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First principles studies of elastic and thermodynamic properties of *fcc*-VH_2 with pressure and temperature

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ABSTRACT

In this work, we study elastic and thermodynamic properties of VH_2 at different pressures and temperatures. Elastic constants and bulk modulus of VH_2 decrease with increase in temperature, and hence increase with pressure. Thermal expansion of the crystal lattice will be suppressed by high pressure. When the temperature is 1500 K, 15.99 GPa of pressure can completely restrain the volume expansion caused by temperature. At a given pressure, the lower the temperature, the easier the cell compression. At low temperatures, C_v is proportional to T^3, and C_v tends to the Dulong–Petit limit at higher temperatures. The Debye temperature increases with pressure, but decreases with temperature. At low temperature and low pressure, thermal expansion coefficient increases sharply with temperature. At high temperature and high pressure, the increasing trend slows down.

1. Introduction

In recent years, energy is a serious problem and hydrogen storage materials have also been widely studied. However, pressure to be applied and cost are too high to apply widely. For example, 70 MPa of high pressure is required while using an ordinary carbon fibre tank to store hydrogen [1]. New hydrogen storage materials should be developed for industrial applications.

With the rapid development of science and technology, hydrogen storage materials, such as metal hydrides are in large demand and application [2,3]. Hydrogen density in metal hydrides is higher than in liquid or solid hydrogen. *fcc*-VH_2 is one of the most important hydrogen storage materials. VH_2 has a high hydrogen density ($\sim 10.5 \times 10^{22}$ Hatom/cm^3), higher than those of liquid or solid hydrogen [3]. Furthermore, VH_2 has an excellent capacity of reversible hydrogen storage, quick hydrogen diffusion in hydride etc. Fabrication and application of VH_2 are usually executed at high temperature and pressure. Structural, elastic, and thermodynamic properties of VH_2 at high temperature and pressure are significant greatly influencing the application of VH_2 in the fields mentioned above. Prediction of good elastic and thermodynamic properties of a crystal is the focus of solid-state science and industrial research. Particularly, these properties at high temperature and pressure are the most significant in many modern technologies. Unfortunately, measurement of elastic and thermodynamic properties of metal hydrides is very difficult, and to our knowledge detailed data on VH_2 at different temperatures and pressures are not available. Therefore, we need to obtain these data through theoretical methods.

First-principle is widely used to predict the properties of hydrogen storage materials [4]. In this work, first-principle and the quasi-harmonic Debye model are employed to investigate elastic and thermodynamic properties of VH_2 at different pressures and temperatures. To our knowledge, research on elastic and thermodynamic properties of VH_2 at high temperature and pressure using this method is an instructive attempt in the corresponding aspects.

2. Theoretical method

In this work, we apply the first-principle CASTEP code [5,6] combined with the quasi-harmonic Debye model [7] to study elastic and thermodynamic properties at different pressures and temperatures. The ultrasoft pseudopotential plane waves, together with the PBE generalized gradient approximation (GGA) exchange-correlation functions, [5,8–10] have been employed. Cut-off energy of the plane waves of 310.0 eV is used to describe the electron–ion interaction. The maximum stress component is 0.02 GPa and the force per atom is less than 0.01 eV. For the Brillouin zone, we use the $10 \times 10 \times 10$ Monkhorst–Pack mesh [11], where self-consistent convergence of

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the total energy is at 5×10^{-6} eV per atom. Pseudoatomic calculations are performed for H $1s^1$, V $3s^23p^63d^34s^2$.

According to Hooke's law [12], for cubic materials, there are only three independent elastic constants (C_{11}, C_{12}, and C_{44}). These constants can be obtained from the deformations caused by forces imposed on the original cell. For small strains, the total energy $E(V,\delta)$ is expressed as a Taylor expansion as follows [13]:

$$E(V,\delta)=E(V_0,0)+V_0\left(\sum_i\tau_i\delta_i\xi_i+\frac{1}{2}\sum_{i,j}C_{ij}\delta_i\xi_i\delta_j\xi_j\right) \tag{1}$$

where $E(V_0,0)$ is the energy of the unstrained system with equilibrium volume V_0, τ_i is an element of the stress tensor, and ξ_i is a factor present to take into account the Voigt index [13]. A detailed description of the calculation method has been reported in Ref. [14]. In this work, the total energy has been calculated for nine different deformations: $\delta=-0.001$, -0.00075, -0.0005, -0.00025, 0, 0.00025, 0.0005, 0.00075, and 0.001. They are too small to cause obvious internal strain effects; as such there may be a minor overestimation of the elastic constants. Then we can obtain the elastic constants and the bulk modulus at different pressures and temperatures.

