

AB INITIO CALCULATIONS ON IMPURITY DOPED NIOBIUM AND NIOBIUM SURFACES*

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Abstract

We develop and apply new tools to understand Nb surface chemistry and fundamental electronic processes using theoretical *ab initio* methods. We study the thermodynamics of impurities and hydrides in the near-surface region as well as their effect on the surface band gap. This makes it possible for experimentalists to relate changes in STM dI/dV measurements resulting from different preparations to changes in subsurface structure. We also calculate matrix elements for electron-impurity scattering in Nb for common impurities O, N, C, and H. By transforming these matrix elements into a Wannier function basis, we calculate lifetimes for a dense set of states on the Fermi surface and determine the mean free path as a function of impurity density. This technique can be generalized to calculate other scattering amplitudes and timescales relevant to SRF theory.

INTRODUCTION

Density Functional Theory (DFT) is a versatile tool that can be used to calculate an array of interesting properties from electronic structure to activation energies to superconducting parameters. This makes it a very useful complement to experimental research of advanced materials such as those used in SRF cavities. In this paper, we describe some of the insights we have gleaned, and discuss their relevance to the future of Nb SRF [1].

HYDRIDE FORMATION

Hydride formation occurs at cryogenic temperatures of around 100K, at which point interstitial hydrogen in niobium is supersaturated, but still mobile enough to diffuse through microns of niobium to form precipitates. When hydride precipitates form within the RF penetration depth, they contribute to RF losses and Q slope [2]. Some methods to mitigate hydride formation, such as degassing and rapid cooling through the hydride formation "danger zone" are relatively well understood, but in order to further suppress hydride formation it is important to understand hydrides in greater detail.

Hydride crystals can be understood as low-energy periodic arrangements of interstitial H, which result in some lattice expansion and distortion to the bcc niobium. The beta hydride phase, for example, consists of hydrogen chains

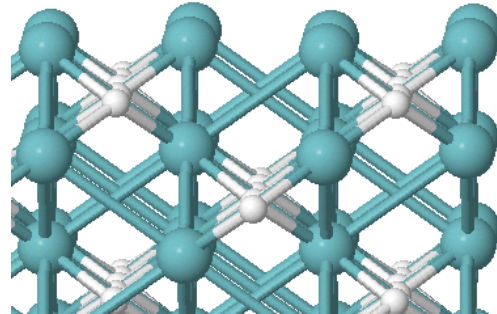


Figure 1: Beta hydride phase viewed along the 110 direction, showing hydride chains (white) within the bcc niobium lattice.

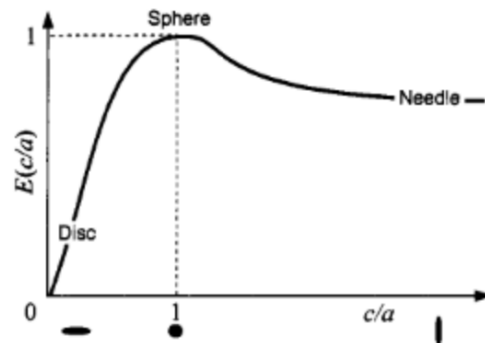


Figure 2: Minimum energy aspect ratio for a critical droplet, as a function of the interface energy to strain energy ratio.

in the 110 direction with an accompanying lattice expansion (Fig. 1) [3]. Because the niobium atoms remain in an approximately bcc arrangement, interface energies with the surrounding bcc niobium is small, and strain energy is the primary factor inhibiting hydride nucleation. One can show that, under these conditions, hydrides will tend to form platelets, which minimize strain energy at the expense of surface area (Fig. 2) [4].

