

# First-Principles Calculation for Thermodynamic Properties of LiD

Lei Jie-Hong<sup>1,2</sup>, Gu Yuqiu<sup>1</sup>

<sup>1</sup>Research Center of Laser Fusion, National Key Laboratory of Laser Fusion, CAEP, Mianyang, China

<sup>2</sup>Physics and Space Science of Institute, West China Normal University, Nanchong, China

## Email address:

jiehonglei@126.com (Lei Jie-Hong)

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**Abstract:** In this paper, the lattice parameter and bulk modulus of LiD at different pressures and temperatures are calculated by using the density functional theory method within the generalized gradient approximation (GGA). Through the quasi-harmonic Debye model, the thermodynamic properties of the LiD are predicted. The dependences of the normalized primitive cell volume  $V/V_0$  on pressure  $P$ , the variation of the thermal expansion coefficient  $\alpha$  with pressure  $P$  and temperature  $T$ , as well as the dependences of the heat capacity  $C_v$  on pressure  $P$  and temperature  $T$  are obtained systematically in the ranges of 0-100GPa and 0-2000K.

**Keywords:** Density Functional Theory, the Quasi-Harmonic Debye Model, Thermodynamic Properties

## 1. Introduction

Lithium hydride thin film is an ideal candidate of the fusion fuel in inertial confinement fusion [1]. Lithium hydride is the lightest of metal hydrides with a high melting temperature of 688°C. It is thermodynamically stable in vacuum and inert atmospheres and is chemically more stable than pure lithium [2-3]. Moreover the isotope <sup>6</sup>Li can react with neutrons to create tritium, which can increase the content of tritium in fusion reaction. Because of these properties, lithium hydride has the most extensive applied foreground in thermonuclear weapons.

Lithium hydride one of the simplest neutral heteropolar diatomic molecules, lightest heteronuclear diatomics and an important candidate in spectroscopic studies to demonstrate the breakdown of the Born-Oppenheimer approximation has long attracted the interest of spectroscopists and theoreticians [4-9].

It is well known that high-pressure and high-temperature studies play an important role in understanding the fundamental physical properties of condensed matter. The high pressure structural phase transformation from a typical metal at ambient pressure to an orthorhombic phase for LiD has been reported to occur at 50GPa [10]. However, there are few literatures reporting on the thermodynamic properties for

LiD at different pressures and temperatures.

In this paper, we investigate the thermodynamic properties of LiD at different pressures and temperatures through the density functional theory method, and the quasi-harmonic Debye model [11]. The brief review of the theoretical methods is presented in Section 2. In Section 3, we make some discussion of calculated results.

## 2. Materials and Methods

In our calculations, the ultrasoft pseudopotentials introduced by Vanderbilt [12] for the interactions of the electrons with the ion cores is applied, together with the generalized gradient approximation (GGA) [13] for exchange-correlation functional in the scheme of Perdew-Burke-Ernzerhof (PBE) [14]. The electronic wave functions are expanded in a plane wave basis set with an energy cut-off of 350eV. As for the Brillouin-zone k-point sampling, the 10×10×10 Monkhorst-Pack mesh [15] are employed, where the self-consistent convergence of the total energy is 10-6eV/Atom. All the electronic structure calculations are implemented through the CASTEP code [16, 17].

In order to investigate the thermodynamic properties, we apply the quasi-harmonic Debye model, in which the non-equilibrium Gibbs function  $G^*(V; P, T)$  can be written as

$$G^*(V; P, T) = E(V) + PV + A_{vib}(\theta(V); T), \quad (1)$$

where  $E(V)$  is the total energy per unit cell of the crystal, which can be determined from the electronic structure calculations. The term  $PV$  corresponds to the constant hydrostatic pressure condition.  $\theta(V)$  is the Debye temperature, and  $A_{vib}$  is the vibrational Helmholtz free energy. It is customary to be written as [18, 19]

$$A_{vib}(\theta; T) = nk_B T \left[ \frac{9\theta}{8T} + 3 \ln(1 - e^{-\theta/T}) - D(\theta/T) \right], \quad (2)$$

