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## CHINA NUCLEAR SCIENCE AND TECHNOLOGY REPORT

金属钒及其氢化物的第一原理研究

FIRST PRINCIPLE STUDIES  
OF METALLIC V AND ITS HYDRIDES



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# 金属钒及其氢化物的第一原理研究

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## 摘 要

用 Castep 程序的局域密度泛函近似方法(LDA)对金属钒及不同原子比的钒氢化物进行了结构优化和总能计算。获得了  $VH_x$  ( $0 \leq x \leq 2$ )体系的各种氢化物的晶体结构的计算结果; 判断了钒氢化物的稳定性; 说明了氢含量对 V-H 体系相组成的影响。与现有的实验结果相比较, 二者是基本相符的。

# First Principle Studies of Metallic V and Its Hydrides

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## ABSTRACT

An initial calculation have been performed to study the crystal structures of V(bcc) and its hydrides  $VH_x(0 \leq x \leq 2)$ . The optimized crystal structures and total energies are obtained. The stability of hydrides and phase transitions of V-H system are discussed with enhancement of hydrogen concentration in the cell. The calculation results are in remarkably close agreement with experiments.

## INTRODUCTION

Metal hydrides have been studied and applied because they can store a large quantity of hydrogen and absorb or desorb hydrogen reversibly. As a kind of advanced hydrogen storing material, vanadium based alloy has widespread prospect in defense and civil uses. Behaviors of hydrogen and its isotopes in V-Cr-Ti alloy was studied by Budykin<sup>[1]</sup>, and this material might be used in fusion reactor; Trapping effect of H in V was studied by Arbutov<sup>[2]</sup>. Behaviors of absorbing and desorbing hydrogen of V(bcc) and its alloys (mainly V-Ti alloy) are observed by Libowitz<sup>[3]</sup>. Behaviors of hydrogen solidifying into V-Nb, V-Cr alloys etc. were studied by Stephen Otto Nelson<sup>[4]</sup>. Phase diagrams of V-D, V-T systems were determined by Carstanjen<sup>[5]</sup>. At room temperature, bcc vanadium based alloys could react rapidly with hydrogen without activation. This fact were proved by Maeland<sup>[6]</sup>. At present, it is difficult to determine atomic ratio of H/V, positions of H atoms in V cell and existing form through experiments. Especially, it is more difficult to test crystal structures of  $VH_x$  ( $x$  are non-stoichiometric). The research works of hydrogen storing alloys mainly focus on experiment description and properties test. There is no report on mechanism of storing hydrogen and material design.

In order to investigate existing form and position of H atom in alloys, stability of hydrides and relationship between H concentration and phases of the system, we have developed and made use of quantum chemical software CASTEP to carry out ab initio calculation of V-H system. Then, we could manage to design the components of alloys to satisfy needs of uses.

## 1 CALCULATION METHODS

All calculation is completed with INDIGO-2 and INDY works stations. To Combine local density function approximation and pseudo-potential technique, BFGS method (BFGS version of New-Raphson calculation algorithm) is used, energy cutoff is 136.0 eV; subspace rotation of wavefunctions is set to promote convergence of total energy; the whole system is considered to be metal, convergence standard of total energy is  $2 \times 10^{-4}$  eV; RMS (room-mean-square) of displacement is 0.01 nm; RMS of Force is less than 5.0 eV/nm. Optimization of cell parameters and atom positions of different H concentration in V-H system is performed. The initial crystal structures of  $VH_x$  system are set up according to different H concentration. When  $x \leq 1.0$ , positions of metal atoms are same as those

of metallic vanadium (bcc), H atoms are set in tetrahedral site of the cell; when  $1.0 \leq x \leq 2.0$ , positions of metal and hydrogen atoms are same as those of  $\text{VH}_2$  (fcc). Superlattice technique is used to build crystal cells of V-H system with different H concentration. After Geometry optimization, band of structure, density of state and population of electrons will be analyzed.

## 2 RESULTS OF CALCULATION AND DISCUSSION

### 2.1 Crystal structure analysis

Firstly crystal models of metallic vanadium and  $\text{VH}_2$  are built respectively by BUILDER1 program of Cerius 2.0 software, according to their experimental results (vanadium:bcc,  $a=0.3029 \text{ nm}^{[4]}$ ;  $\text{VH}_2$ :fcc,  $a=0.4271 \text{ nm}^{[8]}$ , position of H atoms are tetrahedral sites<sup>[9]</sup>). Geometry optimization of them are performed. The calculation results are that the crystal structure of metallic vanadium is body-centered cubic,  $a=0.3027(3) \text{ nm}$ ; the crystal structure of  $\text{VH}_2$  is face-centered cubic,  $a=0.4276(3)$ . These are in remarkably agreement with experiment. Then, the initial models of  $\text{VH}_x$  ( $1 < x < 2$ ) are built, and at the same calculation condition, ab initio calculations of them are performed respectively. Table1 presents the cell parameters, volume of cell and type of crystal of the stable configures. Because the sizes of the calculation systems may be different, in order to compare with each other, the direct calculation results of all models are translated to a cell containing 2 atom.

