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# THE ELECTRONIC STRUCTURE OF VH, NbH AND TaH IN THE β-PHASE *

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ABSTRACT

Calculations of the DOS (Density of States) for the three monohydrides of V Nb and Ta in the orthorhombic β-phase were performed using the LMTO method. In all three systems the hydrogen induced states below the Fermi level split in two maxima as a consequence of the H-H interactions. This fact agrees with photo-emission experiments. We report also the calculated Bulk Modulus and equilibrium lattice parameters. This is the first time that a band structure calculation is reported for the β-VH and β-TaH systems.

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The group of VB metals Nb, Ta and V form monohydrides in a rather complicated diagram of ordered and disordered phases and dihydrides /1-3/.

In particular $NbH_x$ exist as monohydride at 300K in the orthorhombic $\beta$-phase, below 200K in the pseudocubic $\gamma$- phase and also as dihydride in a fcc structure (CaF2-type). In the monohydride phase, the H atom occupy tetrahedral interstices of the bcc host lattice.

The band Structure calculation of the monohydride was first performed for $\gamma$-NbH /4/. This calculation show that the hydrogen-metal induced states produce single narrow peak in the DOS curve far below the Fermi level. This feature is usually observed for other monohydrides. Photoelectron spectra of $NbH_{1.0}$, $VH_{1.0}$ and $TaH_{0.8}$ however present a double peak structure in the hydrogen induced states at 5.5eV and 7.5 eV /5/.

In fact very early SXES (soft x-ray emission spectroscopy) investigations /6/ of $VD_{0.7}$ already revealed a double peak at ~6.5 eV and ~8.5 eV below the Fermi energy in the V-L3 emission spectra. Hydrogen induced states were also observed in electron energy loss spectra of $NbH_x$ and $VH_x$ of unknown concentration at 4eV and 7eV respectively /7/ but one observes less structure than in photoemission spectra. Several explanation were proposed to account for the unusual double peak, among them the formation of surface dihydride. Recently first principles band structure calculations /8/ based on the pseudopotential approach, performed on a cubic beta phase of NbH has show a double peak structure in the hydrogen induced states. The width and double peak structure in the H induced states is well reproduced. It has been ascribed to a splitting of the bands due to shorter distances between the H atoms in the beta phase.

These results have demonstrated the sensitivity of the hydrogen derived bands on the crystal structure and lattice parameters.

In spite of the fact that the $\beta$-phase is not clearly defined in the phase diagram of $VH_x$ and $TaH_x$ for $x \approx 1$ we have performed DOS calculations for all three hydrides using the same orthorhombic structure.

Our calculation was performed with use of the LMTO method /9/ within the local density functional formalism for treating the

exchange-correlation energy of the electrons (The Barth-Hedin form was used /10/).
In the orthorhombic $\beta$-phase of NbH the ratio c/a is approximately $1/\sqrt{2}$. Experimental values for NbH indicate a≈4.88 Åand c≈3.35 Å.
We used the same c/a value for all the three monohydrides.
The ratio between the radii of the overlapping atomic spheres representing the tetrahedral H atom, $S_H$ and the metallic atom $S_M$ is chosen to be $S_H$ / $S_M$ = $\sqrt{\frac{5}{3}} - 1$, which correspond to the radius ratio of touching muffin-tin spheres.
A unit cell of 8 atoms (4 metallic and 4 hydrogen) was used. The value of the atomic radius for the metallic atom was $S_M$ = 0.4884 c.
The atomic positions (given as (x/a,y/a,z/a)) are:
$(0,0,0),(\frac{1}{2},0,\frac{1}{2\sqrt{2}})$, $(0,\frac{1}{2},\frac{1}{2\sqrt{2}})$, $(\frac{1}{2},\frac{1}{2},0)$, $(\frac{1}{4},\frac{1}{4},\frac{\sqrt{2}}{8})$, $(\frac{1}{4},\frac{3}{4},\frac{\sqrt{2}}{8})$, $(\frac{3}{4},\frac{1}{4},\frac{3\sqrt{2}}{8})$, $(\frac{3}{4},\frac{3}{4},\frac{3\sqrt{2}}{8})$,
In the irreducible Brillouin Zone 100k point were used.
The calculation of the equilibrium lattice parameter were made by calculating the pressure p as a function of volume V /11-14 /. By interpolating the equilibrium volume $V_0$ is determined according to: $p(V_0) = 0$ The following equilibrium parameters were obtained:

