

THE INTERACTION AMONG INTERSTITIAL C/N/O/H AND VACANCY IN NIOBIUM VIA FIRST-PRINCIPLES CALCULATION

Hantian Liu, Zhitao Yang, Jiankui Hao[†], State Key Laboratory of Nuclear Physics and Technology
& Institute of Heavy Ion Physics, Peking University, Beijing, China

Abstract

We calculate the interaction among zero dimensional defects in niobium lattice through first-principles calculation. And we compare the trapping effect of hydrogen among carbon, nitrogen, and oxygen as well as the trapping effect of interstitial atoms by vacancy. We find that the interstitial C/N/O have similar effect of trapping interstitial hydrogen in niobium lattice, and the vacancy can trap interstitial C/N/O/H in adjacent protocells and strengthen their chemical bond with Nb. These calculations give some explanation for improving superconducting performance of niobium cavities through medium temperature baking.

INTRODUCTION

In bulk niobium, hydrogen is an active light impurity element that are highly diffusive in baking processes [1]. Insulating at room temperature, niobium hydride behaves as superconductor in bulk niobium below the critical temperature (1-2 K [2, 3]) owing to proximity effect. As SRF cavities are cooled down to liquid helium temperature during operations, niobium hydride form clusters of various sizes. Hundred-nanometer-scaled niobium hydride clusters are considered responsible for low field Q-slope in niobium cavities, while nanometer-scaled hydride clusters are the speculated causes of high field Q-slopes [4]. To reduce the precipitation of niobium hydrides during the cooling process of niobium cavities, various surface treatment methods, such as nitrogen doping [5, 6] and medium temperature baking [5, 6], have been employed. While the mechanisms of such treatments are not yet fully understood, it is speculated that the distribution of defects in niobium bulks may be altered owing to thermal effect and interactions among defects. Based on experiments and simulations, some existing works have demonstrated that both interstitial nitrogen [7, 8] and oxygen [9, 10] atoms trap interstitial hydrogen atoms and suppress the formation of niobium hydride clusters, while vacancies are able to trap the three kinds of interstitial atoms and regulate the superconducting properties of bulk niobium [11, 12]. It is also assumed that interstitial carbon atoms may trap interstitial hydrogen atoms [9]. In this work, we carry out first-principles calculations to better understand the interaction among interstitial carbon, vacancy, and hydrogen.

METHOD

Calculations are conducted in a supercell that consists of $3 \times 3 \times 3$ body-centered cubic (bcc) niobium cells.

Considered as zero-dimensional defects, interstitial atoms and vacancies are introduced into the supercell sequentially. We first introduce a single interstitial carbon atom or vacancy (by simply removing a niobium atom) and conduct geometry optimization [13] to relax the crystal. The interstitial carbon is located at an octahedral point as initial configuration, which was reported to be the lowest energy position for interstitial nitrogen and oxygen [10]. After the convergence of geometry optimization, we redefine the unit cell to put the defect at center (which does not alter any physical property of the crystal) and then introduce an interstitial hydrogen atom.

For hydrogen atom, two types of calculations are conducted, namely stable point energy calculation and two-dimension energy distribution calculation. For stable point energy calculation, hydrogen atoms are first placed at different points as initial configuration. Then, geometry optimizations are conducted with no constraint to relax the entire lattice. It is found that after relaxation, the introduction of the hydrogen atom causes displacements of other atoms by no more than 0.02 Å. The global lowest-energy configuration is found. Furthermore, we calculated the electron density difference and partial density of states (PDOS) of the lowest energy configuration to study the bonding between atoms. For two-dimension energy distribution calculation, the key idea is to ignore the displacement of niobium atoms and other impurity atoms caused by the introduction of the hydrogen atom at unstable points, which is inspired by the result of stable point geometry optimization. A hydrogen atom is placed at different points (not necessarily stable points) on a plane sized 9.9018×9.9018 Å in (0 0 1) direction.

