



Electronic structure calculations of substitutional and interstitial hydrogen in Nb

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ABSTRACT

We report the results of a theoretical study on the effects of substitutional and interstitial hydrogen atoms in niobium. We confirm that any contaminated hydrogen will occupy the interstitial site over the substitutional site in niobium. For interstitial hydrogens, the lattice deformation increases with the percentage content of hydrogen, though it is negligible at low concentrations. Substitutional hydrogens are found to prefer off-center sites in the host lattice.

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1. Introduction

The properties of hydrogen–metal systems have gained much attention in the areas of hydrogen storage, fuel cells, and hydrogen embrittlement [1]. Hydrogen in metals could serve as a model problem for theoretical investigations of more complicated systems. Niobium containing alloys have been extensively used in pressure tubes of CANDU, high performance nuclear fuel cladding, the ITER divertor, and ultra-high temperature materials [2] because of their excellent mechanical properties, high corrosion resistance, high melting point, and small neutron absorption cross section. Hydrogen is generated by corrosion processes in the environments to be used, and some of the hydrogen is absorbed into these alloys. The properties of H-group-V bcc transition metals have been studied extensively, both experimentally and theoretically. In the dilute phase, dissolved hydrogen prefers to occupy tetrahedral sites in the lattice. Hydrogen diffuses rapidly in these materials and retains a high mobility. The change of the activation energy is measured to be 250 K for hydrogen diffusion in Nb [3] and is due to incoherent tunneling between hydrogen ground states localized on neighboring sites [4,5]. Hydrogen in bcc hosts has previously been investigated theoretically [6].

Many recent fourth generation light source programs, such as X-FEL (in DESY, Germany), ERL projects (in USA, UK and Japan) and the proposed International Linear Collider (ILC) have spurred interest in the developments of high performance superconducting radio frequency (SC-RF) cavities. Amongst various superconducting materials, bulk Niobium (Nb) has been the material of choice

for the fabrication of such SCRF cavities. Large sections of such Nb-SCRF cavities [7] are being used in storage rings. In the recent past, there have been surprises when pure Nb-SCRF cavities showed degradations in Q values when kept at 100 K for a long period. This phenomenon is due to hydride precipitation phases in Nb. Degassing of hydrogen at an elevated temperature can eliminate deterioration in cavity but the problem of hydrogen in Nb-SCRF cavities is well known [8,9].

The microscopic super-conducting properties in the Nb sample get changed by absorbing various amounts of hydrogen in a controlled manner. With increasing hydrogen content, flux penetration patterns in NbH_x thin films are observed to become more irregular [10]. It has been known for a long time that hydrogen strongly interacts with open volume defects in a host metallic lattice [11]. Recently, it has been shown that in addition to trapping of hydrogen in existing defects, more complex and new defects can be formed by H-loading [12,13]. However, the nature of defects due to hydrogen continues to elude us. In this paper we study the effects of H impurity in Nb and study the structural deformation. We also investigate the site selectivity of H. In the following section (Section 2), we describe in brief the computational details, which are followed by the discussion of our results in Section 3. In Section 4, conclusions are presented.

2. Computational details

First principle calculations were performed using the density functional theory [14] within the generalized gradient approximation [15,16] as implemented in the Vienna ab initio simulation package (VASP) [17–20]. We have used projector augmented wave (PAW) method [21,22] with GGA given by Perdew et al. [23,24] for

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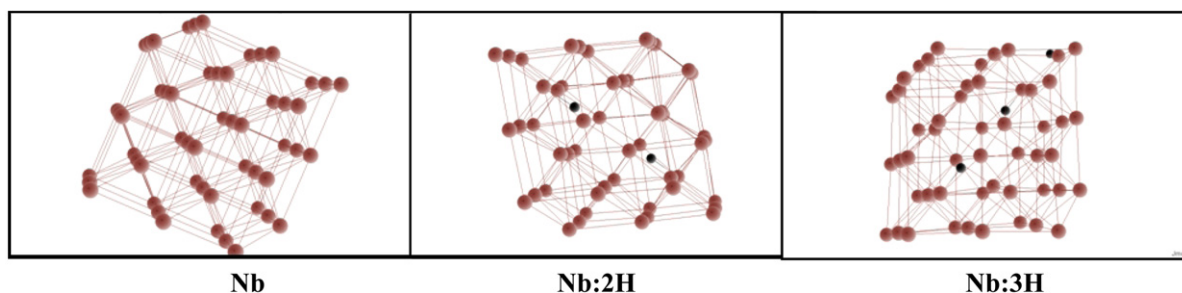


