

B3-B1 phase transition in GaAs: A Quantum Monte Carlo Study

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Abstract. The pressure induced B3-B1 phase transition has been studied using both density functional theory (DFT) and quantum Monte Carlo (QMC) methods. We present results obtained using the local density approximation (LDA), generalized gradient approximation (GGA) generalized gradient approximation, hybrid density functionals (HSE06) and QMC. The changes in the equation of state has also been investigated using the different functionals and from the results obtained, we find that the choice of functional significantly affect the equation of state. The results of the B3-B1 phase transition pressure for DFT using the different functionals and QMC are reported and they demonstrate good agreement with experimental data.

1. Introduction

Advancements and refinements in the Diamond Anvil Cell (DAC) technique have led to increased interest in the study of high-pressure behavior of many materials. These studies have revealed that materials often exhibit new and interesting phase transitions and novel elastic behavior when under pressure [1]. Increase in hydrostatic pressure collapses the open, covalent structure of group-IV and III-V semiconductors to a denser metallic crystal structure, hence when pressure is increased, a range of behaviors is seen. There has been an enormous amount of theoretical and experimental work on high pressure phases and phase transitions done so far [2-7], thereby rekindling greater interest in this field.

Numerous experimental and theoretical investigations have successfully identified high-pressure phases of semiconductors. However high-pressure studies in the case of Gallium Arsenide (GaAs) has been the subject of many speculations [6], since different experiments and *ab initio* studies on pressure induced phase transitions of GaAs have reported varying transition pressure values [2,5-10].

High-pressure X-ray experiments reveal that GaAs transforms from the fourfold-coordinated zinc-blende (B3) structure to a sixfold-coordinated rocksalt (B1) structure at around 11.5-13.5 [5] and 17 GPa [5]. Besson *et al.* [5] and Weir *et al.* [4] have used single-crystal X-ray diffraction, X-ray absorption spectroscopy, and elastic neutron scattering to further investigate this structural transformation in GaAs. When the pressure is decreased, Besson *et al.* [5] observed a reverse transformation from the orthorhombic structure to zincblende structure at around 10 GPa.

Ab initio DFT Studies by [11,12] have found different transition points for GaAs-I (zincblende) to GaAs-II (rocksalt), at about 10.5 GPa [11] and 16.3 GPa [12], while the GaAs-II (rocksalt) to GaAs-III (CsCl) transition was found by [12] to occur at 22 GPa. A molecular dynamics study by Jose *et al* [13]

found the GaAs-I (zincblende) to GaAs-II (rocksalt) transition take place at 17GPa while GaAs-II (rocksalt) to GaAs-III (CsCl) transition has been found to occur at 23.5 GPa for the *Cmcm* structure and 25 GPa for the *Imm2* structure [14].

Density functional theory (DFT) is the standard technique that has been employed in investigating the energetic, atomistic and magnetic properties of materials. DFT replaces the explicit many-body electron interactions with quasi particles interacting via a mean-field potential (the exchange-correlation (XC) potential), which is a functional of the charge density [15]. There is no known universally true XC functional, and DFT studies normally employ approximate functionals based on either the a model or an empirical fit. The most commonly used functionals are based on DMC simulations [16] for the uniform electron gas at different densities, such as, the local density approximation (LDA) [17,18] and gradient expansions which include the generalized gradient approximations (GGA) [19-24]. These local and semi-local functionals have however been found to possess significant self-interaction errors as reflected in the accuracy of their predictions of band gaps [26]. Hybrid functionals are another class of functionals that includes a fraction of the exact exchange into the functionals to improve their accuracy [27,28]

Quantum Monte Carlo (QMC) technique [29,30], has been shown in recent applications to overcome some of the failures of DFT. These applications include; the energetics of point defects in silicon [31] and carbon [32], the reconstruction of the Si (001) surface [33] and its interaction with H₂ [34] and the calculation of optical excitation energies [35]. The two QMC methods; variational Monte Carlo (VMC) and diffusion Monte Carlo (DMC) methods are stochastic approaches for evaluating quantum mechanical expectation values with many-body Hamiltonians and wavefunctions [36]. The details of VMC and DMC methods have been extensively been mention elsewhere [30].

In this work we investigate the pressure B3-B1 induced phase transition using hybrid functional (HSE06) and QMC .

