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UDC 538.956
DOI: 10.15587/1729-4061.2015.44291

ESTIMATION OF ATOMIC CHARGES IN BORON NITRIDES

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Для бінарних сполук виведено вираз ефективних зарядів, залежних від числа молекул в елементарній паралелограмі, площі його перетину поперек зовнішньому полю, модулі Юнга і діелектричній проникності. Для нітридів бору були отримані наступні напівемпіричні оцінки: h-BN – 0.35 і 0.09, c-BN – 0.49, і w-BN – 0.76 і 0.50

Ключові слова: модель точкових атомних зарядів, напівемпіричні оцінки, нітриди бору

Для бинарных соединений выведено выражение эффективных зарядов, зависящее от числа молекул в элементарном параллелограме, площади его сечения поперек внешнему полю, модуля Юнга и диэлектрической проницаемости. Для нитридов бора были получены следующие полуэмпирические оценки: h-BN – 0.35 и 0.09, c-BN – 0.49, и w-BN – 0.76 и 0.50

Ключевые слова: модель точечных атомных зарядов, полуэмпирические оценки, нитриды бора

1. Introduction

Structural modifications of boron nitride (BN) are widely used in various technologies. They belong to the class of binary compounds with chemical bonds of mixed – covalent–ionic type. It has been long noted [1] that, binding polarity is an important characteristic significantly affecting electronic structure and, consequently, most part of physical properties of BN crystals. What a way to find the effective values of static atomic charges in boron nitrides is preferable? It turns out that in this case both experimental and theoretical approaches are associated with difficulties.

Dependences of measurable parameters of the material on the effective charges of constituent atoms (B and N) are so complex that, their credible experimental values are virtually undetectable.

As for the theoretically obtained effective atomic charges in BN, they are characterized by too significant scatter also making them almost unreliable.

A clear physical picture of the coupling between microscopic atomic displacements in a binary compound and macroscopic electric field is provided by Huang's phenomenological model [2], in which the general quadratic expression of the energy as a function of the displacements and the field includes the coupling coefficient known as the Born effective charge of the ions (see, e. g. [3]). Within this approach based on the linear-response theory, charges can be calculated by various first-principles methods. Based on these computations in compounds, the significance of the Born effective charge concept was examined in [4]. It was shown that static and dynamical charges are not driven by the same underlying parameters, and a unified treatment of dynamical charges in periodic solids and large clusters was proposed.

Alternatively, effective charges can be determined theoretically using an approach to the electrostatics of quantum dielectrics based on topological concepts (namely Berry's phase approach to macroscopic polarization – see e. g. [5]). It means the calculation of the change in polarization which occurs upon making an adiabatic change in the Kohn–Sham Hamiltonian of the crystal. The expression for the change in polarization was derived in terms of the valence-band wave functions of initial and final Hamiltonians and shown that, physically such a change can be interpreted as a displacement of the center of charge of the Wannier functions. It can be demonstrated that, within the geometric phase approach, the relevant polarization difference occurs as the circuit integral of a Berry connection, while the corresponding curvature provides the macroscopic linear response. This formulation also has been applied in a number of first-principles calculations.

It was emphasized [6] that, in fact the dipole moment of a crystal is ill-defined quantity and then traditional definition of the macroscopic electric polarization as the dipole of a crystal unit cell should be considered as incorrect. Actually, the quantity measured is differential polarization with respect to so-called reference state of the same crystal. Differential polarization includes either derivatives of the polarization (not only Born effective charges, but also dielectric permittivity, piezoelectricity, and pyroelectricity) or finite differences (ferroelectricity). Polarization is a quantum phenomenon and cannot be adequately treated with a classical model. In the quantum picture, polarization difference is equivalent to a macroscopic current, which is basically a property of the phase of the wave functions, as opposed to the charge, which is a property of their modulus. It is the reason why the theory developed by King–Smith and Vanderbilt in [5] seems preferable than the long-established linear-response theory or e. g. complicated versions of so-called bond charge model.

