Investigations of phase transition, elastic and thermodynamic properties of GaP by using the density functional theory

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The phase transition of gallium phosphide (GaP) from zinc-blende (ZB) to a rocksalt (RS) structure is investigated by the plane-wave pseudopotential density functional theory (DFT). Lattice constant a_0, elastic constants c_{ij}, bulk modulus B_0 and the pressure derivative of bulk modulus B_0' are calculated. The results are in good agreement with numerous experimental and theoretical data. From the usual condition of equal enthalpies, the phase transition from the ZB to the RS structure occurs at 21.9 GPa, which is close to the experimental value of 22.0 GPa. The elastic properties of GaP with the ZB structure in a pressure range from 0 GPa to 21.9 GPa and those of the RS structure in a pressure range of pressures from 21.9 GPa to 40 GPa are obtained. According to the quasi-harmonic Debye model, in which the phononic effects are considered, the normalized volume V/V_0, the Debye temperature θ, the heat capacity C_v and the thermal expansion coefficient α are also discussed in a pressure range from 0 GPa to 40 GPa and a temperature range from 0 K to 1500 K.

Keywords: GaP, phase transition, density functional theory, thermodynamic properties

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1. Introduction

Gallium phosphide is an important semiconductor material. It is often used as the substrate for quantum devices and optoelectronic devices.[1] The structural properties, the phase diagram and the phonon effect in GaP quantum dots have aroused considerable scientific interest. Recently, GaP was described within the density functional theory (DFT) by performing the local density approximation (LDA). Sjakste *et al.*[2] have calculated the phonon density of states (PDOS) by an *ab initio* method, which was proposed to evaluate the electron–phonon scattering time and provide an insight into electronic de-excitation by inter-valley phonons. Rashid *et al.*[3] have investigated the structural and electronic properties of GaP by the DFT and compared the lattice parameters, the bulk modulus and the pressure derivative of the bulk modulus and the cohesive energy per unit cell with the Early values. Garcia and Marvin[4] have found that the phase transition from zinc-blende (ZB) to a rocksalt (RS) structure occurred at 18.8 GPa and the RS structure was unstable. In 1996, Mujica and Needs[5] found that the simple cubic (sc16) phase should be stable between 14.7 GPa and 20.3 GPa. However, to our knowledge, even though GaP has been well known for a long time, its theoretical study of the aspects such as the phase transition, the elastic and the thermodynamic properties under pressure are still rare. In the present paper, the phase transition of gallium phosphide (GaP) from ZB to RS is investigated by the plane-wave pseudopotential density functional theory. Through the quasi-harmonic Debye model, in which the phononic effects are considered, the normalized volume V_P/V_0, the variation of the thermal expansion α, the Debye temperature θ and the heat capacity C_v are studied in a pressure range from 0 GPa to 40 GPa and a temperature range from 0 K to 1500 K. The ZB and the RS structures of GaP are cubic crystal. For the ZB structure, the space group is $F\bar{4}3m$ (216#), the sites of Ga are 4*a* (0, 0, 0) and P is 4*c* (1/4, 1/4, 1/4). Similarly, for the RS structure, the space group is $Fm\bar{3}m$ (225#), the sites of Ga are 4*a* (0, 0, 0), and P is 4*b* (1/2, 1/2, 1/2).

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2. Computational method

In this work, we investigate the transition phase of GaP from ZB to a RS structure by using the plane-wave pseudopotential density functional theory (PP-DFT), together with the Perdew–Wang (1991) (PW91) version of the generalized gradient approximation (GGA) exchange–correlation function.[6,7] The plane-wave basis set with an energy cutoff 400.0 eV is applied. Pseudo atomic calculations are performed for Ga $3d^{10}$ $4s^2 4p^1$ and P $3s^2 3p^3$. For the Brillouin-zone (BZ) sampling, we use the 6×6×6 Monkhorst–Pack mesh points, where the self-consistent convergence of the total energy is at 2.0×10^{-5} eV/atom. All the structures are optimized until the largest residual force on the mobile atoms is less than 0.05 eV/Å (1 Å=0.1 nm), the total stress is less than 0.1 GPa and the maximum displacement is 1.0×10^{-5} Å. All the total energy calculations are performed using the Cambridge Serial Total Energy Package (CASTEP) code.[8,9]

