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Structural and mechanical properties of GaAs under pressure up to 200 GPa

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ABSTRACT

Ab initio calculations were performed for investigating the high pressure phases of GaAs up to 200 GPa. By comparing the minimum free energies of structures, we found the thermodynamically stable phases of GaAs under pressure beyond GaAs-III (*Imm2*) with space groups *Pmma* and *P4/nmm* at the pressure range of 88–146 GPa and 146–200 GPa, respectively. For discussing the difference results of GaAs IV and V in previous studies, we found that *Pmma* and *P4/nmm* are the lower symmetric phases of *P6/mmm* and *CsCl-like*, respectively. For analyzing the *Pmma*→*P4/nmm* phase transition, we observed the approximated path and found that the barrier of transformation from *Pmma* to *P4/nmm* in direction [110] is 0.035 eV. The graph of density of states shows no energy gap in stable phases at 130 and 160 GPa, indicating that *Pmma* and *P4/nmm* are the metallic phases. The contour plots of the electron density difference show some valence electron sharing in *Pmma* which is higher than in *P4/nmm*. Moreover, the results of elastic parameters and modulus ratio suggested that the *Pmma* phase is a ductile material, while the *P4/nmm* phase is a brittle due to the increasing of shear modulus.

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1. Introduction

Gallium arsenide (GaAs) which is one of III–V binary compound semiconductors is widely used in many applications such as solar cell fabrications and diode devices. Stable phase at ambient pressure of GaAs is the zinc blende (*ZB*) phase (space group *F-43m*), which is similar to the other III–V binary compounds such as GaP, InP and InAs [1]. In previous studies of GaAs high-pressure phases, it has been suggested that GaAs–*ZB* transforms to an orthorhombic phase near 17 GPa [2,3]. By studying the X-ray-diffraction pattern from synchrotron radiation, Weir et al. [4] suggested that the evolution of GaAs structures under high pressure is the following: GaAs-I (*ZB*)→GaAs-II (*Pmm2*)→GaAs-III (*Imm2*)→GaAs-IV (*P6/mmm*), with the transitions pressures of 17, 24, and 60 GPa, respectively. The simple hexagonal phase (space group *P6/mmm*) in GaAs-IV from the experiment is similar to the ambient pressure phase of GaSb [5,6]. Zhang and Cohen [7] studied the equilibrium lattice parameters and internal parameters of GaAs-II by using *ab initio* pseudopotential calculations within the local density functional (LDA) in the form of Perdew

and Zunger. They found that GaAs-II is orthorhombic structure which is thermodynamically favored over the rocksalt (Fm$\bar{3}$m) structure. Later, McMahon and Nelmes [8] used the angle-dispersive powder diffraction technique and confirmed that the structure of GaAs-II is a *Cmcm* space group. Mujica and Needs [9] using first principle calculations confirmed that GaAs-II in *Cmcm* structure is more stable than *Pmm2*. Durandurdu and Drabold [10] performed a local-orbital quantum molecular dynamic method with a 216-atom model of GaAs. They used norm-conserving pseudopotentials and Harris functional, and found that the GaAs *ZB* phase transforms to *Cmcm* at 23.5 GPa, and *Cmcm* phase changes to *Imm2* structure at 57 GPa. From the study of the electronic density of states (EDOS), they concluded that both *Cmcm* and *Imm2* phases of GaAs are semimetals. The stability of vibration modes in both high-pressure phases was confirmed by studying the phonon density of states (PDOS). For very high pressure phases (> 80 GPa), Garcia and Cohen [11] studied the *3d* states in Ga compounds with core relaxation effects and predicted that body-centered cubic structure should be stable phase of GaAs above 125 GPa. However, Kim et al. [12] suggested the instability of the *CsCl-like* structure (space group *Pm-3m*) in most III–V semiconductors by using the density-functional linear response method. They focused on InP and InSb in the normalize volume (V/V_0) in range 0.55–0.40. They concluded that the ionic

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compounds such as GaP, GaAs, InP, and InAs are dynamically unstable at high pressures with respect to transverse-acoustic phonon. They suggested two candidate structures that replaced the *CsCl-like* structure at very high pressure are *P4/nmm* and *Pmma*.

