Thermodynamic properties of ZnSe under pressure and with variation in temperature

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The thermodynamic properties of ZnSe are obtained by using quasi-harmonic Debye model embedded in Gibbs-code for pressure range 0–10 GPa and for temperature range 0–1000 K. Helmholtz free energy, internal energy, entropy, Debye temperature, and specific heat are calculated. The thermal expansion coefficient along with Grüneisen parameter are also calculated at room temperature for the pressure range. It is found that internal energy is pressure dependent at low temperature, whereas entropy and Helmholtz free energy are pressure sensitive at high temperature. At ambient conditions, the obtained results are found to be in close agreement to available theoretical and experimental data.

Keywords: density functional theory, Helmholtz energy, Debye temperature, entropy

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1. Introduction

Wide band gap semiconductors are very important due to their large number of applications in optical devices like light emitting diode, optical wave guide, solar cells, solid state lasers, and photodetectors. ZnSe is one member of the family of large band gap semiconductors which can crystallize in the cubic zinc blend structure at the ambient pressure and has a distinct property of reversible transformation thus being used in optical memory devices.[1] Thorough understanding of physical, chemical, and thermodynamical behavior is necessary for the device fabrication and their applications. The thermal property is considered to be one of the basic properties of material, which influences other properties like band gap variation with temperature.

In recent years, ZnSe has been widely studied both by theoretical and experimental ways for their structural, optical, and thermal properties.[2–4] Sarkar *et al.*[4] have studied Helmholtz free energy, entropy, and specific heat capacity at constant volume of ZnSe with variation of temperature using full potential linearized augmented plane wave (FP-LAPW) method in the framework of density functional theory (DFT) with generalized gradient approximation (GGA) as exchange and correlation functional. They concluded that the Helmholtz free energy decreases while entropy increases with increase in temperature. At low temperature, the specific heat shows T^3-law, while at high temperature it approaches to the Dulong–Petit law. Lin *et al.*[5] employed Raman spectroscopy to determine $\frac{\mathrm{d}\gamma}{\mathrm{d}p}$ of ZnSe at room temperature for longitudinal and optical phonon modes at pressure up to 36 GPa. The effect of temperature on entropy and specific heat at constant volume has been investigated by Parashchuk *et al.*[6] using density functional theory (DFT)-based calculations.

The first principle calculation of structural, vibrational, and thermodynamical properties of Zn-based semiconductors was performed by Yu *et al.*[7] and phonon dispersion curve along with phonon density of states was calculated using DFPT. The phonon contribution to entropy, internal energy, and specific heat at constant volume was determined within harmonic approximation.

Wang *et al.*[8] studied the linear expansion of ZnSe and its specific heat at constant pressure using quasiharmonic approximation with local density approximation as exchange correlation functional.

Dinesh *et al.*[9] studied the pressure-induced phase transition of ZnSe from zinc blend structure to rock salt structure.They determined the Debye temperature, Grüneisen parameter, thermal expansion coefficient, compressibility, force constant, and reststrahlen frequency of ZnSe in its zinc blend structure. Hamdi *et al.*[10] employed the DFPT within quasi-harmonic approximation to study the pressure dependence of thermal expansion coefficient and specific heat at constant pressure along with vibrational and elastic properties.

The above literature survey shows that experimental and theoretical studies about thermodynamical properties under pressure with variation of temperature are insufficient. So we study the thermodynamic properties over a wide range of temperature and pressures in order to remove this deficiency. ZnSe is stable in the zinc blend phase up to pressure 11.04 GPa[11] at room temperature and transforms into wurtzite structure when heated above 1698 K.[12] The present study of pressure and temperature dependence of thermodynamical behavior of zinc selenide lies within the stability range of pressure and temperature: pressure range from 0 to 10 GPa and temperature range from 0 to 1000 K.

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2. Theory and computational details

The optimized calculations are performed using DFT implemented in WIEN2k code[13] with FP-LAPW method. The generalized gradient approximation with Wu–Cohen (GGA-WC) parameterization[14] is used as exchange correlation functional. The core and valence states are separated by −9.5 Ry energy and the wave functions in the core for full potential scheme are expanded up to $l_{\max} = 10$ in terms of spherical harmonics. The convergence criterion is set to be $0.0001e$ for charge and 0.0001 Ry for energy where $R_{\mathrm{MT}}K_{\max} = 8.0$. The values of R_{MT} are set to be 1.8 Bohr and 1.88 Bohr for Zn and Se, respectively. The structure has been relaxed up to 1 mRy/Bohr in our calculations. The K-point sampling is $11 \times 11 \times 11$ in the full Brillouin zone.