Hence in order to investigate thermodynamic properties of VH_2, the quasi-harmonic Debye model [15] is applied in this work, the non-equilibrium Gibbs function $G^*(V;P,T)$ can be written as follows:

$$G^*(V;P,T)=E(V)+PV+A_{vib}(\vec{x};T) \tag{2}$$

where $E(V)$ is the total crystal energy per unit cell, P is the constant hydrostatic pressure, $\theta(V)$ is the Debye temperature, and A_{vib} is the vibrational Helmholtz free energy, which includes the vibrational contribution to the internal energy and the $-TS$ constant temperature condition term. Rigorous statistical calculation of A_{vib} is difficult requiring knowledge of the exact vibrational levels, but it is customary to introduce the quasi-harmonic approximation [15]

$$A_{vib}(\vec{x};T)=\int_0^\infty[1/2\hbar\omega+kT\ln(1-e^{-\hbar\omega/kT})]g(\vec{x};\omega)d\omega \tag{3}$$

where $g(\vec{x};\ \omega)$ is the phonon or vibrational density of states. The term quasi-harmonic, in contrast to the rigid harmonic approximation, implies that the density of states is allowed to vary with the crystal configuration, thus including anharmonic contributions to a certain extent.

The phonon spectrum has acoustic and optic branches; the acoustic branches have larger effects on the thermodynamic properties and optic branches have smaller effects. Considering the phonon effect, we apply the Debye model of phonon density of states to express the vibrational contribution A_{vib} as follows [16–20]:

$$A_{vib}=nkT\left[\frac{9\theta}{8T}+3\ln(1-e^{-\theta/T})-D\left(\frac{\theta}{T}\right)\right] \tag{4}$$

where n is the number of atoms per formula unit, $D(\theta/T)$ represents the Debye integral and for an isotropic solid, θ is expressed as [20]

$$\theta=\frac{\hbar}{k}[6\pi^2V^{1/2}n]^{1/3}f(\sigma)\sqrt{\frac{B_s}{M}} \tag{5}$$

where M is the molecular mass per unit cell and B_s is the adiabatic bulk modulus, which is approximately given by static compressibility [17]:

$$B_s\cong B(V)=V\frac{d^2E(V)}{dV^2} \tag{6}$$

$f(\sigma)$ is given in Refs. [19,20] and the Poisson σ is taken as 0.25 [12]. Therefore, the non-equilibrium Gibbs function G^* as a function of $(V;P,T)$ can be minimized with respect to volume V:

$$\left[\frac{\partial G^*(V;P,T)}{\partial V}\right]_{P,T}=0 \tag{7}$$

By solving Eq. (7), one can obtain the thermal equation-of-state (EOS) $V(P,T)$. The heat capacity C_v and thermal expansion coefficient α are given by [21]

$$C_v=3nk\left[4D\left(\frac{\theta}{T}\right)-\frac{3\theta/T}{e^{\theta/T}-1}\right] \tag{8}$$

$$\alpha=\frac{\gamma C_v}{B_TV} \tag{9}$$

where γ is the Grüneisen parameter, which is defined as

$$\gamma=-\frac{d\ln\theta(V)}{d\ln V} \tag{10}$$

The thermodynamic properties of a solid are greatly dependent on phonon density. Using the Debye model, the phonon effect is applied to calculate the total energy of the crystal (E) at different volumes (V). Through the first-principle, we obtain the total energy of different crystal volumes of VH_2 (E–V curve). E–V data are fitted fixed by the Murnaghan equation of state [22], we then, obtain the lattice constant in the ground state and at other pressures.

However, when a first principles method is used, complete minimization of $G^*(V;p,T)$ is currently infeasible. The first principles method ground state calculation is conducted at zero pressure and zero temperature, and the vibrational effect is neglected as it causes lower total energy, which may result in the specific heat deviating from that of the Debye model, especially, at intermediate temperatures. The method will be valid only true when the vibrational effects act as a hydrostatic term, i.e., are isotropic [6]. However, VH_2 is a cubic crystal and it is isotropic. Then the Debye model and first principles can be used to predict the thermodynamic properties of VH_2.

Using the methods mentioned above, we calculate the elastic and thermodynamic properties of VH_2. In our work, the elastic and thermodynamic properties of VH_2 are determined from 0 to 1500 K and 0 to 80 GPa, where the first-principle and quasi-harmonic model remain fully valid.

3. Results and discussion

The equilibrium lattice constant a_0 at $T=0$ K and $P=0$ GPa is obtained and is listed in Table 1. The lattice constant a_0 is 4.249 Å, which agrees well with the experimental value ($a=4.270$ Å) [23]. At the same time, the calculated bulk modulus B_0 and the elastic constants C_{ij} of the ground state are listed in Table 1. Other experimental and theoretical values [23–25] are also shown in Table 1.

Fig. 1(a) and (b) shows the elastic constants C_{ij} and bulk modulus B at different pressures and temperatures. For *fcc*-VH_2, there are only three independent elastic constants: C_{11}, C_{12}, and C_{44}. The three constants, determined by the relationship between deformations and

Table 1
Lattice constant a_0, bulk modulus B_0, and the elastic constants parameters of VH_2 at zero pressure and zero temperature.

	Present work	**Experiment**	**Other theoretical works**
α (Å)	4.249	4.270[a], 4.271[d],	4.10[a], 4.279[b],
B_0 (GPa)	150.589	–	190.8[a], 200.4[c],
C_{11} (GPa)	264.980	–	–
C_{12} (GPa)	93.393	–	–
C_{44} (GPa)	95.317	–	–

[a] Ref. [18].
[b] Ref. [19].
[c] Ref. [20].
[d] Ref. [21].