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First-principles calculations for transition phase and thermodynamic properties of GaAs*

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The transition phase of GaAs from the zincblende (ZB) structure to the rocksalt (RS) structure is investigated by *ab initio* plane-wave pseudopotential density functional theory method, and the thermodynamic properties of the ZB and RS structures are obtained through the quasi-harmonic Debye model. It is found that the transition from the ZB structure to the RS structure occurs at the pressure of about 16.3 GPa, this fact is well consistent with the experimental data and other theoretical results. The dependences of the relative volume V/V_0 on the pressure P, the Debye temperature Θ and specific heat C_V on the pressure P, as well as the specific heat C_V on the temperature T are also obtained successfully.

Keywords: transition phase, thermodynamic properties, GaAs
PACC: 6470K, 6740K

1. Introduction

As a prototyped III-V semiconductor, GaAs is the most suitable candidate for fabrication of photovoltaic devices, heterostructures, semiconductor lasers and light emitting diodes. Despite the technological developments of GaAs, the high pressure behaviour of GaAs has been the subject of considerable attention. Many fundamental problems for GaAs under high pressure condition, such as the structural, electronic and bonding mechanisms, still remain unsolved. Since Froyen and Cohen[1] reported the structural phase of GaAs in 1983, the structural phase transitions of GaAs have attracted much attention from experimental and theoretical investigations over the past decades.

When the applied pressure increases at 300K, the structural phase transforms from zincblende (ZB) structure (GaAs-I) to orthorhombic structure GaAs-II (with proposed space group *Pmm*2),[2,3] this transformation can be taken as a distortion of the rocksalt (RS) structure. Transition pressures of 17 GPa[2] and 11.5–13.5 GPa[3] have been reported. The transformation from GaAs-II (space group *Pmm*2) to GaAs-III (space group *Imm*2) occurs at 24 GPa.[2,4] The angle-dispersive technique[5] has shown that the structure of GaAs-II belongs to the space group *Cmcm*, which was observed in ZnTe and InSb.[6] Mujica and Needs[7] found that the *Cmcm* structure of GaAs is more stable than *Pmm*2 structure. In 1997, McMahon and Nelmes[8] observed a new hexagonal phase, i.e. four-fold coordinated Cinnabar, between *Cmcm* and ZB phases when the pressure was released. They also reported that the Cinnabar phase persists with pressure before transforming to *Cmcm* at about 15 GPa and to ZB phase near 4 GPa when the pressure is further released.

In this work, we only theoretically investigate the structural phase transition of GaAs from the ZB structure to the RS structure by the plane-wave pseudopotential density functional theory method by using the Cambridge Serial Total Energy Package (CASTEP) program.[9,10] Moreover, we calculate the thermodynamic properties of the ZB and RS structures of GaAs through the quasi-harmonic Debye model,[11] which allows us to obtain all thermodynamic quantities from the calculated E–V points.

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2. Theoretical methods

In the electronic structure calculations, the ultrasoft pseudopotentials introduced by Vanderbilt[12] have been employed for all the ion-electron interaction. The effects of exchange-correlation interaction are treated within the generalized gradient approximation of Perdew *et al* (GGA-PBE).[13] A plane wave basis set with energy of cut-off 295.00 eV is applied. Pseudo-atomic calculations are performed for As $4s^2 4p^3$ and Ga $3d^{10} 4s^2 4p^1$. As for the Brillouin-zone sampling, we use the 8×8×8 Monkhorst–Pack mesh, where the self-consistent convergence of the total energy is at 10^{-6} eV/Atom.

In order to investigate the thermodynamic properties, we apply the quasi-harmonic Debye model,[11] where the non-equilibrium Gibbs function $G^*(V;P,T)$ of GaAs is in the form of

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

where $E(V)$ is the total energy per unit cell for GaAs, PV corresponds to the constant hydrostatic pressure condition, the vibrational contribution $A_{\rm Vib}$ can be written as[14,15]

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

where $\Theta(V)$ is the Debye temperature, $D(\Theta/T)$ represents the Debye integral, n is the number of atoms per formula unit. For an isotropic solid, with Poisson ratio $\sigma = 0.25$,[16] Θ is expressed as