Here  $D(\theta/T)$  represents the Debye integral,  $n$  is the number of atoms per formula unit. For an isotropic solid,  $\theta$  is expressed by [20]

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

Where  $M$  is the molecular mass per formula unit,  $B_s$  is the adiabatic bulk modulus,  $f(\sigma)$  and  $B_s$  are given by Ref. [21].

$$B_s \cong B(V) = V \left( \frac{d^2 E(V)}{dV^2} \right), \quad (4)$$

$$f(\sigma) = \left\{ 3 \left[ 2 \left( \frac{21 + \sigma}{31 - 2\sigma} \right)^{3/2} + \left( \frac{11 + \sigma}{31 - \sigma} \right)^{3/2} \right]^{-1} \right\}^{1/3}, \quad (5)$$

Therefore, the non-equilibrium Gibbs function  $G^*(V; P, T)$  as a function of  $(V; P, T)$  can be minimized with respect to volume  $V$ ,

$$\left( \frac{\partial G^*(V; P, T)}{\partial V} \right)_{P, T} = 0, \quad (6)$$

$$P = 2B_0 \left( \frac{V_0}{V} \right) f_N \left[ 1 + \frac{3}{2} (B' - 2) f_N + \frac{3}{2} \left( 1 + B^0 B'' + (B' - 2) + (B' - 2)^2 \right) f_N^2 \right], \quad (11)$$

where  $f_N = \ln(V/V_0)$ , which may be written as  $f_N = \ln(V/V_0)/3$  for hydrostatic compression.

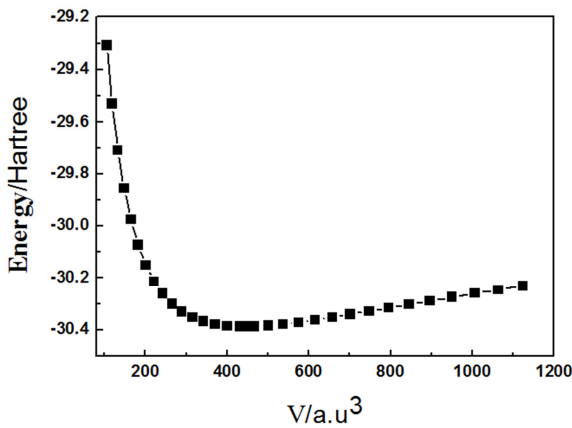


Fig. 1. The energy-volume curves for different of  $a$ .

Thus one could get the thermal equation of state (EOS)  $V(P, T)$  by solving Eq. (6). The heat capacity  $C_V$ , the isothermal bulk modulus  $B_T$ , and the thermal expansion coefficient  $\alpha$  are given by [22]

$$C_V = 3nk_B \left[ 4D(\theta/T) - \frac{3\theta/T}{e^{\theta/T} - 1} \right], \quad (7)$$

$$B_T(P, T) = V \left( \frac{\partial^2 G^*(V; P, T)}{\partial V^2} \right)_{P, T}, \quad (8)$$

$$\alpha = \frac{\gamma C_V}{B_T V}, \quad (9)$$

where  $\gamma$  is the Grüneisen parameter, which is defined as

$$\gamma = \frac{d(\ln \theta(V))}{d(\ln V)}, \quad (10)$$

One could calculate the thermodynamic properties of LiD at different pressures and temperatures from the calculated energy-volume data at  $T=0$  and  $P=0$ . Applying there methods described above, the thermodynamic properties of some materials have successfully been investigated [18-20].

