

Thermodynamic Properties of New Superconductivity Type I Clathrate Compound Ba_8Si_{46}

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Abstract—The ground state properties and equation of state of the silicon clathrate Si_{46} intercalated by Ba atoms are investigated by first-principles calculations based on the plane-wave basis set with the generalized gradient approximation (GGA) for exchange and correlation. Some thermodynamic properties including the heat capacity, the thermal expansion coefficient, Debye temperature and the Grüneisen parameter for Ba_8Si_{46} are obtained. Moreover, the effects of high pressure on these thermodynamic properties are also investigated which will be very helpful for a synthesis of these clathrates in experiments under high pressure and high temperature condition.

Keywords—thermodynamic properties; density functional theory; clathrate compound

I. INTRODUCTION

The type-I silicon-clathrates intercalated by Ba atoms comprised by face-shared polyhedral cages, have the same structure as the methane hydrate $(CH_4)_8(H_2O)_{46}$ [1]. In the cubic cell of Ba_8Si_{46} , the unique Si atoms are located at three distinct Wyckoff symmetry sites: Si 6c, Si 16i and Si 24k. The Ba atoms are assumed to locate at the centers of two small Si_{20} cages and six large Si_{24} cages corresponding to 2a and 6d sites respectively. Such silicon compounds intercalated by Na atoms were first synthesized by Cros et al. early in 1965 [2,3], and they back to the line of sight recently since the discovery of superconductivity in intercalated clathrate $Ba_xNa_ySi_{46}$ [4]. Soon afterwards, due to their potential applications range from superconductivity[5], large gap semiconductors[6], optoelectronics[7], thermoelectrics[8, 9], they become the subject of active experimental and theoretical study. The most known method to synthesize such kind of silicon clathrates is under deep vacuum or at ambient pressure using Zintl compounds as precursors or through different types of chemical reactions.[2,10]. Since the first high-pressure synthesis of type-I Ba_8Si_{46} clathrate was realized in 2000 by the group of Yamanaka [11] in a multi-anvil press, more and more clathrate compounds were synthesized using high pressure techniques[12,13]. However, as declared in the reference [14], a well-controlled clathrate compounds crystal growth need

the knowledge of the p-T domains for thermodynamic stability and the possibility for equilibrium crystal growth, which are still wanting. So, in this letter, we employ first principle calculation combine with quasi-harmonic Debye model to investigate the thermodynamic properties of Ba_8Si_{46} in order to offer some beneficial theoretical reference for experiments.

II. THEORETICAL METHODS

In the electronic structure calculations, the ultrasoft pseudopotentials introduced by Vanderbilt [16] have been employed for all the ion-electron interaction, together with the generalized gradient approximation (GGA) [17] for the exchange-correlation function. A plane-wave basis set with energy cut-off 600 eV is applied. Pseudo atomic calculations are performed for Ba (5s, 5p, 6s) and Si (3s, 3p). For the Brillouin-zone sampling, we use the $6 \times 6 \times 6$ Monkhorst-Pack mesh. The self-consistent convergence of the total energy is 10^{-6} eV/atom. All these total energy electronic structure calculations are implemented through Cambridge Serial Total Energy Package (CASTEP) code [18, 19].

To investigate the thermodynamic properties of Ba_8Si_{46} , we apply the quasi-harmonic Debye model [20], in which the phononic effect is considered, and the non-equilibrium Gibbs function $G^*(V; P, T)$ takes the form of

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

where $E(V)$ is the total energy per unit cell, PV corresponds to the constant hydrostatic pressure condition, $\Theta(V)$ is the Debye temperature, and the vibrational contribution A_{vib} can be written as

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

where the $D(\Theta/T)$ represents the Debye integral, n is the number of atoms per formula unit. The Debye temperature Θ expressed by

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

where M is the molecular mass per formula unit, B_S is the adiabatic bulk modulus, σ is the Poisson ratio and $f(\sigma)$ is given by

$$f(\sigma) = \left\{ 3 \left[2 \left(\frac{2}{3} \frac{1+\sigma}{1-2\sigma} \right)^{\frac{3}{2}} + \left(\frac{1}{3} \frac{1+\sigma}{1-\sigma} \right)^{\frac{3}{2}} \right]^{-1} \right\}^{\frac{1}{3}} \quad (4)$$