2. Analysis of published data and problem statement

In [7] reviewing the status of the first-principles lattice-dynamical calculations in crystals, in particular there is treated the calculation of the response to macroscopic electric fields in polar crystals and demonstrated with a number of applications the capabilities of these methodologies. Effective charges calculated for zinc-blende-structure III–V semiconductors GaAs, GaSb, AlAs, etc. are in good agreement with experiments, where available. Calculated Born effective charges of titanium dioxide TiO_2 in the rutile structure are much larger than the nominal ionic charges of Ti and O ions and those of stishovite in spite of the similar structure. Born effective charges for cubic WO_3 in the defect perovskite structure follow the same pattern. In agreement with experiments, Al_2Ru shows anomalously large Born effective charges, but in contradiction with a valence-charge-density analysis, which leads to the negligible static ionic charges of Al and Ru. There is stated that, in general when used at the same level of accuracy, different approaches (linear-response, Berry's phase, and others) to macroscopic polarization, yield the same results within numerical uncertainties.

But, an uncertainty in numerical coefficient means the uncertainty in effective atomic charges.

The fundamental reason for this is that, charge transfer is an ill-defined quantity not only in interpretation of first principles calculations, but experimental data as well, and then it is impossible to assign unambiguously electrons to different atoms due to the fact that in solids atomic orbitals are no longer the eigenstates of the physical system. Thus, there is no unique way to divide electron density between constituting atoms and determine precisely the charge transfer [8, 9]. That situation pushes for a semiempirical model solution of the problem.

Here we systemize data on effective atomic charge number q, in particular, for boron nitrides available in the literature. For simplicity we use instead the term "effective atomic charge", i. e. measure it in units of elemental charge, – the true effective charges of B and N atoms constituent the binary compound BN are +qe and –qe, respectively. It is expedient to start with finite systems, i. e., BN molecules because B–N bond serves for building block for all the solid state modifications of boron nitride.

Theoretical estimates show [10] some redistribution of the valence electron density between B and N atoms bonded in diatomic molecule. Calculation of the quasi-molecular minimal unit cell of BN crystal within the 2D approximation, i. e., B_1N_1 system or isolated B–N bond, yields following occupancies for the valence states: $s(B)=0.88$, $p_{xy}(B)=0.23$, $p_z(B)=0.69$, $s(N)=1.12$, $p_{xy}(N)=0.77$, $p_z(N)=1.31$. Therefore, for B and N atoms one can find charges of $3–(0.88+0.23+0.69)=+1.20$ and $3–(1.12+1.77+1.31)=–1.20$, respectively, i. e. the configuration $B^{+1.20}N^{-1.20}$. From the electronegativity scale, charge transfer direction is valid, but ionic charge value of 1.20 seems to be too overestimated.

The molecular wave-function calculations [11, 12] lead to the configuration $B^{+0.47}N^{-0.47}$. The transferred charge value of 0.47, of course, has a physical sense.

Analysis of the atomic orbitals population in nonstoichiometric cage molecule $B_{36}N_{24}$ with carbon C_{60}-fullerene structure carried out by X_α-method gives [13] following values of the atomic charges – B(1): +0.47, B(2): +0.41, and N: −0.66 (There are two different B-sites!).

The averaged charges on B (positive) and N (negative) atoms constituting $B_{12}N_{12}$, $B_{24}N_{24}$, and $B_{60}N_{60}$ fullerenes were estimated semiempirically [14] using MNDO (modified-neglect-by-diatomic-overlap) method as ±0.26, ±0.31 and ±0.30, respectively.

Mixed clusters of B and N atoms – B_2N, BN_2, B_3N, B_4N, B_2N_2, and B_3N_2 – can be produced by sputtering of a solid state boron nitride. Atom ordering in these assumed linear species was derived from measurements of the mass distribution of both the positive and negative products from the fragmentation of the anionic clusters in a gas target. Their neutral configurations were calculated [15] as $B^{+0.28}B^{-0.11}N^{-0.17}$, $N^{+0.03}B^{-0.06}N^{+0.03}$, $B^{+0.08}B^{+0.14}B^{-0.03}N^{-0.19}$, $B^{-0.04}B^{+0.07}B^{+0.05}B^{+0.03}N^{-0.11}$, and $B^{-0.07}B^{+0.02}N^{+0.02}N^{+0.03}$ (there are several different B-sites in some linear chains).

