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The high-pressure phase transitions of silicon and gallium nitride: a comparative study of Hartree–Fock and density functional calculations

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Abstract. All-electron Hartree–Fock and density functional calculations are performed to study the high-pressure phase transitions in gallium nitride and silicon within the framework of the linear combination of atomic orbitals using the Gaussian basis sets. Under high pressure, GaN makes a transition from the wurtzite (semiconducting) to the rock-salt (semiconducting) phase, whereas Si makes a transition from the cubic (semiconducting) to the β -tin (metallic) phase. The calculated results suggest that the lattice constants and the bulk moduli can be accurately described by both the methodologies for GaN and Si. Furthermore, both the calculations yield a phase transition pressure for GaN which is in reasonable agreement with the experimental data. However, the transition pressure for Si calculated in the closed-shell (restricted) Hartree–Fock approximation differs significantly from the one calculated using the density functional theory and the experimental data. This is primarily due to the fact that the energy difference between a semiconducting and a metallic state of Si is not well produced in the closed-shell Hartree–Fock approximation.

1. Introduction

Ab initio calculations are now routinely performed on a wide variety of materials to gain an understanding of their structural transformations under high pressure. These calculations are based on either the Hartree–Fock approximation (HF) or the density functional theory (DFT) and are generally in agreement with experimental results for the transition pressure. In some cases, however, HF and DFT calculations do not agree well. For example, a phase transition of GaN from wurtzite to rock-salt structure is calculated to be at 35.4 GPa in the HF approximation including correlation [1] as compared to more than 55 GPa obtained in the DFT calculations [2–4]. Experimental studies, on the other hand, indicate a first-order phase transition at about 37 GPa [5]. It should, however, be noted here that the HF study used a basis set consisting of atom-centred Gaussian functions whereas the DFT studies used either plane waves or muffin-tin orbitals to expand the wavefunction. Therefore the differences between the HF and DFT calculations cannot be attributed with any certainty to either the respective methodologies or the basis sets. In this paper we seek to address this issue by comparing the HF and DFT calculations on an equal footing by using the same basis set, namely via linear combination of atomic (Gaussian) orbitals. For the calculations, we choose gallium nitride (GaN) and silicon (Si) as prototype materials which represent semiconductor-to-semiconductor and semiconductor-to-metal phase transitions respectively

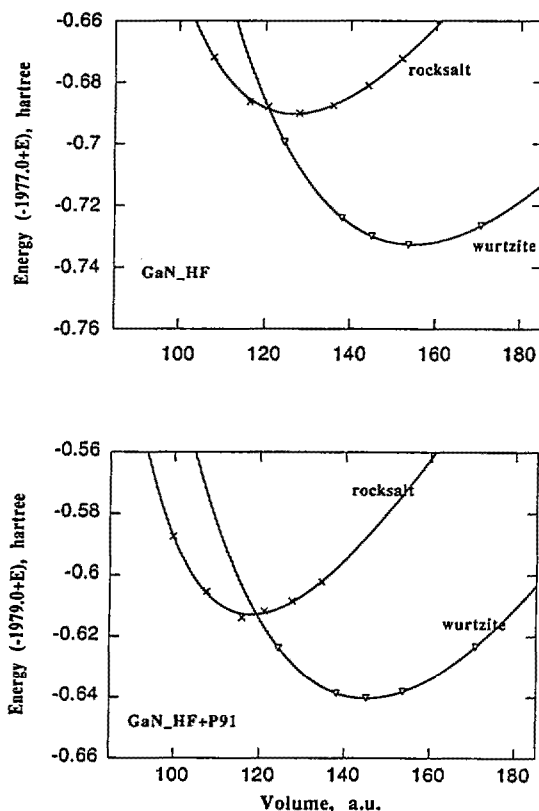


Figure 1. Total energy versus volume for GaN in the wurtzite and rock-salt phases.

under high pressure. This choice of materials is therefore expected to provide a rigorous test for the HF and DFT methodologies for the accurate and reliable prediction of pressure-induced phase transformation in a wide variety of materials.

