ZERO-POINT VIBRATION ENERGY WITHIN QUASI-CLASSICAL APPROXIMATION: BORON NITRIDES

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<u>ABSTRACT.</u> The method of calculation of the substance constituent atoms zero-point vibration energy within the initial quasiclassical approximation is elaborated. By this way the ground state vibration energy values for boron nitride molecule, isolated sheet, hexagonal, cubic and wurtzite-like crystals are found as 0.178, 0.242, 0.266, 0.330 and 0.323 eV/mole, respectively.

1. INTRODUCTION

Boron nitride phases form the class of materials of special scientific and technological interest for their superior bonding, electronic and optical properties. Boron nitride with the general chemical formula BN can exist as one- (diatomic molecule), two-(tubular and fullerene-like surfaces) and three-dimensional (layered hexagonal *h-BN* and rhombohedral *r-BN*, relatively dense cubic *c-BN* and wurtzite-like *w-BN* crystals, turbostratic and amorphous films) structures. The development of theoretical approaches that do not require considerable computational effort but provide a reasonable accuracy in the prediction of main physical characteristics is particularly important for the study of such kind of substance with wide variation of the structure types. A number of structural and electron energy spectrum parameters of boron nitrides were obtained [1-9] by the new effective computing method based on the quasiclassical approximation (summarization of the physical theory is given in [10], the key mathematical aspects see in [11-12]). In the present work the same approach is applied to estimate the energies of zeropoint vibrations in boron nitride modifications. In next section we justify method for this task. Then results of calculations are given in comparison with available data.

2. STANCE OF ZERO-POINT VIBRATION ENERGY WITHIN THE INITIAL QUASICLASSICAL APPROXIMATION

Under the term of 'substance' it is implied atoms and polyatomic structures at the ground state, i.e. molecules and crystals, which can be considered as an interacting electron system affected by the stationary external electrical field of nuclei fixed at the sites in given structure. And so, its physical properties are mainly determined by the electron energy spectrum. The quasi-classical expression for bounded state energies obtained by Maslov [13] yields [14] that for substance inner (self-consistent field) potential the precise and quasiclassical electronic spectra are close to one another. On this basis the scheme of quasi-classical representation of charge density and potential distributions in substance has been elaborated [10] which is useful to estimate energy of atoms vibrating near the equilibrium sites in structure.

The quasi-classical limit means the truncation of electron states wave functions exponentially decaying tails in the classically forbidden regions. In such approximation partial charge densities of the space-averaged atomic orbitals equal zero outside the classical turning points and a nonzero constants within the range between them. Consequently, full charge densities in constituent atoms are expressed by the step-like radial functions. Using the Poisson equation the radial dependencies of the atomic potentials also can be represented as steplike functions if substituted by the space-averaged values inside each of the uniform charge density regions.

Let us assume that $\vec{d}_{(i)}$ are the basis vectors of the unit cell of a crystal with N atoms, (i) = 1, ..., N. In this case, the point $\vec{d}_{(i)} + \vec{t}$ corresponds to the equilibrium position of the center of (i)-type atom belonging to the unit cell with translational vector \vec{t} . Therefore, the total density of the nuclear and electronic charges in the atom and the potential of the field induced by these charges at the point \vec{r} can be represented by the functions $\rho_{(i)}(\vec{r} - \vec{d}_{(i)} - \vec{t})$ and $\varphi_{(i)}(\vec{r} - \vec{d}_{(i)} - \vec{t})$. If the affecting atoms are fixed at their sites (this is equivalent to the time averaging of their vibrations), the potential energy of the (i) th

atom of the central unit cell (i.e. with $\vec{t} = 0$) displaced by the vector \vec{r} from the equilibrium position is defined as

$$U_{(i)}(\vec{r}) = \sum_{\vec{t}}^{/} \sum_{(k)=1}^{(k)=N} \int d\vec{r}' (\rho_{(i)}(\vec{r}' - \vec{d}_{(i)} - \vec{r}) \varphi_{(k)}(\vec{r}' - \vec{d}_{(k)} - \vec{t}) + \rho_{(k)}(\vec{r}' - \vec{d}_{(k)} - \vec{t}) \varphi_{(i)}(\vec{r}' - \vec{d}_{(i)} - \vec{r}))/2.$$

The prime on the summation sign indicates that the term with $\vec{t} = 0$ and (k) = (i) corresponding to the self-action is omitted (besides, the formula is symmetrized with respect to the contributions of interacting charges, because the approximations not related by the Poisson equation were used upon quasi-classical parameterization of the charge density and potential).

