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Construction of the interatomic potential of the ferroelectric barium titanate based on the temperature dependence of the heat capacity near the phase transition

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The article presents the results of studying the temperature dependence of the heat capacity of the ferroelectric $BaTiO_3$ in the vicinity of the phase transition in order to construct the interatomic potential. An effective interatomic potential is introduced to take into account the type of chemical bond (covalent for Ti-O or ionic for Ba-O bond). To assess the correctness of the choice of the effective potential, it is proposed to calculate the enthalpy of the phase transition taking into account the presence of several activation processes in the vicinity of the phase transition. The presence of two activation processes when approaching the Curie temperature in the ferroelectric phase with activation energies U is established. The first is due to the motion of oxygen vacancies ($U_1 = 0.99$ eV). The second begins at the critical temperature $T_{\text{crit.}}$ (5 K below the Curie temperature T_C) and is associated with the electron-phonon interaction in the presence of electron orbital degeneracy and mixing of the electron bands of the $2p$-states of O with the d-states of Ti ($U_2 = 2.46$ eV). The activation process in the paraelectric phase ($U_3 = 2.87$ eV) is associated with the relaxation of the structure after a change in the symmetry of the crystal lattice. The results obtained are discussed within the framework of the vibronic theory of ferroelectricity, taking into account the Jahn-Teller effect (or pseudo-effect).

Keywords: heat capacity, barium titanate, interatomic potential, entropy, phase transition, ferroelectric, activation energy.

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1. Introduction

In the modern condensed matter physics the fact that the ferroelectric phase transitions are accompanied by an abnormal surge of dielectric permittivity and heat capacity of ferroelectric crystal is generally recognized. In the dynamic theory of crystalline lattices the maximum dielectric permittivity is explained by softening of ferroelectric mode of oscillations at phase transition temperature, and the heat capacity jump for the second-order phase transition may be determined from the thermodynamic theory of ferroelectricity [1]. The experimental study of the heat capacity dependence on temperature in the proximity of the phase transition is especially critical to study the nature and mechanism of the ferroelectric phase transition. In particular, the value of ΔS transition entropy enables to conclude the type of the phase transition: order-disorder or shift, and usually in the first case ΔS is much higher [2]. And determination of ΔH transition enthalpy makes it possible to estimate the spontaneous polarization jump value P_s in the Curie point.

Temperature dependence of heat capacity in a rather wide range of temperatures is described well by the function of free energy (which is the expression of the medium field) [3]. This function was used to calculate the molar heat capacity $BaTiO_3$ at temperature of second-order phase transition ($1.58\,\text{J/mol}\cdot\text{K}$), and the value of this jump makes it possible to conclude that the ferroelectric ion Ti is in the single-well potential in absence of interaction with other titanium ions [3]. Also the dependence of heat capacity on temperature $C_p(T)$ may also be used to calculate the changes to enthalpy, entropy, free Gibbs energy and equilibrium constant. Using the example $KNbO_3$, for which purpose the dependence $C_p(T)$ is approximated at separate temperature ranges by temperature polynomials of different degree (up to T^9) [4].

Another use of phase transition calorimetry results is the testing of the model interatomic potential and the dependent crystal Hamiltonian, the functionality of which it is. Besides, the substantial electron-phonon interactions and phonon anharmonicity in the proximity of the phase transition must be reflected in the density of phonon states (PDOS). Thus, in particular, when the dynamics of the lattice, the structural phase thermodynamic and thermodynamic properties $BaTiO_3$ were studied by methods of the density functional theory (DFT) methods, the calculation of the partial density of phonon states demonstrated that the main contribution to the imaginary optical phonon frequencies is made by the distortion of the perovskite cell (Ti-O) [5]. Another example of modeling based on the first principles using the current polarization theory is the Berry phase method and maximum localized Vanier functions, which are used to study electronic, chemical bonds, ferroelectric and piezoelectric properties of $PbTiO_3$ [6].

