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Polymorphism in chalcogenides of alkaline-earth metals

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Abstract. Calculations of structural phase transitions B1 - B2 under pressure in chalcogenides of alkaline-earth metals were carried out on the basis of approach of the local density functional theory, where as a fitting used was the constructive amendments of the potential by means of the electronic density received in a self-coordinated calculation using the approximation of the local density.

Keywords: alkaline-earth metal chalcogenides, local density functional theory.

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The standard calculation procedure of the band structure E_k (for example, [1]) was used. In specific points of the Brillouin zone, the secular equation 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 the factors of decomposition of pseudowavefunction 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 the number of a band, \vec{k} is the wavevector in the first Brillouin zone, \vec{g} , \vec{g}' are vectors of a reciprocal lattice. The Fourier-image of potential $W(\vec{k}_1, \vec{k}_2)$ includes the Fourier-image potentials such as: Hartree W_H , exchange-correlation W_{xc} , and pseudopotential named as Bachelet-Hamann-Schlüter W_{BHS} [2].

The total energy using the density functional theory (DFT) is represented as follows:

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

where N is a number of atoms of various grades in an elementary cell.

The Hartree energy has the form

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

The exchange-correlation contribution is expressed as

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

where Ω is the volume of an elementary cell, $\varepsilon_{xc}(\vec{g})$ is the density of the exchange-correlation energy, $\rho(\vec{g})$ is the Fourier-image of the electronic density, z is the mean number of the valent electrons per atom, E_{es} is the electrostatic energy.

The non-Coulomb part of electron-ion interaction can be written as

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

The local density functional theory (LDFT) is the standard approximation method of calculation of the exchange-correlation energy (5). And therewith the lacks of this approach are well-known [3-6]. From the viewpoint of research of polymorphism, we shall note some of them: undervaluation of the forbidden band; understating the lattice parameters; different influence of the LDFT on the calculation of different states that especially strongly affects the size of the forbidden band and peculiarities of the electron band structure [4]. Some lacks are inherent directly to LDFT, others result from the DFT [5].

Recently offered were some methods that allowed us both to avoid application of LDFT, and to try removing the existing lacks within the framework of LDFT. Among the latter, we shall note self-action corrected (SAC) pseudopotentials [7-10]. SAC eliminates nonphysical self-action of every electron and reduces the energy of filled orbitals. The energy functional received

Table 1. Results of calculations for the structure B1.

Connection	Ω_0 , (a.u.) ³	$\Delta\Omega_0/\Omega_0$, %	B_0 , GPa	$\Delta B_0/B_0$, %	E_{tot} , Ry	Ω_{pt} , (a.u.) ³
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

in this approach power is non-invariant in unitary transformation of the filled orbitals, and it is possible to design a set of decisions. Thus, p -orbitals of an anion do not change practically, however d -orbitals of a cation can be strongly changed [9]. It is necessary to note that distortion of the band structure is related both with the p - d hybridization that was wrong estimated using LDFT and the wrong calculation of s -states that forms a bottom of the conduction band [6]. Special interest can be demonstrated in calcium chalcogenides, because Ca has no d -electrons yet, which results sometimes in rather bad convergence of results in calculations that both not take into account and take into account the elimination of p - d hybridization.

Thus, the iterative solution of Eq. (1) insufficiently precisely describes the localized states because of non-physical self-actions. Entering the SAC pseudopotentials [10]:

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

unitary repeats the calculation for electron densities of separate atoms ρ^{at} . Such pseudopotentials cannot be used in solid-state calculations because of long interaction of Coulomb tails, which should be compensated by introduction of the additional component $1/r_{\text{loc}}$ that shifts an energy scale and is taken into account only in the region $r < r_{\text{loc}}$.

The addition of complementary contributions to the pseudopotential, whose action may be thought of as “destroying” in part or completely by application of the LDFT, it is modeled by a fitting procedure further. These contributions are designed from the electron density derived in the LDFT-calculation. At each step of iterative procedure, the density changes in view of a correction factor that depends on the volume of an elementary cell. That part, which in [10] was received from nuclear calculations, is modeled and keeps r_{loc} as the second fitting parameter.

To research polymorphism, performed was the self-coordinated calculation in 80 points for each connection

in the interval from $0.4\Omega_0$ up to $1.2\Omega_0$ with a step $0.01\Omega_0$ where Ω_0 is the experimental volume of an elementary cell in the structure B1. Results of calculation were fitted to the equation using the Berch 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 the pressure, B_0 is the bulk modulus of compression at $P = 0$, Ω is the volume of an elementary cell, Ω_0 is the volume of an elementary cell at $P = 0$.

In the structure B1, the calculations of Ω_0 and B_0 were adjusted with the corresponding experimental data, in the structure B2, the parameters determine the total energy E_{tot} and B_0 . Table 1 represents the equilibrium volumes of elementary cells Ω_0 , bulk modulus of compression B_0 , deviations $\Delta\Omega_0$ and ΔB_0 from the corresponding experimental values, arising basically from the limited word length of the parameters, total energy E_{tot} and volumes of elementary cells at the phase transition B1 to B2 for the structure B1. Table 2 contains the same data for the structure B2. Results of our calculation for polymorphism are summarized in Table 3. Listed are the deviations only with known

Table 2. Results of calculations for the structure B2.

Connection	E_{tot} , Ry	B_0 , GPa	Ω_0 , (a.u.) ³	Ω_{pt} , (a.u.) ³
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

Table 3. Pressure of phase transitions B1-B2 and changes of volumes at phase transitions (in %).

Con- nection	p_{tr} , GPa	$\Delta p_{tr}/p_{tr}$, %	$\Omega_{pt1}/\Omega_{0B1}$	$\Omega_{pt2}/\Omega_{0B1}$	$\Delta\Omega/\Omega_{pt1}$	$\Delta\Omega/\Omega_{0B1}$	$\Delta\Omega_{B1}/\Omega_{0B1}$	$\Delta\Omega_{B2}/\Omega_{0B2}$
CaO	63.65	+1.0	73.8 (-0.8%)	66.1 (-1.6%)	10.5	7.7	26.2	23.4
SrO	37.38	+3.8	77.9 (-4.4%)	71.5 (+0.1%)	8.3	6.4	22.1	18.8
CaS	38.34	+3.6	73.7	64.0	12.0	8.7	27.3	28.1
SrS	17.82	-1.0	81.5	71.7	12.0	9.8	18.5	16.9
BaS	6.73	+3.5	89.9 (+0.3%)	79.1 (+2.3%)	12.0 (-12%)	10.8	10.1	11.1
CaSe	33.45	-1.6	72.3	63.5	12.0	8.6	27.8	29.6
SrSe	13.21	-5.6	81.8	76.0	7.1	5.8	18.2	15.0
BaSe	5.83	-2.8	88.9	80.3 (-8.5%)	9.7 (-30%)	8.6	11.1	11.6
SrTe	11.20	-6.7	82.7	80.3	3.9	2.4	17.3	15.0
BaTe	4.51	-6.0	90.9	84.2 (-7.2%)	7.4 (-44%)	6.7	9.1	8.0

experimental data (see [11-18] where resulted are the calculations of other authors, too). Designations of these characteristics: Ω_{0B1} , Ω_{0B2} are the equilibrium volumes of elementary cells in the structures B1 and B2; Ω_{pt1} , Ω_{pt2} are the volumes at the pressure of phase transition in corresponding structures. They have the following form:

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

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