Ground State Parameters of Wurtzite Boron Nitride: Quasi-Classical Estimations

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ABSTRACT: Using quasi-classical approach the ground state parameters are obtained for wurtzite boron nitride (w-BN) crystal. The calculated total energy gain with respect to the boron nitride zinc-blende structure is with A£ =0.617 eV/mole. The estimations of zero-point vibration energy and lattice constants are found to be respectively E_m = 0.328 eV/mole, and a=2.537Å and c =4.143 A.

1 INTRODUCTION

The class of boron modifications and boron products contains many important molecular compounds and crystalline materials with extremely wide variations of electronic structure types. Among them the boron nitrides (BN) are of special scientific and technological interest due to its properties making mem useful for applications. Boron nitride exists in forms of diatomic molecule, fullerene-like nanoparticles and some solid state modifications. At standard conditions boron nitride crystallizes usually in a graphite-like hexagonal structure (h-BN) with two-layer stacking sequence, but a rhombohedral form (r-BN) with a three layer stacking also occurs. The denser cubic zinc-blende (c-BN) and wurtzite (w-BN) phases are thermodynamically stable at high pressure and high temperature. Besides the amorphous boron nitride films may be prepared. The ground state static and zero-point vibration energies and bonds equilibrium lengths of BN diatomic molecule (Chkhartishvili et al. 1999, Chkhartishvili et al. 2000), b-BN (Chkhartishvili et al. 2000, Chkhartishvili & Lezhava 2001) and c-BN (Chkhartishvili, in press) crystals were obtained using new quasi-classical approach.

In the present work in same way we calculate ground state parameters of wurtzite phase of boron nitride. This material is known for their superior mechanical properties that are especially valuable in high-temperature applications (Xu & Ching 1993). The hardness, high melting point, high thermal conductivity, large bulk modulus, etc. make w-BN useful for protective coatings. It is chemically inert and does not react with iron. As a result the super-hard materials made from w-BN found wide applications in metal cutting operations. Furthermore, the electronic properties of w-BN characterized by large band gap and relatively low dielectric constant indicate its device applications in short-wavelength (green, blue, and ultraviolet) electroluminescent optics and high-temperature microelectronics (Chen et al. 1995).

The paper is organized as follows. In next Section we briefly review the theoretical method used. Then results of w-BN ground state energy quasi-classical calculations are presented in comparison with earlier theoretical data for the ground state parameters. Finally conclusions are given concerned the method accuracy in case of boron compounds.

2 QUASI-CLASSICAL APPROACH

The quasi-classical expression for bounded states energies obtained by Maslov (1965) yields (Elyutin & Krivchenkov 1976) that for the atomic potential

the precise and quasi-classical electronic spectra are close to one another. On this basis the quasi-classical approach to calculation of molecular and crystalline electronic structures has been developed (Chkhartishvili 1996, Chkhartishvili 1997, Chkhartishvili 1999a, b). Its essential content can be described as follows.

The quasi-classical limit means the truncation of atomic nucleus and electron states wave functions exponential tails in the classically forbidden regions. In this case space-averaged nucleus and orbitals charge densities equal zero outside the classical turning points and a nonzero constant within the range between them. Consequently full atomic charge density is expressed by the step-like radial function

$$\rho(r) = \rho_K \quad (R_{K-1} < r < R_K) \quad K = 1,2,3,...,Q. \quad (1)$$

r is the distance from the center of atom. p_K and R_K denote known constants that depend on the nucleus and electrons classical turning points radii $(R_o = 0, R_0 < R_1 < R_2 < ... < R_g, R_Q < \infty)$. Q is the number of charge spherical layers in atom.

Using the Poisson equation the radial dependence of the full atomic potential $<p(r)$ also can be approximated by the step-like function if substituted by the space-averaged values $<p_K$ inside each of the Äir, $<r<R_K$ regions,

$$\varphi(r) = \varphi_K \quad (R_{K-1} < r < R_K) \quad K = 1,2,3,...,Q. \quad (2)$$

In the quasi-classical limit in the region $r > R_g$ charge density and potential vanish identically $(p(r) m 0$ and $<p(r) = 0)$. Thus finite parameter R_Q is the quasi-classical atomic radius.

