

BK-Spectrum XANES and Electron Structure of the Polytypes of the Boron Nitride

V.V. Ilyasov and T.P. Zhdanova

Department of Physics,
Don State Technical University,
Rostov-on-Don, 344010, Russia
E-mail: viily@mail.ru, victor.ilyasov@rost.ru

Abstract

The electronic power structure of a vicinity XANES of polytypes BN as graphite (h-BN), wurtzite (w-BN) and sphalerite (c-BN) is designed by a method local coherent of potential with use cluster of the version of MT-approach, in frameworks multiple scattering theory. Comparison of peculiarities of electronic structure 2H is spent, 4H and 3C of polytypes with x-ray to - spectra of absorption boron and interpretation of their peculiarities is given. Is shown, that the electronic power structure in a vicinity XANES in 2H, 4H and 3C polytypes boron nitride is formed in the basic free 2p-condition of atoms boron.

1. Introduction

Problems of the analysis of electronic structure and physical properties wide-gap of semi-conductor materials (BN, SiC and other) for steel the most urgent with development of solid-state electronics, as for interpretation, for example, optical properties of these materials knowledge of peculiarities of their electronic structure is necessary.

In this connection the interest is represented by(with) electronic structure in a vicinity XANES of polytypes boron nitride

It is known, that in B K-spectra of absorption boron as in hexagonal [1], and in sphalerite [2] updatings boron nitride selective maxima are observed which can communicate as with occurrence of an exited condition boron 1s electron [1], Wannier exciton [2], and with process of transition 1s electron on free condition arising due to vacancies [3].

Besides there is without an explanation the number of bands of thin structure in experimental to - spectra of absorption boron 2H boron nitride polytypes.

In the present work we offer interpretation of peculiarities X-ray emission of a to K -band and absorption near-edge structure (XANES) of boron in considered boron nitride polytypes.

2. Method of calculation

The electronic energy structure of considered boron nitride crystal modifications is studied within the framework of one approximation with use local coherent potential method [4]. Effective crystal potential each boron nitride polytype was determined as a sum of the Coulomb potential, the exchange component, and the Madelung potential.

The account crystal muffin-tin (MT) - of potential came true for an equilibrium condition with experimental meanings of parameters of lattices, submitted in Table 1.

The account of the contributions in DOS from the next atoms and Coulomb potential 30 coordination spheres was made. Exchange potential was under construction in X-approach Slater with the exchange amendment $\alpha = 2/3$. Madelung potential is calculated on Ewald method and takes into account the electrostatic contribution various sublattices in crystal potential boron nitride similarly [5].

Constructed crystal MT-potentials were used at the decision of the radial equation Schrodinger for $l=0,1$ in an interval energy from 0.02 Ry up to 3 Ry with a constant step 0.02 Ry. Local partial the density of condition (PDOS) boron in boron nitride polytypes were calculated for cluster, consisting from more 250 atoms, on the basis of the formula [3]:

$$n_l^A(E) = \frac{\sqrt{E}}{\pi} \int_0^{r_{ws}} [R_l^A(r, E)]^2 dr \frac{\text{Im Tr} T_{LL'}^{A,00}(E)}{\text{Im } t_l^A(E)}$$

Where l - orbital quantum number; $R_l^A(r)$ - radial wave functions of atom of a grade A (boron); $T_{lm, l'm'}^{A,00}$ - matrix element of the scattering operator. Complete density of condition (TDOS) electrons on an elementary cell for one projection a back was determined as a sum of local density of condition (LDOS) similarly to work [3].

