Theoretical calculation for the phonon spectrum and thermodynamic functions of vanadium and its hydride

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Abstract: Based on density functional theory (DFT), using virtual crystal approximation and generalized gradient approximation (GGA) with pseudopotential method, the lattices and energies for five crystallines of vanadium hydrides are optimized and calculated. The phonon densities of states are calculated based on density functional perturbation theory (DFPT). The standard Heat capacities, Entropies, Helmholtz free energies and Gibbs functions of vanadium and its hydride are deduced at 298.15K. The calculated results are discussed and compared with experimental data.

1 Introduction

Vanadium is an excellent material favored by people because of its hard texture, high temperature resistance, low specific gravity, high strength and stable chemical properties, as an advanced hydrogen storage material, vanadium-based hydrogen storage alloys have a broad application prospect in national defense and civil industry. In recent years, many scholars have made researches on them, Budykin et al. have studied the behavior of hydrogen isotopes in V-Cr-Ti alloys, this material has been successfully applied to the treatment of hydrogen isotopes in fusion reactors; the "trap" effect of H in V has been studied by Arbuzov et al., the hydrogen absorption and desorption behavior of vanadium and vanadium-based alloys with cubic centers have been studied by Libowitz et al.. The behavior of dissolved hydrogen in alloys such as V-Nb and V-CR was studied by Stephen.; the vanadium-based BCC alloys can react rapidly with hydrogen without activation at room temperature was studied by Maeland et al.

In this paper, the lattice structure and energy of Vanadium and vanadium hydrides are calculated respectively by using the Density Functional theory method, and the density functional perturbation theory (DFPT) method is used, the densities of phonon states of vanadium and vanadium hydrides and their thermodynamic functions such as heat capacity, entropy, Helmholtz free energy and Gibbs Free Energy at 298.15K are calculated.

2 Method of calculation

In the debye theory, the debye Spectrum \( D(\omega) = \frac{\hbar \omega}{e^{\frac{\hbar \omega}{kT}} - 1} \) is quite different from the actual lattice vibrational spectrum. In order to calculate the thermodynamic function of crystal accurately, the actual vibrational spectrum (phonon density of states), i.e. \( f(\varepsilon) \), should be used instead of the debye spectrum, the vibrational frequency here corresponds to the energy of the phonon \( \varepsilon = \hbar \omega \). The grand partition function of the Phonon is

\[
Z = \prod_i (1 - e^{-\beta \varepsilon_i})^{g_i} \tag{1}
\]

Among them \( \beta = \frac{1}{kT} \), \( \varepsilon_i = \hbar \omega_i \), \( g_i \) is the degree of degeneracy of the phonon at the vibrational frequency \( \omega_i \) . The logarithm of the grand partition function

\[
\ln Z = -\sum g_i \ln (1 - e^{-\beta \varepsilon_i}) \tag{2}
\]

If the phonon is regarded as a quasi-particle with continuous energy distribution, and its degeneracy is \( f(\varepsilon) \) \( d\varepsilon \), then the upper formula can be rewritten as an integral form

\[
\ln Z = -\int_0^\infty f(\varepsilon) \ln (1 - e^{-\beta \varepsilon}) d\varepsilon \tag{3}
\]

The internal energy of the system is \( U_{\text{elect}} + U_{\text{heat}} \), where \( E \) is the energy of electrons in the system and \( U_{\text{heat}} \) is the energy of thermal motion of lattice vibrations

\[
U_{\text{heat}} = -\frac{\partial}{\partial \beta} \ln Z = \int_0^\infty f(\varepsilon) \frac{\epsilon}{e^{\frac{\epsilon}{kT}} - 1} d\varepsilon \tag{4}
\]

The contribution of lattice vibration to the heat capacity of the system is

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\[ C_V = \frac{\partial U_{\text{heat}}}{\partial T} = \int_0^\infty f(\varepsilon) \cdot e^{\varepsilon kT} \cdot \frac{e^\varepsilon}{(e^{\varepsilon kT} - 1)^2} d\varepsilon \]  
(5)

The contribution of lattice vibration to the entropy of the system is

\[ S = k \left( \ln Z - \beta \frac{\partial}{\partial \beta} \ln Z \right) = -k \int_0^\infty f(\varepsilon) \cdot \ln \left( 1 - e^{\varepsilon kT} \right) + \frac{\varepsilon}{(e^{\varepsilon kT} - 1) kT} \right) d\varepsilon \]  
(6)

The Free Energy of the system is zero if the effect of temperature is ignored

\[ F = U - TS = E + \int_0^\infty f(\varepsilon) \cdot \frac{\varepsilon}{e^{\varepsilon kT} - 1} - \ln \left( 1 - e^{\varepsilon kT} \right) \cdot kT + \frac{\varepsilon}{(e^{\varepsilon kT} - 1)} \right) d\varepsilon \]  
(7)

Gibbs free energy

\[ G = U - TS + PV = E + PV + \int_0^\infty f(\varepsilon) \cdot \frac{\varepsilon}{e^{\varepsilon kT} - 1} - \ln \left( 1 - e^{\varepsilon kT} \right) \cdot kT + \frac{\varepsilon}{(e^{\varepsilon kT} - 1)} \right) d\varepsilon \]  
(8)