Our calculations show that in the absence of external constraints, it is energetically favorable for interstitial hydrogen to precipitate into a beta hydride crystal, as expected from the experimentally determined phase diagram. We find that an infinite hydride platelet, constrained along the surface parallel directions but free to expand along the surface normal direction, has a smaller magnitude but still significantly negative formation energy. A hydride constrained along all three directions, however, is not an energetically favorable

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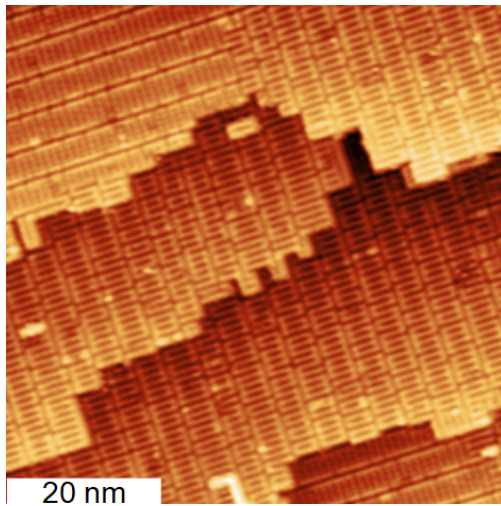


Figure 3: Image showing the atomically ordered "ladder structure" surface that forms on the Nb 100 surface as prepared by the Sibener group.

precipitate, which confirms our understanding that hydrides should tend to form platelets (Table 1).

Table 1: Hydride Formation Energies

Constraints	Formation Energy (eV/H)
Unconstrained	-0.12 eV
2D Constrained (Platelet)	-0.07 eV
3D Constrained	0.16 eV

A hydride platelet of finite diameter can approach the low formation energy of an infinite platelet if it forms on the surface, where it is free to expand along the surface normal. This suggests that the critical droplet size for hydrides is smallest on the surface, where strain energy is minimized. If this is the case, and hydride precipitates preferentially form on the surface, then even a fast cooldown that successfully freezes most interstitial hydrogen into the bulk may result in many nanohydrides at the surface.

HYDRIDE DETECTION

In order to develop methods to minimize the formation of surface nanohydrides, it is important to be able to precisely measure the abundance of nanohydrides in the near-surface area. The Sibener group at the University of Chicago specializes in creating atomically ordered niobium oxide surfaces (Fig. 3), making them perfectly equipped to perform such measurements [5]. They have detected changes in the physical structure of the surface during hydride nucleation by continuously scanning the surface, and they have also performed dI/dV measurements to determine the effect of hydrides on the surface electronic structure.

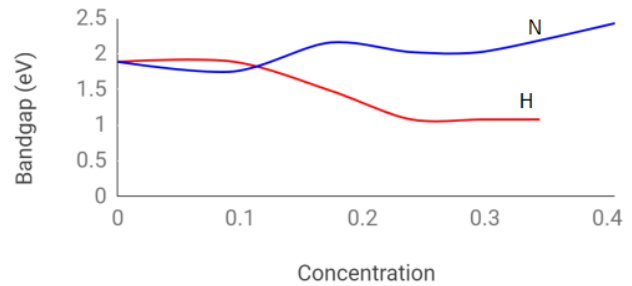


Figure 4: Bandgap as a function of sub-surface hydrogen and nitrogen concentrations.

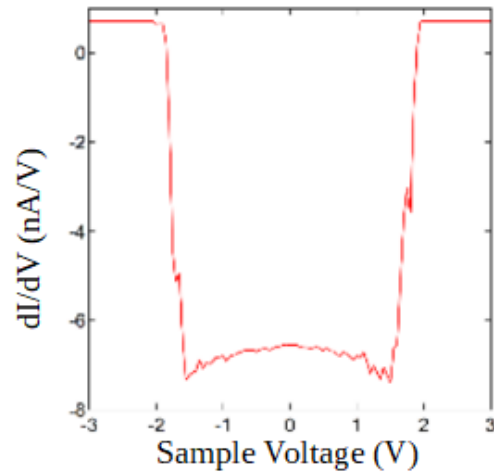


Figure 5: Example dI/dV measurement by the Sibener group.

Because the surface they study has a periodic structure, we have successfully constructed a unit cell of the material and used DFT to calculate the effect of different sub-surface hydrides and hydrogen concentrations on the surface bandgap. We have had some success correlating our calculated changes in surface bandgap (Fig. 4) with their experimentally measured changes in surface bandgap, making it possible to link their observations to the presence of hydride structures that they cannot directly observe. These measurements and calculations are being finalized in preparation for publication.