Table. Parameters of the lattice and of the crystal potentials of the studied compounds

Parameters	Lattice type					
	sphalerite		wurtzite		graphite	
	B	N	B	N	B	N
Lattice parameters, nm	0.3615		a = 0.2551 c/a = 1.633		a = 0.2504 c/a = 2.67	
Coordination number	4		4		3	
Number of atoms per unit cell	8		4		4	
Radii of MT-spheres, at. units.	1.449	1.449	1.327	1.327	1.367	1.367
Radii of Wigner-Seitz spheres, at. units.	2.121	2.121	1.898	1.898	1.849	1.849
Число валентных электронов в MT-сфере	2.97	5.19	3.076	4.864	2.844	4.979
Potential beyond MT-spheres, Ry	0.00985		-0.10626		-1.48600	
Density of electron charge beyond the spheres	0.07061		0.10770		0.13229	

3. Results and discussion

On Fig. 1 comparison of complete density of filled and free condition electrons for polytypes investigated by us is resulted. The analysis of electronic spectra on the given drawing allows to note presence of wide power cracks between top TDOS strips and bottom of a zone of conductivity: h-BN (3.4 eV), c-BN (4.5 eV) w-BN (5.2 eV), that quite corresponds(meets) to their semi-conductor nature.

On Fig. 2 are resulted experimental X-ray a spectrum (XPS) real crystal c-BN_{1-x}, complete density of electronic condition (TDOS) non-stoichiometric c-BN_{0.99} (for an nonequilibrium condition) and spectrum of a quantum output B K- XANES in c-BN.

The analysis of electronic spectra non-stoichiometric $c\text{-BN}_{0.99}$ in comparison with) $c\text{-BN}$ shows, that the electronic structure non-stoichiometric boron nitride $c\text{-BN}_{0.99}$ in a vicinity XANES gets thin structure, not peculiar $c\text{-BN}$.

It is connected to localization free s - and p -condition boron of 1-th type (peaks a and b) and condition on vacancy (1,34 Ry) similarly data of work [6]. It is essential, that the free condition with energy, arising at scattering on vacancies, energetically coincide with a rule of a resonance "CE in BK- XANES in $c\text{-BN}$.

It allows to assume, that exited $1s$ electron can pass to free condition of p -symmetry (caused by vacancy). The peculiarities x-ray absorption near-edge of structure of boron can be defined(determined) by structure $1s$ and $2s$ internal Wannier exciton [2]. Not stopping here on exciton's to a nature of a resonance we shall note only, that these exciton's the levels cannot be described through one-electronic condition of $2s$ -symmetry of atoms of boron, located with energy 1.22 Ry and 1.46 Ry. It is necessary to notice, that the absence of a resonance "CE (1.34 Ry) in zoned accounts, marked in work [4], on our sight, can be connected to use of the one-electronic approach. Last, gives one-electronic condition, which can not coincide with exciton's by condition, belonging to the whole crystal. As in real crystals (at presence of defects of a lattice) the rules of selection for quantum transitions can be broken, it is possible to admit(allow) existence of the above described process exciton's of excitation, i.e. transition $1s$ electron of atom B on exciton's a level according to representations of the authors [1,2].

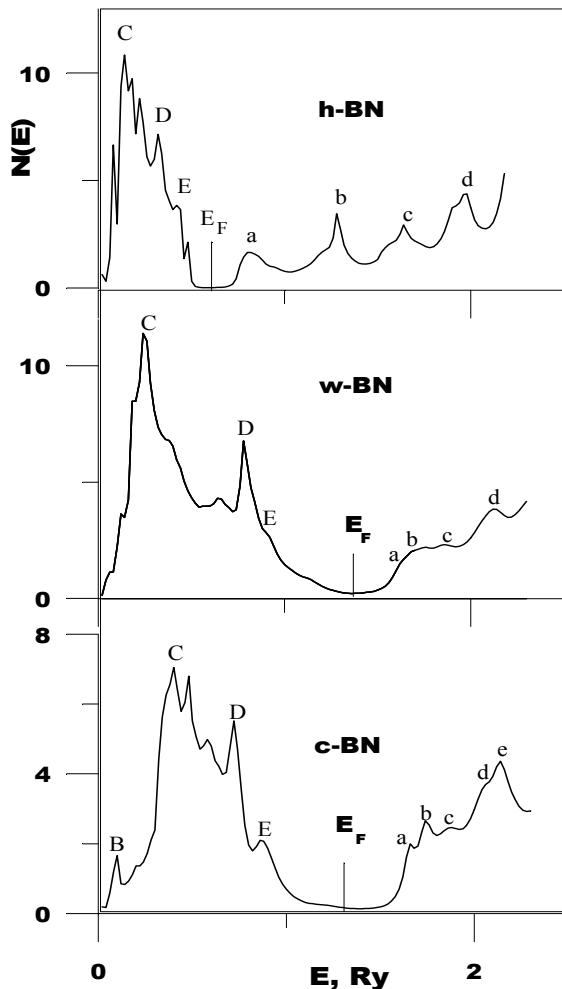


Fig. 1. Total density of states in boron nitride polytypes.