The thermodynamic properties are determined by using quasi-harmonic Debye model which is implemented in Gibbs code.[15] The energy volume optimization data is used as input to determine the pressure and temperature dependence of Helmholtz free energy, internal energy, entropy, Debye temperature, and heat capacity. In the quasi-harmonic Debye model, the non-equilibrium Gibbs function $G^*(V;P,T)$ can be written as[16]

$$G^*(V;P,T) = E(V) + PV + F_{\mathrm{vib}}(\theta_{\mathrm{D}},T), \tag{1}$$

where $E(V)$ represents the total energy per unit volume of ZnSe, P represents the hydrostatic pressure,

$$F_{\mathrm{vib}}(\theta_{\mathrm{D}},T) = nk_{\mathrm{B}}T\left[\frac{9}{8}x + 3\ln\left(1-\mathrm{e}^{-x}\right) - D(x)\right]$$

is the vibrational Helmholtz free energy with $\frac{\theta_{\mathrm{D}}}{T} = x$ which is a dimensionless parameter, n is the number of atoms per formula unit,

$$D(x) = \frac{3}{x^3}\int_0^x \frac{y^3\mathrm{e}^{-y}}{1-\mathrm{e}^{-y}}\mathrm{d}y$$

is Debye integral, and

$$\theta_{\mathrm{D}} = \frac{\hbar}{k_{\mathrm{B}}}\left[6\pi V^{1/2}n\right]^{1/3} f(\sigma)\sqrt{\frac{B_s}{M}}$$

is Debye temperature where B_s is adiabatic bulk modulus, σ is Poisson ratio, M is molecular weight per unit cell, and

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

is an explicit function.

The equilibrium geometry is achieved by minimizing the Gibbs function with respect to volume of unit cell at constant pressure and temperature, i.e.,

$$\left[\frac{\partial G^*(V;P,T)}{\partial V}\right]_{P,T} = 0. \tag{2}$$

By using minimizing condition in Eq. (2), vibrational contribution to heat capacity, entropy, internal energy, and thermal expansion coefficient can be computed and expressed as[16]

$$C_v = 3nk_{\mathrm{B}}\left[4D(x) - \frac{3x}{\mathrm{e}^x - 1}\right], \tag{3}$$

$$S_{\mathrm{vib}} = nk_{\mathrm{B}}\left[4D(x) - 3\ln\left(1-\mathrm{e}^{-x}\right)\right], \tag{4}$$

$$U_{\mathrm{vib}} = 3nk_{\mathrm{B}}\left[\frac{3}{8}\theta_{\mathrm{D}} + TD(x)\right], \tag{5}$$

$$\alpha = \frac{\gamma C_v}{B_T V} \quad \text{with} \quad \gamma = -\frac{\mathrm{d}\ln\theta_{\mathrm{D}}(V)}{\mathrm{d}\ln V}, \tag{6}$$

where γ is Grüneisen parameter.

3. Results and Discussion

The Helmholtz free energy is important to determine the stability of a structure. A structure with more negative value of Helmholtz free energy will be considered more stable. The Helmholtz free energy at any temperature T can be written easily in the scope of standard thermodynamics as

$$F(Z;T) = E(Z) + F_{\mathrm{el}}(Z;T) + F_{\mathrm{vib}}(Z;T). \tag{7}$$

Here Z represents the crystal configuration vector which consists of geometric information for crystal structure and $E(Z)$ is the static energy. F_{el} represents the electronic contribution to free energy which can be ignored in case of a semiconductor, and F_{vib} is the vibrational contribution. The vibrational contribution in the Helmholtz and internal energy are related as

$$F_{\mathrm{vib}} = U_{\mathrm{vib}} - TS, \tag{8}$$

where S is entropy. The pressure and temperature dependence of F_{vib} and U_{vib} is displayed in Figs. 1 and 2, which is in excellent agreement to reported data[7] for $P = 0$ GPa.

The Helmholtz and internal energies are increasing with the increase of temperature. The internal energy is found insensitive to pressure above 200 K, while Helmholtz energy increases with pressure from 0 to 10 GPa. At low temperature limit, F_{vib} weakly depends upon pressure, while at high temperature limit it strongly depends on pressure, whereas U_{vib} is found more sensitive to pressure at low temperature. At low temperature limit, the atomic oscillators have small amplitude of oscillations and hence an increase in pressure induces a prominent effect on the internal energy and insensitive to Helmholtz energy of the system. While at high temperature limit, pressure has negligible effect on the internal energy and prominent effect on Helmholtz energy of the system, because harmonicity is now converted into anharmonicity.