3. Purpose and objectives of the study

The key purpose of this paper is to determine unambiguously the effective atomic charges in crystalline modifications of boron nitride.

In accordance with this goal the following research objectives have been identified:

– Construction of a point charge model useful for crystalline binary compounds;

– Elaboration of a model-based phenomenological theory expressing the effective charges in a crystalline binary compound via experimentally measurable parameters of the material;

– Quantitative estimations of effective atomic charges in crystalline boron nitrides.

4. Research materials

We have studied three main structural modifications of boron nitride such as hexagonal (h-BN), cubic (c-BN), and wurtzite-like (w-BN) boron nitrides. Here are collected the data available on electron charge transfer in these crystalline solids.

4. 1. Hexagonal boron nitride

According to the 11B NMR (nuclear-magnetic-resonance) studies [16, 17], net charges at atomic sites of the h-BN structure equals to ±0.45. While according to the EPR (electron-spin-resonance) studies [18], F-center in form of nitrogen vacancy in h-BN lattice possesses the effective charge of –1.00 at the ionicity of bonding of ±0.61.

Periodic small cluster calculations performed within a semi-empirical tight-binding approach showed [19] that total atomic charges in BN hexagonal layer equal to ±0.30.

Analysis of the ESCA (electron-spectroscopy-for-chemical-analysis) and SXS (surface-X-ray-scattering) experiments also has proved [20] the conclusion that h-BN is partially covalent and partially ionic compound with effective charges of ±0.30.

Calculation of the quasi-molecular cells $B_{12}N_{12}$ and $B_{16}N_{16}$ of the h-BN crystal within the 2D approximation, i. e., for fragments of the hexagonal layer, yields [10] following occupancies for the valence electron states: $s(B)=0.69$, $p_{xy}(B)=0.55$, $p_z(B)=0.32$, $s(N)=1.25$, $p_{xy}(N)=1.48$, $p_z(N)=1.68$. Therefore, for B and N atoms one can find charges of $3-(0.69+0.55+0.32)=+1.44$ and $3-(1.25+1.48+1.68)=-1.41$, respectively, i. e. the configuration $B^{+1.44}N^{-1.41}$. If the electron charge defect of 0.03 is distributed in the inter-atomic space the compound has to behave as a semimetal. Thus, we have to assume that, the charge of –0.03 is transferred to the model hydrogen pseudoatoms placed at edges of the cell.

Utilizing the OLCAO (orthogonalized-linear-combinations-of-atomic-orbitals) method within the LDA (local-density approximation), values of valence charges in h-BN were determined [21] as B: 0.19, N: 6.70, and in the inter-atomic space: 1.11 (which correspond to 1.4, 22.3 and 76.3 % of the volume, respectively). Thus, atomic charges are B: $3-0.19=+2.81$, N: $5-6.70=-1.70$, and in the inter-atomic space: $-1.70-(+2.81)=-1.11$. This situation corresponds to the configuration $B^{+2.81}N^{-1.70}$ with the charge of –1.11 distributed in the inter-atomic space. These values seem to be significantly overestimated if compared with ±0.30, according to Mulliken population analysis B: $3-2.70=+0.30$ and N: $5-5.30=-0.30$.

On basis of MTO (muffin-tin-orbital) calculations of energy distributions in h-BN, it was estimated [22] ratios of anionic and cationic electron-states in valence band (B/N≈0.45) and conduction band (B/N≈1.18). Assuming that in insulating h-BN almost all the electron charge is concentrated in the valence band, we can estimate atomic charges as B: $3-(3+5)\cdot0.45/(0.45+1)\approx+0.52$ and $(3+5)\cdot1/(0.45+1)-5\approx-0.52$. This situation corresponds to the configuration $B^{+0.52}N^{-0.52}$.

4. 2. Cubic boron nitride

Semiempirical description of the electronic structure of a tetrahedral crystal expresses the electron–lattice-ion interaction in the form of $\pm mZ/R$, where Z is the effective charge number of ions, R is the distance, and m is a fitting coefficient. At $R\to\infty$, m equals to Madelung constant M≈1.64. For c-BN, at m=0, 1.1, 1.2, and M, there are found [23] Z=0.16, 0.46, 0.51, and 0.93, respectively. Thus, c-BN has to correspond to the configuration $B^{+0.93}N^{-0.93}$.