From the literature reviews, the theoretical and experimental investigations of GaAs in I, II and III phases under high pressure have been widely conducted. However, the studies of structural and mechanical properties under extremely high pressure (80–200 GPa) in GaAs-IV and V phases are not yet completed. In this work, the thermodynamic stability of GaAs in IV and V phases are discussed up to 200 GPa. The relations of similar structures (*Pmma-P6/mmm* and *P4/nmm-CsCl-like*) were explained. We predicted the mechanism of path transformation in GaAs from *Pmma* to *P4/nmm* which is well above the experimental observation. In order to analyze the physical properties of GaAs IV and V, the elastic parameters, namely, the bulk modulus and shear modulus are studied to classify the metallization of the phases IV and V.

2. Calculation details

In this work, the *ab initio* calculations are performed based on the density functional theory (DFT) as implemented in the CASTEP code [13,14]. In DFT, all ground states properties of a solid system such as the electron density, effective potential and total energy were evaluated by self-consistently solving the Kohn–Sham equations. First of all, the exchange–correlation functionals which contained in Kohn–Sham equations were observed by comparing the results with the previous experiments. At ambient pressure condition (0 GPa), the cutoff energy and k-point grid were used at 500 eV and $6 \times 6 \times 6$, which gave the energy convergence at 5 meV/atom. The lattice parameters ($a = b = c$) in *ZB* at ambient pressure were determined as 5.576 and 5.729 Å by using the LDA functional and the generalizaed-gradient approximation of Perdew–Burke–Ernzerhof (GGA-PBE) functionals [15–17]. Bulk modulus of GaAs from the experiments [18,19] is 74.7 GPa, while the calculation results are 75.5 GPa (LDA) and 60.3 GPa (GGA-PBE) as shown in Table 1.

From Table 1, we found that the LDA functional gives a better agreement with the experimental results than the GGA-PBE. The LDA functional was therefore selected for the rest of this study. The ultrasoft pseudopotentials that included the electronic configurations $3d^{10}4s^24p^1$ for Ga and $4s^24p^3$ for As were used. The cutoff energy of 500 eV was found to be suitable for calculating the geometry optimizations, single point energies and elastic parameters. Forces on the optimized atomic positions were calculated by using the Hellmann–Feynman theorem [20]. The Brouillion zone integration was performed using the Monkhorst–Pack grids [21] of $6 \times 6 \times 6$ for *ZB*, $10 \times 10 \times 8$ for *Cmcm*, $12 \times 12 \times 10$ for *Imm2*, $10 \times 10 \times 5$ for *P6/mmm*, $10 \times 10 \times 10$ for *CsCl-like* and $6 \times 6 \times 11$ for *P4/nmm* and *Pmma* structures. These were sufficient to converge the total energies to within 5 meV per atom for all structures. For the example of study the effect of k-point on the wide pressure range, the Fig. 1 shows the k-point of the example structure (*CsCl-like*) in the pressure 120, 160 and 200 GPa. The total
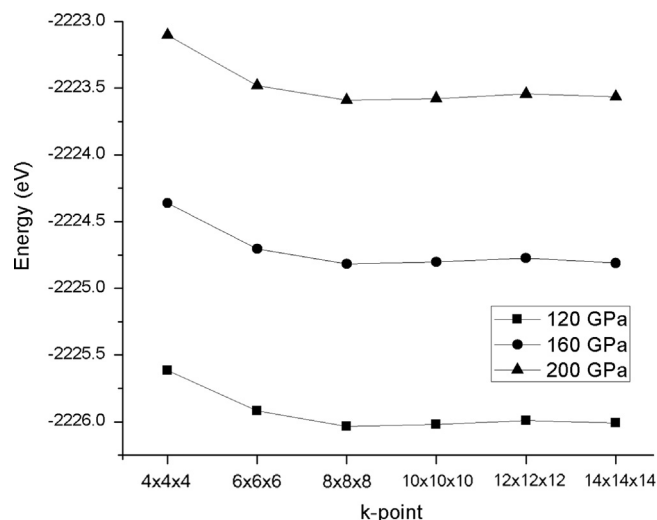
Table 1
The lattice parameter and bulk modulus of GaAs–ZB at ambient pressure from DFT calculations compared with the previous experiments [18,19].