Studies of the system $BaTiO_3$ are still relevant today, which is supported by the results of the recent studies. Thus, for example, using the data on the local structure and taking into account the strictional interaction, the statistical-thermodynamic model was developed for formation of ferroelectric phases in perovskites $BaTiO_3$ and $KNbO_3$ [7]. And the study of the perovskite and hexagonal phases $BaTiO_3$, using the density functional theory (DFT) in the local density approximation (LDA) and generalized gradient approximation (GGA) schemes has shown that in the hexagonal phase the oxygen vacancy of O(1) type (joint use of facets) is more stable that vacancy of O(2) type (joint use of angles) in the octahedral structure [8]. Construction of interatomic potentials is of specific interest, which is confirmed by the presentation of the new set of interatomic potentials for modelling of the perovskite system $BaTiO_3$, where the potential model is adjusted using several parameters on the row of experimental and *ab initio* data, including the cohesion energy and parameters of the lattice $BaTiO_3$, BaO and rutile TiO_2 [9].

For theoretical prediction of macroscopic properties of the crystal using molecular-dynamic modeling, first of all, a high-precision interatomic potential is necessary, which for the perovskite structure was obtained within the valent bond theory with calculation of the lattice parameters and elastic constants [10]. The structure and electronic configurations may be calculated using hybrid exchange-correlation equipment and reoptimized basic sets of atomic (Gaussian) orbitals, which is done for $SrTiO_3$, $BaTiO_3$ and $PbTiO_3$ [11]. At the same time, a certain problem here is the accounting of electron-phonon interactions, the private solution to which was found by DFT calculation in a combination with the Frohlich and Boltzmann-Onsager approaches, temperature dependence of Seebeck coefficient and conductivity of the electron-doped perovskites $SrTiO_3$, $BaTiO_3$ and $CaTiO_3$ [12].

Another significant problem in selection of the interatomic potential of ferroelectric is the correct accounting of the chemical bond type. The calculation of the electronic structure of ferroelectric perovskites $BaTiO_3$ and $PbTiO_3$ demonstrated that the hybridization between $3d$-states of titanium and $2p$-states of oxygen is the important condition for balance between long-distance Coulomb forces (which support the ferroelectric state) and short-distance repulsion forces (which support the nonpolar cubic structure) [13]. Besides, in $PbTiO_3$ the lead and oxygen states are hybridized (Pb-O bond is covalent), which causes significant strain that stabilizes the tetragonal phase, while in $BaTiO_3$ the Ba-O bond is fully ionic, which supports the rhombohedral structure [13]. For the quantum ferroelectric $SrTiO_3$ the calculation of the phononic density of states showed that Sr-O bond was ionic, and Ti-O bond-covalent [14].

It should be noted that the definition of the density of phonon states in the Bose system (or phonon spectrum of the crystal), except for the theoretical calculation based on the first principles, as, for exemple, for $BaTiO_3$ in [15] and for $PbTiO_3$ and $PbZrO_3$ in [16], is also possible from the experimental data on the system heat capacity in the wide temperature range [17,18]. And the calorimetry method is relevant in the study of phase transitions in ferroelectrics (for example, $PbTiO_3$ in [19] and $BaTiO_3$ in [20]) and multiferroics (for example, $CoFe_2O_4$-$PbTiO_3$ in [21]).

The above confirms the feasibility of performing the studies in the proposed paper to obtain the numerical values of enthalpy and entropy from the temperature dependence of the ferroelectric heat capacity in the proximity of the phase transition to build the interatomic potential.

2. Experimental procedures

For the study, ceramic specimens of barium titanate $BaTiO_3$ were prepared by solid-phase method. The original reagents were barium carbonate $BaCO_3$ and titanium dioxide TiO_2. The synthesis was done at temperature of 1670 K for 3 hours. Completeness of synthesis and production of single-phase powder $BaTiO_3$ were monitored by X-ray diffraction method (DRON-3, CuK_α-emission).

The temperature dependence of specimen heat capacity was measured in the heating cell, coupled with a computerized setup for differential thermal analysis (DTA) and thermogravimetric analysis (TGA) „Termoskan-2" („Analitpribor") in the mode of differential scanning calorimetry (DSC) in the temperature range from 300 to 500 K.