GaN crystallizes at ambient conditions in the wurtzite phase and at high pressure (>35 GPa) it makes a transition to the rock-salt phase [5, 6]. This structural transformation does not change the semiconducting nature of the gallium nitride as the rock-salt phase has an indirect band gap [1]. On the other hand, Si has been subjected to numerous experimental [7–9] and theoretical studies [10–13] on its phase transformation under high pressure. At room temperature and pressure, silicon has (cubic) diamond structure, and it undergoes a structural transformation to the β -tin structure at about 11 GPa where it changes from the semiconducting to the metallic state.

In the following section, we provide details of the HF and DFT calculations, and we discuss the results in section 3.

2. Computational details

Our computational approach is based on total energy calculations as a function of volume (or pressure) in the cubic and β -tin phases of silicon. The respective point-group symmetries of these phases are $Fd3m$ and $I41/amd$. The cubic phase is characterized by a single structural parameter, the lattice constant a . For the β -tin phase, there are two parameters, namely

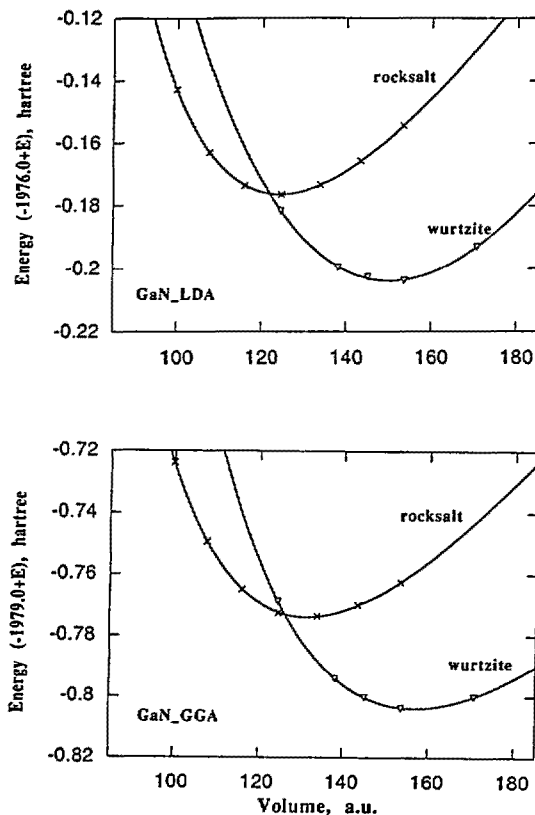


Figure 1. Continued.

the basal-plane lattice constant a and the uniaxial lattice constant c . Total energy for the β -tin phase is therefore minimized with respect to c/a at fixed volume for each volume that we consider in this work. The equilibrium structural parameters, i.e. lattice constants, bulk modulus and its pressure derivative, are then obtained by fitting the calculated potential energy surface to the Murnaghan equation of state [14]. For GaN, we follow a similar approach where the wurtzite phase is described by two lattice constants, a and c , and the high-pressure rock-salt phase is described by the lattice constant a .

A linear-combination-of-atomic-orbitals (LCAO) approach is employed for the HF and DFT all-electron calculations. In the LCAO approach the Bloch functions are constructed as linear combinations of atom-centred Gaussian orbitals. For Si, the Gaussian basis set consists of four shells of s-type, three shells of p-type, and two shells of d-type functions (i.e. an 8411/411/11 set) in both the cubic and β -tin phases [15]. For GaN, the basis sets consist of four s and three p functions for N (a 7311/311 set) and six s-, five p-, and two d-type functions for Ga (an 864111/64111/41 set) in both the wurtzite and rock-salt phases [16].