To set initial position of H atom in the V cell, interstices of the bcc structure are considered. There are two kinds of interstice sites, 12 tetrahedral sites and 8 octahedral sites, and their maximum radiuses are  $0.291R$  ( $0.0382 \text{ nm}$ ) and  $0.154R$  ( $0.0202 \text{ nm}$ ),  $R$  is the diameter of metal atom. But the radius of H atom is  $0.046 \text{ nm}^{[9]}$ , according to the theory, hydrogen of atomic state entering into metal<sup>[10]</sup>, H atom only can enter into interstice sites, and impossibly replace the metal atom and occupy lattice position. Obviously, H atom is prior to occupying the tetrahedral site. H atom is putted into tetrahedral and octahedral sites respectively to build the initial models, then optimization of their structure are completed. The results show that no matter whether the crystal structures of them were distorted or not, H atoms occupy the tetrahedral site. Even if H atom is fixed at octahedral site, during the process of optimization, the volume of the cell expands beyond that of  $\text{VH}_2$  cell, and calculation can not be converged. This is in closely agreement with the metallic theory.

**Table 1 The cell parameters, volumes and crystal types of VH<sub>x</sub> system**

	Cell parameters						Cell volume $V/\times 10^3 \text{ nm}^3$	Crystal structure
	$a/\text{nm}$	$b/\text{nm}$	$c/\text{nm}$	$\alpha/^\circ$	$\beta/^\circ$	$\gamma/^\circ$		
V	0.3026	0.3026	0.3030	90.00	90.00	90.00	27.73	bcc
VH <sub>0.125</sub>	0.3045	0.3045	0.3032	89.99	89.99	90.04	28.11	bcc
VH <sub>0.25</sub>	0.3048	0.3048	0.3034	90.03	90.00	90.00	28.18	bcc
VH <sub>0.50</sub>	0.3065	0.3066	0.3113	89.97	90.02	90.09	29.26	Bct <sup>1)</sup>
VH <sub>0.75</sub>	0.3167	0.3162	0.3168	89.94	89.88	89.77	31.71	distortion bcc
VH	0.3171	0.3170	0.3154	90.00	89.99	89.99	31.71	bcc
VH	0.4102	0.4102	0.4102	90.00	90.00	90.00	34.50 <sup>2)</sup>	fcc
VH <sub>1.25</sub>	0.4127	0.4110	0.4110	90.02	89.97	89.99	34.87	fcc
VH <sub>1.50</sub>	0.4104	0.4104	0.4104	89.99	89.99	89.99	34.56	fcc
VH <sub>1.75</sub>	0.4200	0.4200	0.4200	90.28	90.09	90.15	37.05	distortion fcc
VH <sub>2.0</sub>	0.4276	0.4279	0.4279	89.99	90.00	90.01	39.09	fcc

1) body -centered tetragonal structure.

2) The volumes of fcc structures are divided by 2.

From Table 1 we can see that with the increase of  $x$  in  $\text{VH}_x (0 \leq x \leq 2)$  system, cell parameters  $a$ ,  $b$ ,  $c$ , volume of the cell increase, and  $\alpha$ ,  $\beta$ ,  $\gamma$  maintain invariable. When symmetry of  $\text{VH}_x$  is high, crystal structure is cubic; conversely distorted cubic crystal. When  $x < 1.0$ , crystal structures of vanadium hydrides are body of center cubic. When  $x$  is 0.5 or so, structure of hydride translates from bcc to bct, and with increase of  $x$ , changes into bcc structure. This is in agreement with phase diagram of V-H system<sup>[5]</sup>. When  $x = 1.0$ , structure of hydride possibly translate from bcc to fcc, but bcc structure is relatively stable (this will be explained in analysis of energy later). When  $x > 1.0$ , structures of hydrides are face of center cubic. From literature 3, we see that when alloys with bcc structure to absorb hydrogen, there are two platforms on P-C-T curves. This is closely in agreement with calculation.