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

where M is the molecular mass per formula unit, $B_{\rm S}$ is the adiabatic bulk modulus, $f(\sigma)$ and $B_{\rm S}$ are given by Ref.[17,18]. For both ZB and RS phase structure of GaAs, n=2, M =24.0268×10^{-26}kg, and $f(\sigma)$=0.85995. Then the non-equilibrium Gibbs function $G^*(V;P,T)$, as a function of $(V;P,T)$, can be minimized with respect to volume V

$$\left(\frac{\partial G^*(V;P,T)}{\partial V}\right)_{P,T} = 0. \quad (4)$$

Thus one could get the thermal equation of state (EOS) by solving Eq.(4). The heat capacity $C_{\rm V}$ is given by

$$C_{\rm V} = 3nk\left[4D(\Theta/T) - \frac{3\Theta/T}{{\rm e}^{\Theta/T}-1}\right]. \quad (5)$$

Applying the above method, we have successfully investigated the structural phase transition and thermodynamic properties of GaN.[19]

3. Results and discussion

For the ZB and RS structures of GaAs, a series of different values of lattice constant a are set to calculate the total energy E and the corresponding volumes V. The calculated E–V points are fitted to the natural strain EOS developed by Poirier and Tarantola.[20] The obtained lattice constant a, the bulk modulus B_0, the pressure derivative of bulk modulus B_0' and the elastic constants for the ZB structure and the RS structure of GaAs at zero pressure are listed in Table 1. For the ZB structure of GaAs, It is obvious that the calculated lattice constant is consistent with the calculated values[21,22] and the experimental data.[23] The bulk modulus B_0 and pressure derivative of bulk modulus B_0' are also consistent with the calculated results[1,22,24–26] as well as the experimental data.[27,28] For the RS structure of GaAs, the calculated lattice constant is consistent with the calculated values,[21,22] and the bulk modulus B_0 and pressure derivative of bulk modulus B_0' is less than the other result.[22]

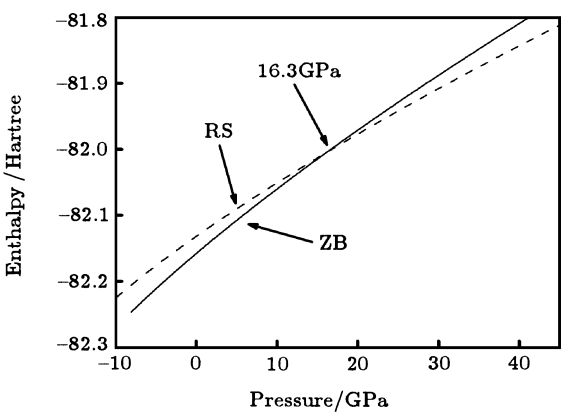


Fig.1. Enthalpy as a function of pressure for GaAs.

An estimate of the zero-temperature transition pressure between the ZB and the RS structures of GaAs may be obtained from the usual condition of equal enthalpies. In Fig.1, we show the enthalpy as a function of pressure. It is found that the structural phase transformation from the ZB structure to the RS structure of GaAs occurs at 16.3 GPa. This kind of phase transition also occurs for GaN[29] and GaP.[30]

The obtained transition pressure is close to the experimental values of 16–19 GPa[1,2] and the other calculated results,[1,30,31] but different from the calculated results by Mujica and his co-workers.[7,26] We find that in the range of pressure from 10 GPa to 19 GPa, there exist several structural phases of GaAs. The differences in enthalpy among these structural phases are very small. Therefore, we think that it is not very suitable to determine the thermodynamical stability for these phases only according to the lowest enthalpy under a given pressure. In this work, we do not discuss the thermodynamical stability of GaAs when the structural phase transformation from the ZB structure to the RS structure occurs at 16.3 GPa. Considering that the GaAs-III (space group *Imm*2) occurs at 24 GPa,[2,4] we thus discuss the thermodynamic properties of the ZB structure of GaAs over the range of pressures from 0 GPa to 16.3 GPa and the RS structure of GaAs over the range of pressures from 16.3 GPa to 24 GPa in order to check the influences of pressure on the thermodynamic properties of GaAs.

Table 1. Lattice constants, bulk modulus, pressure derivative of bulk modulus and elastic constants of the ZB and RS structures of GaAs at zero pressure.