The program package CRYSTAL [17–19] is used for the calculations. This program package has been applied successfully to a wide variety of ionic and semi-ionic materials [20] calculating accurate structural properties within the framework of the HF approximation. An *a posteriori* correlation correction can be added to the total energy obtained from the HF calculations which is based on the density functional correlation energy functional, such

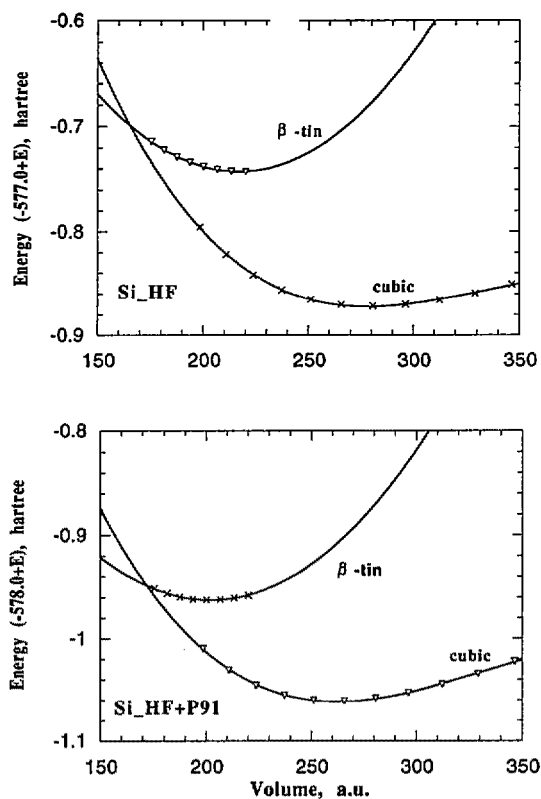


Figure 2. Total energy versus volume for Si in the cubic and β -tin phases.

as Perdew's general gradient approximation [21]. Causa' and co-workers have described in detail this integration of *a posteriori* functionals of the electronic density obtained with the Hartree–Fock method [22], and the implementation of the DFT method in a periodical LCAO scheme [23, 24]. Density functional calculations are performed in both the local and non-local density approximations. In particular, we have considered the Perdew–Zunger parametrization [25] of Ceperley–Alder results [26] for the local functional (referred to as the LDA), and the combination of the Becke exchange functional [27] with the Perdew–Wang correlation functional [21] (referred to as the GGA) for the non-local case. We note here that the residual numerical uncertainty in these calculations is approximately 0.01 eV per atom leading to uncertainties in the phase transition pressure of about 0.5 GPa.

3. Results and discussion

Figures 1 and 2 show the dependence of total energy on cell volume for GaN and Si obtained using the closed-shell Hartree–Fock (HF), correlated Hartree–Fock (HF+P91), local density (LDA), and non-local density (GGA-P91) approximations. These potential energy surfaces are then fitted to the Murnaghan equation of state [14] to obtain the equilibrium structural parameters (volume, and bulk modulus and its pressure derivative) for the Si (cubic), Si (β -tin), GaN (wurtzite), and GaN (rock-salt) phases which are listed in tables 1 and 2. The calculated lattice constant follows the expected trend; it is overestimated by the HF