However, if to admit, that in researched crystals boron nitride could be observed non-stoichiometric in sublattice of nitrogen, it is possible to assume vacance's a nature of a resonance "CE (1.34 Ry) [5]. As have shown our accounts, of an equilibrium condition presence of a power interval in 2 eV between vacance's by peak and free one-partial electronic condition of atom boron with energy 1.5 eV is characteristic. For relaxation's of a condition density of free electronic condition of atoms B with energy 1.34 Ry appear very small. Thus, for non-relaxation's of a condition of a crystal c-BN_{0.99} there is some probability of transitions 1s electron of atom boron on free condition, formed both vacancy, and atom B (peak a).

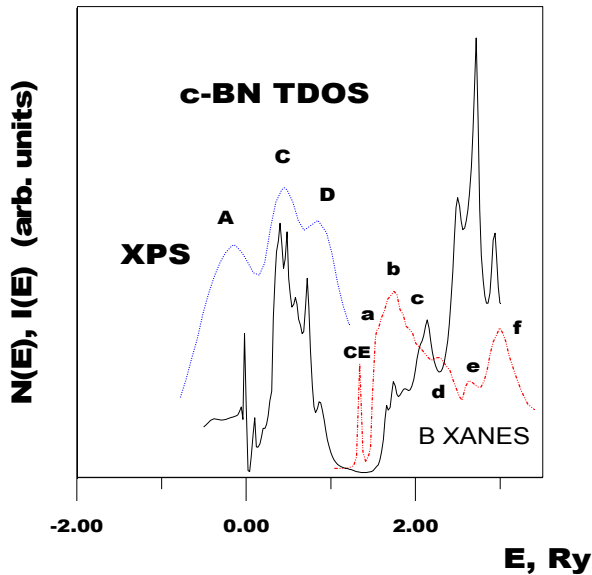


Fig. 2. Total density c-BN and x-ray spectrum: XPS and B XANES.

Size of a power interval between a resonance "CE and level Fermi in c-BN_{0.99} is of interest which makes 4.6 eV B And there is on 1.4 eV less power break between short-wave border emission's of a band and selective maximum (in a quantum output) for 2H polytype of BN [1]. The given distinction can be explained by structure of zones in h-BN, for which is characteristic wider band gap [7,8].

On Fig. 3 experimental x-ray K-band emission and absorption by boron's atom and designed in the given work 2p-DOS boron in 2H boron nitride polytypes are submitted.

The submitted here results will be coordinated with a conventional treatment of near thin structure, determined (for example in 2H BN) narrow π -zone and two wide σ -zones. Last are poorly blocked with a high-energy tail - of a zone. Last are poorly blocked with a high-energy tail of a π -zone. The most "wash out" there is the spectrum of free condition in 4H a polytype BN. Opposite, in a polytype 2H BN peaks "a", "b", "c" and "d", formed by p-condition of atoms boron, find out "oscillations" with a step on energy 0.5 Ry.

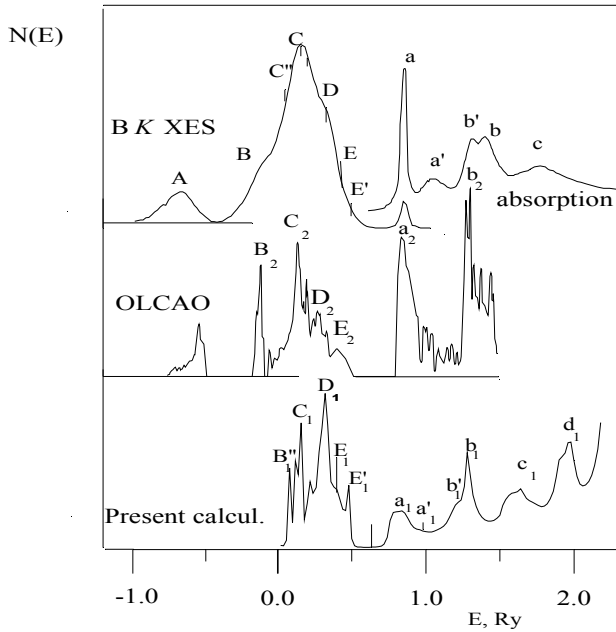


Fig. 3. Experimental B K XES, B K XANES, and local partial density of boron 2p states for the h-BN modification.