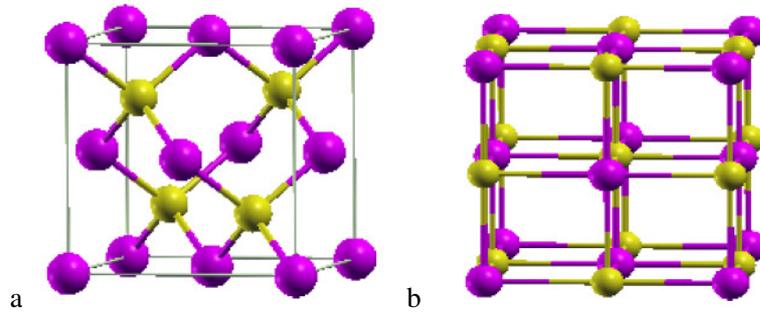


Figure 1. GaAs structures a) ZincBlend (B3) and b) RockSalt (B1)

2. Computational Method

Hartree-Fock norm conserving pseudopotentials for As $4s^2 4p^3$ and Ga $3d^{10} 4s^2 4p^1$ were used to perform pseudoatomic calculations for the two structures of GaAs, namely, Zincblende (B3) and Rocksalt (B1). The DFT calculations were performed using Quantum Espresso code [37], while QMC calculations were performed using CASINO code [30]. Convergence tests were initially done at the DFT level without the hybrid part, on all the structures based on k-point mesh ($n \times n \times n$) and for plane-wave cut-off energy, to an accuracy of 10^{-6} Ry in the computed total energies. Plane-wave cut-off energy of 60 Ry was chosen and k-point meshes $n = 8$ were chosen. All the QMC calculations were performed using 128 atoms. In QMC, the only essential inputs are the trial wave functions (a

determinant of DFT orbitals) and pseudopotentials for the core electrons. In the case of hybrid functionals, k-mesh corresponding to $n=8$ was chosen due to hybrid calculation being computationally expensive.

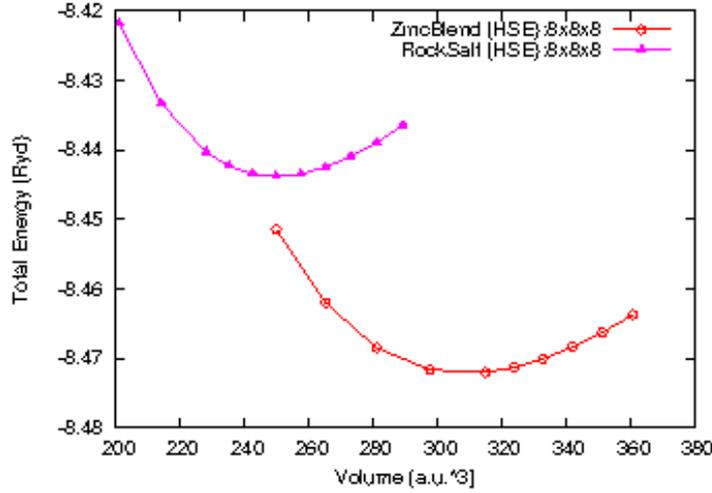


Figure 2. graph showing E-V data obtained by HSE06

Bulk properties were obtained by fitting the obtained energy-volume $E-V$ data from DFT and QMC to the Vinet equation of state (EOS) (eq. 1.0),

$$E(V) = -\frac{4B_0V_0}{(B'_0-1)^2} \left(1 - \frac{3}{2}(B'_0-1) \left(1 - \left(\frac{V}{V_0} \right)^{\frac{1}{3}} \right) \right) \exp \left(\frac{3}{2}(B'_0-1) \left(1 - \left(\frac{V}{V_0} \right)^{\frac{1}{3}} \right) \right) \quad (1.0)$$

the equilibrium lattice constant (a_0), equilibrium volume (V_0), bulk modulus (B_0), pressure derivative of the bulk modulus (B'_0), the Enthalpy and Pressure were obtained. The transition pressure were obtained via the common tangent method of the $E-V$ curves since

$$P = -\left(\frac{\partial E}{\partial V} \right) \quad (2.0)$$

3. Results and Discussion

As seen in Table 1, the bulk properties of the B3 and B1 structures obtained computationally at 0K are compared to experimental values. For B3 structure, the value lattice constant (a_0) obtained from DFT (GGA, LDA and HSE06), and QMC (VMC and DMC) calculations, are consistent with experimental values. It is, however, important to note that all the calculations reported in this study were carried out at ground-state (T=0K), while experiments are done at elevated temperatures.