	Our Calc.	Other Calc.	Expt.
ZB Structure			
a/Å	5.648	5.59[a], 5.653[b]	5.653[c]
B_0/GPa	76.03	73.4[b], 81.8[c], 72.5[d], 74.6[f], 74.0[g]	75.7[h], 74.8[i]
B_0'	3.9	4.5[b], 4.8[e], 4.71[f], 4.6[g]	4.00[h], 4.56[i]
C_{11}	117.32	123.7[b], 117.9[f]	120.7[h], 118.1[i]
C_{12}	40.57	48.2[b], 53.0[f]	53.3[h], 53.2[i]
C_{44}	64.53	39.1[b], 68.6[f]	60.2[h], 59.2[i]
RS Structure			
a/Å	5.31	5.251[a], 5.32[b]	
B_0/GPa	73.54	95.63[b]	
B_0'	4.05	4.77[b]	
C_{11}	157.93		
C_{12}	25.15		
C_{44}	16.74		

[a] Ref.[21], [b] Ref.[22], [c] Ref.[23], [d] Ref.[1], [e] Ref.[24], [f] Ref.[25], [g] Ref.[26], [h] Ref.[27], [i] Ref.[28].

The bulk modulus B_0 of the ZB structure for GaAs from the quasi-harmonic Debye model is 75.5GPa, which is well consistent with the experimental data.[27,28] Correspondingly, for the RS structure, the bulk modulus B_0 is 72.59 GPa, which is less than that by Albe *et al*[22] and the obtained value 73.54 GPa from the natural strain equation of state.[20] In Fig.2, we present the pressure dependences of the normalized volumes of the ZB and RS structures of GaAs at several temperatures. We have simulated the relative volumes V/V_0 of the ZB and the RS structures of GaAs at 300K, and 1200K respectively, where V_0 is the primitive cell volume at zero pressure and a given temperature. It is shown from Fig.2(a) that, as the pressure increases, the relative volume decreases at a given temperature for the two structures, and the relative volume V/V_0 of the RS structure is less than the relative volume V/V_0 of the ZB structure at the same pressure and temperature. It suggests that the RS structure is more compressible than the ZB structure for GaAs. Considering that the phase transition from the ZB structure to the RS structure of GaAs occurs at the pressure of 16.3GPa, we obtain Fig.2(b). For the ZB structure, it is shown that our obtained results are in well agreement with the results obtained by Mujica *et al.*[26]

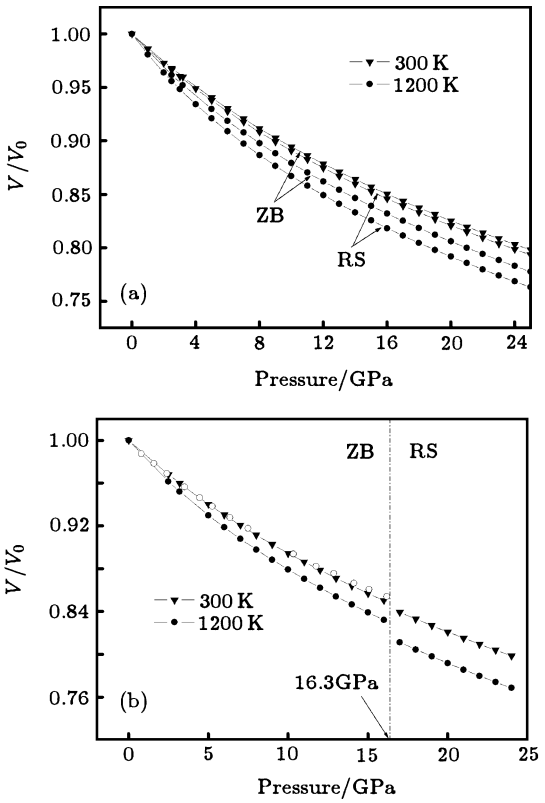


Fig.2. The normalized volume-pressure diagram of the ZB and RS structures for GaAs at various temperatures: (a) suppose that there exists no phase transition over the range of pressures from 0 to 24 GPa, and (b) the phase transition between the ZB and the RS structures occurs at 16.3 GPa. Open circles are for ZB structure from Ref.[26].

