

Pressure effects on the absorption of α -phase Nb-H system

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An *ab initio* calculation is performed on the α -phase Nb-H system with the hydrogen concentrated to 1/16 based on density functional theory, to investigate the pressure effects on the geometry, electronic structure and optical properties. The results show structural phase changes from triclinic, monoclinic to orthorhombic symmetry with the increasing of pressure from 0GPa to 200GPa. A low-lying band hybridized by 1s of H with 4d, 5s of the first four neighbored Nb and s-, p-, d-states of the second ones is observed, which is separated from the metallic valence bands. The electronic structure is strongly pressure dependent in two aspects: when the pressure increases, the low-lying band is distorted and covers larger energy area, the 4d-states of Nb move downward relatively to its 4s-states; the total density of s-states is more intensive than that of p-states around the Fermi level. The absorption spectra is drastically intensified by external pressure.

1 Introduction

The study of hydrogen solution in metal and metal hydrides is an important area in basic theoretical understanding of materials as well as in technological applications (Alefeld and Völkl, 1978, p1). Among metal-hydrogen systems, group VB metals V, Nb and Ta played important roles in the past decades due mainly to the self-trapping and high mobility of H in the host metal lattices (Kehr, 1978, p197). While the electronic structure and basic properties of metal hydrides MH (M=V, Nb, Ta) and low concentrated hydrogen-metal alloys MH_x have been extensively studied under ambient conditions, the pressure effects on the MH_x system remain unclear. This work presents the pressure dependence of the geometry, electronic structure and optical absorption spectra of an α -phased Nb₁₆+H model.

Three different structures of NbH_x were suggested depending on the hydrogen concentration x (Hauck, 1976, p208). Basically, hydrogen atoms occupy tetrahedral sites in bulk Nb as interstitials, causing slight host lattice distortion when $x \leq 1$. For $x \sim 1$, β or γ monohydride is formed (Hauck, 1976, p208), but the related band structure calculations show poor agreement with experimental results of the low-lying band induced by hydrogen in either β or γ phase (Ho et al, 1984, p1586; Tao et al, 1986, p8394), so the phase of NbH is still under dispute. A fluorite structure of dihydride NbH₂ was supported by both theoretical and experimental results. In case $x \ll 1$, NbH_x system is proved to favor α -phase where the hydrogen atoms randomly distribute onto interstices in Nb lattice, occupying tetrahedral sites (T-wells), each formed by four Nb atoms.

The electronic structure of niobium hydrides were calculated previously in order to interpret the experimental observed phenomena in Nb-H systems (Gupta and Chatterjee, 1982, p1923; Gupta, 1982, p1027; Ho et al, 1984; Smithson et al, 2002, p144107-2). Ho et al (1984) applied first-principles method to investigate the H-Nb interactions and the electronic structure of NbH. Tao et al (1986) studied its anharmonic vibration modes. Gupta and Chatterjee (1982) calculated the electronic energy bands of transition metal dihydrides VH₂ and NbH₂. Their results were utilised to calculate the optical absorption spectra. In all the works on NbH and NbH₂ the low-lying bands induced by the hydrogen were found. The low-lying bands were interpreted by the hybridization of s-states of H and d-states of Nb. The low-lying band splitting in NbH₂ was explained to be the s-s antibonding of neighbored hydrogen atoms by Gupta (1982). But the electronic structure of NbH does not well agree with the experimental photoemission energy distribution data, especially in the low-lying valence band that is most important in H-Nb, H-H and Nb-Nb interactions.

Although we have known much about niobium hydrides, the interactions in low hydrogen concentrated Nb-H system has not been thoroughly resolved. In order to understand deeply into the behavior of hydrogen atoms in metal, it is of great importance to study the basic

properties, such as the geometry, electronic structure, dielectric response and the pressure effects.