3. Results and discussion

3.1. Phase transition and elastic properties

We present the ground state lattice parameter a_0 for the ZB and the RS structures of GaP by optimizing the geometry. For both structures, a series of different lattice constants are set to calculate the total energy E and the corresponding primitive cell volume V, and the curves for E versus V are shown in Fig. 1.

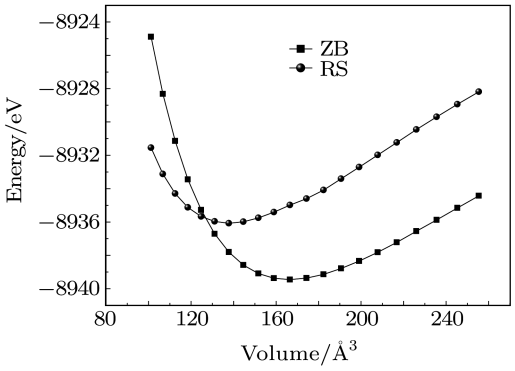


Fig. 1. Energy as a function of the primitive cell volume for GaP.

It is seen from these EV curves that the RS structure of GaP is unstable as compared with the ZB structure, which is consistent with the previous theoretical work.[1] We obtained the zero pressure bulk modulus B and its pressure derivative B' by fitting the calculated E–V points to the Birch–Murnaghan EOS,[11] all the results are listed in Table 1. It is observed that our results are in good agreement with numerous theoretical[3,5,12,13] and experimental[14,15] data. It is indicated that our calculated method is reasonable.

Table 1. Values of lattice constant a_0, bulk modulus B_0, and pressure derivative B_0' for ZB and RS structures of GaP at 0 GPa.

	Compound	a_0/Å	B_0/GPa	B_0'
ZB structure	Present work	5.502	75.8	4.59
	Ref. [3]	5.512	76.0	4.60
	Ref. [12]	5.358	–	–
	Ref. [13]	5.322	92.0	4.34
	Ref. [14]	5.560	95.0	–
	Ref. [5]	5.411	90.0	4.50
	Exp.[15]	5.447	91.0	–
	Exp.[4]	5.451	88.7	–
RS structure	Present work	5.165	87.3	3.78
	Ref. [1]	5.160	87.59	4.54

The zero-temperature phase transition pressure between the ZB and RS structures of GaP may be estimated from the usual condition of equal enthalpies, i.e. the pressure P at which the enthalpies, $H = E + PV$ of the ZB and the RS structures are both the same.

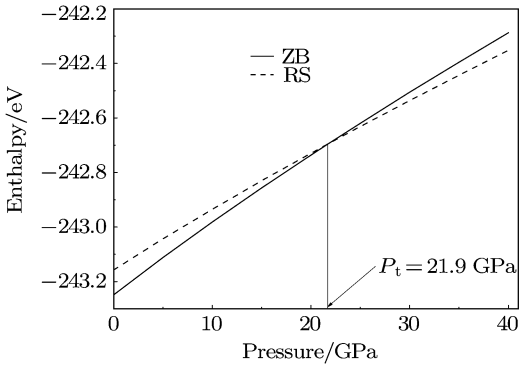


Fig. 2. Enthalpy as a function of pressure for GaP.

Table 2. Transition pressures for zinc-blende to rocksalt transitions in GaP (where CC stands for core corrections).

		P/GPa
Present work	ZB →RS	21.9
Ref. [4] (CC)	ZB →RS	18.8
Ref. [4] (no CC)	ZB →RS	24.8
Ref. [2]	ZB →RS	21.7
Exp.[16]		24±0.3
Exp.[17]		21.5±0.8
Exp.[18]	ZB →RS	22.0

Figure 2 shows the enthalpy as a function of pressure. It is found that the phase transition pressure from the ZB structure to the RS structure is about 21.9 GPa. The result is consistent with the experimental results[16−18] and the theoretical calculations,[4,19] which are shown in Table 2.