### 3. Results and Discussion

First of all, we set a series of different values of lattice constant to calculate the total energy  $E$  and the corresponding primitive cell volume  $V$  for the metal LiD at  $P=0$  GPa and  $T=0$  K. In Fig. 1, we present the  $E$ - $V$  curves for several values of  $a$ . Then by fitting the calculated  $E$ - $V$  curves to the natural strain EOS [23], we have

Now, we investigate the thermodynamic properties of LiD by applying the quasi-harmonic Debye mode described above. The normalized volume-pressure diagrams of LiD at the temperature ranges of 0-2000K are illustrated in Fig. 2. It is noted that, as the temperature  $T$  changes, the relative volume  $V/V_0$  of LiD doesn't change at the same pressure. On the other hand, as the pressure  $P$  increases, the relative volume  $V/V_0$  of LiD decreases at a given temperature. The relationship between the bulk modulus  $B$  and pressure  $P$  at different temperatures are shown in Fig. 3. The results indicate that  $B$  increases with  $P$  at a given temperature, and at a given pressure,  $B$  increases with  $T$ . We illustrate the variations of the thermal expansion  $\alpha$  with temperature and pressure in Fig. 4. It is shown that, for a given pressure,  $\alpha$  increases rapidly with temperature at low temperature especially at zero pressure. As the pressure increases, the increase of  $\alpha$  with temperature becomes smaller, especially at higher temperatures.  $\alpha$  decreases drastically with the increase of pressure at a given

temperature. The temperature of dependence of  $\alpha$  is small at high pressure and high temperature.

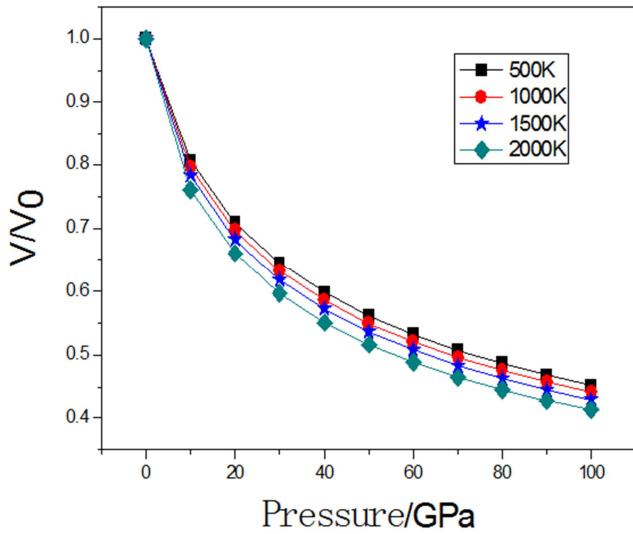


Fig. 2. The normalized volume  $V/V_0$ - $P$  diagrams of LiD at the temperature ranges of 0-2000K.

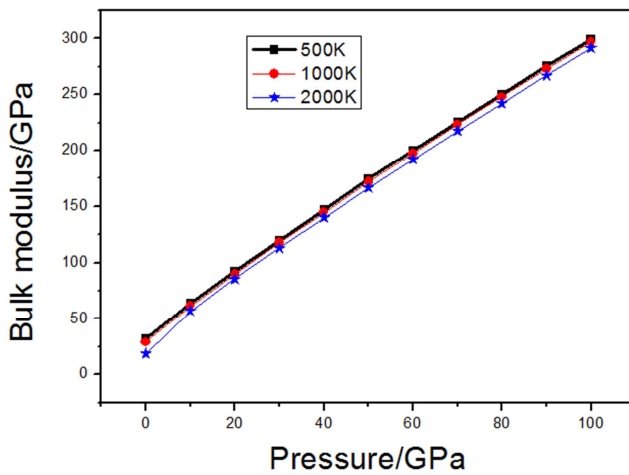


Fig. 3. The relationships between bulk modulus  $B$  and pressure  $P$  at temperatures of 500, 1000, and 1500K.