Table 1: Bulk Properties of B3 and B1 structures

		$a(\text{\AA})$	$B_0(\text{GPa})$	B'_0
B3	Present work LDA	5.53	69.16	4.5
	Present work GGA	5.74	66.19	4.7
	Present work HSE06	5.67	73.8	4.3
	Present work (DFT) DMC	5.65	72.8	4.2
	Other Calculations	5.56a, 5.648b	79.75a, 76.03b	3.5a, 3.9b
	Experiment.	5.653c	75.7c	4c
B1	Present work LDA	5.63	82.95	4.3
	Present work GGA	5.72	78.26	4.3
	Present work HSE06	5.29	90.4	4.2
	Present work (DFT) DMC	5.27	87.3	4.3
	Other Calculations	5.28a, 5.31b	69.95a, 95.63b	4.87a, 4.05b

a Ref[12],b Ref [11],c Ref [39]

From the table it is evident that for the B3 structure, the choice of the XC functional has an effect on the calculation of the bulk properties. This is also evidenced by earlier *ab initio* studies by Gupta *et al* [11], Lai-Yu *et. al* [12] and Mujica *et al* [10]. Gupta *et al* [11] and Mujica *et al* [10] used LDA pseudopotentials, and although Lai-Yu *et al* [12] used PBE-GGA pseudopotentials, they obtained the equilibrium bulk properties via the quasi-harmonic Debye (QHD) model. HSE06 and DMC calculations are much consistent with experimental results [39] in comparison to other XC functionals. This is because HSE06 functional has a fraction of the exact-exchange (a Hatree-Fock exact-exchange) in them that improves the accuracy of the calculations. There were no experimental data for the B1 structures but from the comparison of our calculated results for the B3 structure with experimental data, HSE06 and DMC gives better results.

In this work we also studied the effect of the k-point mesh on phase transitions since all previous studies have been done with different meshes. For the calculations of bulk properties the results indicate that increasing the k-mesh does not appreciably improve the results.

The phase transition pressure from the B3 to B1 structures of GaAs was also obtained using DFT (LDA, GGA and HSE06) and QMC (DMC) and as seen in table 2, the choice of the XC significantly affects the calculated phase transition pressures. There were two experiential data available [5, 6], which gave the B3 to B1 phase transition pressures to be 12 ± 1.5 GPa and 17 GPa respectively. These were values were used a benchmark of our calculations. We also compared our results to previous *ab initio* studies too.

Our calculations as seen in Table 2, indicate that GGA and LDA give different transition pressures, these transition pressure differ by ~ 4 GPa. From the results obtained we also found that LDA calculations are consistent with the experiment [4] and calculations [11] which were also done using LDA XC, GGA results were found to be more consistent with the experiment [5] and calculations [12] which used GGA XC. The HSE06 and DMC results were found to be consistent with calculations using GGA XC and that Lai-Yu *et al* [14] who reported a transition pressure of 16.3 GPa but were smaller compared to the experiment of Weir *et al* [8] who obtained a value of 17 GPa. The HSE06 and DMC results also vary from those of an experiment conducted by Besson *et al* [9] who obtained a

transition pressure of 12 ± 1.5 GPa and also with calculations of Gupta *et al* [3] who got a transition pressure of 10.5 GPa. The experiments of Besson *et al* [9] and Weir *et al* [8] did not give the same result, but incidentally our study gave values that lie within the range of experimentally obtained results (11.5 GPa and 17 GPa). HSE06 and QMC gave better results and this can be attributed to their accuracy.

Table 2: Phase transition pressure in GPa

	GGA	LDA	HSE06	DMC
Present work	13.99	10.1	15.99	15.05 \pm 0.15
Other Calculations	16.3a	10.5b		
Experiment.	17c	12 \pm 1.5d		

a ref [12], b Ref[11], c Ref [5], d Ref [4]

The choice of the k-point mesh was also found not to significantly affect the transition pressures at the DFT level.

4. Conclusions

Hybrid functionals and QMC methods present an accurate tool for calculation of phase transition pressures provided care is taken to control the accuracy of all underlying approximations. The choice of XC functional is also important in the calculations of transition pressures. Further studies however need to be done in controlling the finite-size effects in HSE06 and DMC.

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