By solving the following equation with respect to V

$$\left(\frac{\partial G^*(V; P, T)}{\partial V} \right)_{P, T} = 0 \quad (5)$$

one could obtain the thermal expansion coefficient α as follows

$$\alpha = \gamma C_V / (B_T V) \quad (6)$$

where the isothermal bulk modulus B_T , the heat capacity C_V and the Grüneisen parameter γ are expressed as

$$B_T(P, T) = V \left[\frac{\partial^2 G^*(V; P, T)}{\partial V^2} \right]_{P, T} \quad (7)$$

$$C_V = 3nk \left[4D(\Theta/T) - \frac{3\Theta/T}{e^{\Theta/T} - 1} \right] \quad (8)$$

$$\gamma = \frac{d \ln \Theta(V)}{d \ln V} \quad (9)$$

III. RESULTS AND DISCUSSION

For clathrate compounds Ba_8Si_{46} , a series of lattice constants are set to obtain the total energy E and the corresponding primitive cell volume V through GGA schemes, and then the obtained E - V data are fitted to the Birch–Murnaghan equation of state (EOS) [21]. From the EOS we find that when the pressure applied to 30 GPa, the volume of clathrate compound Ba_8Si_{46} just reduced about 20 % which show this compound is not easy to compressed. The obtained equilibrium lattice constant a equals to 10.375 Å, zero-pressure bulk modulus B_0 and its pressure derivative B_0' are 75.5 GPa and 5.2 respectively.

We plot the dependence of both heat capacity at constant volume C_V and heat capacity at constant pressure C_p on temperature from 0 to 700 K in Figure 2. The calculated heat capacity C_p and C_V at ambient condition are 1317.9 J Mol⁻¹ K⁻¹ and 1255.6 J Mol⁻¹ K⁻¹ respectively. The experimental heat capacity is that at constant pressure, i.e., C_p , but the more meaningful quantity to discuss lattice dynamics is C_V . For a cubic solid, the relationship between them can be expressed by $C_p - C_V = KTV(\alpha_V)^2$. The difference between C_p and C_V is about 4.9 % at room temperature, when the temperature decrease to about 100 K, the difference between them can hardly be found. Moreover, it can be found that when the temperature is below 300 K, the heat capacity C_V is strongly dependent on temperature, which is due to the anharmonic approximations. However, under higher temperature, the

anharmonic effect on C_V is suppressed, and the C_V is close to a constant at high temperature.

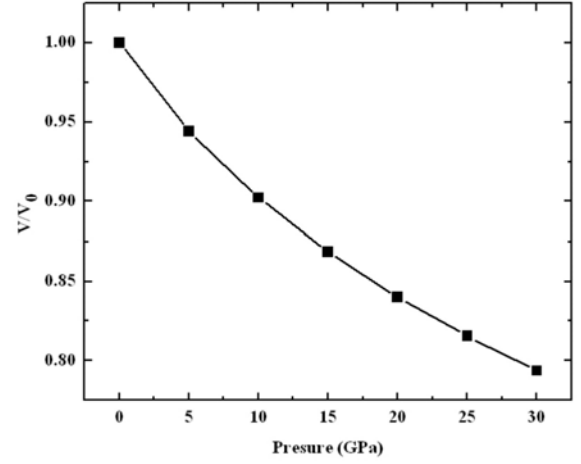


Figure 1. Calculated equation of state of Ba_8Si_{46}

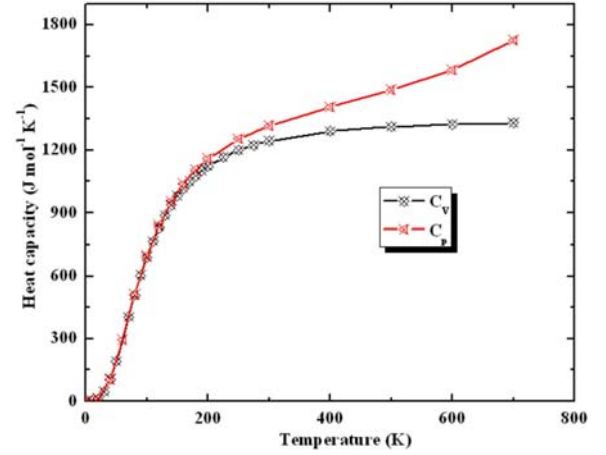


Figure 2. Dependences of specific heat for Ba_8Si_{46} on temperature

In Figure 3, The temperature dependences of thermal expansion coefficient α_V of Ba_8Si_{46} under different pressures are illustrated. It can be found that the thermal expansion coefficient α_V increases with T^{-3} at low temperatures and gradually approaches a very slow increase at high temperature. At low temperatures, the effects of pressure on the thermal expansion coefficient α_V are very small. The pressure can suppress such thermal expansion obviously. The variation of Grüneisen parameter γ with pressure and temperature are displayed in Figure.4, from which it can be found that the Grüneisen parameter γ increases as the temperature increases, however, as the pressure enhanced, the effect of temperature becomes more and more infirm because at high pressure, the increasing trend becomes rather gentler.