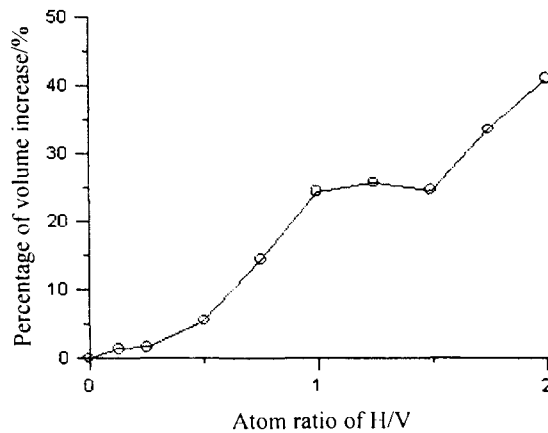


Fig. 1 Percentage of volume increase of  $\text{VH}_x (0 \leq x \leq 2)$

Volume variability before and after absorbing hydrogen is a brief standard to judge anti-pulverization ability of metal hydride. We can see from Fig. 1 that volume increase percentage from V to  $VH_x$  can be simulated by structure optimization calculation. Volume increase percentage of V-H system increases with the increase of ratio of H/V. When ratio of H/V is less than 0.75, volume increase percentage is less than 10%. Volume increase percentage of VH with bcc structure is 14% (the plot of VH with fcc structure in Fig. 1). Ratio of H/V from 1.0 to 1.5, volume variability is small, and from 1.5 to 2.0, volume increase percentage of hydride enhances rapidly. Volume increase percentage of  $VH_2$  is 41%, which is 3 times of that of VH (bcc). Therefore, on the bcc stage, hydrides have the better anti-pulverization ability, and on the fcc stage, lower anti-pulverization ability.

## 2.2 Total energy analysis

The total energies of V-H system are listed in Table 2. Forming process of vanadium hydride can be expressed by following equation (1).



The stability of  $VH_x$  is determined by  $\Delta H$  of this reaction. The total energy of the gas state hydrogen can not be directly obtained in the calculation of the solid. We only can investigate the variability of total energy from metallic vanadium to vanadium hydride. In this process,  $\Delta V(V_{\text{vib}} - V_V)$  is very small, and  $p^* \Delta V$  (commonly  $p=0$  or 1 atm) is also small, so  $\Delta H$  is nearly equal to  $\Delta E$ . To compare with stability of vanadium hydrides each other, the average total energy variability of each hydride caused by unit H atom is calculated, labeled  $\delta E (E_{\text{vib}} - E_V)$ . When gas-solid reaction gets equilibrium, the equilibrated pressure ( $p$ ) abides by equation (2). At room temperature, the absolute value of  $\Delta H/RT$  is much bigger than that of  $\Delta S/R$ . Obviously,

$$\ln p = \Delta H/RT - \Delta S/R \quad (2)$$

$p$  is mainly determined by  $\Delta H$ . The total energy of one H atom is fixed, therefore, the equilibrium pressure can be reflected by  $\delta E$ .

**Table 2** The total energies of  $VH_x$

$VH_x$	$VH_{0.125}$	$VH_{0.25}$	$VH_{0.5}$	$VH_{0.75}$	VH(bcc)	VH(fcc)	$VH_{1.25}$	$VH_{1.5}$	$VH_{1.75}$	$VH_2$
$\Delta E/eV$	-3.26138	-6.31190	-10.73754	-19.79203	-25.71911	-25.67697	-31.08305	-37.51589	-42.97255	-52.72340
$\delta E/eV$	-13.04552	-12.62380	-10.73754	-13.19468	-12.85955	-12.83899	-12.43322	-12.50530	-12.65653	-13.18085

It is obvious that the stable metal hydrides can be formed, when the atom ratio of H/V is between 0 and 2. The stability of  $VH_x$  hydrides is nearly same except  $VH_{0.5}$



(may be caused by phase transition). Therefore, when there is hydrogen source,  $VH_2$  can be formed spontaneously. When the structures of hydrides are fcc structures, P-C plateau at room temperature is plane. When the structures of hydrides are bcc structures, P-C plateau is not obvious, and the equilibrium pressure increases with an increase of the atom ratio of H/V. Under this calculation condition, the thermodynamic parameters can not be obtained, so the equilibrium pressure can not be calculated correctly. Therefore the stability and relative size of the equilibrium of metal hydride can only be judged by  $\delta E$ .

### 3 CONCLUSION

Through the first principle calculation of V-H system, the crystal structures of  $VH_x(0 \leq x \leq 2)$  hydrides are obtained. When  $x < 1.0$ , the structures of hydrides are bcc structures, the volume increase percentages are less than 14%, anti-pulverization ability is better. When  $x > 1.0$ , the structures of hydrides are fcc structures, the volume increase percentages enhance obviously, even up to 41%, anti-pulverization ability is lowered. According to the total energy analysis of V-H system, it shows that the structures of hydrides are bcc structures, the P-C plateau at room temperature is not obvious, and the structures of hydrides are fcc structures, the plateau is better.

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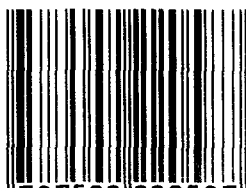
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