In the following, we investigate the elastic properties of the ZB structure of GaP over a range of pressures from 0 GPa to 21.9 GPa, and those of the RS structure over a range of pressures from 21.9 GPa to 40 GPa through using the stress-strain method.[20,21] To investigate the elastic constants under hydrostatic pressure P, we use the strains which are non-volume conservative because this method is consistent with our calculated elastic constants using the stress-strain coefficients, which are applicable for the calculation of the elastic wave velocities. The elastic constant c_{ijkl} with respect to the finite strain variable is defined as,[22,23]

$$c_{ijkl} = \left(\frac{\partial \sigma_{ij}(x)}{\partial e_{kl}}\right)_X, \tag{1}$$

where σ_{ij} and e_{kl} are the applied stress and Eulerian strain tensors, and X and x are the coordinates before and after the deformation. For the isotropic stress, we have[23−25]

$$c_{ijkl} = C_{ijkl} + \frac{P}{2}(2\delta_{ij}\delta_{kl} - \delta_{il}\delta_{jk} - \delta_{ik}\delta_{jl}), \tag{2}$$

$$C_{ijkl} = \left(\frac{1}{V(x)}\frac{\partial^2 E(x)}{\partial e_{ij}\partial e_{kl}}\right)_X, \tag{3}$$

where C_{ijkl} denotes the second-order derivatives with respect to the infinitesimal strain (Eulerian). The fourth rank tensor $\boldsymbol{c}$ generally has 21 independent components. However, this number is greatly reduced with the symmetry of the crystal taken into account. In the case of cubic crystal, there are only three independent elastic constants. In our calculations, the values of total energy E are calculated for six different values of deformation $\delta = \pm 0.0006\delta = \pm 0.0018\delta = \pm 0.003$. They are too small to cause an obvious internal strain effect, 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. In Fig. 3, we obtain the E–δ curve of the ZB structure GaP at 21.9 GPa.

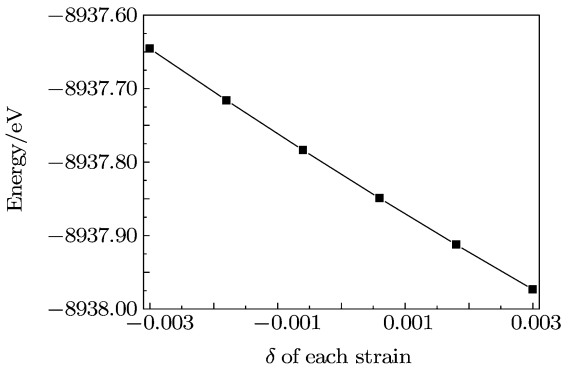


Fig. 3. Energy as a function of deformation δ of each strain under 21.9 GPa for the ZB structure.

In the case of hydrostatic pressure P, the observable elastic constants c_{ij} are related to the elastic constants C_{ij} as follows:[24,25]

$$c_{11} = C_{11}, \quad c_{12} = C_{12} + P, \quad c_{44} = C_{44}P/2. \tag{4}$$

We obtain three independent observable elastic constants (c_{11}, c_{12}, c_{44}), the adiabatic bulk $B_S = (c_{11}+2c_{12})/3$ and the shear modulus $G = (G_{\rm V}+G_{\rm R})/2$ for the ZB structure of GaP over a range of pressures from 0 GPa to 21.9 GPa, and those of the RS structure over a range of pressures from 21.9 GPa to 40 GPa, where $c = (c_{11}c_{12})/2$, $G_{\rm V} = (2c + 3c_{44})/5$, and $G_{\rm R} = 15 \times (6/c + 9/c_{44})^{-1}$, with $G_{\rm V}$ being the Voigt shear modulus and $G_{\rm R}$ the Reuss shear modulus. The results are listed in Table 3. In the ground state, the elastic constants c_{11}, c_{12}, and c_{44} for the ZB structure of GaP are consistent with those reported in Refs. [22] and [23]. As is well known, for a cubic crystal, the mechanical stability under isotropic pressure is judged by the following relation:[22,24]