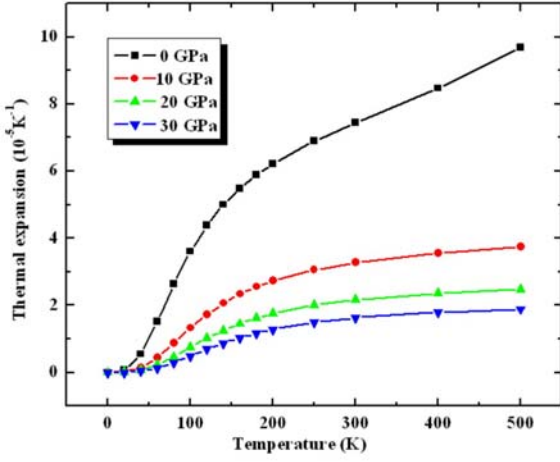


Figure 3. Temperature dependences of thermal expansion coefficient for Ba_8Si_{46} under different pressures

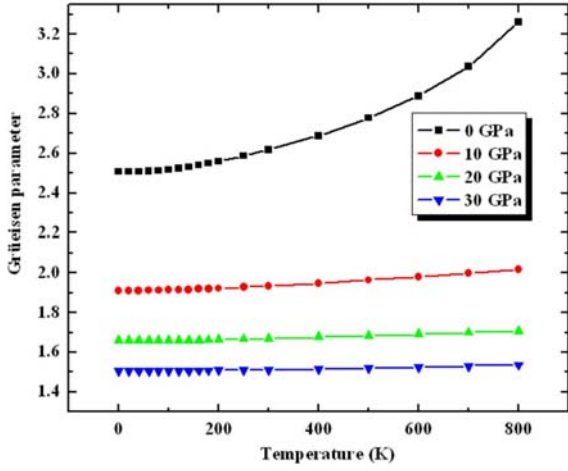


Figure 4. Temperature dependences of the Grüneisen parameter for Ba_8Si_{46} under different pressures

The dependence of Debye temperature on temperature under different pressures are shown in Figure 5. The value of Debye temperature can represent inter-atomic binding forces thus it is related to hardness of material, in general, a higher Debye temperature indicates a higher hardness[22]. The dependence of Debye temperature on temperature at zero pressure shows a soften of the Ba_8Si_{46} crystal and the pressure can suppress such effect. At room temperature, the calculated Debye temperature Θ_D is 395 K. From Figure 5, it can be found that the pressure has a more distinct effect on Θ_D than temperature. When the pressure applied to 30 GPa, although the temperature enhanced, the Debye temperature is almost a constant.

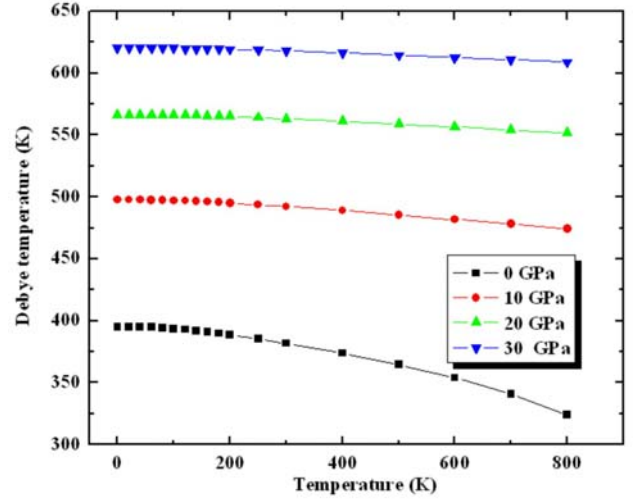


Figure 5. The dependence of Debye temperature on temperature at 0, 10, 20 and 30 GPa

IV. SUMMARY

In summary, the thermodynamics properties of silicon clathrate intercalated by Ba atoms are obtained by first-principles calculations combine with quasi-harmonic Debye model. The EOS, heat capacity, thermal expansion coefficient and Debye temperature are calculated. The dependence of them pressure on are also discussed, it is found that the effects of pressure on thermal expansion of Ba_8Si_{46} are very small at low temperatures, but as the temperature increases the effects become more prominent. As for the variation of Grüneisen parameter, pressure plays a dominant role.

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