Semiempirical estimates of the B–N bond ionicity in c-BN, according to Phillips and Pauling, scales are ±0.26 and ±0.22, respectively [24].

Within the Coulson approach, bonding in c-BN can be described by the sp^3-hybridization leading to the ionic charges of ±0.43 [25].

A semiempirical approach [26] to the chemical bonding in the class of tetrahedrally coordinated compounds A^nB^{8-n}, which includes c-BN (n=3), leads to the effective charges of ±0.80 (at the binding covalence of 0.76).

By the LCAO (linear-combinations-of-atomic-orbitals) method, the static ionic charge in c-BN is estimated as 0.26–0.50 [27]. The self-consistent electron density distribution yields the electron state configurations B $1s^{2.00}2s^{0.65}2p^{1.75}3s^{0.12}3p^{0.13}$ and N $1s^{2.00}2s^{1.71}2p^{3.52}3s^{0.08}3p^{0.04}$, i.e., charge configuration $B^{+0.35}N^{-0.35}$.

According to the well-known interpolation scheme by Harrison [28], effective atomic charges in c-BN equal to ±0.36.

By a HF (Hartree–Fock) type method ionic charges of B and N atoms in c-BN crystal were estimated [29] as ±0.48, what significantly exceeds the value determined from the Mulliken population analysis.

Numbers of valence s- and p-electrons on B and N atoms in c-BN crystals were determined [30] on the basis of semiempirical calculations of electron density components: s(B)=1.13, p(B)=2.60, s(N)=1.73 and p(N)=2.54. Consequently, B and N atoms possess 1.13+2.60=3.73 and 1.73+2.54=4.27 valence electrons, respectively; and charges of $3-3.73=-0.73$ and $5-4.27=+0.73$. But, the configuration $B^{-0.73}N^{+0.73}$ contradict the usual electron charge transfer direction and relative electronegativity of B and N atoms.

It was assumed that, contradictions between results of different band structure calculations performed for c-BN mainly are related with neglecting by the partial ionicity of bonding. In the work [1], calculations were conducted using a version of the APW (augmented-plane-wave) method for the configuration $B^{+0.35}N^{-0.35}$ (some of experimental data support the configuration $B^{+0.32}N^{-0.32}$, while according to the G. Perkins private communication to Authors of [1] $B^{+0.36}N^{-0.36}$ can be released).

By the semiempirical OLCAO method of calculations, the numbers of valence electrons in B and N atoms in c-BN were determined [31] as n_B=1.91 and n_N=6.09. Consequently, the fractional ionicity coefficient for this compound equals to $FIC=(n_N - n_B)/(n_N + n_B)\approx 0.52$. As for the effective charge configuration, it is determined as $B^{+1.09}N^{-1.09}$ because 3–1.91=+1.09 and 5–6.09=–1.09.

Analysis of the XRD (X-ray-diffraction) data for c-BN reveals [11] electron charge transition from B to N and formation of the configuration $B^{+0.46}N^{-0.46}$. When the slightly different model of analysis with minimal atomic radii of R_B=0.74Å and R_N=0.82Å is used [12], the predicted configuration has to be $B^{+(0.44\pm0.02)}N^{-(0.44\pm0.02)}$.

Within the LDA based on KS (Kohn–Sham) equations and non-local PP (pseudopotential), the valence charge density in c-BN was calculated [32]. Its distribution was found to be with asymmetry of ≈0.26. Thus, the configuration $B^{+0.26}N^{-0.26}$ can be assumed.

A SCF (self-consistent-field) calculation for c-BN leads [33] to the configuration $B^{+0.48}N^{-0.48}$ with ionic charges higher than those according to the Mulliken analysis.

Utilizing the OLCAO method within LDA, valence charges in c-BN were determined [21] as B: 0.20, N: 6.40, and in the inter-atomic space: 1.40 (they correspond to 2.3, 34.0, and 63.7 % of the volume, respectively). Thus, atomic charges values are B: 3–0.20=+2.80 and N: 5–6.40=–1.40, and in the inter-atomic space: –1.40. This situation corresponds to the configuration $B^{+2.80}N^{-1.40}$ with the charge of –1.40 distributed in the inter-atomic space. Obtained values seem to be significantly overestimated if compared, e. g., with ±0.20 according to Mulliken population analysis (B: 3–2.80=+0.20 and N: 5–5.20=–0.20).

