GENERAL PROBLEMS OF THEORETICAL PHYSICS

ELECTRON ENERGY BAND STRUCTURE OF GaN AND InN EVALUATED WITHIN THE MIXED BASIS APPROACH WITH A NEW EXCHANGE-ENERGY FUNCTIONAL

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The electron energy band spectra of GaN and InN crystals are calculated within the mixed basis (MB) consisting of core Bloch functions and plane waves. The exchange potential is obtained on the basis of a new exchange-energy functional including electron density gradient corrections (*Generalized* Generalized Gradient Approximation, GGGA). The obtained parameters of the energy band structure of crystals are in better agreement with the data calculated using the exact exchange potential than those obtained in the Local Density Approximation (LDA). The calculated energies of semicore d-electrons are close to the experimental data.

1. Introduction

The electron energy band spectra of GaN and InN crystals were calculated in the LDA approximation using the pseudopotential method, as well as the exact-exchange approach [1] with the help of the full-potential linear muffin-tin orbital (FP-LMTO) method [2]. We calculated the electron energy bands of GaN and InN crystals within the mixed basis consisting of the Bloch functions of core electrons and plane waves [3–5].

The aims of the given work are as follows: 1) to use the recently proposed exchange potential, being more exact for crystals [6], with gradient corrections (GGA) in the calculation algorithms of the MB formalism; 2) to use a generalization of GGA, i.e. GGGA, recently proposed in [7] in the MB calculation scheme; 3) to perform calculations using a new exchange-energy functional obtained in [7] and successfully applied to atoms; 4) to test if the parameter β of the new exchange-energy functional [7] successfully used for atoms is appropriate for the calculation of the properties of crystals; 5) to propose the values of the parameter β which will allow one to im-

prove the results of calculations for crystals. Section 2 briefly describes the mixed-basis formalism. Section 3 deals with the exchange potential obtained on the basis of the new exchange-energy functional [7]. In Section 4, we compare the results for the electron band energies in GaN and InN crystals with those obtained with the help of various theoretical methods and with experimental data.

2. Hamiltonian Matrix in the Mixed Basis

The electron energy band spectrum is obtained from the Kohn–Sham equation

$$(T + V(\mathbf{r})) \Psi_{\mathbf{k}\alpha}(\mathbf{r}) = E_{\mathbf{k}\alpha} \Psi_{\mathbf{k}\alpha}(\mathbf{r}), \qquad (1)$$

where $T = -\nabla^2/2$ denotes the kinetic energy operator, V is the potential of a crystal, $\Psi_{\mathbf{k}\alpha}$ and $E_{\mathbf{k}\alpha}$ represent the eigenvector and the eigenvalue (the energy of an electron at the point $\mathbf{k}$ of the first Brillouin zone), respectively, and α denotes the number of the electron spectrum branch. The unknown wave function $\Psi_{\mathbf{k}\alpha}$ is presented in the mixed basis as

$$\Psi_{\mathbf{k}\alpha}(\mathbf{r}) = \sum_t \sum_{\mathbf{a}} a_{\mathbf{k}t\mathbf{a},\alpha} \mid \mathbf{k}t\mathbf{a}\rangle + \sum_{\mathbf{G}} a_\alpha(\mathbf{k} + \mathbf{G})|\mathbf{k} + \mathbf{G}\rangle, \qquad (2)$$

where $a_{\mathbf{k}t\mathbf{a},\alpha}$ and $a_\alpha(\mathbf{k} + \mathbf{G})$ are the coefficients of the Bloch states

$$|\mathbf{k}t\mathbf{a}\rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{A}} e^{i\mathbf{k}(\mathbf{a}+\mathbf{A})} \varphi_t(\mathbf{r} - \mathbf{a} - \mathbf{A}) \qquad (3)$$

and the plane waves

$$|\mathbf{k} + \mathbf{G}\rangle = \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}}, \tag{4}$$

respectively. Here, $t = \{lmn\}$ represent the quantum numbers of the Bloch states, $\mathbf{a}$ determines the coordinates of an atom in the unit cell, $\mathbf{A}$ are vectors of the Bravais lattice, whose number in a crystal is equal to N, $\mathbf{G}$ is a vector in the reciprocal space, and Ω is the crystal volume. The atomic functions of core electrons are chosen in the form of Cartesian Gaussians with the center at a site $\mathbf{A}$

$$\varphi_{lmn}(\mathbf{r} - \mathbf{A}) = \sum_i c_i N_i (x - A_x)^l (y - A_y)^m \times$$

$$\times (z - A_z)^n e^{-\alpha_i(\mathbf{r}-\mathbf{A})^2}, \tag{5}$$

where the coefficients c_i and α_i are calculated by the Hartree–Fock method [8,9], whereas $N_i = N(\alpha_i)$ denote the normalization constants. Substituting (2) in (1), we obtain the system of linear equations in the block form [3-5]