$$c_{11} + 2c_{12} > 0, \quad c_{11}c_{12} > 0, \quad c_{44} > 0. \tag{5}$$

According to the mechanical stability criteria, it is noted that c_{44} and shear modulus G for the RS structure of GaP are negative, suggesting that the RS structure of GaP is unstable when $P \geq 21.9$ GPa at zero temperature. The result is consistent with those in Fig. 1 and Ref. [9]. It is found that c_{11} and c_{12} increase with pressure increasing, the variation of c_{12} is obvious as compared with that of c_{11}, but the variation of c_{44} is very little for both structures. The elastic constant c_{11} represents elasticity in length. A longitudinal strain produces a change in c_{11}. The elastic constants c_{12} and c_{44} are related to the elasticity in shape, which is a shear constant. A transverse strain causes a change in shape without a change in volume.

Table 3. The calculated elastic constants and aggregated elastic modulus at 0 GPa and 21.9 GPa.

Structure	P/GPa	c_{11}/GPa	c_{12}/GPa	c_{44}/GPa	B_s/GPa	G/GPa
ZB	0	123.5	50.9	70.9	75.1	54.2
	Ref. [26]	146.1	63.6	69.6	–	–
	Ref. [27]	137.5	59.4	72.2	–	–
	5	145.6	77.5	73.4	100.2	53.9
	10	166.6	102.6	75.8	123.9	53.6
	15	185.5	126.9	73.8	146.4	51.1
	20	202.1	150.9	72.6	168.0	47.8
	21.9	208.8	160.3	72.3	176.4	46.7
RS	0	164.6	43.5	9.6	83.8	49.2
	21.9	212.1	177.8	–21.0	189.2	–99.6
	25	224.2	192.9	–21.1	203.3	–182.8
	30	249.0	212.1	–21.4	224.4	–82.4
	35	282.7	230.7	–17.9	248.1	–27.8
	40	316.2	243.6	–17.6	267.8	112.1

3.2. Thermodynamic properties

According to the quasi-harmonic Debye model,[28] the non-equilibrium Gibbs function $G^*(V;PT)$ of GaP is in the form of

$$G^*(V;P,T) = E(V) + PV + A_{\rm vib}(V;T), \quad (6)$$

where $E(V)$ is the total energy per unit cell for GaP, PV corresponds to the constant hydrostatic pressure condition, V and T are the volume and the temperature respectively and $A_{\rm vib}$ is the vibrational Helmholtz free energy. Considering the quasi-harmonic approximation[28] and using the Debye model of phonon density of states, $A_{\rm vib}$ can be written as[28–31]

$$A_{\rm vib}(\theta;T) = nKT\left[\frac{9}{8}\frac{\theta}{T} + 3\ln(1-{\rm e}^{-\theta/T}) - D\left(\frac{\theta}{T}\right)\right], \quad (7)$$

where $\theta(V)$ is the Debye temperature, $D(\theta/T)$ represents the Debye integral, n is the number of atoms per formula unit, and θ is expressed as

$$\theta = \frac{\hbar}{K}[6\pi^2 V^{1/2} n]^{1/3} f(\sigma)\sqrt{\frac{B_{\rm S}}{M}}, \quad (8)$$

where M is the molecular mass per formula unit, $B_{\rm S}$ is the adiabatic bulk modulus, the expression of $f(\sigma)$ is given by Ref. [32] or Ref. [33]. For Poisson ratio $\sigma = 0.25$,[34] $f(\sigma) = 0.85995$ is obtained. The heat capacity C_v and the thermal expansion coefficient α are given by[12]

$$C_V = 3nk\left[4D\left(\frac{\theta}{T}\right) - \frac{3\theta/T}{\exp(\theta/T)-1}\right], \quad (9)$$

$$\alpha = \frac{\gamma C_V}{B_T V}, \quad (10)$$

where γ is the Grüneisen parameter. By applying this method, the thermodynamic properties of other materials[35–38] were also investigated.