In the present work, we construct a periodic cell of α -phased 16Nb+H to simulate dilute hydrogen in Nb metal. By applying first-principles method, the properties are investigated under pressures up to 200GPa. The equilibrium geometry of the system is more complicated than NbH is, and changes towards orthorhombic structure when the pressure increases. The transition from clinic to orthorhombic occurs at about 120GPa. The structural transition and the contract of the cell cause drastic distortion in metallic valence band structure, the low-lying H-Nb hybridization band and the composition of the density of states (DOS) near the Fermi level, which in turn affect the absorption spectra. The rest of the paper is organized as follows: in Sec. 2, the model and method used in the present work are described; in Sec. 3, the results of structure, electronic structure and optical properties are discussed; finally the conclusions are summarized in section 4.

2 Model and method

The periodic supercell consists of 16 Nb atoms and an interstitial H atom, as shown in Fig. 1. All Nb atoms are initially arranged at perfect body-centered cubic sites, while the hydrogen occupies a tetrahedral site formed by four niobium atoms. The host lattice parameter is 3.3006 Angstroms, equals to the experimental value of pure Nb. The supercell is made P_1 symmetry in order to make all lattice parameters (a , b , c and α , β , γ) and internal geometry (atom coordinates) variable. The electronic structure of the system is calculated using the HSC type norm-conserving pseudopotential (Hamann et al, 1979, p1494) and generalized-gradient approximation (GGA) of PBE (Perdew et al, 1996, p3865). The quasi-Newton geometry-optimization scheme of BFGS (Fischer and Almlof, 1992, p9768) is used to handle out the equilibrium states of the system under pressures from 0GPa to 200GPa. A kinetic cutoff energy of 600eV and 4X4X4 Monkhorst-Pack k-points grid are used in all geometry optimization processes. Since structure phase transition occurs, the geometries at 0GPa and 80GPa (approximately the transition pressure) are re-optimized at higher precision (880eV of cutoff energy) to confirm the convergences. The results are in agreement with the less precise (600eV cutoff energy) ones. The band structure and optical absorption spectra are calculated in the relaxed supercell at different pressures with a higher cutoff kinetics of 800eV. The excited states are calculated up to about 30eV above the Fermi level. Only interband contributions to the absorption spectra is considered. The CASTEP code (Segall et al, 2002, p2717) is used for the *ab initio* calculations.

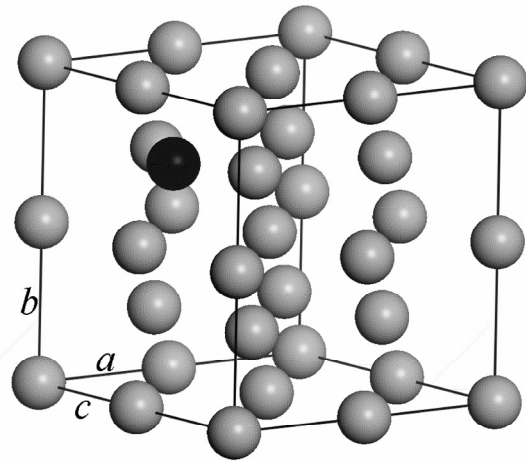


Figure 1. The supercell of Nb16+H, the black ball denotes Hydrogen.

3 Results and discussions

3.1 Structural phase transitions under pressure

We have firstly checked the structure of NbH (in both the phase β and γ) using first-principles method in order to test the efficiency and applicability of pseudopotential plane-wave method in transition metal hydrogen systems. Our theoretically optimized structure of the *orthorhombic* NbH is in acceptable agreement with the experimental data and other theoretical predictions.