$$\begin{pmatrix} H_{\mathbf{kta},\mathbf{kt'a'}} - ES_{\mathbf{kta},\mathbf{kt'a'}} & H_{\mathbf{kta},\mathbf{k}+\mathbf{G'}} - ES_{\mathbf{kta},\mathbf{k}+\mathbf{G'}} \\ H_{\mathbf{k}+\mathbf{G},\mathbf{kt'a'}} - ES_{\mathbf{k}+\mathbf{G},\mathbf{kt'a'}} & H_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G'}} - E\delta_{\mathbf{G},\mathbf{G'}} \end{pmatrix} \times$$

$$\times \begin{pmatrix} a_{\mathbf{kta},\alpha} \\ a_\alpha(\mathbf{k} + \mathbf{G}) \end{pmatrix} = 0, \tag{6}$$

where H is the Hamilton matrix, and S is the overlapping matrix. The mixed basis is nonorthogonal; therefore, the overlapping matrix is present in all blocks of system (6). The use of the Bloch functions (3) allows one to substantially reduce the number of plane waves (to about 1000). We start practical calculations of the spectrum for fcc crystals from $N_g = 609$. After that, the number N_g is gradually increased, by covering full coordination spheres in the reciprocal space and reaching 941 ($h^2 + k^2 + l^2 = 91$). The further increase of the number of plane waves in the basis does not result in the change of the band energies more than by 0.01 eV, i.e. the spectrum is stabilized in all energy bands.

In addition, we separately control the spectrum of the overlapping matrix. The eigenvalues are positive, i.e. the Hamiltonian spectrum problem is positive definite. The determinant of the overlapping matrix is calculated by the factorization method and differs from zero. This is another evidence of the fact that the mixed-basis method has no internal threats in view of the redundancy.

The potential of a crystal acting on an electron at a site $\mathbf{c}$ of the unit cell is a superposition of one-site terms

$$\nu(\mathbf{r}-\mathbf{c}) = \sum_{\mathbf{C}} \nu(\mathbf{r} - \mathbf{c} - \mathbf{C}), \ \nu(\mathbf{r}) = \nu_n(\mathbf{r})+\nu_e(\mathbf{r})+\nu_{xc}(\mathbf{r}), \tag{7}$$

i.e. the sum of the Coulomb potentials of nuclei (n), electrons (e), and the exchange-correlation potential (xc).

3. Exchange-correlation Potential

The exchange potential is derived from the exchange-energy functional proposed in [7],

$$E_x^{\mathrm{GGGA}}[\rho] = -C_x \int \rho^{4/3} F(s_0) e^{\beta(\rho-\rho_0)/\rho_0} d\mathbf{r}, \tag{8}$$

where $C_x = 3/4(3/\pi)^{1/3}$, ρ is the electron density, and F is the exchange enhancement factor defined (Perdew, Burke, Ernzerhof, PBE) in [8]

$$F(s) = 1 + k - k/(1 + x/k), \ k = 0.804. \tag{9}$$

For this factor, a better dependence of the parameter x on the electron-density gradient was recently proposed in [6]:

$$x = \frac{10}{81}s^2 + \left(\mu - \frac{10}{81}\right) s^2 \exp(-s^2) + \ln(1 + cs^4). \tag{10}$$

Here,

$$s = |\nabla\rho|/(2k_{\mathrm{F}}\rho) \tag{11}$$

denotes the measure of nonuniformity of the electron density, k_{F} is the quasimomentum of an electron on the Fermi sphere, $\mu = 0.2195149727645171$, and $c = 0.0079325$. The exchange potential is obtained from Eq. (8) [7] as

$$v_x^{\mathrm{GGGA}}[\rho_0] = \frac{\delta E_x^{\mathrm{GGGA}}[\rho]}{\delta\rho}|_{\rho_0} = (4/3 + \beta)\varepsilon_x(\rho_0), \tag{12}$$

where the exchange-energy density $\varepsilon_x = -C_x \rho_0^{1/3} F(s_0)$. The authors of [7] proposed to assume $\beta = 2/3$ in order to satisfy the global demands of the compensation of the Coulomb self-interaction energy in atoms. But we found that the best value of this parameter for GaN and InN crystals is $\beta = 1/3$. The correlation-energy functional was used in the form given in [10].

T a b l e 1. Electron energies in GaN, eV

Level	MB GGGA	LDA+d[d]	EXX+d[d]	HF[c]	LDA[12]	LDA[13]	LDA[10]	GW[11]	LDA[a]GW	exp[a]
$\Gamma 15d$	−17.58								−15.7	−17.7
$\Gamma 12d$	−17.41	−13.8[a]	−12.2[a]						−15.7	−17.7
		−16.9[b]	−14.8[b]	−23.3					−16.4	−17.1
$\Gamma 1\nu$	−16.03	−15.85	−17.8		−16.3		−15.5	−16.7		
$\Gamma 15\nu$	0.00	0.00	0.00		0.00		0.00	0.00	0.00	0.00
$\Gamma 1c$	2.40	2.20	3.1		2.1	1.9	2.0	3.1	2.88	3.2
$\Gamma 15c$	10.46				10.6	10.2	10.5	12.0		
X1ν	−12.44				−13.0		−12.4	−13.5		
X3ν	−5.64				−6.5	−6.2	−6.1	−6.8		
X5ν	−2.40				−2.8	−2.6	−2.4	−2.7		
X1c	4.73				3.2	3.2	3.3	4.4		
X1c	7.50				6.9	6.6	6.7	8.1		
X3c	11.82				12.2		11.9	14.0		
L1ν	−13.18				−13.8		−13.2	−14.3		
L1ν	−6.30				−7.4	−7.0	−6.8	−7.6		
L3ν	−0.88				−1.0	−0.9	−0.8	−0.9		
L1c	5.35				5.0	4.7	4.8	6.1		
L1c	10.04				9.1	8.9	8.9	10.8		
L3c	10.95				10.6	10.3	10.3	11.9		