The lattice dynamic instabilities are considered to be responsible for the phase transition with drastic motion and lattice distortion induced by pressure. The values of normalized volume V_P/V for the RS and the ZB structures of GaP at various pressures are shown in Fig. 4. It is found that as pressure P increases the normalized volume V_P/V decreases for the two structures where V is the ground-state volume. When the phase transition occurs, V_P/V_0(ZB)=0.827, V_P/V_0(RS)=0.694, and the volume collapse is 13.3%, indicating that the ZB structure of GaP is more compressible than the RS structure.

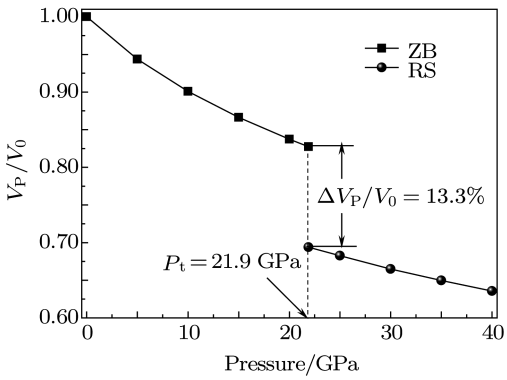


Fig. 4. Phase transition between the ZB and RS structures at 21.9 GPa.

Figure 5 shows the relations between normalized Debye temperature $(\theta - \theta_0)/\theta_0$ and pressure P at

300 K and 1500 K for the ZB and RS structures of GaP. For both the structures, when the temperature keeps constant, the Debye temperature increases almost linearly with applied pressure. The normalized Debye temperature $(\theta - \theta_0)/\theta_0$ for both structures of GaP at 1500 K are much more higher than 300 K, so is the frequency variation of the particles in GaP changing with pressure and temperature. The relevant investigation on the heat capacity of crystal is an old topic of condensed matter physics.[20,39,40] Knowledge of the heat capacity of substance not only provides an essential insight into its vibrational properties but is also mandatory for many applications. Two famous limiting cases are correctly predicted by standard elastic continuum theory.[40] At high temperatures, the constant-volume heat capacity C_v approaches to the Dulong–Petit limit.[21] At sufficiently low temperature C_v is proportional to T^3.[40] At intermediate temperatures, however, the temperature dependence of C_v is governed by the details of vibration of the atoms and has long been determined only in experiment. From Fig. 6, we can find that when $T < 400$ K, the increase of heat capacity C_v is dependent on temperature and pressure, owing to the anharmonic approximation of the Debye model used. At higher temperatures, the anharmonic effect on C_v is suppressed. C_v is very close to Dulong–Petit limit ($\approx$ 49.90 J·mol^{-1}·K^{-1}), which is common to the properties of all the solids at high temperatures. At 0 GPa and 300 K, C_v(ZB)=43.43 J·mol^{-1}·K^{-1}, C_v(RS)=43.04 J·mol^{-1}·K^{-1}, θ(ZB)=507.2 K, and θ(RS)=523.71 K.

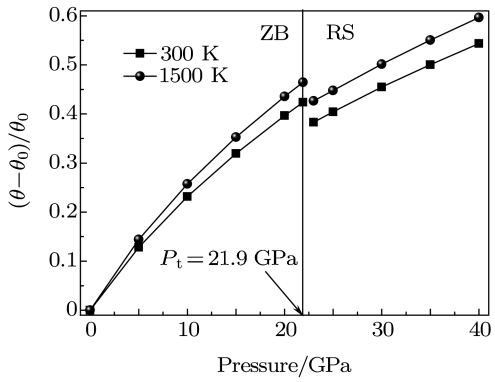


Fig. 5. Curves for normalized Debye temperature $(\theta - \theta_0)/\theta_0$ versus pressure for the ZB and RS structures of GaP at 300 K and 1500 K.

