

## CALCULATION PROCEDURE FOR THE QUANTUM-DIMENSIONAL SYSTEMS

Calculations of structural phase transitions B1 - B2 under pressure in halcogenids Alkali and Metals are carried out on the basis of approach of the local functional density theory, using as adjustment designing of amendments to potential by means of the electronic density received in self-coordinated calculation using approximation of local density. The results has interest for nanosystems.

The standard calculation procedure of the energy of zoned structure  $E_{\mathbf{k}}$  (for example, [1]) is used. In special points of Brillion's zone equation the secular was solved

$$\left[ \frac{1}{2}(\vec{k} + \vec{g})^2 - E_n(\vec{k}) \right] C_{n,\vec{k}}(\vec{g}) + \sum_{\vec{g}'} W(\vec{k} + \vec{g}, \vec{k} + \vec{g}') C_{n,\vec{k}}(\vec{g}') = 0, \quad (1)$$

where  $C_{n,\vec{k}}(\vec{g})$  are factors of decomposition of pseudo-wave function as a number of plane waves

$$\varphi_{n,\vec{k}} = \sum_{\vec{g}} C_{n,\vec{k}}(\vec{g}) \left| \vec{k} + \vec{g} \right\rangle, \quad (2)$$

$n$  is then number of a zone,  $\mathbf{k}$  is a wave vector in the first Brilluon's zone,  $\mathbf{g}$ ,  $\mathbf{g}'$  - are vectors of a return lattice. The Furies-image of potential  $W(\mathbf{k}_1, \mathbf{k}_2)$  includes Furies -images potentials such as:  $W_H$  — Hartree,  $W_{xc}$  — exchange-correlation,  $W_{BHS}$  [2] — pseudo-potential which is named as Bachelet — Hamann — Schlüter.

Full energy using the density functional theory (DFT) is represented as

$$E = \frac{1}{N} \sum_{\vec{k}} E_{\vec{k}} - E_H + E_{xc} + E_{es} + \alpha_1 z, \quad (3)$$

where  $N$  is a number of atoms of various grades in an elementary cell, energy Hartree

$$E_H = \frac{\Omega}{2} \sum_{\vec{g}} \frac{4\pi}{g^2} \left| \rho(\vec{g}) \right|^2, \quad (4)$$

The exchange-correlation contribution is the following

$$E_{xc} = \Omega \sum_{\vec{g}} \left[ \varepsilon_{xc}(\vec{g}) - W_{xc}(\vec{g}) \right] \rho(\vec{g}), \quad (5)$$

where  $W$  is the volume of an elementary cell,  $\varepsilon_{xc}(\mathbf{g})$  is the density of exchange -correlation energy,  $r(\mathbf{g})$  is a Furies -image of electronic density,  $z$  is the average number of the valent electrons on atom,  $E_{es}$  is electrostatic energy.

Non Coulomb part of electron-ionic interaction is the following

$$\alpha_1 = \lim_{\vec{g} \rightarrow 0} \left\{ W_{BHS}^{loc}(\vec{g}) + \frac{8\pi z}{\Omega g^2} \right\}. \quad (6)$$

The local density functional theory (LDFT) is the standard approximation methods of calculation of exchange-correlation energy (5). And the same lacks of this approach [3] are well-known. From the point of view of research of polymorphism we shall note some of them: underestimation of the forbidden zone; understating of parameters of a lattice; different influence LDFT on the calculation of different conditions, that especially strongly affects the size of the forbidden zone and details of a structure of electronic zoned structure. Some lacks are peculiar directly LDFT, others result from DFT.