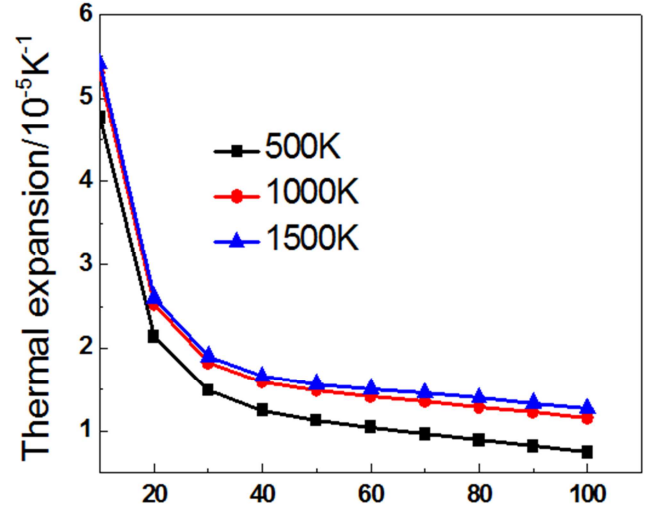
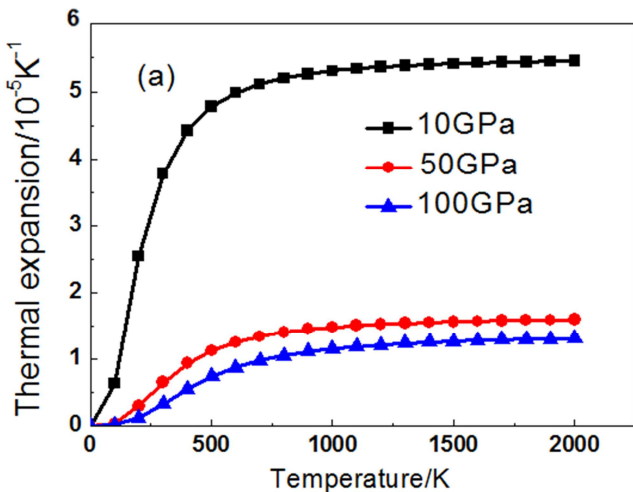


Fig. 4. The thermal expansion versus pressure and temperature (a) and (b) for LiD.

The heat capacities of the metal LiD at various pressures and temperatures are plotted in Fig. 5, which shows that when  $T < 1500$ K, the heat capacity  $C_V$  is dependent on temperature and pressure. This is due to the anharmonic approximations of the Debye model here. However, under higher temperatures, the anharmonic effect on heat capacity  $C_V$  is suppressed, and  $C_V$  is very close to the Dulong-Petit limit.

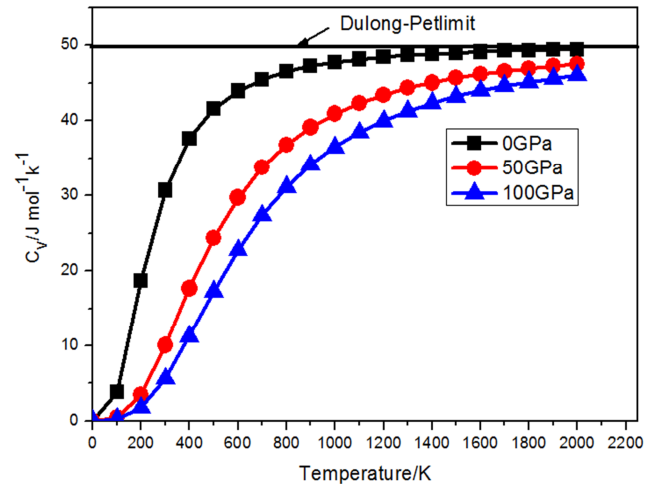


Fig. 5. The heat capacity of LiD at various pressures and temperatures.

## 4. Conclusion

In summary, the thermodynamic properties of the metal LiD at different pressures and temperatures are investigated by using density functional theory method within the generalized gradient approximation (GGA). Applying the quasi-harmonic Debye model, we predict the thermodynamic properties of the metal LiD. The dependences of the relative volume  $V/V_0$  on pressure, the variations of the thermal expansion coefficient  $\alpha$  and the  $C_V$  with pressure and temperature have been obtained systematically in the ranges of 0-100GPa and 0-2000K.

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