Utilizing CASTEP module [14] of Materials Studio 2020, all first-principles calculations in this work are based on density function theory (DFT) [15, 16]. Perdew-Burke-Ernzerhof (PBE) functional under Generalized Gradient Approximation (GGA) [17] is used to estimate the exchange-correlation interaction. For high accuracy, norm-conserving pseudopotential is used. The cut-off energy of the plane wave basis set is set to 440 eV. For self-consistent field (SCF) calculations, the SCF tolerance is set to 5.0×10^{-7} eV/atom. Geometry optimization accuracy is set to ‘ultra-fine’ setup, the most accurate set of preset convergence parameters. To be specific, the energy tolerance is set to 5.0×10^{-6} eV/atom, atom force tolerance 0.01 eV/Å, maximum pressure 0.02 GPa, and single atom displacement 5.0×10^{-4} Å. To compare the C-H interaction with the O-H and N-H interaction, the carbon atom with interstitial nitrogen and oxygen atoms in the same niobium lattice configuration undergoes the same calculation procedure. In this work, carbon, nitrogen, and oxygen atoms are referred to as ‘heavy impurity atoms’ for being

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[†] jkhao@pku.edu.cn

significantly heavier than hydrogen atoms.

RESULT

We calculate the interaction between C/N/O and H, and the interaction between C/N/O/H and vacancy respectively. In this section, we will introduce the 2D system energy distribution and electron density distribution in real space, as well as the electron density of states in various niobium lattice configurations.

C/N/O-H Interactions

The results of 2D energy distribution with and without center impurity atom are presented in Fig. 1. The light blue 3D spheres represent niobium atoms, impurity atoms, namely carbon (3D gray sphere), nitrogen (3D blue sphere), and oxygen (3D red sphere), are placed at the center respectively. The 2D dots are colored by the system free energy when one hydrogen atom is located at that position. The blue end of the color scale is set to the minimum free energy E_{\min} of the system, and the red end is set to $E_{\min} + 15$ eV. Lowest-energy positions of hydrogen atoms are marked with green-cored blue dots.

Without center impurities, the lowest-energy positions of the hydrogen atom are the tetrahedral sites, 36 of which are on the plane, as shown in Fig. 1 (a). When center impurity atoms are introduced, regardless of its element, the translation symmetry of the system is broken. In such cases, the lowest-energy hydrogen positions are tetrahedral sites in the second-nearest-neighborhood prime cell of the center impurity atoms. There are 24 such sites in a supercell, 8 of which are in the 2D plane, as shown in Fig. 1(b) (c) and (d).

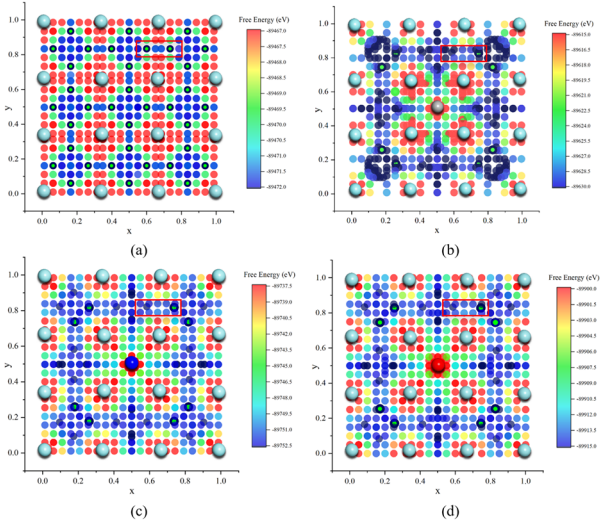


Figure 1: The 2D system energy distribution of when hydrogen distributed as various positions with no center impurity atom (a), single carbon (b), single nitrogen (c) and single oxygen (d).