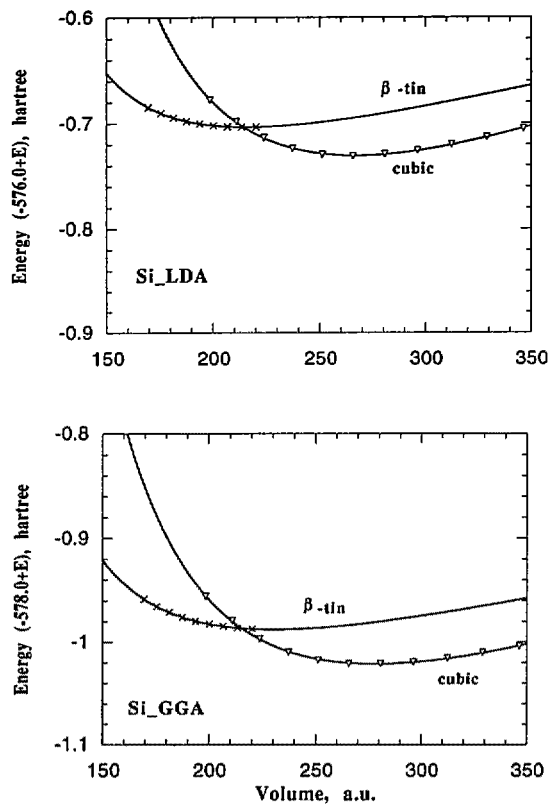


Figure 2. Continued.

approach and underestimated by LDA. For GaN(wurtzite), the HF value is 0.3% larger and the LDA value is 0.6% smaller than the experimental value. For Si(cubic), the HF value is 1% larger and the LDA value is 0.5% smaller than the experimental value. The addition of the correlation corrections to the HF makes the lattice constant about 1% smaller in both GaN and Si whereas the GGA values are about 1.0% larger than the corresponding experimental values. This variation in the lattice constant is also reflected in the calculated values of the bulk modulus which are well within the range of $\pm 10\%$ of the experimental data except the correlated HF results. The correlation correction enlarges the discrepancy with experiments to about 16% in GaN(wurtzite) and about 28% in Si(cubic).

Tables 3 and 4 compare the calculated high-pressure transitional pressure (p^T) which is determined from the common-tangent construction for the energy surfaces shown in figures 1 and 2. For GaN, p^T -HF is 51.9 GPa as compared to p^T -LDA which is 32.4 GPa. The correlated HF decreases p^T to 35.3 GPa whereas the GGA yields a higher value of 40 GPa. Overall, the correlated HF, LDA, and GGA values are in agreement with each other as well with the experimental value of 37 GPa. However, this is not the case for Si where the LDA and GGA values are much closer to p^T -experiment than are the HF and the correlated HF values, which are seven and five times larger than p^T -experiment.

A close examination of table 4 reveals that although the HF and LDA calculations yield about the same equilibrium volume for the cubic and β -tin phases, they do not yield the same energy difference between these two phases. In fact, the energy difference turns out

Table 1. Structural properties of GaN. (All extensive quantities are per formula unit.)

Method	Total energy E_0 (Hartree)	Equilibrium lattice constant			Bulk modulus B_0 (GPa)	Pressure derivative B'
		a (Å)	c/a	u		
Wurtzite						
HF-LCAO†	-1977.732 63	3.199	1.618	0.38	251.0	2.70
HF + correlation(PW91)	-1979.640 35	3.137	1.608	0.38	271.8	5.43
LDA-LCAO	-1976.203 92	3.169	1.614	0.38	252.4	1.66
GGA(PW91)-LCAO	-1979.803 96	3.215	1.614	0.38	210.6	3.75
Experiment:						
Xia <i>et al</i> [5]	—	3.190	1.626	—	188	3.2
Ueno <i>et al</i> [6]	—	3.190	1.627	0.377	237 ± 31	4.3 ± 2.0
Rock salt						
HF-LCAO†	-1977.690 20	4.219	—	—	287	4.3
HF + correlation(PW91)	-1979.612 88	4.119	—	—	364	5.4
LDA-LCAO	-1976.176 39	4.189	—	—	272	4.47
GGA(PW91)-LCAO	-1979.773 85	4.268	—	—	236	4.23
Experiment:						
Xia <i>et al</i> [5]	—	4.234	—	—	248	5.5

† Pandey *et al* [1].**Table 2.** Structural properties of Si.