The observable peculiarities of a power spectrum are possible to consider as strongly located excited condition of a crystal. The nature of dominant bands of absorption "a" and "b" of a x-ray spectrum of absorption boron in 2H polytype of BN, is caused by transition B K-electron in marked excited condition π - and σ - of symmetry of a crystal.

Comparison of a settlement electronic spectrum of considered polytypes BN and with experimental x-ray to K-spectra of absorption boron have shown [5], that the electronic structure of a vicinity XANES in 2H, 4H and 3C polytypes boron nitride is formed in the basic free 2p-condition of atoms boron.

The near thin structure of a to - spectrum of absorption boron (area XANES), in the given work, is interpreted on the basis of results of account of electronic structure. First of all it is necessary to note, that the power rule of peaks a, b and c on theoretical and experimental spectra coincides.

From the analysis of data, submitted on drawings, it is possible to assume, that the appreciable influence to electronic structure h-BN should render π -interaction of atoms boron and nitrogen (on that specifies concurrence on energy of peaks "a"), and also it is possible to expect an appreciable role of interaction of atoms boron and nitrogen (rule(situation) of peaks "b and "c").

4. Conclusions

Thus, in the present work is shown, that the electronic energy structure of area filled DOS in h-BN, w-BN and c-BN polytypes has general laws, which are displayed in presence on a curve TDOS characteristic for BN of peculiarities, in particular of peaks C and D, describing basic condition of nitrogen and boron in a crystal.

The presence of short-wave inflow E on experimental x-ray spectra of issue boron, and theoretical spectra electrons of 2p-symmetry in the given polytypes BN testifies to general(common) character of formation short-wavelength shoulder, in particular, so-called "external" collective band, not only at nitrides of transitive metals [9], but also at a wider class binary nitrides, including considered polytypes BN.

The reduction of width of a forbidden strip at transition from wurtzite and sphalerite to hexagonal h-BN, from our point of view, is connected to change of coordination number of components, which result(bring) in change of a power rule(situation) of bottom of a zone of conductivity, in particular(personally) to its(her) shift on size about 7 eV in area low energy.

In formation of electronic structure in area of the x-ray absorption near-edge structure (XANES) in considered polytypes of BN determining free 2p-condition of atoms boron are.

References

1. Fomichev, V. A., Зимкина, Т. М. and Lyakhovskaya I. I. *Fiz. Tverd. Tela (Leningrad)* **12**, 156 (1970).
2. Agui, A., et al., *Phys. Rev. B.* **55**, 2073 (1997).
3. Илясов, В. В., Никифоров, И. Я., *Fiz. Tverd. Tela (Leningrad)* **43**, 598 (2001).
4. Ilyasov, V. V., Safontseva, N. Yu. And Nikiforov, I. Ya., *Phys.stat.sol (b)*. **185**, 171 (1994); *J. Phys.: C.* **7**, 6035 (1995).
5. Илясов, В. В., Zhdanova, Т. Р. and Nikiforov, I. Ya., *Fiz. Tverd. Tela (Leningrad)* **45**, 777 (2003).
6. Илясов, В. В., Никифоров, И. Я., *Fiz. Tverd. Tela (Leningrad)* **43**, 233 (2001).
7. Fomichev, V.A., Rumsh., N. A., *J. Phys. Chem. Solids* **29**, 153 (1972).
8. Yong-Nian Xu and Ching, W. Y., *Phys. Rev. B.* **44**, 7787 (1991-I).
9. Vinogradov, A.C., et al., *Fiz. Tverd. Tela (Leningrad)* **33**, 896 (1991).