The central-field approximation for the constituent atoms permits us to represent this potential energy as the sum of the contributions that depend only on the squares of the distances from the point $\vec{r} + \vec{d}_{(i)}$ to the point $\vec{d}_{(k)} + \vec{t}$:

$$U_{(i)}(\vec{r}) = \sum_{\vec{t}}^{/} \sum_{(k)=1}^{(k)=N} U_{(ik)\vec{t}} \left(r_{(ik)\vec{t}}^2 - 2(\vec{r}_{(ik)\vec{t}} \vec{r}) + r^2 \right),$$

where $\vec{r}_{(ik)\vec{t}} = \vec{d}_{(k)} + \vec{t} - \vec{d}_{(i)}$ denotes the radius vector of the (k)th atom with respect to the (i)th atom. In order to estimate the energy of small-amplitude lattice vibrations, we expand each contribution into a power series of the variable parts of the arguments and retain only constant and linear terms. The terms responsible for the vibrations are as follows:

$$U_{(i)Vibration}(r) = \sum_{\vec{t}}^{/} \sum_{(k)=1}^{k=N} r^2 dU_{(ik)\vec{t}}(r_{(ik)\vec{t}}) / 2dr_{(ik)\vec{t}}$$

In quasi-classical scheme, the pair potential energies $U_{(ik)\bar{t}}(r_{(ik)\bar{t}})$ are linear combinations of the functions $V(r_{(i)j}, r_{(k)l}, r_{(ik)\bar{t}})$, which determine the volumes of the intersection of the layers with uniform charge density and potential in the interacting atoms:

$$V_{(ik)jl}(r_{(ik)\bar{t}}) = V(r_{(i)j}, r_{(k)l}, r_{(ik)\bar{t}}) + V(r_{(i)j-1}, r_{(k)l-1}, r_{(ik)\bar{t}}) - -V(r_{(i)j}, r_{(k)l-1}, r_{(ik)\bar{t}}) - V(r_{(i)j-1}, r_{(k)l}, r_{(ik)\bar{t}}).$$

Here $r_{(i)j}$ are the outer radii of the atomic layers, $j = 1,...,q_{(i)}$ ($q_{(i)}$ is the total number of uniform layers in (*i*) th atom), and $V(R_1, R_2, D_{12})$ is the continuously differentiable piecewise analytical algebraic function determining the volume of the intersection of two spheres with radii R_1 and R_2 whose centers are spaced at D_{12} (this universal geometrical function was derived in an explicit form in [15] when formulating the problem regarding the quasi-classical calculation of the band structure of a crystal). Consequently, by introducing the charge density $\rho_{(i)j}$ and the potential $\varphi_{(i)j}$ values in the atomic layers the molar energy of zero-point vibrations in the crystal can be written in the form