Method	Total energy E_0 (Hartree)	Equilibrium lattice constant		Bulk modulus B_0 (GPa)	Pressure derivative B'
		a (Å)	c/a		
Cubic					
HF-LCAO	-577.871 75	5.497	—	108.8	3.54
HF + correlation(PW91)	-579.060 89	5.374	—	126.6	3.65
LDA-LCAO	-576.730 50	5.406	—	100.6	4.54
GGA(PW91)-LCAO	-579.021 27	5.479	—	89.9	4.42
Experiment:					
Hu <i>et al</i> [8]	—	5.435	—	98.0	4.24
β-tin					
HF-LCAO	-577.742 82	4.808	0.59	121.5	3.75
HF + correlation(PW91)	-578.962 20	4.656	0.59	159.7	3.89
LDA-LCAO	-576.703 65	4.666	0.63	66.2	5.00
GGA(PW91)-LCAO	-578.987 62	4.767	0.63	58.1	4.58

to be 3.5 eV in the HF calculation and 0.73 eV in the LDA calculation. We therefore conclude that this large energy difference between between the cubic and β -tin phases is leading to a much higher value of the phase transition pressure for the HF and correlated HF calculations. For GaN, the energy difference between the wurtzite and rock-salt phases is about the same (0.8 eV) yielding the same phase transition pressure in the correlated HF, LDA, and GGA calculations (table 3). Since Si makes a transition from a semiconducting to a metallic state under high pressure, it appears that the energy difference between a semiconducting and a metallic state is not well produced by the closed-shell Hartree–Fock

Table 3. The phase transition (from wurtzite to rock salt) pressure, volume contraction at the transition (ΔV^T), equilibrium volumes per formula unit, and the energy difference between the minima of the wurtzite and rock-salt phases of GaN.

Method	p^T (GPa)	ΔV^T (%)	$V_{\text{eq}}(\text{wurt})$ (au)	$V_{\text{eq}}(\text{rs})$ (au)	$\Delta E_{\text{eq}}(\text{wurt-rs})$ (eV)
HF-LCAO†	51.9	14	154.9	126.8	-1.150
HF + correlation(PW91)	35.3	14	145.1	118.0	-0.747
LDA-LCAO	32.4	16	150.2	124.2	-0.749
GGA(PW91)-LCAO	40.0	16	156.2	131.3	-0.819
Experiment: Xia <i>et al</i> [5]	37.0	17	154.4	128.1	—

† Pandey *et al* [1].**Table 4.** The phase transition (from cubic to β -tin) pressure, volume contraction at the transition (ΔV^T), equilibrium volumes per formula unit, and the energy difference between the minima of the cubic and β -tin phases of Si.

Method	p^T (GPa)	ΔV^T (%)	$V_{\text{eq}}(\text{cubic})$ (au)	$V_{\text{eq}}(\beta\text{-tin})$ (au)	$\Delta E_0(\text{cubic-}\beta\text{-tin})$ (eV)
HF-LCAO	78.7	20.8	280.3	221.3	-3.50
HF + correlation(PW91)	54.6	25.0	261.8	200.9	-2.70
LDA-LCAO	15.0	21.9	266.8	216.2	-0.73
GGA(PW91)-LCAO	20.0	20.4	277.6	230.5	-0.92
Experiment: Hu <i>et al</i> [8]	11.2–12.5	22.4	271.1	—	—

approximation. For GaN, this situation does not arise, as it undergoes a phase transition from a semiconducting to a semiconducting state.

In summary, both the Hartree–Fock and density functional calculations using the atom-centred Gaussian functions obtain structural properties for GaN(wurtzite) and Si(cubic) which are in reasonable agreement with the corresponding experimental values. However, the closed-shell Hartree–Fock approximation does not satisfactorily describe the stability of the β -tin phase with respect to the cubic phase for Si. It may well be that the open-shell (unrestricted) description of the metallic (β -tin) phase is more appropriate than the closed-shell one in the Hartree–Fock approximation.

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