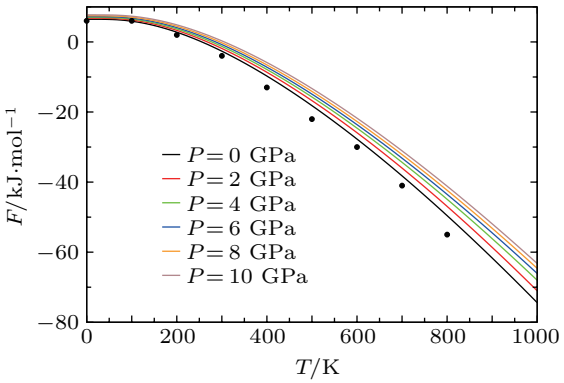


Fig. 1. (color online) The pressure and temperature dependence of Helmholtz energy. The doted line is from Ref. [19].

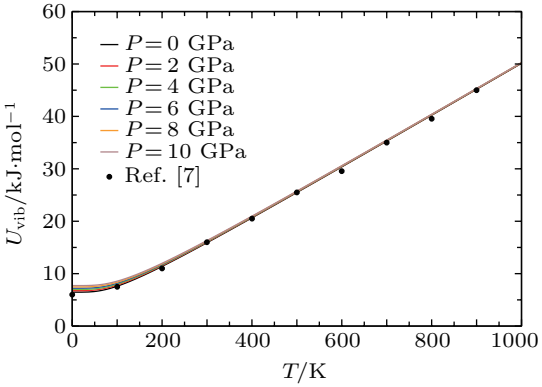


Fig. 2. (color online) The pressure and temperature dependence of the internal energy.

The internal energy at 0 K is attributed to the existence of zero point motion and calculated $F_{\rm vib}$ and $U_{\rm vib}$ at absolute zero is 5.47 kJ/mol, which is in agreement with the value 5.3 kJ/mol reported in Ref. [7]. The increase in Helmholtz energy with increasing pressure is attributed to the decrease in entropy at certain temperature. The effect of hydrostatic pressure and temperature on entropy of ZnSe is shown in Fig. 3, which shows an increasing trend with the increase of temperature due to the increase of heat energy. At any temperature, the entropy of ZnSe decreases with the increase of pressure, which is due to the decrease of volume that consequently decreases the amplitude of vibration of atoms. Since anharmonicity of the system becomes very large at high temperature, the entropy is more pressure sensitive.

The Debye temperature is a key quantity in the quasi-harmonic Debye model, which is related to many properties like elastic constants, thermal expansion, melting temperature, and specific heat. The Debye temperature at zero Kelvin and zero Pascal is 390.53 K, which is close to the value 383 K reported in Ref. [9]. The effect of temperature and pressure on Debye temperature is displayed in Fig. 4, which shows that it decreases on increasing the temperature. When pressure is raised from 0 to 10 GPa, it increases. It should be noticed that Debye temperature is found to be more sensitive compared to temperature.

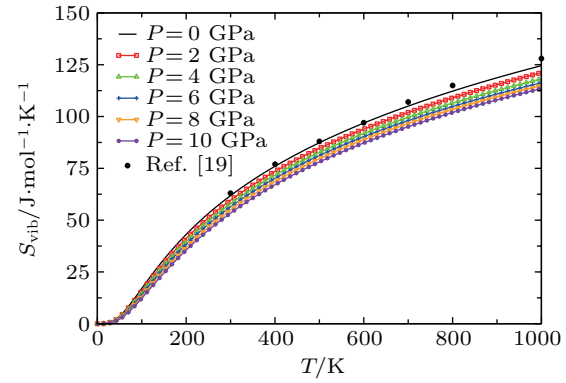


Fig. 3. (color online) The effect of hydrostatic pressure and temperature on entropy.

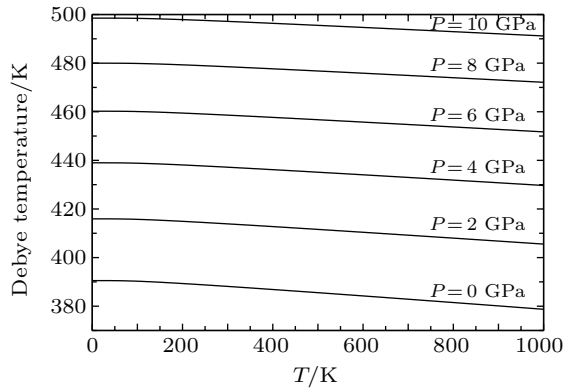


Fig. 4. The effect of temperature and pressure on Debye temperature.

The Grüneisen parameter reflects the anharmonicity in the crystal, that is, how much phonon vibrations are deviating from harmonic oscillations. Table 1 shows the Grüneisen parameter and thermal expansion coefficient at room temperature under pressure varied from 0 to 10 GPa. It shows strong pressure dependence, which is in close agreement to the other calculated and experimental results.[9,17] It can be seen that both quantities decrease with the increase of pressure.

Table 1. Grüneisen parameter and thermal expansion coefficient at $T = 300$ K.