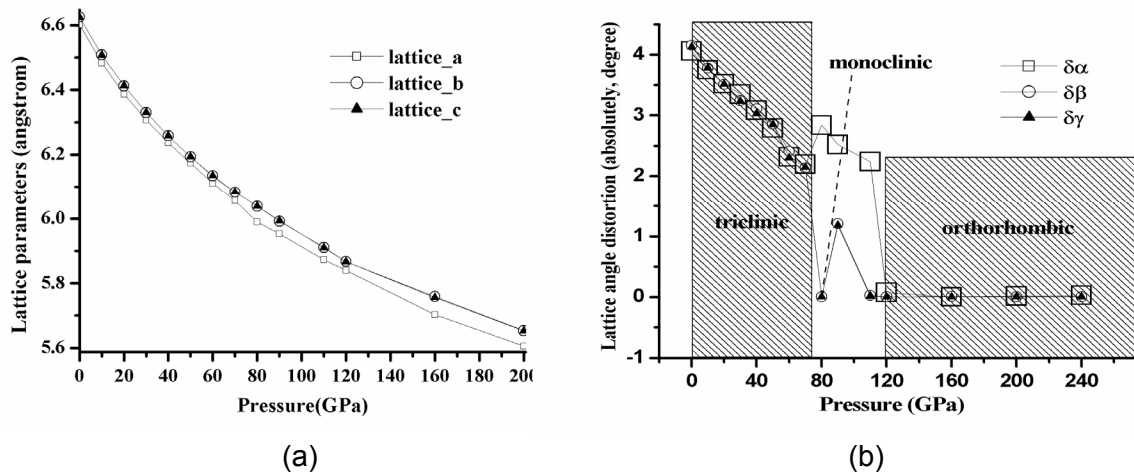


Figure 2. The pressure dependence of lattice parameters of the Nb16+H system

The Nb16+H system is *triclinic* after geometry optimization under ambient pressure and shows complex structural transformations with the increasing of pressure: below 80 GPa, the cell is triclinic; at 80 GPa, it changes into monoclinic; from 80 GPa to 120 GPa, the cell changes back to triclinic and over 120 GPa, the cell is orthorhombic, as shown in Fig. 2. All of the lattice angles are distorted when P is lower than 120 GPa except the pressures around 80 GPa, deviating by about 4° under 0 GPa. The deviation goes down with pressure, and approach 0° when a pressure of more than 120 GPa is applied. At the pressure of 80 GPa, where $b = c > a$, $\alpha > 90^\circ$ and $\beta = \gamma = 90^\circ$, the cell changes into monoclinic symmetry. The lattice parameters a , b and c decrease with the pressure with $a < b = c$ that are similar to the starting b - c relations. When the external pressure increases above 80 GPa, the parameter a tends to be more pressure sensitive than b and c . The pressure dependence of the structure shows complicated interactions between H and the host lattice.

3.2 Electronic structure

The band diagram along special axes is shown in Fig. 3. There are a low-lying band below the metallic valence bands, band splittings and band distortions induced by the lowering of symmetry in comparison with perfect bcc metals. The low-lying band has been identified to be s - d binding between H and Nb in the dihydrides NbH₂ and VH₂ (Gupta, 1982). The electronic band structure is deeply investigated by analysis of the DOS and partial density of states (PDOS). The overall PDOSs are shown in Fig. 4. In order to understand the effects of hydrogen and the lattice distortion respectively, the electronic structure of Nb sublattice is also calculated by simply removing the hydrogen atom away from the relaxed supercell.

In all PDOS diagrams, the $4d$ -states of Nb play the dominant roles in the metallic valence band are clearly shown. Hence the system is metallic due primary to the strong d bands around the Fermi level. The low-lying band is the hybridization of the s -states of H and s -, p - and d -states of Nb, separated by a band gap from the metallic bands. All bands tend to be expanded by the pressure. The low-