Charge transfer in c-BN should be related to the depletion of B p-states. First principle asymmetry coefficient for c-BN is estimated [8, 9] as g≈0.48, which exceeds its Phillips's ios nicity. Thus, the configuration $B^{+0.48}N^{-0.48}$ can be assumed.

The baric dependence of the c-BN band gap width is possible to obtain taking into account partial ionicity of this compound. Its ionicity, calculated by the SC (self-consistent) linear MTO-method, is 0.38 [34]. This value is placed between Phillips ionicity and electron charge distribution asymmetry coefficient. It corresponds to the configuration $B^{+0.38}N^{-0.38}$.

Within the DFT (density-functional-theory), ionicity of c-BN calculated by a PP PW (pseudopotential-plane-wave) method equals to 0.49 [35]. Thus, the configuration $B^{+0.49}N^{-0.49}$ can be assumed.

Using first-principles total energy calculations to investigate electronic properties of c-BN, the Born effective charge was determined in [36]. The ionicity factor of c-BN was also estimated by a semiempirical tight-binding method and first principle PP method within the LDA was used for studying of the ionicity effect on c-BN surface states [37].

On basis of MTO-calculations of energy distributions in c-BN, it was estimated [22] ratios of anionic and cationic electron-states in valence band, B/N≈0.51, and conduction band, B/N≈1.25. Assuming that in insulating c-BN almost all the electron charge is concentrated in the valence band, we can estimate atomic charges as B: 3–(3+5)·0.51/(0.51+1)≈+ +0.30 and (3+5)·1/(0.51+1)–5≈–0.30. This situation corresponds to the configuration $B^{+0.30}N^{-0.30}$.

4. 3. Wurtzite-like boron nitride

Utilizing the OLCAO method within LDA, valence charges in w-BN were determined [21] as B: 0.20 and N: 6.00, and in the inter-atomic space: 1.80 (they correspond to 2.3, 37.7, and 63.0 % of the volume). Thus, atomic charges values are B: 3–0.20=+2.80 and N: 5–6.00=–1.00, and in the inter-atomic space: –1.80. This situation corresponds to the configuration $B^{+2.80}N^{-1.00}$ with the charge equal to –1.80 distributed in the inter-atomic space. These values seem to be significantly overestimated if compared with ±0.01, according to Mulliken population analysis, which indicates practically no charge transfer (B: 3–2.99=+0.01 and N: 5–5.01=–0.01).

Numbers of valence electrons on B and N atoms in w-BN crystal were determined [38] as n_B=1.47 and n_N=6.53. Thus, characteristic of the partial ionicity of bonding equals to $CPI=|n_B - n_N|/(n_B + n_N)\approx 0.63$ (according to the Mulliken scheme CPI≈0.25). As for the effective charge configuration, it was determined as $B^{+1.53}N^{-1.53}$ (3–1.47=+1.53 and 5–6.53=–1.53).

Within the DFT, ionicity of w-BN calculated by a PP PW method equals to ≈0.49 [35]. Thus, the configuration $B^{+0.49}N^{-0.49}$ can be assumed. It should be noted that, the difference between w-BN and isostructural AlN phonon dispersions cannot be explained by a simple mass-approximation, i. e., assuming that the force-constants of BN and those of AlN are very similar and that one can obtain the dynamical properties of AlN using the force constants of BN and the masses of AlN or vice versa. Instead, the quite different degree of ionicity of the two crystals, namely, the marked ionicity of w-AlN bonding yields a pronounced anisotropy, larger than that of w-BN.

Using first-principles total energy calculations to investigate electronic and elastic properties of the w-BN, the Born effective charge was determined in [39] as well.

Above presented data on boron nitride species are systemized in the Table 1. There are also shown references and type of method of evaluation: E – experimental, T – theoretical, and ET – when in the determination experimental data were used together with a special theoretical model. When effective charges of B and N atoms differ in absolute value, it means that in the structure there are nonequivalent atomic positions or some part of electron charge is distributed in interatomic space.