| Hydride | a(Å) | c(Å) |
|---|---|---|
| VH | 4.469 | 3.160 |
| NbH | 4.947 | 3.498 |
| TaH | 4.931 | 3.487 |

The Bulk modulus B was also calculated from the slope of the p vs V curve at V = $V_0$ ($B = -V\frac{dp}{dV}$).
The values obtained are:
$B_{VH}$ = 1.99 Mb, $B_{NbH}$ = 1.83 Mb, $B_{NbH}$ = 2 Mb.
Available experimental data is found only for $\beta$-NbH, $B^{exp}_{NbH}$ = 1.87 Mb./1-3/
The Figs.1-3 show the DOS (States/(Ry cell)) for the 3 different



hydrides. The partial DOS due to the H-atoms reveals the splitting of the H induced states below the fermi energy. The DOS at the fermi energy (indicated by the small arrows) decreases as compared with the pure metallic elements as a consequence of an increasing of the fermi level. This fact has been observed by measurements of the $\gamma$ coefficient of the electronic specific heat in $VH_x$ and $NbH_x$ systems/15/.
The splitting of the H-states is 1.7 eV in VH, 2.0 eV in NbH and 2.4 eV in TaH. This splitting is a consequence of the 1s-1s orbital interaction between the H-atoms.
The position of the first peak of the H-induced states from the fermi level is located at 5.3 eV for VH, 5.5 eV for NbH and 5.9 eV for TaH.
The values obtained agree very well with the experimental results of photoemission experiments / 5/.

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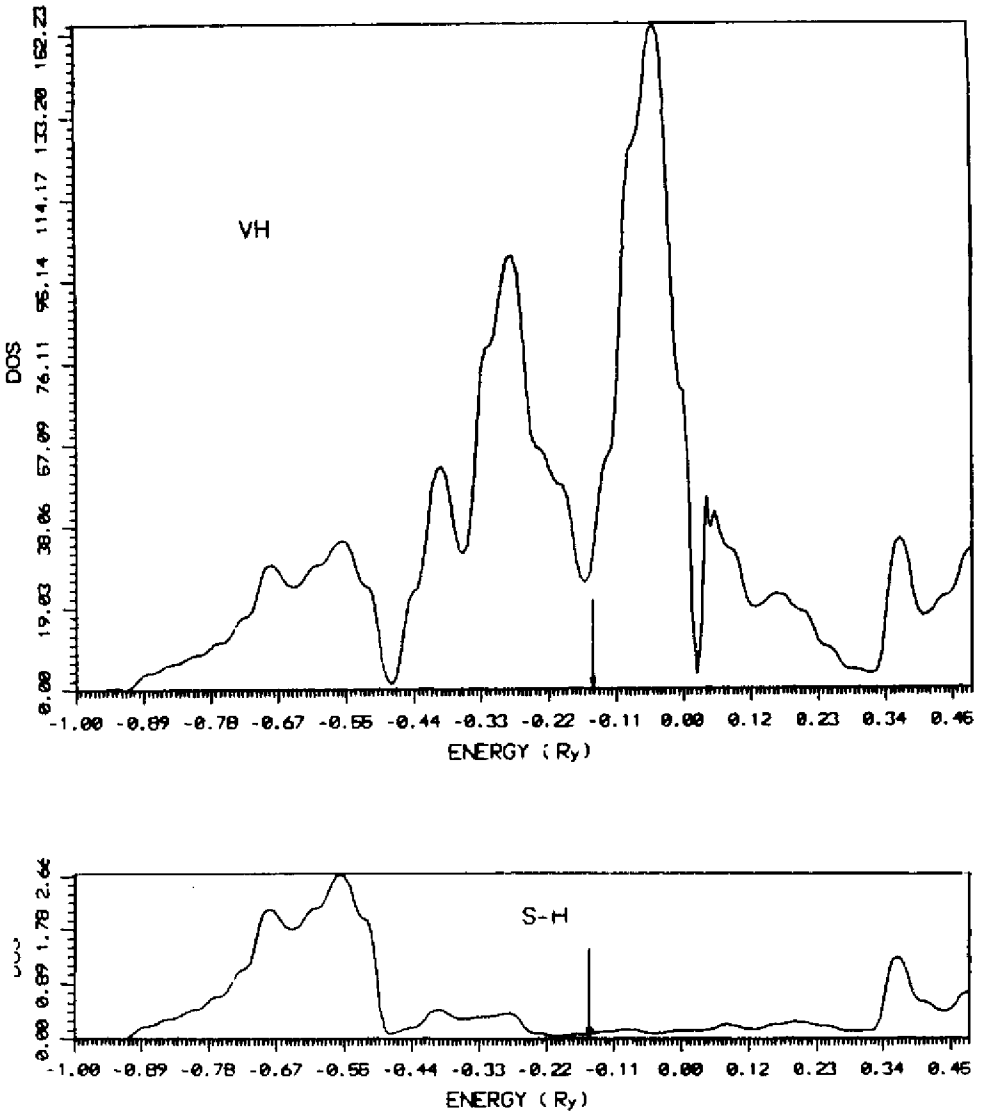