The electron energy \( E \) and the phonon density of states are calculated using the Density functional theory ABINIT package, The Troullier-Martins pseudo-potential and the generalized gradient approximation (GGA) are used in the computation. The computational results show that the kinetic energy truncation \( E_{\text{cut}} = 30 \text{hartree} \) and the \( k \) sampling at \( 4 \times 4 \times 4 \) can ensure sufficient convergence for the computation of \( \text{VH}_x \) with all different types of structures. The convergence requirement of the total energy in self-consistent computation is less than \( 10^{-4} \text{hartree} \), the so-called virtual crystal method \(^7\) is introduced, in which the number of nuclear charge and the number of electron is \( x \), which is not necessarily an Integer, and the purpose is to characterize the average distribution of hydrogen atom in the crystal lattice, in this way, it is not necessary to construct a supercell, so the amount of calculation is greatly reduced, and it is suitable for the calculation of solid solution system. When the density functional perturbation theory is used to calculate the phonon energy, the selection of \( q \) sampling is consistent with that of \( k \) sampling.

### 3 Results and Discussion

When the hydrogen atom enters the vanadium crystal to form the hydride \( \text{VH}_x \), the Crystal Structure of vanadium may be BCC and FCC. In this paper, the lattice structures of five possible types of \( \text{VH}_x \) have been calculated. BCT and FCT are the two structures with \( x = 0 \sim 1 \), the three structures between \( x = 0 \sim 1 \) are BCC, FCC and FCT. The relative coordinates of

| Table 1 Relative coordinates of hydrogen atoms in five lattice structures |
|------------------|------------------|------------------|
| BCT VH\(_{0.1}\) | (0.75, 0.25, 0.5) |                  |
| FCT VH\(_{0.1}\) | (0.5, 0.5, 0.5)  |                  |
| BCC VH\(_{1.2}\) | (0.75, 0.25, 0.5), (0.25, 0.75, 0.5) |                  |
| FCC VH\(_{1.2}\) | (0.25, 0.25, 0.25), (0.75, 0.75, -0.25) |                  |
| FCT VH\(_{1.2}\) | (0.5, 0.5, 0.5), (0.25, 0.25, 0.25) |                  |

Fig. 1 shows the relationship between the hydrogen content \( x \) and the lattice parameter \( a \) of the optimized vanadium hydride \( \text{VH}_x \). It can be seen that with the increase of hydrogen content \( x \) in Vanadium, the lattice parameter \( a \) of the five vanadium hydrides increases gradually; it is shown that the addition of hydrogen makes the vanadium crystals swell, which is consistent with the results in the literature\(^1\). Fig. 2 shows the relationship between the hydrogen content \( x \) and the lattice energy \( E \) of the optimized vanadium hydride \( \text{VH}_x \). When \( x = 0 \sim 1 \), the energy of BCT structure is very close to that of FCT structure. There is an intersection point at \( x = 0.103 \) (see the small figure in figure 2). When \( x = 1 \sim 2 \), the energy of BCC structure is obviously lower than that of FCC and FCT structure. According to the energy minimum principle, \( \text{VH}_x \) should be BCT structure when \( x = 0 \sim 0.103 \), when \( x = 0.103 \sim 1 \), the structure is FCT. When \( x = 1 \sim 2 \), the BCC structure is observed. The volume of BCC system increases with the increase of \( x \), but when
$x=1$, the BCT structure changes to BCC structure, so there is a sudden change in the volume of BCC system

\[\text{Fig.1 Relationship between } x \text{ and } a\]

In the low frequency range of 0~126 cm$^{-1}$, the phonon state density of the vanadium BCC structure is relatively low and increases monotonously, there are two peaks of phonon density of state at 152 cm$^{-1}$ and 201 cm$^{-1}$, respectively. The peak height of 201 cm$^{-1}$ was higher than that of 152 cm$^{-1}$, the low frequency part of the debye spectrum of BCT VH$_{0.1}$ is enlarged from 0~126 cm$^{-1}$ to 0~126 cm$^{-1}$, and the two acoustic peaks are changed from 152 cm$^{-1}$ and 201 cm$^{-1}$ to 181 cm$^{-1}$ and 272 cm$^{-1}$, respectively, and the height of the low energy peak is higher than that of the high energy peak. The optical wave band of BCT VH$_{0.1}$ forms two optical wave density peaks. With the increase of hydrogen atom content, the peak energy of the density of states in the LO wave band changes from 1109 cm$^{-1}$ to 1041 cm$^{-1}$, the peak of the TO wave band was split from 1747 cm$^{-1}$ to 1363 cm$^{-1}$ and 1397 cm$^{-1}$.