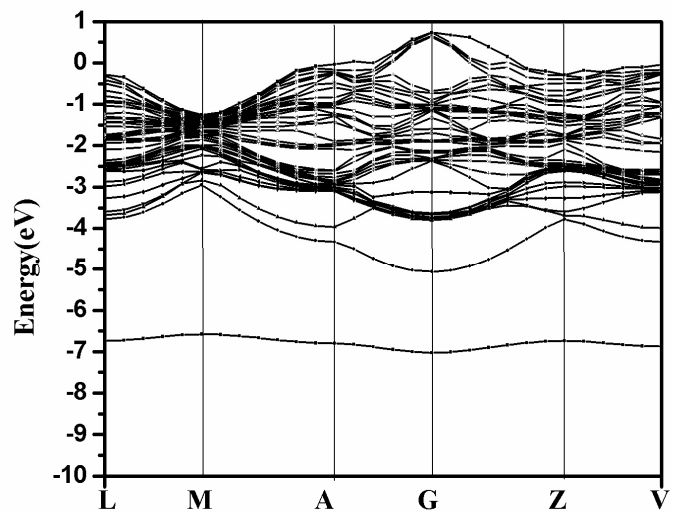


Figure 3. The band structure under 0 GPa of Nb16+H

lying band moves leftward (downward in energy level, in respect to the Fermi levels) with the increase of pressure. The *s*-like peak shrinks from about 4 electrons/eV to 1.5 electrons/eV and the band gap is widened from about 1eV to 2eV. The *4d*-states are more sensitive to the pressure, moving downward from the Fermi level when the pressure increases to 120GPa. It should be emphasized that, a peak of *s*-states is formed about -0.4 eV below the Fermi level, and a shoulder of *d*-states under 120GPa.

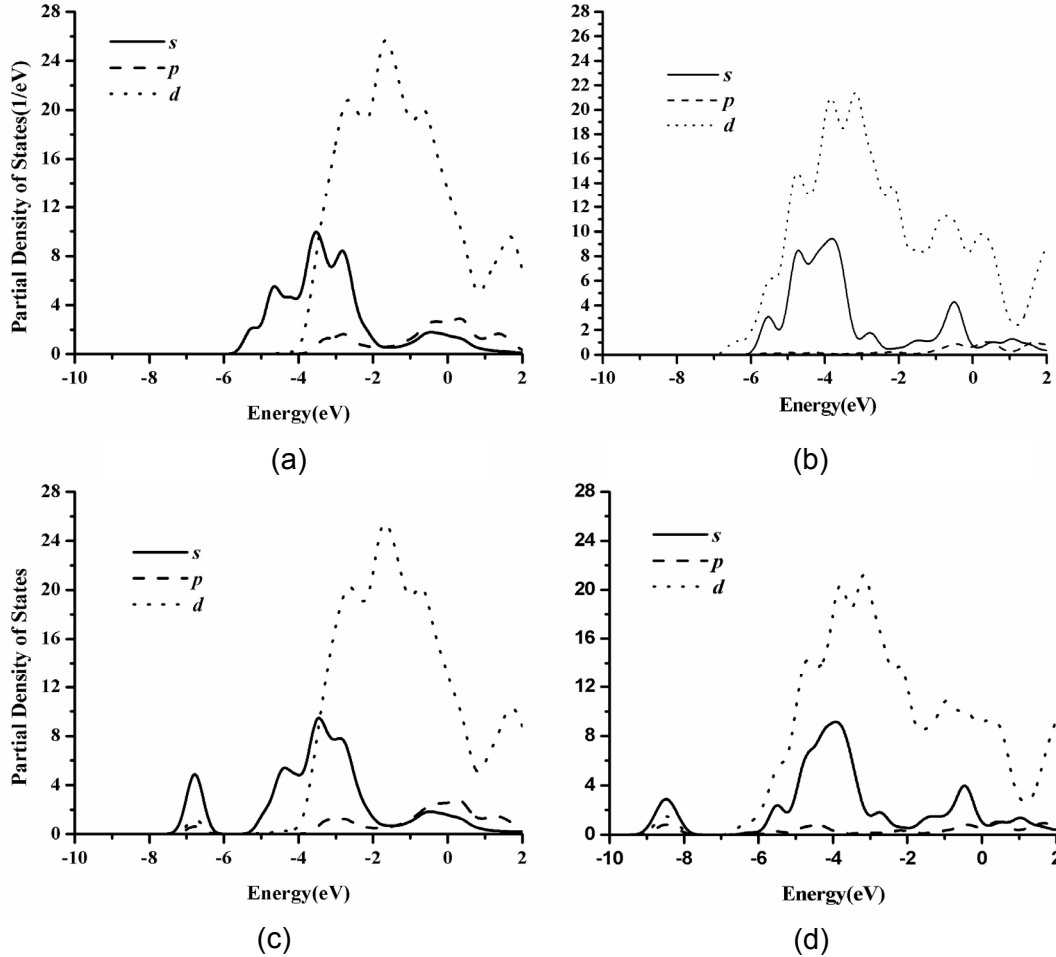


Figure 4. Partial density of states of Nb16 under (a) 0GPa and (b) 120GPa, Nb16+H under (c) 0GPa and (d) 120GPa