In Fig. 7, we present the values of thermal expansion coefficient α at different temperatures and pressures for the ZB and RS structures of GaP. With temperature increasing, the values of thermal expansion coefficient α increase at various pressures, while the increase rate gradually slows down. At a certain temperature, the pressure P increases, the thermal expansion coefficient α decreases. The thermal expansion coefficient α for the RS structure of the GaP is 1.20×10^{-5}/K while the ZB structure is 1.24×10^{-5}/K at 0 GPa and ambient temperature.

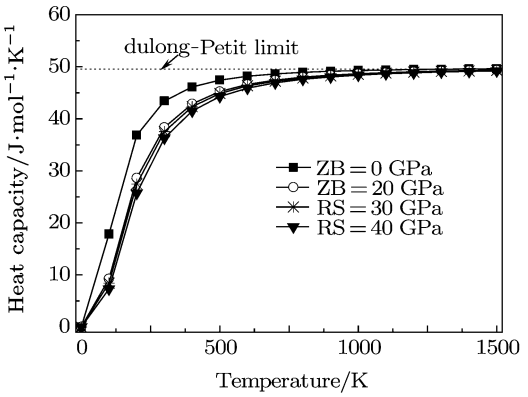


Fig. 6. Heat capacity of the ZB and RS structures of GaP at some pressures and temperatures.

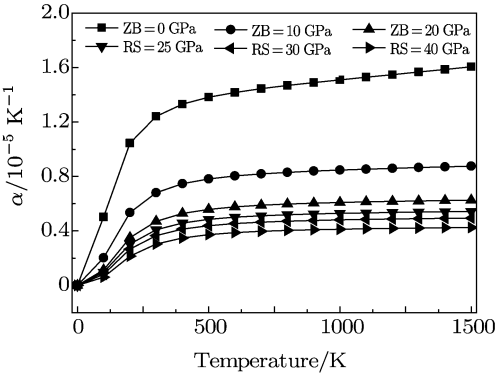


Fig. 7. Thermal expansion coefficients at different pressures and temperatures.

4. Conclusion

We have investigated the phase transition from the ZB structure to the RS structure of GaP by the plane-wave pseudopotential density functional theory using the CASTEP code. From the usual condition of equal enthalpies, the phase transition from the ZB structure to the RS structure occurs at 21.9 GPa. The elastic properties for the ZB structure of GaP over a pressure range from 0 GPa to 21.9 GPa, and those of the RS structure over a range of pressures from 21.9 GPa to 40 GPa are investigated through the stress-strain method. According to the Debye quasi-harmonic model, in which the phononic effects are considered, the thermodynamic properties of the ZB

and RS structures are successfully obtained. The normalized Debye temperature $(\theta-\theta_0)/\theta_0$ increases with pressure P increasing, which takes place at different temperatures, as shown by the vibration frequency of the particles in GaP changing with pressure and temperature. At sufficiently low temperatures C_v is proportional to T^3. At intermediate temperatures, however, the temperature dependence of C_v is governed by the details of vibration of the atoms. At high temperatures, the heat capacity C_v is close to the Dulong–Petit limit (≈ 49.90 J·mol^{-1}·K^{-1}). For a given pressure, thermal expansion coefficient increases with temperature, but the increase rate gradually slows down. At 0 GPa and 300 K, C_v(ZB)=43.43 J·mol^{-1}·K^{-1}, C_v(RS)=43.04 J·mol^{-1}·K^{-1}, θ(ZB)=507.2 K, and θ(RS)=523.71 K. The thermal expansion coefficient α for the RS structure of GaP is 1.20×10^{-5}/K and for the ZB structure it is 1.24×10^{-5}/K at 0 GPa and ambient temperature.

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