It is obvious that, we ignore the limit values as erroneous because they point to the wrong, in view of electronegativity scale of elements, direction of electron charge transfer from the nitrogen atoms to boron atoms (first 5 rows in the Table 1), and too large values of the transferred charge and/or free electron charge in the interatomic space in BN crystals known as good insulators (last 6 rows).

After this, there is still too significant variety in values of effective charge number. Situation like this is not peculiar exclusively to boron nitrides, but is typical for binary compounds. The reason is that in such case both the theoretical calculation and interpretation of the measurement results require a division of space between atoms constituting the crystal. But, this procedure cannot be done unambiguously, as it has been mentioned in the Introduction.

Table 1

Effective charge numbers of B and N atoms in BN molecules and crystals

Molecules of BN			Crystal of h-BN			Crystal of c-BN			Crystal of w-BN		
B	N	Ref.	B	N	Ref.	B	N	Ref.	B	N	Ref.
–	–	–	–	–	–	–0.73	+0.73	ET[34]	–	–	–
–0.07	+0.03	E[15]	–	–	–	–	–	–	–	–	–
–0.07	+0.02	E[15]	–	–	–	–	–	–	–	–	–
+0.02	+0.03	E[15]	–	–	–	–	–	–	–	–	–
+0.02	+0.02	E[15]	–	–	–	–	–	–	–	–	–
–	–	–	–	–	–	+0.22	–0.22	ET[24]	–	–	–
+0.26	–0.26	ET[14]	–	–	–	+0.26	–0.26	ET[24]	–	–	–
–	–	–	–	–	–	+0.26	–0.26	T[32]	–	–	–
+0.30	–0.30	ET[14]	+0.30	–0.30	ET[19]	+0.30	–0.30	T[22]	–	–	–
–	–	–	+0.30	–0.30	E[20]	–	–	–	–	–	–
–	–	–	+0.30	–0.30	T[21]	–	–	–	–	–	–
+0.31	–0.31	ET[14]	–	–	–	–	–	–	–	–	–
–	–	–	–	–	–	+0.32	–0.32	E[1]	–	–	–
–	–	–	–	–	–	+0.35	–0.35	T[27]	–	–	–
–	–	–	–	–	–	+0.35	–0.35	T[1]	–	–	–
–	–	–	–	–	–	+0.36	–0.36	ET[28]	–	–	–
–	–	–	–	–	–	+0.36	–0.36	T[1]	–	–	–
–	–	–	–	–	–	+0.38	–0.38	T[34]	–	–	–
+0.41	–0.66	T[13]	–	–	–	–	–	–	–	–	–
–	–	–	–	–	–	+0.43	–0.43	T[25]	–	–	–
–	–	–	–	–	–	+0.44	–0.44	E[12]	–	–	–
–	–	–	+0.45	–0.45	E[16,17]	–	–	–	–	–	–
–	–	–	–	–	–	+0.46	–0.46	E[12]	–	–	–
+0.47	–0.47	T[11, 12]	–	–	–	–	–	–	–	–	–
+0.47	–0.66	T[13]	–	–	–	–	–	–	–	–	–
–	–	–	–	–	–	+0.48	–0.48	T[29]	–	–	–
–	–	–	–	–	–	+0.48	–0.48	T[33]	–	–	–
–	–	–	–	–	–	+0.48	–0.48	T[8,9]	–	–	–
–	–	–	–	–	–	+0.49	–0.49	T[35]	+0.49	–0.49	T[35]
–	–	–	+0.52	–0.52	T[22]	–	–	–	–	–	–
–	–	–	+0.61	–0.61	E[18]	–	–	–	–	–	–
–	–	–	–	–	–	+0.80	–0.80	ET[26]	–	–	–
–	–	–	–	–	–	+0.93	–0.93	ET[23]	–	–	–
–	–	–	–	–	–	+1.09	–1.09	ET[27]	–	–	–
+1.20	–1.20	T[9]	–	–	–	–	–	–	–	–	–
–	–	–	+1.44	–1.41	T[10]	–	–	–	–	–	–
–	–	–	–	–	–	–	–	–	+1.53	–1.53	T[38]
–	–	–	–	–	–	–	–	–	+2.80	–1.00	T[21]
–	–	–	–	–	–	+2.80	–1.40	T[21]	–	–	–

5. Research methods

5. 1. Point charges model

The impossibility of unambiguous division of the electron density between atoms of elements constituting compound pushes the search for a model semiempirical solution of the problem. In the model proposed here, the using of the static effective charge concept for the atoms constituting a material involves the introduction of a crystalline structure, in which the atomic sites are considered as fixed point electric charges, like the well-known Madelung model for ionic crystals. Polarization of such a structure in an external static electric field means displacements of charges in new equilibrium positions, where the mechanical stresses that accompany the polarization-related deformation of the structure, are balanced by the electric force.