Figure 2 shows the electron density distribution difference on a 2D slice in niobium lattices with different impurity configuration. Impurity atoms tend to attract electrons and form bonds with neighbouring niobium atoms. Qualitatively, C-Nb, N-Nb, and O-Nb bonds share

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similar structures. These bonds are also significantly stronger than H-Nb bonds. Bonding significantly lowers the energy and immobilizes interstitial atoms at high symmetry sites.

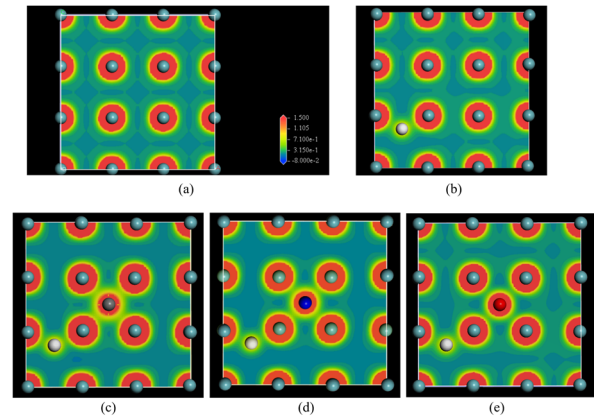


Figure 2: the 2D electron density distribution of various lowest energy niobium lattice configurations: (a) pure niobium (3D light blue atoms), (b) niobium lattice with one hydrogen atom (3D white sphere), (c) niobium lattice with one carbon atom (3D gray sphere) and one hydrogen atom, (d) niobium lattice with one nitrogen atom (3D blue sphere) and one hydrogen atom, (e) niobium lattice with one oxygen atom (3D red sphere) and one hydrogen atom.

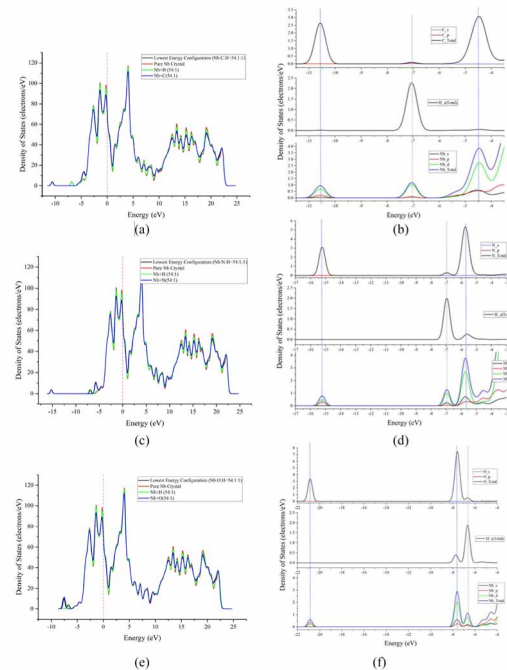


Figure 3: Global density of states and partial density of states (PDOS) by element and orbital in different doping configurations. (a) and (b) show the C-H-doped system, (c) and (d) show the N-H-doped system, (e) and (f) show the O-H-doped system.

To better understand bonding in the systems, partial density of states (PDOS) is calculated. The results are shown in Fig. 3, and the corresponding parameters in Table 1. We could obtain the knowledge as below:

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1. Low concentration doping of all interstitial atoms involved in this work (H, C, N, and O) has no significant influence on the DOS on the Fermi surface ($E=0$).
2. In energy region $-21 \sim -3$ eV, multiple new peaks shared by neighbouring atoms are found in systems with interstitial atoms, confirming the bonding between such atoms. For example, niobium and hydrogen atoms share the DOS peak at -7 eV, representing Nb-H bonds.
3. Heavy impurities (C, N, O) and niobium atoms form two types of bonds, as represented by two shared DOS peaks with different energy. The group of bonds with higher energy (further below the Fermi surface) mostly consists of s orbital electrons of C/N/O and p orbital electrons of the 4 second-nearest-neighbour niobium atoms. Such bonds have larger peak areas. The group of bonds with lower energy, or closer to the Fermi surface, mostly consists of electrons of p orbital electrons of C/N/O and d orbital electrons of the 2 nearest-neighbour niobium atoms. Such bonds have smaller peak areas.
4. The global lowest-energy positions of hydrogen atoms are in proximity to heavy impurity atoms. However, no bonding is observed between impurity atoms.