Parameter/Method	Exp.	LDA	GGA-PBE
Lattice parameter (Å)	5.653 (Ref. [18])	5.576	5.729
Bulk modulus GPa	74.7 (Ref. [18,19])	75.5	60.3

Fig. 1. Graph of total energy (*y*-axis) and k-point (*x*-axis) of GaAs in the example (*CsCl-like*) structure shows that the total energies converged at k-point set $8 \times 8 \times 8$ in a wide pressure range (120–200 GPa).

energies confirmed that the k-point set $10 \times 10 \times 10$ which was used to calculate in *CsCl-like* still converges in this pressure range. The total energies in the wide pressure range were observed and found that these k-point sets still converge in this pressure range. However, the k-point in a direction (*k*) of some space groups was carefully varied under wide pressure range by controlling actual spacing ($1/k$) at about 0.04 Å in all dimensions (*x*, *y* and *z*).

3. Results and discussion

For finding the mechanism of GaAs phase transitions, we optimized the possible space groups to find the total energy per primitive cell (*E*) and their volume (*V*) at a given pressure (*P*). The total energies of GaAs structures in *ZB*, *Fm-3m, Cmcm, Cinnabar* (*P3₁21*), *Imm2*, *P6/mmm*, *CsCl-like*, *P4/nmm* and *Pmma* were observed. *E*–*V* curves were fitted by using the third order Birch–Murnaghan equation of state [22,23]. For analyzing phase stabilities, the enthalpy (*H*) per a formula unit of a GaAs space group was calculated from the relation $H = E + PV$, which is the free energy of system at 0 K. The enthalpies of GaAs structures were compared under pressure up to 200 GPa. The *Fm-3m* structure has also been observed with remarkably higher in energy compared to the *ZB* (about 4 eV). Our calculation found that the *Cinnabar* and *Fm-3m* phases are not stable structures under this condition (0 K) because *ZB* transforms directly to the *Cmcm* without going through the *Cinnabar* phase that has the higher free energy (> 1 eV). We found the minimum enthalpy structures between 0 and 200 GPa as shown in Fig. 2, which consist of GaAs I-*ZB* (0–12 GPa), GaAs II-*Cmcm* (12–37 GPa), GaAs III-*Imm2* (37–88 GPa), GaAs IV-*Pmma* (88–146 GPa) and GaAs V-*P4/nmm* (146–200 GPa), respectively. Therefore, for lower pressure range, we report the transition sequence from *ZB→Cmcm→Imm2* which confirmed Durandurdu and Drabold's work [10]. We found that the enthalpy of *ZB* compared to the *Cmcm* and the volume reduction during the *ZB-Cmcm* phase transition is larger than those of the *Cmcm-Imm2*. This can be understood since the *ZB* to *Cmcm* transition is a structural reconstruction, but *Cmcm-Imm2* transition is a distortion from the orthorhombic structure.

Under extremely high pressure ($P > 80$ GPa), we found that *Imm2* changes to the *Pmma* space group with atomic positions Ga (0.25, 0.00, 0.75) and As (0.25, 0.50, 0.75) at 88 GPa which confirms the suggestion of Kim et al. [12]. However, the experiment of