**Figure1.**
The DOS (States $Ry^{-1}$ $cell^{-1}$) for the $\beta$-VH system, the fermi level is indicated by the small arrows. The lower panel shows the s projected DOS on the 4 equivalent H atoms.

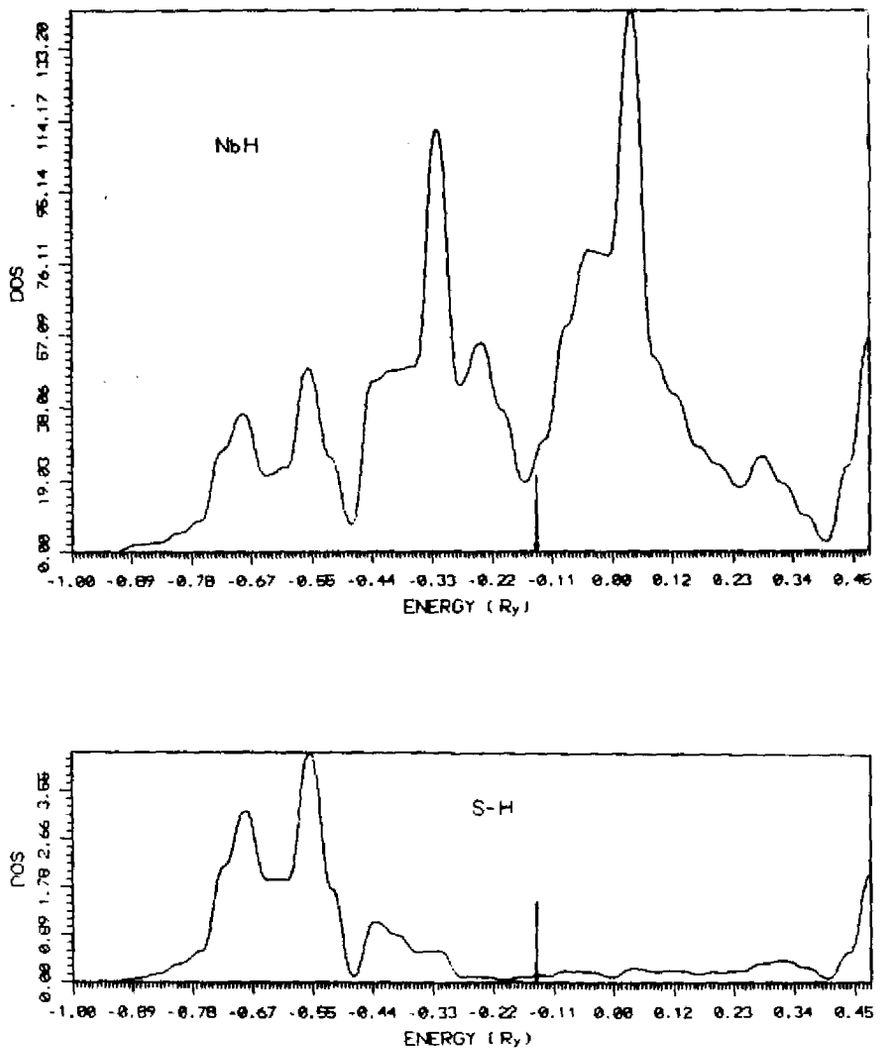