C/N/O/H-Vacancy Interactions

Similar to the previous calculation procedure, we further studied the interactions between vacancy (V) and interstitial atoms. We first removed the niobium atom at the center of the cell to introduce a vacancy, and then doped the system with an impurity atom (H, C, N, and O). Through geometry optimization and 2D energy distribution calculation, we find the most stable structure of a vacancy coexisting with one impurity atom in $3 \times 3 \times 3$ niobium supercells. The 2D energy distribution of impurities are shown in Fig. 4. The vacancy is placed at the center of the 2D plane, and one impurity atom is placed at different points on the plane.

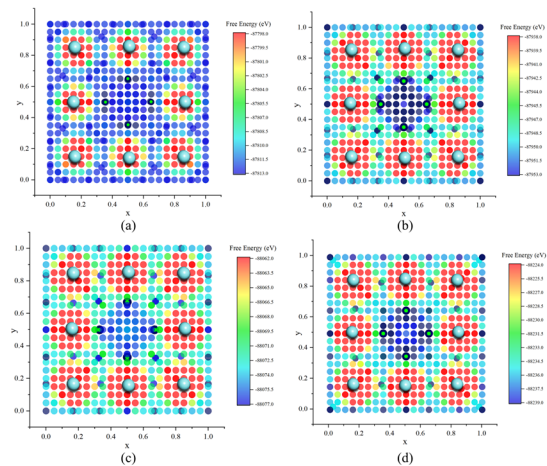


Figure 4: the 2D impurity atom energy distribution in niobium lattice with a center vacancy and one interstitial atom: (a) hydrogen, (b) carbon, (c) nitrogen, (d) oxygen. The light blue 3D spheres are niobium, and the 2D circles with color scale are impurities atoms. Dark blue circles with green heart represent the lowest energy positions in stable configurations.

As Fig. 4 shows, putting an impurity atom (H, C, N, or O) at the position of the missing niobium atom does not result in a stable structure. The 6 nearest-neighbour octahedral sites (4 of which are on the 2D plane) of the vacancy, on the other hand, are the global lowest energy site of C, N, O, and H impurity atoms studied in this work.

Based on the lowest energy configuration of Nb-V-C/Nb-V-N/Nb-V-O, we add one hydrogen atom into the supercell and search for the lowest energy position. Through geometry optimization and energy calculation (results shown in Fig. 5), the lowest energy configurations are found. The crystal structure and electron density difference of the lowest energy configurations are shown in Fig. 6.

Table 1: Peak Searching Calculation Results of States of Density in Niobium Lattice with Interstitial Atoms

System	Element	Peak 1		Peak 2		Peak 3	
		Center(eV)	Area (e)	Center(eV)	Area(e)	Center(eV)	Area(e)
C+H+Nb	C	-10.576	1.295	-	-	-4.480	2.186
	H	-	-	-7.063	1.097	-	-
	Nb	-10.577	0.482	-7.063	0.608	-4.465	2.153(?)
N+H+Nb	N	-15.240	1.589	-6.960	0.149	-5.739	6.035
	H	-	-	-6.966	1.026	-5.613	0.265
	Nb	-15.240	0.402	-6.960	0.657	-5.729	2.547
O+H+Nb	O	-20.858	1.666	-7.695	4.100	-6.662	0.214
	H	-	-	-7.732	0.183	-6.667	0.944
	Nb	-20.274	0.308	-7.608	1.636	-6.667-	0.669

* Note that the question marks “?” refer to the condition that the peak baseline cannot be deducted properly, which may result in inaccuracy of the integral area, same as Table 2.