Recently a number of methods both avoiding application LDFT is offered, and trying to remove existing lacks of frameworks LDFT. Among the last we shall note self-action corrected (SAC) pseudo-potentials [4]. SAC eliminates not physical self-action of every electron and reduces energy filled orbitals. Received in this approach power functional is noninvariant at unitary transformation filled orbitals it is possible to design a set of decisions too. Thus p-orbitals of an anion practically do not change, however d-orbitals of a cation can strongly be changed. It is necessary to note, that distortion of zoned structure is connected as with p-d-hybridization, which wrong estimates using LDFT, and to a wrong calculation of s-conditions which form a bottom of a zone of conductivity. Special interest can be shown to halcogenids of calcium because in Ca still there are no d-electrons. Calculation results sometimes to bad enough convergence of results in settlement circuits both not taking into account, and taking into account elimination of p-d-hybridization. Thus, the iterative decision of the equation (1) insufficiently precisely describes the located conditions because of not physical self-actions. Entering SAC pseudo-potentials [5]:

$$V_{ps}^{SIC} = V_{BHS} - V_H[\rho^{at}] - V_{xc}[\rho^{at}], \quad (7)$$

unitary repeat calculation for electronic density of separate atoms  $r^{at}$ . Such pseudo-potentials cannot be used in solid-state calculations because of long interaction of Coulomb tails which should be compensated to introduction additional composed  $1/r_{loc}$ , which shifts a power scale and it is taken into account only in area  $r < r_{loc}$ .

The addition of additional contributions to pseudo-potential, which action could be counted «is destroyed» in part or completely application LDFT further it is modeled by fit procedure. These contributions are designed from the electronic density received in LDFT-calculation. On each step of iterative procedure the density changes in view of correction factor which depends on volume of an elementary cell. That part which in [5] is received from nuclear calculations is modeled and kept  $r_{loc}$  as the second fitting parameter.

For research of polymorphism the self-coordinated calculation in 80 points for each connection in an interval  $0,4 W_0 - 1,2 W_0$  with a step 0,01

$W_0$  where  $W_0$  is the experimental volume of an elementary cell in structure B1 was carried.

Results of calculation were adjusted under the equation using Berch's condition

$$P = \frac{3}{2} B_0 \left[ \left( \frac{\Omega_0}{\Omega} \right)^{7/3} - \left( \frac{\Omega_0}{\Omega} \right)^{5/3} \right], \quad (8)$$

where P is pressure,  $B_0$  is the volumetric module of compression at  $P=0$ ,  $W$  is the volume of an elementary cell,  $W_0$  is the volume of an elementary cell at  $P=0$ . In structure B1 the calculation of  $W_0$  and  $B_0$  are adjusted under the corresponding experimental information, in structure B2 parameters determined full energy  $E_{tot}$  and  $B_0$ . Table 1 represents equilibrium volumes of elementary cells  $W_0$ , volumetric modules of compression  $B_0$ , deviations  $DW_0$  and  $DB_0$  from the corresponding experimental values, arising basically because of the limited word length of the parameters, full of energy  $E_{tot}$  and volumes of elementary cells at phase transition B1-B2 for structure B1. Table 2 contains the same data for structure B2. Deviations only with known experimental data (see [6,7] where are resulted as well results of calculations of other authors) are specified. Designations of volumetric characteristics:  $W_{0B1}$ ,  $W_{0B2}$  — equilibrium volumes of elementary cells in structures B1 and B2;  $W_{pt1}$ ,  $W_{pt2}$  — volumes at pressure of phase transition in corresponding structures are given

$$\Delta\Omega = \Omega_{0B1} - \Omega_{0B2}; \Delta\Omega_{B1} = \Omega_{0B1} - \Omega_{pt1}; \Delta\Omega_{B2} = \Omega_{0B2} - \Omega_{pt2}. \quad (9)$$

Table 1. Results of calculation in structure B1.