The acoustic wave density of the FCC vanadium has two peaks at 89 cm$^{-1}$ and 242 cm$^{-1}$, respectively, the boundary between the two peaks is not easy to distinguish. The addition of hydrogen atoms makes the distinction between the two acoustic peaks obvious, the optical phonon density of states of the two acoustic peaks, VH$_{0.1}$ with FCT structure, varies from 89 cm$^{-1}$ and 242 cm$^{-1}$ to 180 cm$^{-1}$ and 280 cm$^{-1}$, with the increase of hydrogen atom content, the two peaks of 1380 cm$^{-1}$ and 1410 cm$^{-1}$ merge into one peak of 1020 cm$^{-1}$.

The density of phonon states of VH$_{1-x}$ with BCC structure has little change with hydrogen atom content, the density of states of the optical waveband is mainly distributed over a wide energy range of 620 cm$^{-1}$~1398 cm$^{-1}$, in which the peaks of 823 cm$^{-1}$ and 1059 cm$^{-1}$ decrease with the increase of hydrogen atom content.

The acoustic wave density of VH$_{1-x}$ with FCC structure has two peaks, with the increase of hydrogen atom content, the peak shape changes from 100 cm$^{-1}$ and 241 cm$^{-1}$ to 167 cm$^{-1}$ and 247 cm$^{-1}$, respectively, the optical wave density of states of VH$_{1-x}$ has two main peaks of 1495 cm$^{-1}$ and 1547 cm$^{-1}$. With the increase of hydrogen atom content, the optical wave density of states of VH has a wide range of 1050 cm$^{-1}$~1278 cm$^{-1}$.

The density of states of FCT VH$_{1-x}$ is composed of three peaks. The peak energy of acoustic wave with lower energy is changed from 203 cm$^{-1}$ to about 155 cm$^{-1}$ with the increase of hydrogen atom content, the peak energy of the acoustic wave with higher energy changes from 344 cm$^{-1}$ to 218 cm$^{-1}$, and the shape of the acoustic wave becomes lower and flatter. There are two peaks in the density of state of the two groups of optical waves, and the energy decreases with the increase of hydrogen atom content.
Fig. 3 The density of states $VH_x$ ($x = 0 \sim 2$)

Fig. 4 shows the internal energy $U$, entropy $S$, isobaric heat capacity $C_P$ of $VH_x$ at 298.15 K using the density of states of phonons, the thermodynamic functions of Helmholtz Free Energy $F$ and Gibbs Free Energy $G$ vary with hydrogen atom content $x$, where the entropy of BCC Structure Vanadium is 31.668 J/mol.K is 9% larger than the experimental value (29.022 J/mol.K), which is equivalent to the result obtained by atomic displacement method in reference [10](31.324 J/mol.K) and the heat capacity is 23.058 J/mol.K, is 8% smaller than the experimental value (24.995 J/mol.K), the results obtained by the S-P wave method and the atomic displacement method (23.178 J/mol.K and 23.451 J/mol.K) are comparable to those obtained by the s-wave-p-wave method and the atomic displacement method in reference [10], the results show that the thermodynamic functions of the crystal can be obtained by both the atomic displacement method and the phonon spectrum calculation method. When $x = 0 \sim 1$, the internal energy $U$ of $VH_x$ with BCT Structure and FCT structure, the Helmholtz Free Energy $F$ and Gibbs Free Energy $G$ are very close. The relationship between the Gibbs free energy of BCT $VH_{x=1}$ and FCT $VH_{x=1}$ and the hydrogen atom content $x$ is as follows.

$$G_{BCT} = -15.7656 - 0.05236x - 1.53263x^2$$
$$G_{FCT} = -15.7618 - 0.13737x - 1.45137x^2 \quad x = 0 \sim 1$$

The results show that when $x$ equals 0.0468, the crystal structure will change from BCT structure to FCT structure, when $x = 0.0468$, and the Gibbs free energy of BCC structure is lowest, when $x = 1$, the increase of hydrogen atom will change the crystal structure from FCT to BCC. The relationship between the Gibbs free energy of $VH_{x=2}$ and hydrogen atom content $x$ is as follows:

$$G_{BCC} = -18.7741 - 0.02159x + 0.00365x^2 \quad x = 1 \sim 2$$

The BCC structure of $x = 0 \sim 1$ and FCC structure of $VH_x$ crystal in $x = 1 \sim 2$ are calculated by local density functional approximation in Castep program, it shows that the crystal structure and its change of $VH_x$ in hydrogen storage need further study.
4 Conclusion

By introducing the virtual crystal approximation, the pseudopotential method of Density functional theory is adopted. BCT and FCT crystal forms $\text{VH}_0$ and BCC FCC and FCT crystal forms $\text{VH}_1$ are optimized and calculated the structures and energies. The internal energy, entropy, heat capacity, Helmholtz Free Energy and Gibbs free energy of vanadium and its hydrides are calculated by using the obtained phonon structures, the variation of thermodynamic function with hydrogen storage capacity $x$ and its effect on the crystal structure in hydrogen storage process are analyzed. The results show that at 298.15 k, the crystal structure of vanadium metal is BCC, the structure of vanadium metal ($x = 0.0468$) will change from BCT to FCT. When $x = 1$, the structure of vanadium hydride will change from FCT to BCT. This is the same as that of BCC calculated in reference [9], the conclusion that $x = 1\sim 2$ is a FCT structure is inconsistent and needs further study.

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