[a]Work [1] was carried out with the use of pseudopotentials in the LDA formalism. [b]Work [1] was carried out with the use of pseudopotentials in the exact-exchange approach (EXX). [c] Work [2], Hartree–Fock method. [d] Work [2], EXX formalism.

4. Results and Discussion

We calculated the electron energy band spectra of GaN and InN crystals within the mixed basis of one-particle states (3), (4). The exchange potential was calculated on the basis of the new exchange-energy functional (12) in the GGGA. The results obtained in the mixed basis with regard for the exchange potential (12) and the correlation potential [10] are presented in Tables 1 and 2.

As one can see from Table 1, the direct interband gap in a GaN crystal obtained within the mixed-basis approach is somewhat better than that found by other authors in the LDA approximation. Table 2 demonstrates that the interband gaps in an InN crystal calculated in the LDA approximation with semicore d-electrons considered as core (LDA-d) or valence (LDA+d) ones contradict the fact that this crystal is a semiconductor. Our results (MB GGGA) are in good agreement with the values of the band energies obtained in the exact exchange potential approximation (EXX+d). The energies of semicore d-states in GaN and InN crystals calculated in the MB GGGA approach agree well with those obtained with the help of the LDA GW method and with experimental data. Why do the energies of semicore d-states obtained in the MB GGGA approach agree with experiment much better than the direct interband gaps? What is the reason for that the excited state energies in the conduction bands obtained using corrections in

T a b l e 2. Electron energies in InN, eV

Level	MB GGGA	LDA-d[a]	LDA+d[b]	EXX-d[c]	EXX+d[d]	exp [1]
$\Gamma 15d$	−16.54					
$\Gamma 12d$	−16.40		−13.5		−12.2	−14.9
			−14.9		−14.4	−16.7
$\Gamma 1\nu$	−15.02	−13.99	−14.60	−14.37	−14.74	
$\Gamma 15\nu$	0.00	0.00	0.00	0.00	0.00	0.00
$\Gamma 1c$	0.91	0.17	−0.43	1.49	0.61	0.7
		−0.13	−0.39	1.89	0.81	1.0
			−0.36			1.9
$\Gamma 15c$	10.28					
X1ν	−11.43					
X3ν	−4.10					
X5ν	−1.55					
X1c	5.15	2.87	2.82	4.63	4.20	
X1c	7.38					
X3c	10.89					
L1ν	−12.20					
L1ν	−4.83					
L3ν	−0.63					
L1c	4.39	3.51	2.95	4.75	4.14	
L1c	8.34					
L3c	10.70					

[a]Work [1] was carried out with the use of pseudopotentials in the LDA formalism. [b]Work [1], EXX formalism. [c]Work [2], EXX formalism, d-electrons are considered as core ones. [d]Work [2], EXX formalism, d-electrons are considered as valence ones.

the GW method are close to experimental data, whereas the energies of d-states are not so close to the measured

values? We suppose that the corrections to the energies obtained in the GW approach are of decisive importance for the calculation of excited states. However, in the case of localized semicore d-states, the key role is played by a correction to the exchange potential due to the Coulomb self-interaction. The new exchange-energy functional [7] gives a possibility to compensate this energy. The good results we obtained for the energies of semicore d-states are of practical importance for the application to the phenomenon of core-valence luminescence [5].

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ЕЛЕКТРОННА ЕНЕРГЕТИЧНА СТРУКТУРА НІТРИДІВ ГАЛІЮ ТА ІНДІЮ, ОТРИМАНА У ЗМІШАНОМУ БАЗИСІ З НОВИМ ФУНКЦІОНАЛОМ ОБМІННОЇ ЕНЕРГІЇ

С.В. Сиротюк

Р е з ю м е

Електронні енергетичні спектри кристалів GaN та InN розраховано у змішаному базисі (MB), що складається з функцій Блоха глибоких електронних оболонок і плоских хвиль. Обмінний потенціал було отримано на основі нового функціонала обмінної енергії, що включає градієнтні поправки електронної густини (*Generalized* Generalized Gradient Approximation, GGGA). Отримані значення параметрів енергетичної структури кристалів краще зіставляються із даними, розрахованими з точним обмінним потенціалом, ніж аналогічні, знайдені у наближенні локальної електронної густини (Local Density Approximation, LDA). Значення енергій напівостовних d-електронів близькі до експериментальних даних.