To calibrate the calorimeter, a standard reference Al_2O_3 was used. Temperature detection error $\sim \pm 1$ K. Thermal effect value detection accuracy ~ 3 J/g. Studied weighed quantity mass $BaTiO_3$ ~ 0.5 g.

The experimental results were analyzed using the original method proposed in this article.

3. Results and discussion

It is known that molar heat capacity of crystalline chemical compound is equal to the sum of atomic heat capacities of its elements, and according to the Joule-Kopp law it is equal to $C_p = 3nR$, where n is number of chemical elements, $R = 8.31\,\text{J/mol}\cdot\text{K}$. If for $BaTiO_3$ it is assumed that $n = 5$, then $C_p \approx 115\,\text{J/mol}\cdot\text{K}$. As you can see from the experimental data (Figure 1) on the temperature dependence of heat capacity for $BaTiO_3$ this value is achieved at 350 K, then in the temperature range from 350 to 420 K the heat capacity surge is observed with maximum value $C_p \approx 135\,\text{J/mol}\cdot\text{K}$, and which is related to the surge of spontaneous polarization in a ferroelectric phase transition, and starting from temperature 420 K, slow growth of molar heat capacity occurs, which is caused by the growth of anharmonicity of the phonon contribution to the heat capacity at higher temperatures.

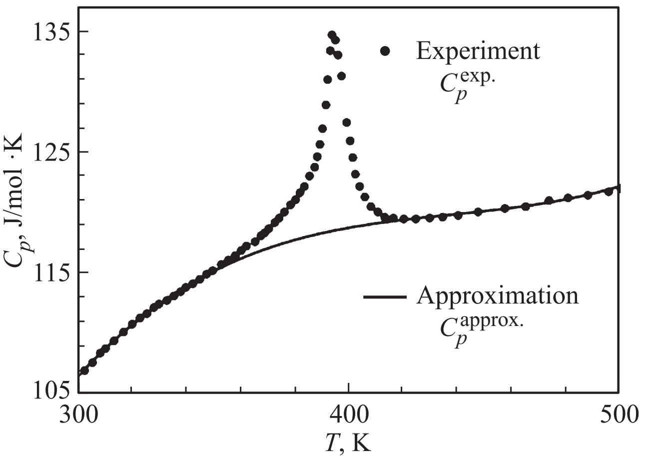

Figure 1. Temperature dependence of heat capacity $C_p(T)$ ceramic $BaTiO_3$.

To assess the surge of heat capacity in the proximity of the phase transition $\Delta C_p(T)$, it is necessary to identify a part of heat capacity caused by phonon contribution and not related directly to the surge of the spontaneous polarization. Based on this, the dependence $\Delta C_p(T)$ is calculated as:

$$\Delta C_p(T) = C_p^{\text{exp}}(T) - C_p^{\text{approx}}(T), \tag{1}$$

where $C_p^{\text{exp}}(T)$ is experimentally determined temperature dependence of heat capacity; $C_p^{\text{approx}}(T)$ is part of experimental dependence (Figure 1), except for the temperature range from 350 to 420 K, approximated by equation:

$$C_p^{\text{approx}}(T) = 3.87 \cdot 10^{-6}T^3 - 5.08 \cdot 10^{-3}T^2 + 2.25T - 215, \tag{2}$$

where T is temperature, K.

The selection of such approximating function may be justified by the fact that to build the analytical dependence $C_p(T)$ in the wide temperature range based on experimental data, usually, polynomials of various temperature degrees are used, besides, at different temperature intervals the coefficients and indicators of the polynomial degree for one and the same substance may differ substantially, which is, for example, shown for $KNbO_3$ in article [4].