For concreteness, let's consider a crystalline binary compound, whose unit cell (Fig. 1) contains N atoms of each of two chemical elements with charges +qe and –qe, respectively (e is the elementary charge). Effective charge number q is the only parameter of the model, the numerical value of which can be uniquely identified semiempirically. In addition, we assume that the external electric field $\vec{E}_0$ is weak enough, so that deformations caused by electric polarization remain elastic.

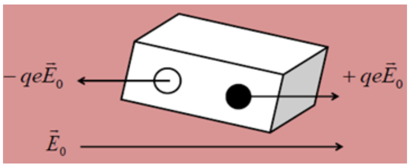

Fig. 1. Point charges model of crystalline binary compound

Let's perform the transition from microscopic quantities to the macroscopically averaged ones for the crystalline unit cell in the form of parallelepiped with volume of V. Assume that, the external field is applied in the direction of the edge with length of a. That is the lattice constant in this direction. Corresponding cross-sectional area will be equal to

$$S = \frac{V}{a}.$$

Therefore, if the Young's modulus of the crystal along the vector $\vec{E}_0$ is Y, then the linear extension caused by the tensile force

$$\vec{F} = Nqe\vec{E}_0$$

equals to

$$\Delta a = \frac{Fa}{SY} = \frac{NqeE_0a^2}{VY}.$$

As a result, the electric dipole moment

$$p = Nqe\Delta a = \frac{(Nqea)^2E_0}{VY}$$

is induced in the elementary parallelepiped.

By definition, the polarization vector $\vec{P}$ is the density of the induced electric moment. Therefore, we find it as

$$\vec{P} = \frac{\vec{p}}{V} = \left(\frac{Nqea}{V}\right)^2 \frac{\vec{E}_0}{Y}.$$

Here we have neglected by the expansion of the unit cell volume assuming deformations to be sufficiently weak. Now we can determine the polarization field strength $\vec{E}'$ (ε_0 is the electric constant):

$$\vec{E}' = -\frac{\vec{P}}{\varepsilon_0} = -\left(\frac{Nqea}{V}\right)^2 \frac{\vec{E}_0}{\varepsilon_0 Y}.$$

The minus sign indicates that this field is directed opposite to $\vec{E}_0$. The resulting macroscopically averaged field in the crystal is equal to

$$\vec{E} = \vec{E}_0 + \vec{E}' = \left(1 - \frac{1}{\varepsilon_0 Y}\left(\frac{Nqea}{V}\right)^2\right)\vec{E}_0 .$$

Hence, at the first it is determined the permittivity of the crystal along the direction of external electric field:

$$\varepsilon = \frac{1}{1 - \frac{1}{\varepsilon_0 Y}\left(\frac{Nqea}{V}\right)^2},$$

and then the corresponding effective charge number

$$q = \frac{V}{Nea}\sqrt{\varepsilon_0 Y\left(1 - \frac{1}{\varepsilon}\right)}.$$

5. 2. Empirical parameters

Values of the room temperature lattice parameters, elastic constants, and dielectric permittivity of boron nitride crystals were provided from the data-base [40]. Values of Young's modulus were recalculated utilizing general crystallographic formulas [41] with the exception of h-BN, for which we have used results of direct measurements presented in the Handbook [42].

The axial Young's modulus of an individual multi-walled BN nanotube (with very few defects) also was determined experimentally [43] and obtained the value, 1.22±0.24TPa, consistent with theoretical estimates. It exceeds Young's modulus of any other known insulating fiber. On the other hand, partial polarity of the chemical bonding distinguishing BN from C makes nanotubular boron nitride a new excellent piezoelectric material with response values larger than those of piezoelectric polymers and spontaneous polarization comparable to that of wurtzite bulk semiconductors (references see, e. g., in the Review [44]). Unfortunately, we fail to estimate effective atomic charges in BN nanotubes because of absence of reliable information on their dielectric permittivity.