**Figure2.**
Same as Fig.1 but for the $\beta$-NbH system.



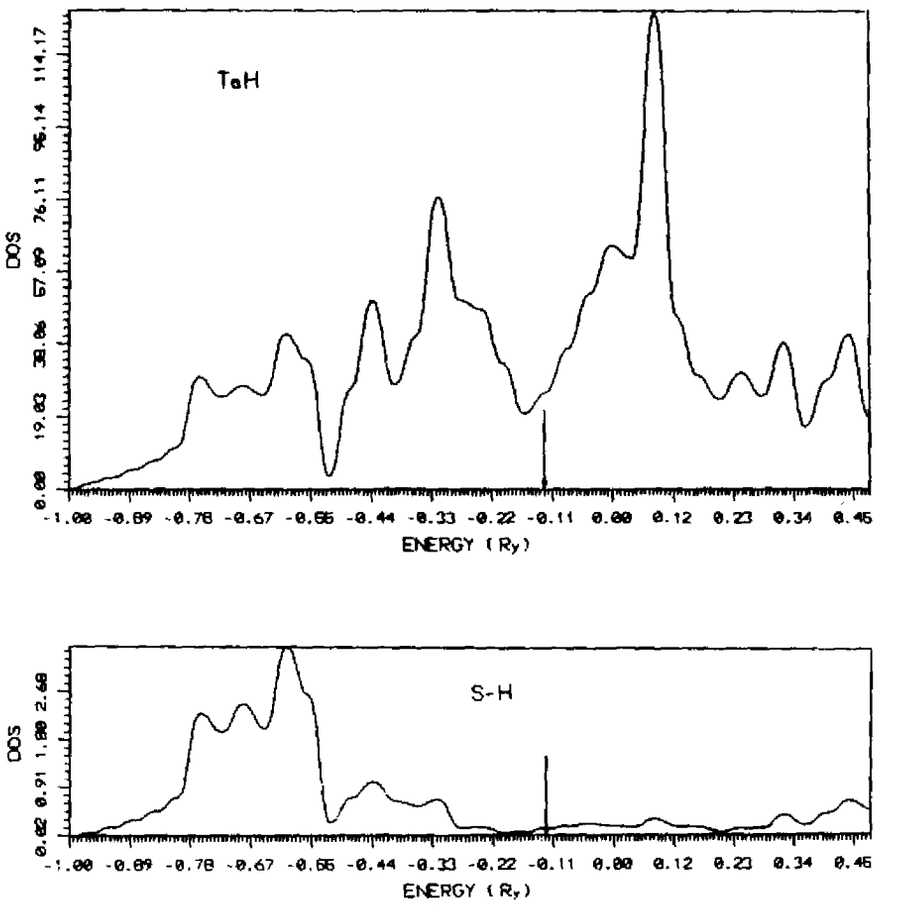


**Figure3.**
Same as Fig.1 but for the $\beta$-TaH system.

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