$$\begin{split} E_{Vibration} &= \\ &= \sum_{(i)=1}^{(i)=N} \frac{3}{2} \sqrt{\sum_{\vec{i}}^{/} \sum_{(k)=1}^{(k)=N} \sum_{j=1}^{j=q_{(i)}} \sum_{l=1}^{l=q_{(k)}} \frac{\rho_{(i)j}\varphi_{(k)l} + \rho_{(k)l}\varphi_{(i)j}}{2M_{(i)}r_{(ik)\vec{t}}} \frac{\partial V_{(ik)jl}(\vec{r}_{(ik)\vec{t}})}{\partial \vec{r}_{(ik)\vec{t}}}, \\ \partial V_{(ik)jl}(r_{(ik)\vec{t}}) / \partial \vec{r}_{(ik)\vec{t}} &= \\ &= \partial V(r_{(i)j}, r_{(k)l}, r_{(ik)\vec{t}}) / \partial r_{(ik)\vec{t}} + \partial V(r_{(i)j-1}, r_{(k)l-1}, r_{(ik)\vec{t}}) / \partial r_{(ik)\vec{t}} - \\ &- \partial V(r_{(i)j}, r_{(k)l-1}, r_{(ik)\vec{t}}) / \partial r_{(ik)\vec{t}} - \partial V(r_{(i)j-1}, r_{(k)l}, r_{(ik)\vec{t}}) / \partial r_{(ik)\vec{t}} \,. \end{split}$$

 $M_{(i)}$ denotes the mass of the (*i*) th atom, and the frequencies of lattice vibrations are expressed through the partial derivative $\partial V(R_1, R_2, D_{12}) / \partial D_{12}$ which is the continuous piecewise analytical algebraic function:

$$\begin{split} \partial V(R_1,R_2,D_{12})/\partial D_{12} &= 0 & D_{12} \leq R_2 - R_1 \\ &= 0 & D_{12} \leq R_1 - R_2 \\ &= -\pi ((R_1 + R_2)^2 - D_{12}^2)(D_{12}^2 - (R_1 - R_2)^2)/4D_{12} \\ &\quad |R_1 - R_2| \leq D_{12} \leq R_1 + R_2 \\ &= 0 & R_1 + R_2 \leq D_{12} \,. \end{split}$$

These relations obtained for infinite crystalline structure can be reduced for case of molecule fixing translational vector at $\vec{t} = 0$.

3. QUASI-CLASSICAL ZERO-POINT VIBRATION ENERGIES IN BORON NITRIDES

The quasi-classical parameters of charge density and potential distributions in constituent atoms B and N (necessary for calculations) were determined within the scheme of Coulomb-like potentials by fitting quasi-classical electron energy levels to the ab initio, namely, Hartree–Fock [16]) ones for isolated atoms (as it is known, need for the large programming resources makes such kind of calculations unrealizable in case of crystals). The obtained values are listed in Table 1. Then using these parameters the molar ground state vibration energies have been calculated for following boron nitride structures (see Table 2):

- diatomic molecule, i.e. isolated B-N bond, what is important object being the building 'block' for any boron nitride solid phase;

 hypothetic two-dimensional hexagonal crystal which also is of special interest because the three-dimensional layered modifications are formed by similar boron nitride sheets and, moreover, fullerene and nano-tube aggregates are bounded by flat or curved fragments of such a sheet;

 hexagonal crystal with two-layer stacking sequence (value found for rhombohedral one with three-layer stacking sequence is almost the same due to substantially weakness of the inter-layer bonding in comparison with intra-layer interactions);

Table 1. Quasi-classical parameters of the charge density and
potential distributions in *B* and *N* atoms (in *atomic units*)

$\varphi_{(B)j}$	$\rho_{(B)j}$	$r_{(B)j}$	j	$r_{(N)j}$	$ ho_{(N)j}$	$\varphi_{(N)j}$
210.546	5(0(5.1	0.02759	1	0.00044	100250	070 450
210.546	56865.1	0.02/58	1	0.00944	198258	8/8.458
8	4	5	2	6	9	1
8.88232	-	0.50980	3	0.35772	-	20.2252
9	3.61095	2	4	4	10.4497	3
3.65292	_	0.74412	5	0.54980	-	8.46469
0	0.00734	2		3	0.01939	8
0.20607	—	4.02134		2.90907	-	0.50966
2	0.01028	6		4	0.04127	8
0.00061	—	4.33706		3.20448	—	0.00399
4	0.00294	0		9	0.02188	3

Table 2. Quasi-classically calculated zero-point vibration energiesof boron nitride structural modifications (in eV/mole)

Modification	$E_{Vibration}$
molecule BN	0.178
sheet BN	0.242
h-BN	0.266
c-BN	0.330
w-BN	0.323

cubic crystal;

- wurtzite-like crystal for which the ratio of lattice constants *a* and *c* and internal parameter *u* were fixed at the 'ideal' values: $(a/c)^2 = u = 3/8$.