Fig. 1. The structural configurations of Nb and doped Nb with substitutional hydrogens (Hs). (Grey: Nb, blue: substitutional H). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

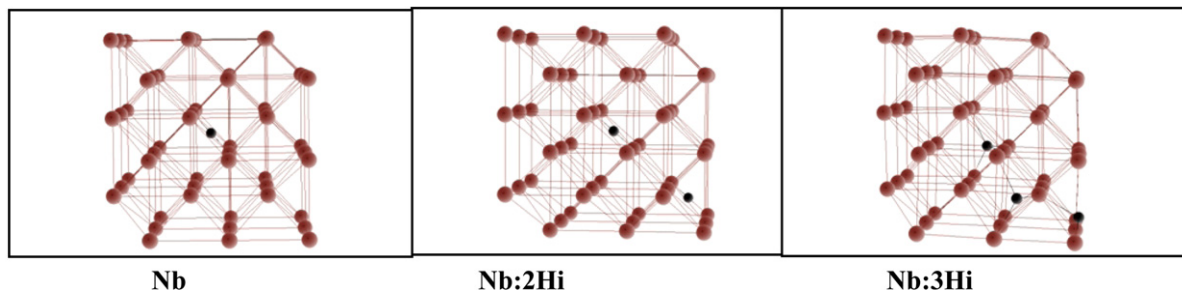


Fig. 2. The structural configurations of Nb and doped Nb with interstitial hydrogens (Hi). (Grey: Nb, blue: substitutional H). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the exchange–correlation functionals. In the course of both the cell parameters and atomic positions optimization, the k -space integration were carried out using the method of Methfessel and Paxton in the first order, with employed smearing width of 0.01 eV.

We constructed a 54 atom super-cell using the experimental value of 3.3 Å for the lattice parameter of Nb. Numerical integration of the Brillouin Zone (BZ) was performed using $7 \times 7 \times 7$ Monkhorst–Pack k -point sampling, and the plane-wave cut off energy was 175 eV. The lattice was allowed to relax in the process of reaching self consistency. Substitutional hydrogen impurities were studied by replacing a niobium by hydrogen at the niobium site and the initial interstitial hydrogen were randomly introduced in the lattice.

3. Results

Fig. 1 shows the optimized structure for the Nb lattice with the calculated bond length ($R_{\text{Nb-Nb}}$) of 3.23 Å, as compared to the experimental value of 3.3 Å. When hydrogen is substituted at the niobium site, the near-neighbor distance, $R_{\text{Nb-H}}$ is 3.19 Å and that between the host atoms, $R_{\text{Nb-Nb}}$ is 3.23 Å. No change in $R_{\text{Nb-Nb}}$ is expected due to hydrogen substitution owing to the smaller size of hydrogen. When we add another H at the substitutional site in the lattice (Fig. 1), we see that the hydrogen atoms move away from the center towards the niobium atoms owing to greater electrostatic attraction. $R_{\text{H-H}}$ is 5.17 Å. The distance between the hydrogen and nearest niobium atom is reduced to 1.97 Å. $R_{\text{Nb-Nb}}$ in the neighborhood of the substitutional hydrogen are 2.8 Å and 3.1 Å, respectively.

We now focus on three niobium sites substituted by hydrogen atoms. Energetically, it is very unlikely that the third H would prefer to occupy the lattice site near the other two hydrogen atoms. Therefore, we let two hydrogen atoms stay close and then let the third one occupy a distant site as depicted in Fig. 1. The optimized geometry in Fig. 4b shows that the distance between the two neighboring hydrogen atoms are now 4.86 Å. The distance between hydrogen and its nearest niobium atom is 1.95 Å and the distance between the same niobium and the 3rd hydrogen atom is 3.54 Å and 3.87 Å. $R_{\text{Nb-Nb}}$ distances are 2.96, 3.16 and

3.24 Å respectively, depending on their proximity to the hydrogen atoms.

Fig. 2 shows the structural configurations considered for the interstitial hydrogen atoms in Nb. Owing to the small size of H, no deformation of the host lattice is predicted for very small quantities of interstitial H. $R_{\text{Nb-H}}$ is calculated to be 1.43 Å. Two interstitial hydrogen atoms are found at two different distances from the neighboring niobium atoms. The hydrogen closer to the center of the cluster is at 1.43 Å and the one closer to the outer side is 1.54 Å from its neighboring niobium atoms. $R_{\text{Nb-Nb}}$ closer to the hydrogen atoms is 2.86 Å and the ones further away are at 3.3 Å as depicted in Fig. 2. The optimized configuration as depicted in Fig. 2 shows that the third H does not occupy a symmetric position due to the presence of other hydrogen atoms. The hydrogen has bond distances of 1.88, 1.98, 1.9 Å with its nearest niobium atoms. $R_{\text{Nb-Nb}}$ close to the hydrogen atoms are 2.83 Å. As we move away from the H interstitial $R_{\text{Nb-Nb}}$ increases to 3.24 and then to 3.27 Å, respectively.