Analysis of $\Delta C_p(T)$ dependence data in coordinates $\ln(\Delta C_p) - 1/T$ showed that in the dependence $\Delta C_p(T)$ three temperature intervals (1st: 350–389 K; 2nd: 389–394 K; 3rd: 394–420 K), where this dependence is exponential (Figure 2, *a*):

$$\Delta C_p(T, U) = C_0 \exp\left(\pm\frac{U}{kT}\right), \tag{3}$$

where C_0 is coefficient, J/mol · K; U is heat capacity activation energy, eV; k is Boltzmann constant, eV/K; T is temperature, K. Sign „±“ before the activation energy U takes into account the inclination of dependence $\Delta C_p(T)$ in the ferroelectric phase ($T < T_C$) and paraelectric phase ($T > T_C$). Besides, in the dependence $\Delta C_p(T)$, except for Curie temperature T_C, where the ferroelectric heating causes the phase transition from the ferroelectric to the paraelectric state, the critical temperature $T_{\text{crit.}}$ is also identified (where index „crit.“ means „critical“), in which, probably, the activation processes changes, which preceded the phase transition to T_C.

When there is the exponential dependence (3) available, which is met at certain temperature intervals of dependence $\Delta C_p(T)$, the equation may be proposed to calculate the heat capacity surge in the entire temperature interval with account of empirically defined coefficients C_0 and activation energy U:

$$\Delta C_p(T) = \sum_{i=1}^{3}\left[C_{0_i} \exp\left(\pm\frac{U_i}{kT}\right)\delta(U - U_i)\right], \tag{4}$$

where $\delta(U - U_i)$ is Dirac delta function. The calculation result is shown in Figure 2, *b*.

Numerical values of enthalpy ΔH (Figure 3) and entropy ΔS (Figure 4) of the processes in the identified areas are determined using the available formulas:

$$\Delta H = \int \Delta C_p(T)dT, \tag{5}$$

$$\Delta S = \int \frac{\Delta C_p(T)}{T}dT. \tag{6}$$

When values of enthalpy ΔH and entropy ΔS are calculated in ferroelectric phase ($T = 350-394$ K) it was taken into account that in process of transition through the critical temperature $T_{\text{crit.}} = 389$ K the initial activation process with activation energy $U_1 = 0.99$ eV may both stop (Figure 3, *a*, Figure 4, *a*) and continue to the phase transition temperature (Figure 3, *b*, Figure 4, *b*), which is possible in interaction of ferroelectric subsystems, activated by heating and responsible for the activation processes in the first and second temperature intervals (Table).

Now it is necessary to find out the microscopic mechanisms responsible for identified activation processes observed in the proximity of the phase transition. Therefore, in process of ferroelectric heating its domain structure near the Curie temperature becomes very unstable and, as it is known, its equilibrium is considerably affected by the point defects of the crystalline lattice. In particular, for the oxygen-containing ferroelectrics with perovskite structure, which is barium titanate $BaTiO_3$, the most significant are oxygen vacancies. At the same time the activation energy of such vacancies movement has value of 0.91 eV, which was established by the method of electron paramagnetic resonance [22]. And in ferroelectric $KNbO_3$ that is isostructural to $BaTiO_3$ the low-frequency dielectric relaxation with activation energy 0.84 eV is explained by relaxation of dipoles also related to oxygen vacancies [23]. The study of temperature dependence of dielectric permittivity of ceramic $BaTiO_3$ generated the values of activation energy 2.07 eV for the process close to the temperature of phase transition, and the activation process was related