Table 2: Peak Searching Calculation Results of States of Density in Niobium Lattice with Vacancy and Interstitial Atoms

System	Element	Peak 1		Peak 2		Peak 3		Peak 4	
		Center (eV)	Area (e)	Center (eV)	Area (e)	Center (eV)	Area (e)	Center (eV)	Area (e)
C+H+V +Nb	C	-10.892	1.383			-4.022	2.890		
	H	-	-	-7.536	1.120				
	Nb	-10.892	0.513	-7.536	0.581	?	?		
N+H+V +Nb	N	-14.678	1.616			-5.334	2.463	-4.671	3.732
	H			-6.081	0.893			-4.524	1.052
	Nb	-14.678	0.415	-6.071	0.544	-5.334	1.819	-4.608	1.238
O+H+V +Nb	O	-19.981	1.759	-6.724	3.749			-5.661	2.354
	H					-6.440	0.424	-5.619	1.521
	Nb	-19.981	0.277	-6.703	1.678	?	?	-5.640	0.734

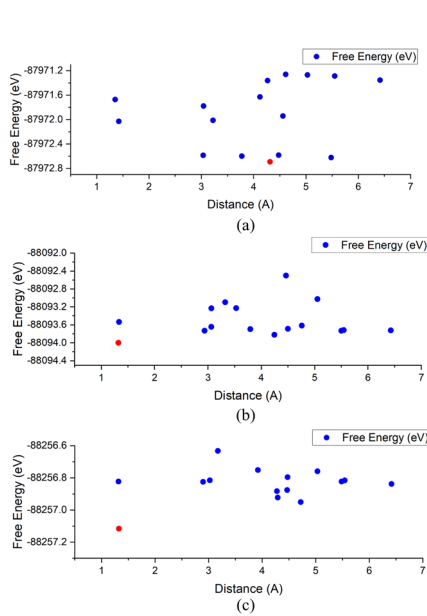


Figure 5: the distance between hydrogen and vacancy in stable configurations of (a) Nb-C, (b) Nb-N, (c) Nb-O. the red points represent the situation of the lowest energy, while the blue points represent other situations.

In the lowest energy structure of Nb-V-C-H (Fig. 6(a) and 6(c)), hydrogen locates at a tetrahedral site near the vacancy, similarly to the situation without vacancy. While in the lowest energy structure Nb-V-N-H (Fig. 6(b) and 6(d)) and Nb-V-O-H (Fig. 6(b) and Fig. 6(e)), hydrogen locates at the octahedral site near the vacancy. We further conducted PDOS calculation to better understand bonding properties.

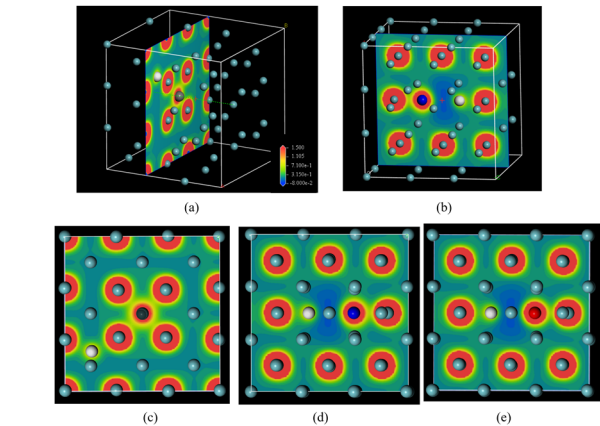


Figure 6: The 2D electron density distribution of various lowest energy niobium lattice configurations: (a) shows the lowest energy structure of Nb-V-C-H, and (b) shows the lowest energy structure of Nb-V-N/O-H. Red crosses represent vacancy, and atoms are represented by 3D spheres in different colors (H: white, C: gray, N: deep blue, O: red, Nb: light blue). (c), (d), and (e) shows the electron density difference distribution on a 2D slice of Nb-V-C-H, Nb-V-N-H, and Nb-V-O-H respectively.