In Table 2, we list the heat capacities and the Debye temperatures at different temperatures (300, 600, 900, 1200K) and different pressures (0, 6, 10, 16, 18, 20, 24GPa). The obtained heat capacities for the ZB structure and the RS structure of GaAs at various pressures and temperatures are plotted in Fig.3, which shows that when T <600K, the heat capacity C_{V} is strongly dependent on the temperature and pressure. This is due to the anharmonic approximations of the Debye model used here. However, under higher pressures and higher temperatures, the anharmonic effect on C_{V} is suppressed, and C_{V} is very close to the Dulong–Petit limit.

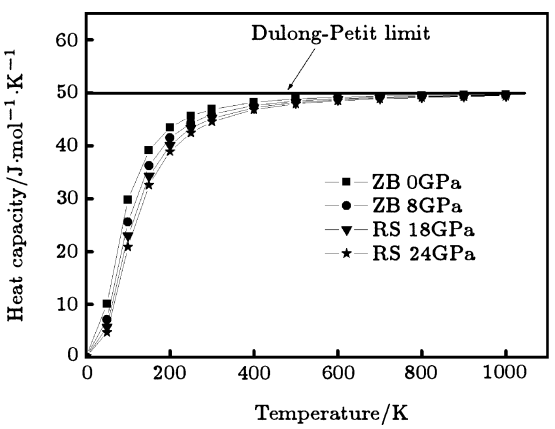


Fig.3. The heat capacity of the ZB and RS structures for GaAs at various pressures and temperatures.

Table 2. The heat capacity C_{V} (J·mol^{-1}·K^{-1}) and the Debye temperature Θ(K) over a wide range of temperatures and pressures for the ZB and RS structures of GaAs.

T/K			P/GPa						
			0GPa	6GPa	10GPa	16GPa	18GPa	20GPa	24GPa
300	ZB	C_{V}	46.91	46.14	45.68	45.04			
		Θ	335.13	378.16	402.16	433.62			
	RS	C_{V}					45.18	44.99	44.63
		Θ					426.70	435.88	453.17
600	ZB	C_{V}	49.15	48.94	48.84	48.63			
		Θ	327.39	372.31	397.05	429.27			
	RS	C_{V}					48.68	48.62	48.52
		Θ					421.52	430.94	448.63
900	ZB	C_{V}	49.58	49.48	49.42	49.34			
		Θ	318.94	366.08	39.63	424.68			
	RS	C_{V}					49.36	49.33	49.29
		Θ					416.02	425.69	443.81
1200	ZB	C_{V}	49.72	49.66	49.63	49.58			
		Θ	309.80	359.56	386.01	419.94			
	RS	C_{V}					49.60	49.58	49.56
		Θ					410.32	420.25	438.83

It is found from Table 2 that, as pressure increases, the heat capacity C_V decreases and the Debye temperature Θ increases. For the ZB structure, at the temperatures of 300, 600, 900, and 1200K, when the applied pressure is from 0 to 16GPa, the heat capacity decreases by 4.0%, 1.1%, 0.4% and 0.3% respectively, and the Debye temperature increases by 29.4%, 31.1%, 33.2% and 35.6% respectively. Correspondingly, for the RS structure, when the pressure from 18 to 24GPa, the heat capacity decreases by 1.2%, 0.3%, 0.1% and 0.08% respectively, and the Debye temperature increases by 6.2%, 6.4%, 6.7% and 7.0% respectively. The heat capacity C_V in this work is $46.91 \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ at zero pressure and ambient temperature. As temperature increases, the heat capacity C_V approaches approximately to the Dulong–Petit result $3k_B (\approx 49.90 \mathrm{J \cdot mol^{-1} \cdot K^{-1}})$, which is followed by all solids at high temperature. Moreover, the Debye temperature Θ obtained here is 335.13K. Unfortunately, to our knowledge, there are no experimental and theoretical data of the heat capacity C_V and the Debye temperature Θ for our comparison.

In summary, we investigate the transition phase of GaAs from the ZB structure to the RS structure by using the *ab initio* plane-wave pseudopotential density functional theory method. It is found that the phase transformation from the ZB structure to the RS structure occurs at 16.3 GPa. The obtained lattice constant, the bulk modulus, the pressure derivative of bulk modulus and the elastic constants for the ZB structure at zero pressure are in good agreement with the experimental data and those calculated by others. Through the quasi-harmonic Debye model, the dependences of the relative volume on pressure, the thermodynamic properties (including the special heat capacity and the Debye temperature) on pressure, as well as the specific heat on the temperature have also been obtained successfully.

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