The local partial density of states contributed by atoms are obtained by projecting the wavefunctions onto different atoms, shown in Fig. 5. It can be seen that the 1*s*-states of H is expanded by the pressure, and an increase in higher states at about -1.2 eV can be observed. The integration of *s* DOS of H over the low-lying band energy area gives about 1.3 electrons, showing that the hydrogen atom acts as an anion as in NbH and NbH₂ (Gupta, 1982). The hydrogen atom contributes most to the low-lying band in comparison with any Nb atom, about 4 times than that of the first neighbor and 10 times of the seconds. The second neighbor Nb atoms are less affected by the screened proton, although their bands are affected by the distorted lattice. Atoms outer than the second neighbors have little contribution to the low-lying band.

The hybridization of the low-lying band is dependent on the distance from H to different Nb atom. The first neighbor Nbs contribute *4d*-, *5s*-states to the low-lying band, while the second neighbors contribute *5s*-, *5p*-states under ambient pressure and only *p*-states under 120GPa. Much attention should be paid on the dependence of DOS near the Fermi level, where *s*-states increases drastically over the *p*-states with external pressures, affecting mainly the optical profile at the low frequency area, which will be discussed below.

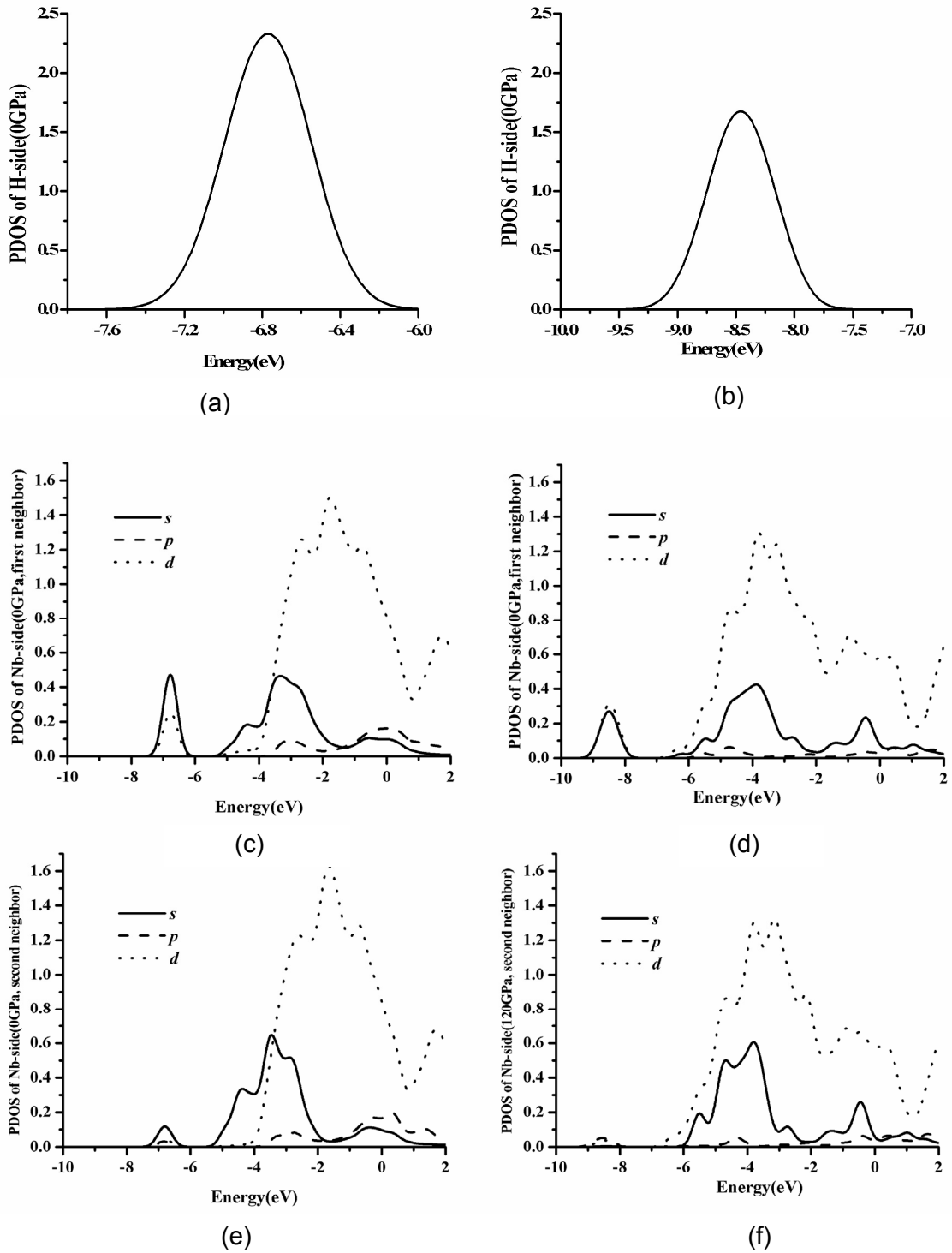


Figure 5. Local density of states on different atoms.

3.3 Optical absorption

Fig. 6 shows the hydrogen and pressure effects on the absorption spectra of the α -phase Nb-H systems. Under ambient pressure, the overall spectra of α -phase Nb-H is similar to that of Nb16 under ambient pressure, except the slightly intensive shoulder at about 1 eV. The absorption spectra of α -phase Nb-H is more intensive than that of Nb16 under the pressure