In the case of expressing molecular or crystalline potential by the superposition of the step-like atomic potentials the electronic structure is determined by solving the secular equation in which matrix elements are the linear combinations of the overlapping volumes for every possible triad of spheres with radii R_K centered at the atomic sites. These matrix elements are calculated using the universal function which expresses the dependence of the three spheres' intersection region volume upon their radii and inter-central distances. The

explicit solution of this geometrical problem has been obtained by Chkhartishvili (2001).

The quasi-classical ground-state static energy $E\&$ and its zero-point vibration correction E_{va} for molecule or crystal unit cell

$$E_{ST} = \frac{1}{4} \sum_{IIKLT} \rho_{(I)J} \varphi_{(K)L} V_{(IK)JL}(R_{(IK)T}^2), \quad (3)$$

$$E_{VIB} = \frac{3}{2} \sum_I \sqrt{\frac{1}{M_{(I)}} \sum_{JKLT}' \frac{\rho_{(I)J}\varphi_{(K)L}}{R_{(IK)T}^2} \frac{\partial V_{(IK)JL}(R_{(IK)T}^2)}{\partial R_{(IK)T}^2}} \quad (4)$$

are calculated using another universal function $W = W(r_1, r_2, d_n)$ (and its partial derivative $\partial W(r_1, r_2, d_{12})/\partial d_{12}$),

$$\begin{aligned} V_{(IK)JL}(R_{(IK)T}^2) &= W(R_{(I)J}, R_{(K)L}, R_{(IK)T}^2) \\ &+ W(R_{(I)J-1}, R_{(K)L-1}, R_{(IK)T}^2) \\ &- W(R_{(I)J}, R_{(K)L-1}, R_{(IK)T}^2) \\ &- W(R_{(I)J-1}, R_{(K)L}, R_{(IK)T}^2). \end{aligned} \quad (5)$$

W expresses the dependence of two spheres' intersection region volume upon their radii r_1 and r_2 and inter-central distance d_{12} (see (Chkhartishvili 2001)). IV and dW/dd_{12} are the continuous piecewise algebraic functions. Here indexes in parentheses (/) and (K) are the numbers of atoms İn molecule or crystal unit cell, T is the crystal transnational vector (in case of molecule TsO), Ä,,,,f is a distance between atomic sites and M_{0i} is the mass of atom. The pruned summation symbol denotes the elimination of the term with $T = 0$ and $I = K$. As the quasi-classical atomic radii are a finite parameters the above stated expressions of En- and E_{VIB} contain a finite number of nonzero summands without series termination.

3 GROUND STATE ENERGY VERSUS LATTICE CONSTANTS

Using the parameterization based on the Coulomb-like atomic potentials and fitting quasi-classical energetic levels to the Hartree-Fock ones (see (Froese Fischer 1977)) we have obtained the requisite quasi-classical parameters of the charge
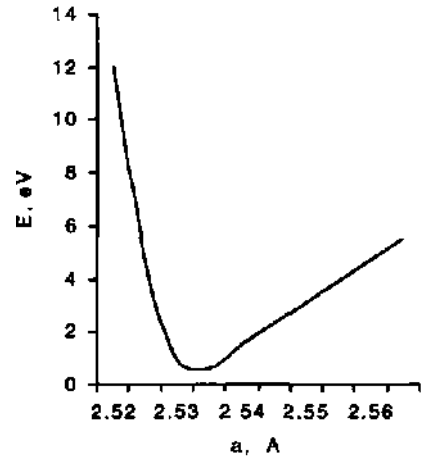
density and potential distributions *m the* constituent atoms B and N. The values are presented in Table 1.

Consequently, $c \approx \sqrt{8/3}\, a = 4.143$ A. The vibration energy correction equals to E_{VIB} s= C.328 eV/mole.