HYDRIDE MITIGATION

Moving beyond understanding sub-surface hydrides, we next turn to the structure of a hydride-free surface, with a goal of understanding the mechanisms by which various bakes and nitrogen doping procedures can suppress hydride formation and improve cavity performance. To this end, we have begun studying sub-surface nitrogen, relating its concentration to the surface bandgap and studying its energetics in the near-surface region. Our preliminary results show that nitrogen has a different effect than hydrogen on the bandgap (Fig. 4), making it possible to distinguish between hydrogen-rich, nitrogen-rich, and clean surfaces even without a visible change to the surface oxide. The trend we observe with nitrogen doping is also in agreement with preliminary dI/dV measurements by the Sibener group (Fig. 5).

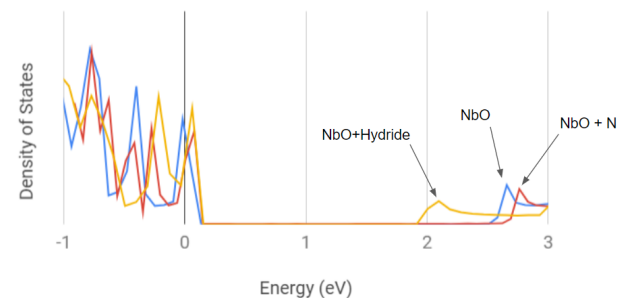


Figure 6: Example density of states calculations for the same monolayer oxide surface with different sub-surface impurities.

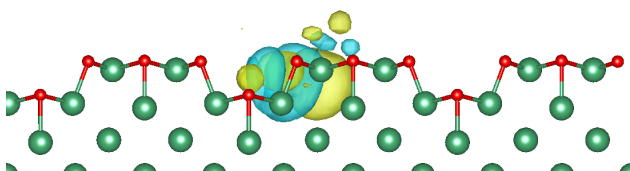


Figure 7: A Wannier orbital on the niobium oxide surface.

A limitation to our bandgap calculations at the moment is the relatively low density of states on the upper end of the bandgap (Fig. 6). This makes small changes in the bandgap difficult to resolve. To overcome this, we are transitioning to a Wannier function approach which describes surface electrons in terms of maximally localized orbitals, making much more precise calculations of the surface electronic structure possible (Fig. 7) [6]. Our calculations on the energy of nitrogen interstitials reveal an energy minimum a few lattice constants from the surface (Fig. 8). This suggests an approximate lengthscale of about 2 nm on which a low-temperature nitrogen infusion might affect the surface.

The introduction of a thin nitrogen-rich layer could have a significant impact on hydride nucleation behavior. It is possible to show that the strain energy of a hydride near the surface increases with the cube of depth (Fig. 9) on a lengthscale related to the thickness of the hydride platelet. Therefore, a nitrogen-rich layer passivated layer that forces nanohydrides to nucleate slightly further from the surface would significantly reduce the energetic advantage of nucleating in this region. Looking forward, we are optimistic that the ability to produce and analyze pristine atomically ordered surfaces in tandem with these computational techniques will make it possible to analyze the effect of other bakes and infusions geared towards creating a thin dirty surface layer with specific beneficial properties.

ELECTRON-IMPURITY SCATTERING CALCULATIONS

In addition to studying niobium surfaces, we also use DFT to study fundamental processes in bulk niobium. In particular, we have calculated elastic mean free path due to scattering with the common impurities O, N, C, and H. To do this, we calculate overlaps of pure niobium electronic

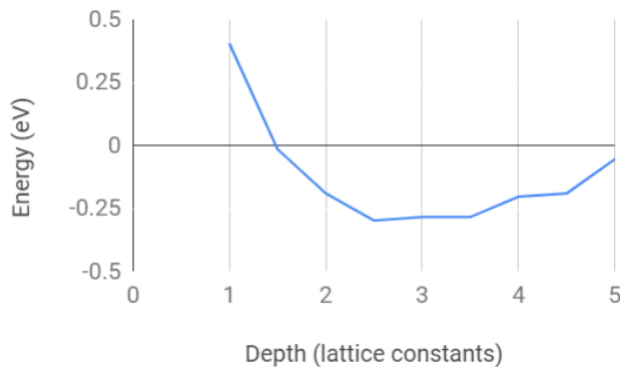


Figure 8: Calculated energy for nitrogen interstitials as a function of depth in lattice constants beneath the surface.