Con- nection	$\Omega_p$ (a.u.) <sup>3</sup>	$\Delta\Omega_p$ / $\Omega_p$ %	$B_0$ GPa	$\Delta B_0$ / $B_0$ %	$E_{tot}$ Ry	$\Omega_{pt}$ (a.u.) <sup>3</sup>
CaO	98,12	+4,3	113,01	0,0	-17,071	72,44
SrO	115,59	-0,3	90,29	-0,8	-16,996	90,02
CaS	155,91	+0,1	63,78	-0,3	-10,830	113,30
SrS	183,92	-0,1	57,90	-0,2	-10,537	149,93
BaS	219,28	-0,2	52,65	+1,3	-11,056	197,13
CaSe	175,21	-0,1	53,70	+5,3	-9,870	126,65
SrSe	205,25	-0,1	44,62	-0,8	-9,685	167,86
BaSe	242,81	+0,1	39,18	+0,5	-9,357	215,83
SrTe	249,34	+0,1	40,77	+1,9	-8,638	206,17
BaTe	289,42	-0,1	38,03	+0,1	-8,430	263,15

Table 2. Results of calculation in structure B2.

Con- nection	$E_{\text{tot}}$ Ry	$B_0$ GPa	$\Omega_0$ (a.u.) <sup>3</sup>	$\Omega_{\text{pt}}$ (a.u.) <sup>3</sup>
CaO	-17,029	138,74	84,62	64,85
SrO	-16,972	120,32	101,65	84,59
CaS	-10,790	59,68	138,66	99,70
SrS	-10,517	65,65	158,64	131,89
BaS	-11,045	44,74	195,12	173,44
CaSe	-9,832	46,71	158,09	111,32
SrSe	-9,671	59,94	183,39	155,88
BaSe	-9,349	37,85	220,56	194,96
SrTe	-8,631	49,27	235,61	200,27
BaTe	-8,424	46,14	265,09	243,79

**Conclusion.** In structure B1 the calculation of  $W_0$  and  $B_0$  are adjusted under the corresponding experimental information, in structure B2 parameters determined full energy  $E_{\text{tot}}$  and  $B_0$ . Table 1 represents equilibrium volumes of elementary cells  $W_0$ , volumetric modules of compression  $B_0$ , deviations  $DW_0$  and  $DB_0$  from the corresponding experimental values, arising basically because of the limited word length of the parameters, full of energy  $E_{\text{tot}}$  and volumes of elementary cells at phase transition B1-B2 for structure B1. Table 2 contains the same data for structure B2. Deviations only with known experimental data (see [6,7] where are resulted as well results of calculations of other authors) are specified.

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### **Abstract**

Calculations of structural phase transitions B1 – B2 under pressure in halcogenids Alkali and Metals are carried out on the basis of approach of the local functional density theory, using as adjustment designing of amendments to potential by means of the electronic density received in self-coordinated calculation using approximation of local density. The results has interest for nanosystems.

**Key words:** phase, transition, density, optics

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## **РОЗРАХУНКОВА ПРОЦЕДУРА ДЛЯ КВАНТОВО-РОЗМІРНИХ СИСТЕМ**

### **Резюме**

Представлені результати розрахунку структурних параметрів фазових переходів типу B1 – B2 під тиском у халькогенідах лужних металів. Значення отримані у наближенні функціоналу електронної густини. Використано підгоночні параметри до потенціалів взаємодії щодо усереднення розподілу електронної густини за самоузгодженою схемою. Результати мають інтерес для наносистем.

**Ключові слова:** фаза, переходи, густина, оптика

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## **РАССЧЕТНАЯ ПРОЦЕДУРА ДЛЯ КВАНТОВО-РАЗМЕРНЫХ СИСТЕМ**

### **Резюме**

Представлены результаты расчетов структурных параметров фазовых переходов типа B1 – B2 под давлением в халькогенидах щелочных металлов. Значения получены в приближении функционала электронной плотности. Использованы подгоночные параметры к потенциалам взаимодействия для усреднения распределения электронной плотности в сасосогласованной схеме. Результаты интересны для наносистем.

**Ключевые слова:** фаза, переходи, плотность, оптика