The quasi-classically calculated B-N inter-atomic vibration energy, 0.178 eV/mole, is in good agreement (with a deviations ~5%.) with the values experimentally found for neutral BN molecule 0.187 eV/mole [17] and 0.188 eV/mole [18]. According to the original (self-consistent-field-type) theoretical method of [19] ground state vibration energy in molecular boron nitride estimated as 0.179 eV/mole which is

almost our quasi-classical result. In [20] it was suggested higher theoretical value 0.217 eV/mole what is close with 0.216 eV/mole measured in ionized molecule BN^+ [21].

The present calculations of vibration energy are the first for boron nitride crystalline modifications. Earlier these values were only estimated according to the semi-empirical models and/or theoretical phonon spectra.

It is natural that the molar vibration energies quasi-classically found for sheet and hexagonal boron nitrides, 0.242 eV/mole and 0.266 eV/mole, are close one to another. When comparing these energies, it should be taken into account that inter-layer bonds in layered boron nitride structure are substantially weaker than intra-layer bonds and, consequently, inter-layer interaction may be ignored. On the other hand, the atoms of the isolated layer which is a two-dimensional system, nevertheless, can execute vibrations in three independent directions in the physical space. Thus, it is expedient to analyze these predictions jointly (especially because there is no experimental studies for boron nitride sheet being the hypothetic structure). Both of them agree well with semi-empirical value of 0.225 eV/mole for the energy of zero-point vibrations in real *h-BN* crystal found within the model of a classical force field potential [22] and coincide in order of magnitude with the estimate 0.350 eV/mole made from the theoretical phonon spectrum [23].

It is also natural that determined vibration energies of *c-BN* and *w*-BN crystals, 0.330 eV/mole and 0.323 eV/mole, are almost the same. Boron and nitrogen atoms are tetrahedrally surrounded in both of densely packed forms of boron nitride and in considered 'ideal' case, that mimics the real stable wurtzite-like lattices, the w-BN structure differs from the *c*-BN structure only in the stacking sequence of the B atoms. Correspondingly, the nearest-neighbor and N atomic environments and bonding types in both crystals are sufficiently close and it may be taken for guarantee that their ground state parameters are also similar (the lower symmetry and small deviations of bond lengths in the *w-BN* structure can result only in some unique features of its properties). It urges on analysis of *c-BN* and *w-BN* vibration energies together (especially as w-BN bonding parameters have not been measured). Aforementioned quasi-classical values coincide only in order of magnitude with the semi-empirical estimates based

on the model of a classical force field potential: 0.130 eV/mole and 0.210 eV/mole, respectively [22]. However, there is excellent agreement with equal values of 0.320 eV/mole found from the theoretical phonon spectrum [23] and early semi-empirical Debye model [24] for *c-BN*.

Summarizing the obtained results we can conclude that quasiclassical calculation would be useful for determination of lattice zeropoint vibration energy which is important ground state parameter hardly lended itself to measurement in crystals.

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ლ. ჩხარტიშვილი

ნულოვანი რხევების ენერგია კვაზიკლასიკურ მიახლოებაში: ბორის ნიტრიდები

დასკვნა

დამუშავებულია საწყის კვაზიკლასიკურ მიახლოებაში ნივთიერების შემადგენელი ატომების ნულოვანი რხევების ენერგიის გამოთვლის მეთოდი. ამ გზით ბორის ნიტრიდის დიატომური მოლეკულის, განმხოლოებული ფენის, ჰექსაგონალური, კუბური და ვიურციტისებრი კრისტალების რხევითი ენერგიები ძირითად მდგომარეობაში შეფასებულია, როგორც 0.178, 0.242, 0.266, 0.330 და 0.323 eV/mole, შესაბამისად.