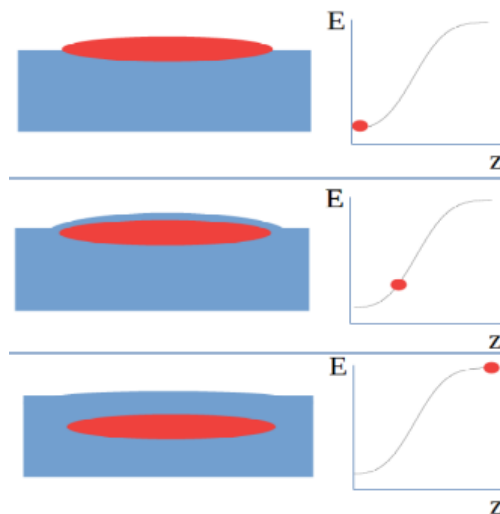


Figure 9: Strain energy of a hydride platelet as a function of depth.

states with the perturbing potential of an impurity in a large supercell. The resulting matrix elements are then recast into a Wannier function basis [6], which makes it possible to calculate scattering processes on a much finer momentum space grid. This fine resolution allows us to obtain the electron scattering amplitude as a smooth function over the Fermi surface, as Fig. 10 illustrates.

Integrating over these amplitudes results in mean free paths (Table 2) in reasonable agreement with those implied by experimental resistance measurements [7].

Table 2: Calculated Electron-impurity Mean Free Paths

Impurity (1 at. %)	Mean Free Path (nm)
Oxygen	28
Nitrogen	34
Carbon	38
Hydrogen	780

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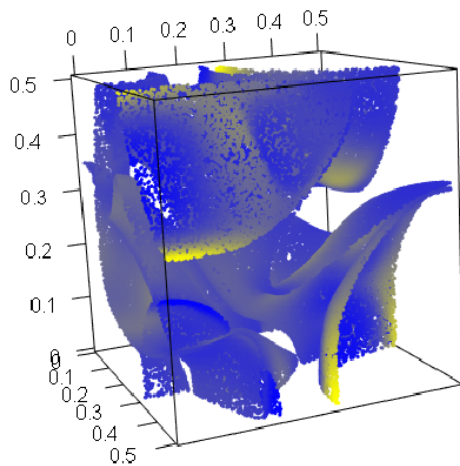


Figure 10: Oxygen impurity scattering amplitudes as a smooth function of crystal momentum k across the Fermi surface. Yellow corresponds to higher amplitudes, while blue corresponds to lower amplitudes.

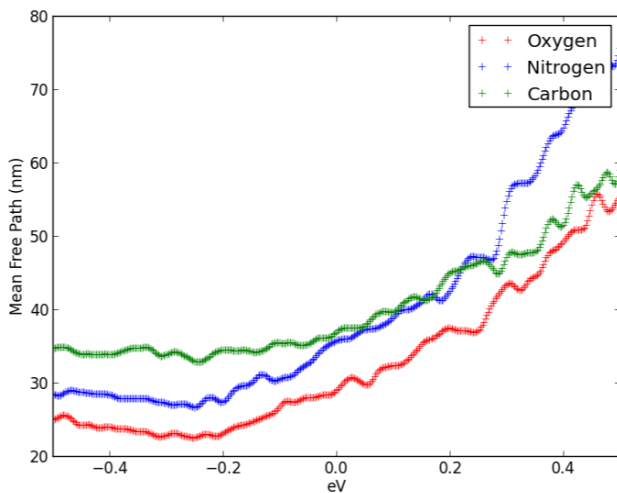


Figure 11: Calculated mean free path as a function of energy in eV near the Fermi level.

We also find a significant dependence of the mean free path on the position of the Fermi level (Fig. 11). This implies that strain and surface effects could indirectly play a role in determining scattering rates.

In the future, these same techniques will enable calculation of scattering amplitudes for other important processes,

including inelastic impurity scattering, an important mechanism in thermal transport. First principles results for inelastic scattering will provide useful input parameters to new theories attempting to explain important SRF phenomena such as the anti-Q slope.

CONCLUSIONS

We have demonstrated the fruitful application of DFT to open problems in Nb SRF related to hydride formation and electron-impurity interactions. By improving our understanding of the fundamental physics at work, these results and future *ab initio* calculations will help develop new recipes to maximize cavity Q and quench field.

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