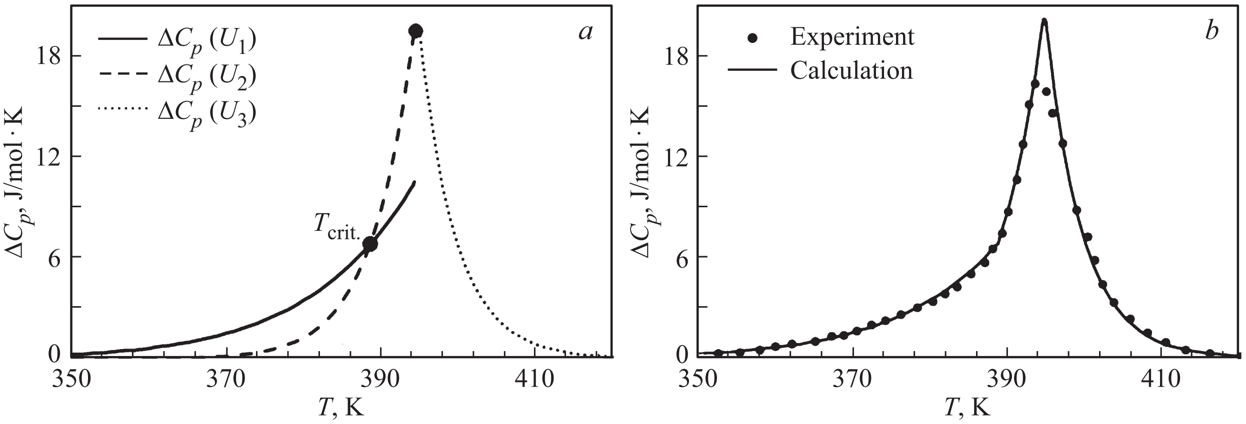

Figure 2. Model temperature dependences of heat capacity surge $\Delta C_p(T, U)$ for $BaTiO_3$ with different coefficients of activation process (a). Comparison of temperature dependences of heat capacity surge $BaTiO_3$ obtained experimentally and from the calculations using the equation (4) (b).

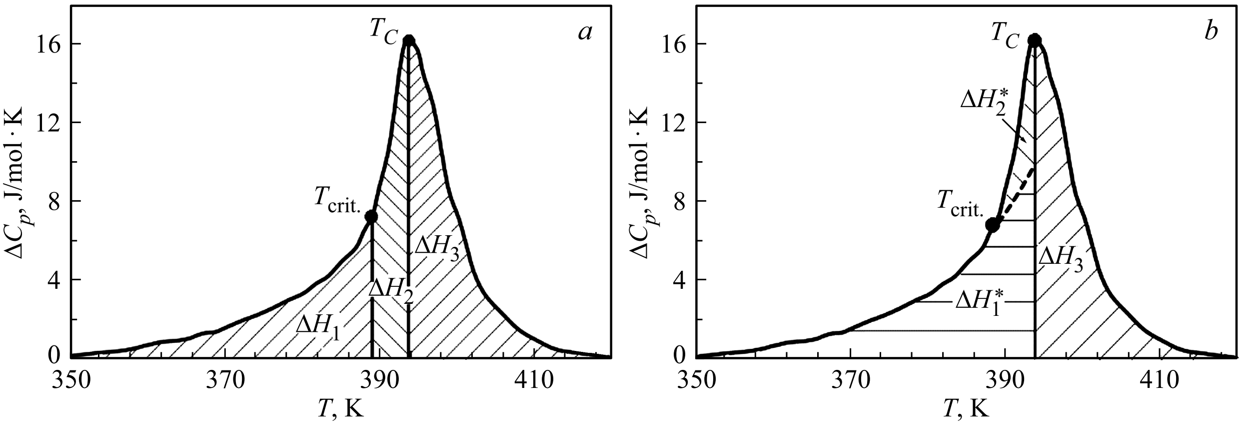

Figure 3. Calculation of enthalpy ΔH for $BaTiO_3$ in three temperature intervals without the interaction of activation processes in ferroelectric phase (a) and with account of such interaction (b).