Table 1. Quasi-Classical Parameters of the Charge Density and Potential Distributions in Atoms (in Atomic Units)

K	R_K	ρ_K	φ_K
Boron			
i	0.027585	56865 14	210 5468
2	0.509802	−3 61095	8 882329
3	0 744122	−0.00734	3.652920
4	4 021346	−001028	0.206072
5	4.337060	−000294	0.000614
Nitrogen			
1	0009446	1982589	878 4581
2	0 357724	−10.4497	20.22523
3	0 549803	−001939	8 464698
4	2.909074	−0.04127	0.509668
5	3.204489	−002188	0.003993

Then we have calculated the ground state total energy of w-BN crystal unit cell $E = E\& - E_m$ as function of lattice constant *a*. A most demanding -approach involves minimization of such energy with respect to the both of lattice constants *a* and c and the internal parameter *u* . But İn our calculations the ratio *cla* and parameter *u* were fixed at the 'ideal values', $cla = J\%H> = 1.633$ and $u = 3/8 = 0.375$. As it İs known, it is a good approximation for stable wurtzite structures. As m 'ideal case' the w-BN structure differs from the c-BN structure only in the stacking sequence of the B and N atoms in the [111] direction the calculated for w-BN curve $E = E(a)$ in Figure 1 is shown with respect to me c-BN equilibrium energy (see (Chkhartishvili, in press)). According to this quasi-classical curve w-BN has an equilibrium energy slightly higher than c-BN: $AE = 0.617$ eV/mole. The lattice constant *a* equilibrium value is found to be $a = 2.537$ A.

There are some other investigations for w-BN concerned the theoretical determination of ground state parameters. To best of our knowledge the work of Park et al. (1987) ıs the first ab initio calculation. Appling the full-potential linear APW method they obtained total energy for three different lattice parameters *a* and fitted them with parabolic curve (the c/a ratio was fixed at the experimental value). The equilibrium lattice constant was found to be $a = 2.55$ A. Using the orthogonalized LCAO method within the LDA Xu & Ching (1991) had calculated total energy of w-BN as a function of crystal unit cell volume $V = Sa^2c/2$. The determined equilibrium volume factor was $V/V_{EXP} = 1.015$, where V^. is the experimental unit cell volume. According to this approach the difference between unit cell energies of w-BN and c-BN equals to A£ = 0.3045 eV/mole. The self-consistent linear MTO calculations of Christensen & Gorczya (1994) for boron nitride wurtzite structure gave the effective cubic lattice constant defined through $a_{EFF}^3 = \sqrt{3}a^2c = 2V$: $_sEFF = 3\,6\,i\,9\,^A$- Karch & Bechstedt (1997) used the plane-wave PP approach within the framework of the DFT. The minimization of the total energy had been performed by a two-step procedure. For a given unit-cell

volume the total energy was minimized with respect to *c/a* and *u*, and the theoretical ground state parameters had been finally determined by fitting the calculated total energy as a function of volume to the equation of state: *a~* 2.531 A, *c/a* = 1.657, « = 0.3751 and A£= 0.037 eV/mole. Using the total energy DFT method the equilibrium properties of w-BN crystal was derived by Albe (1997) by systematic optimization of unit cell parameters and atomic positions: *a*= 2.532 A, *cla-* 1.654 and A£= 0.022 eV/mole. A short-range classical force-field for the modeling of boron nitrides had been derived by Marian et al. (2000) on the basis of expérimenta] and ab initio solid state and diatomic molecular data. The wurtzite modification was not used for this fitting but was included later in the test set: *a*= 2.567 A, *c*= 4.141 A, A£= -0.13 eV/mole and £$_{WH}$ = 0.21 eV/mole.

CONCLUSIONS

Awareness concerning the energy differences between the crystallographic modifications of a substance has a great significance for applications. On the other hand the parameter under the consideration hardly lends itself to experimental determination. For this reason it is extremely important to calculate it. The results of present study and previous calculations (except the empirical estimation of Marian- et al. (2000)) show the identical trend of energy difference between w-BN and c-BN: A£ > 0, however with a wide spread of values for A£. Summarizing theoretical results concerning w-BN lattice constants, we can infer that all of them are in sufficient agreement with the experimental data (tffxp- 2.553 A and c_{EXP}= 4.199 A). But the accuracy of the value of constant *a* obtained using a quasi-classical method is especially remarkable: its deviation from experimental one is only -0.6%. This fact allows us to conclude that quasi-classical approach would be also preferable for estimation of energy differences between various structural modifications of boron compounds.

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