with increasing H concentration, is \( \sim \) equal for the disordered and ordered hydrogen configurations of the same concentration.