To understand the effect of both substitutional and interstitial H on the electronic properties of the host Nb lattice, we plot total density of states in Fig. 3. In the host lattice, the contribution to the top of the valence band is mainly from the d states of Nb. The d states appear between -3 to 0.5 eV. A large peak appears at -1.5 eV and a second major peak appears in the valence band at -2.5 eV. There seems to be overlap between the p states and d states around the Fermi energy. For singly substituted H, Nb s-states hybridize with H s-states between -6 and -5 eV in the valence band. The multiple bands between -5 eV and the Fermi energy is predominantly Nb s states whereas the conduction bands above the Fermi energy are predominantly associated with Nb d-states. On the other hand, the Nb d-states are pulled down into the valence band for the doped Nb with interstitial H, though the H s states continue to reside near -6 eV in the valence band. There are two major peaks: one at -1.4 eV and the other at -0.5 eV. Both these peaks have major contributions from Nb d- and p-states. The effect of additional H does not change the nature of density of states; Nb p–d hybridization continues to persist near the Fermi energy but reduces in the valence band. The s–p hybridization

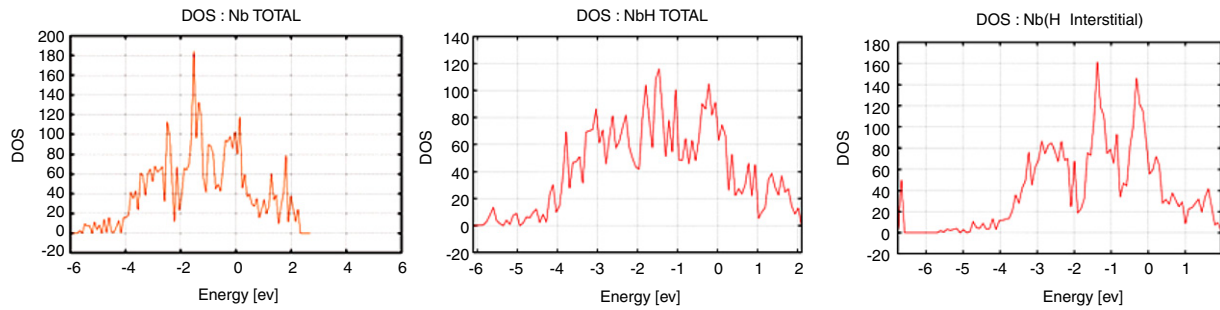


Fig. 3. Total density of states for Nb, doped Nb with substitutional (Hs) and interstitial hydrogen (Hi).

above the Fermi energy is stronger in the substitutional than in the interstitial case for Nb:2H.

Total energies of the optimized configurations find that hydrogen occupancy at the interstitial site is energetically favored. The difference in energy increases sharply from 7.87 eV to 8.27 eV to 9.65 eV, respectively as we compare the energy difference between the single, double and triple interstitial hydrogen with their corresponding substitutional configurations.

The quantity of hydrogen found in various metals is known to be a function of temperature and pressure [25]. Experimentally [26] it has been inferred that hydrogen exists in the metal as individually dissolved atoms located in interstitial lattice positions. In the case of the palladium hydrogen system these positions have been identified as octahedral interstitial positions of the face centered cubic lattice from neutron scattering [27] and channeling [28] experimental measurements. Our calculations confirm that H occupies the interstitial site over the substitutional site as seen in experiments. It has been reported that in Nb, randomly distributed hydrogen atoms expand the Nb lattice and retains most of Nb's cubic symmetry [29]. As the concentration of hydrogen increases, the lattice is orthorhombically distorted. Our calculations reveal little distortion of the lattice for low concentration of H impurity. The deformation increases for higher concentration of H and is in consistent with experimental results.

4. Summary

We have reported the electronic structure of niobium and the effects of substitutional and interstitial hydrogen atoms in niobium in terms of the structural parameters, energetics and density of states. It is evident that low concentration of interstitial hydrogen barely impacts the host lattice. The deformation increases with the percentage of hydrogen content, as expected. For substitutional hydrogen, other theoretical calculations [18] performed indicate that a hydrogen atom trapped at the niobium vacancy site is located off-center. In the future, we would like to study hydrogen clustering and the impact of vacancy-interstitial effects on the host lattice.

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