The unit cell volume for h-BN layered crystals can be calculated from the formula

$$V = \frac{\sqrt{3}\,a^2 c}{2},$$

where a and c are intra- and interlayer lattice constants. If Y_a and Y_c, and ε_a and ε_c denote, respectively, Young's modulus and permittivity values in plane of layers and direction normal to this plane, then corresponding effective atomic charge numbers are calculated as

$$q_a = \frac{ac}{4e}\sqrt{3\varepsilon_0 Y_a\left(1 - \frac{1}{\varepsilon_a}\right)}$$

and

$$q_c = \frac{a^2}{4e}\sqrt{3\varepsilon_0 Y_c\left(1 - \frac{1}{\varepsilon_c}\right)}.$$

Same formulas work for w-BN crystals, unless lattice constants a and c are of different crystallographic meanings.

The unit cell volume for c-BN crystal is

$$V = a^3,$$

i. e., expressed with single structural parameter a. Correspondingly, effective atomic charge number is

$$q = \frac{a^2}{4e}\sqrt{\varepsilon_0 Y\left(1 - \frac{1}{\varepsilon}\right)}.$$

6. Research results

In the present work, we have construct a phenomenological theory, based on which we can derive the expression for the effective charge number in a crystalline binary compound depending on the number of molecules in the primitive parallelogram, its sectional area transverse to the direction of the applied external electric field, the Young's modulus and the static dielectric constant in same direction. Then utilizing the empirical values of mentioned characteristics, we can estimate the effective charges of B and N atoms.

The used input data together of calculation results – semiempirically estimated effective atomic charge numbers for three crystalline modifications of boron nitride – are presented in Table 2.

Table 2

Calculated effective atomic charge numbers in boron nitrides

Crystal	N	a, Å	c, Å	ε_a	ε_c	Y_a, GPa	Y_c, GPa	q_a	q_c
h-BN	2	2.50	6.66	5.06	6.85	85.9	33.9	0.35	0.09
c-BN	4	3.62		7.10		749		0.49	
w-BN	2	2.55	4.23	5.10	6.80	960	1070	0.76	0.50

7. Discussion of results

Semiempirically estimated values of q are physically reasonable – are less than 1: h-BN – 0.35 and 0.09, c-BN – 0.49, and w-BN – 0.76 and 0.50.

Also quite natural are qualitative results:

– in h-BN, in-layer bonds polarity is much stronger than that between hexagonal layers;

– bonds are stronger polarized in denser modifications c-BN and w-BN, which are characterized by higher coordination numbers as well;

– bonds polarities in c-BN and along c-axis in w-BN are almost indistinguishable;

– bonds polarities in a- and c-directions in w-BN are different.

8. Conclusions

In summary, we have constructed a point charges model for binary compounds, which allows the theoretical expressing of the static charges associated with constituent atoms through experimentally available parameters of the material, such as number of atoms in unit cell, lattice constants, Young's modulus and permittivity. The derived formula has been used for semiempirical estimates of effective charges of B and N atoms in crystalline modifications of boron nitride BN. Results of calculations are physically meaningful both from quantitative and qualitative points of view (hexagonal boron nitride – 0.35

and 0.09, cubic boron nitride – 0.49, and wurtzite-like boron nitride 0.76 and 0.50).

The obtained effective charges can be used in the refinement of calculations of the electronic structure of boron nitrides. In particular, we indent to revise our previous band structure calculations (performed using quasi-classical approach), which did not take into account polarity of bonding in crystalline modifications of boron nitride: h-BN [45, 46], c-BN [47], and w-BN [48].

Acknowledgment

One of the authors, Prof. Levan Chkhartishvili, is thankful to Dr. Norman A. Draeger, Materials Scientist of the Lab in Oregon, WI, US. Just his question about values for the permanent dipole moment of various structures of boron nitride was an invocation for searches for a reliable estimation scheme of effective atomic charges of boron nitrides.

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