According to the density of states in Fig. 7 and the corresponding parameters in Table 2, there is a bond between interstitial carbon and niobium atoms, represented by the shared DOS peak at -10.892 eV. There is also a new peak in the DOS of carbon atom at -4.022 eV, where the peak of niobium DOS is not that apparent. One possible explanation may be that the high DOS background at that energy region makes the peak unobservable.

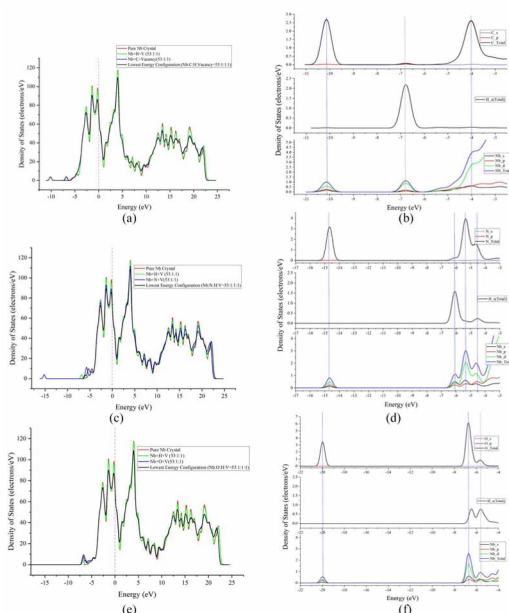


Figure 7: Global states of density and bond states of density by element and orbital in various niobium lattice configuration with vacancy. (a) and (b) show the situation with interstitial carbon and hydrogen. (c) and (d) give the situation with interstitial nitrogen and hydrogen. (e) and (f) present the situation with interstitial oxygen and hydrogen.

As for the situations of nitrogen and oxygen, there are 3 shared peaks between N/O atoms and Nb atoms, corresponding to 3 kinds of bonds. The absent Nb contributed to bonding with N/O before being removed, and a new shared peak emerged near the fermi face after being removed, implying the formation of a new bond due to the introduction of vacancy. We postulate that there is a double bond between N/O and Nb.

Hereby we summarize the conclusions about the interaction between vacancy and interstitial atoms:

1. The introduction of vacancy traps interstitial atoms at the global lowest energy positions adjacent to its position.
2. In the lowest energy structure, niobium atoms form bonds with impurity atoms close to the vacancies, but in different bonding manners from the lattice configuration without vacancies.

CONCLUSION

We study the interaction among interstitial C/N/O (heavy impurities) atoms, H atoms, and vacancy in niobium bulk utilizing first-principles calculation based on density functional theory. In terms of trapping interstitial H atoms to their neighborhood, interstitial C, N, and O atoms exhibit similar behaviors: the global lowest energy positions of H atoms are the tetrahedral sites second nearest to the interstitial heavy impurity atoms. Vacancies, on the other hand, tend to trap all interstitial C/N/O/H atoms to its nearest neighbour octahedral sites.

In other words, during medium temperature baking,

interstitial C and O atoms could serve as mild trapping sites for H atoms similarly to artificially doped N atoms. On the one hand, uniform doping of heavy impurity atoms at low concentration may compete with the self-trapping of hydrogen atoms, reduce the formation of hydrogen clusters and the precipitation of hydrides, and improve the superconducting performance of niobium cavities. Vacancies, on the other hand, exhibit significant trapping effect to all im-purity atoms, which is too strong that may result in the formation of impurity clusters and in turn jeopardize the suppression of hydride precipitation. To achieve better superconducting performance, it is important to reduce vacancies with proper baking recipes such as medium temperature baking.

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