of 120GPa because of the increase of *s*-component of DOS and the decrease of *p*-states around the Fermi level. The main peak positions between α -phase Nb-H and Nb16 are similar, it can be concluded that the the peak locations are probably determined by the host lattice distortion and the magnitude is affected mainly by the selection rules modified by the impurity H. The absorptions of Nb16 at frequency area lower than 1.5eV have the same magnitude under 0GPa and 120GPa, showing the important role played by the *d*-bands of Nb around Fermi Level. It should be pointed out that the absorption of Nb16+H under 120GPa is enhanced in comparison with both the Nb16 and Nb16+H results under 0GPa, showing the structural phase transition effects. The absorption shoulder appears at the special frequencies of ~ 1 eV at 0GPa, and becomes the strongest peak at pressure of 120GPa.

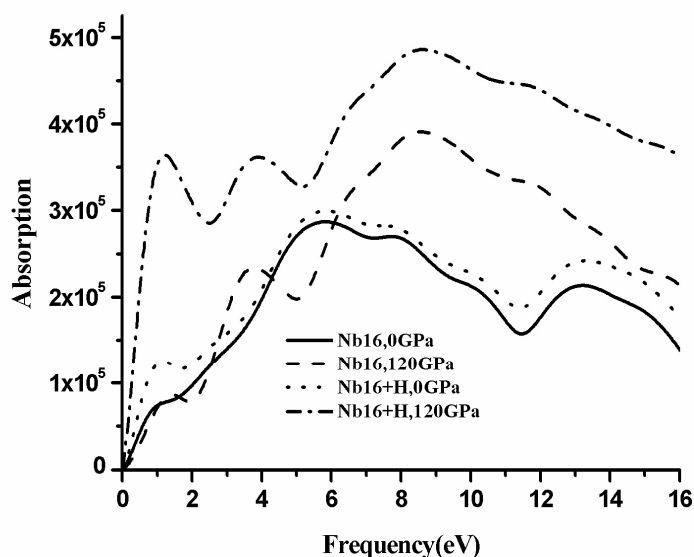


Figure 6. The absorption spectra contributed by interband transitions

4 Conclusion

The geometry, electronic structure, optical absorption and the pressure effects on an α -phase Nb-H system are studied using first-principles method. The system is shown to be triclinic under 0GPa, differing from niobium monohydride NbH. Pressure induced phase transitions are observed within the pressure range from 0GPa to 200GPa. Under pressures over 120GPa, the system changes to orthorhombic crystalline. A low-lying band is observed to be the hybridization of 1*s* of H and 4*d*, 5*s* states of the first neighbored Nb and *p*-states of the second neighbors, and the relevant DOS peak height decreases with the external pressure due to the band distortion. The absorption spectra show strong pressure dependence both in magnitude and structure.

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