P/GPa	Calculated results		Other results	
	γ	$\alpha/10^{-6}$ K^{-1}	γ	$\alpha/10^{-6}$ K^{-1}
0	1.9	6.9	1.55[17]	7.2,[18] 7.0[10]
2	1.65	5.1		
4	1.56	4.3		
6	1.4	3.0		2.6[10]
8	1.31	2.1		
10	1.22	1.5		

The heat capacity at constant volume on the basis of Debye quasi-harmonic approximation as a function of temperature at different pressure is shown in Fig. 5. It obeys T^3 law at low temperature, whereas it approaches to Dulong–Petit limit at high temperature. It should be noted that C_v appears to be independent of pressure at high temperature, so converging to

the same value of classical limit of $C_v = 49.9$ J/(mol·K). But at the temperature range of 100–400 K, there is a decrease in specific heat on increasing pressure.

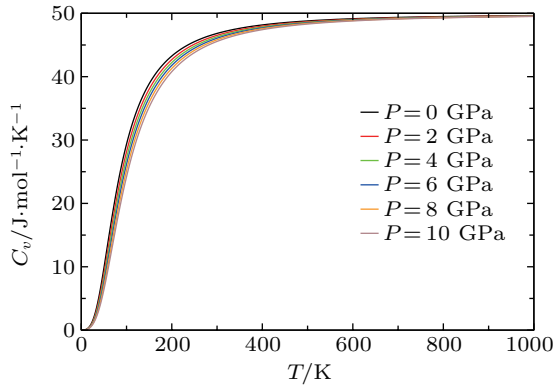


Fig. 5. (color online) The pressure and temperature dependence of C_v.

Figure 6 shows Helmholtz energy, internal energy, and entropy varying with pressure at $T = 300$ K, which is in agreement to Eq. (9). The decreases in entropy at room temperature ($T = 300$ K) at hydrostatic pressures of 2 GPa, 4 GPa, 6 GPa, 8 GPa, and 10 GPa are 3.667%, 6.413%, 8.792%, 11.16%, and 13.63%, respectively. The decrease in entropy on rise of pressure is due to decrease in spread of energy.

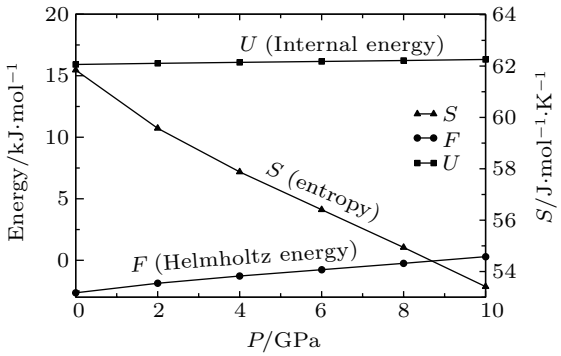


Fig. 6. The pressure dependence of Helmholtz, internal energy, and entropy at $T = 300$ K.

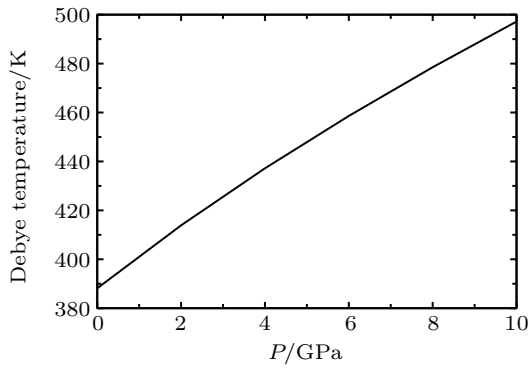


Fig. 7. The pressure dependence of Debye temperature at $T = 300$ K.

The effect of pressure on Debye temperature at $T = 300$ K is shown in Fig. 7. The increases in Debye temperature at room temperature on increasing pressure through 2 GPa, 4 GPa, 6 GPa, 8 GPa, and 10 GPa are 6.629%, 12.634%, 18.153%, 23.285%, and 28.09%, respectively.

4. Conclusion

The pressure and temperature dependence of thermodynamic properties of zinc selenide in zinc blende phase have been calculated by using FP-LAPW+lo method in the framework of density functional theory and Debye quasi-harmonic approximation which are implemented in WIEN2k and Gibbs codes respectively. The Helmholtz free energy and Debye temperature are found to decrease with increasing temperature, but both have increasing behavior with rise of pressure, whereas internal energy and entropy of ZnSe have increasing trend with increase of temperature. The internal energy almost remains insensitive to pressure over most of the temperature range and entropy decreases with rise of pressure. The specific heat at constant volume approaches to classical limit at $T = 300$ K. The Grüneisen parameter and thermal expansion coefficient decrease with rise of pressure. The calculated thermodynamic properties are in good agreement with available theoretical and experimental data at ambient conditions.[7,19]

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