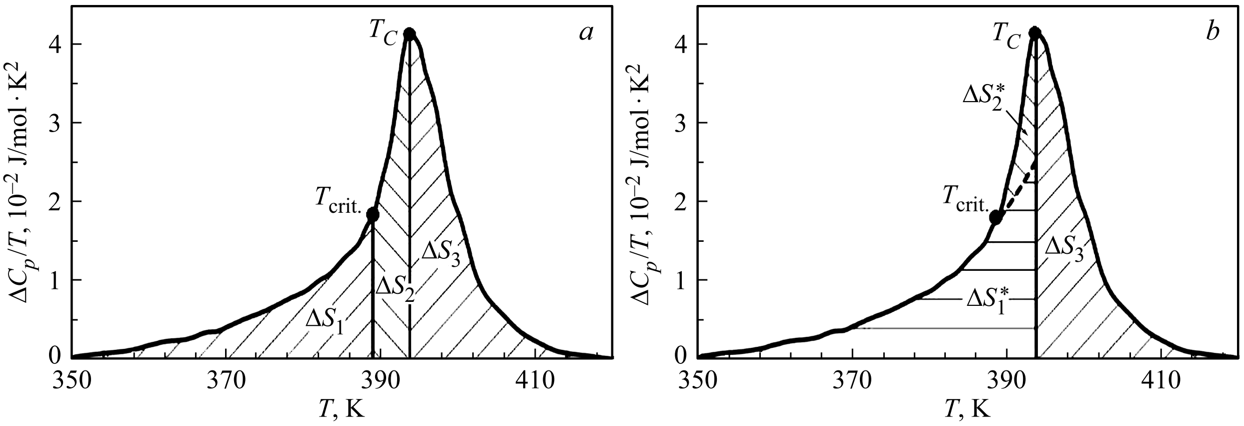

Figure 4. Calculation of entropy ΔS for $BaTiO_3$ in three temperature intervals without the interaction of activation processes in ferroelectric phase (a) and with account of such interaction (b).

Values of coefficient C_0, activation energy U from equation (3) in three sections of calculated dependence $\Delta C_p(T, U)$ (Figure 2, *a*), and also enthalpy ΔH (Figure 3) and entropy ΔS (Figure 4) of ceramic $BaTiO_3$

№	ΔT, K	C_0, J/mol · K	U, eV	ΔH, J/mol	ΔH^*, J/mol	ΔS, J/mol · K	ΔS^*, J/mol · K
1	350–389	$5.21 \cdot 10^{13}$	0.99	82	126	0.218	0.327
2	389–394	$5.41 \cdot 10^{32}$	2.46	60	16	0.151	0.042
3	394–420	$3.98 \cdot 10^{-36}$	2.87	108		0.271	

to the interaction of the defective and domain structures of ferroelectric in the temperature area of instability of spontaneous polarization [24].

Based on this, one may assume that the first identified activation process with activation energy $U_1 = 0.99\,\text{eV}$ is caused by the activation of movement and subsequent migration of oxygen vacancies. This disturbs the equilibrium of the crystalline lattice as a result of arising stretching and compressing stresses. However, for the critical change in the rigidity of interatomic bond, necessary for the phase transition at Curie temperature, as shown by the calculation of the activation energies, the second activation process is necessary with the higher activation energy $U_2 = 2.46\,\text{eV}$.

To establish the microscopic mechanism of this process, it is necessary to refer to the existing ferroelectricity theories. The dynamic theory, known also as the Ginzburg-Anderson-Cochrane (GAC) theory, established the existence of low-frequency temperature-dependent transverse optical oscillation („of soft" phononic mode), in which the crystal loses dynamic stability in the point of the phase transition. The microscopic reason for occurrence of the „soft" mode was explained by compensation of some forces of interionic interaction in the frequency of the active mode with subsequent accounting of phononic anharmonicity. Further the electron-phonon (vibron) interaction was also taken into account, which resulted in development of the vibron theory of ferroelectricity (Christoffel and Konsin [25], as well as Bersuker and Vechter [26]). This theory is also called pseudo-Jahn-Teller theory for the reason that as noted in [27], the Jahn-Teller pseudo-effect (JTPE) is the only source of polar instability, which initiates the spontaneous polarization of the crystal. At the same time the local phase transition occurs in electron-phonon (vibron) interaction with the available electronic orbital degeneracy (or quasi-degeneracy) and mixing of electron zones. Such mechanism of phase transition is also specified in article [28]. According to this mechanism, the presence of ferroelectric state in perovskites is mainly affected by the following: 1) hybridization of $2p$-states of oxygen with d-states of transition metals (covalence effect); 2) chain binding of oxygen ions with the adjacent ion of transition metal (anisotropy effect). Besides, paper [28] indicates the central role of oxygen ions in ferroelectric phase transitions in virtue of the fact that more than 90 % of all known ferroelectrics and antiferroelectrics contain oxygen.

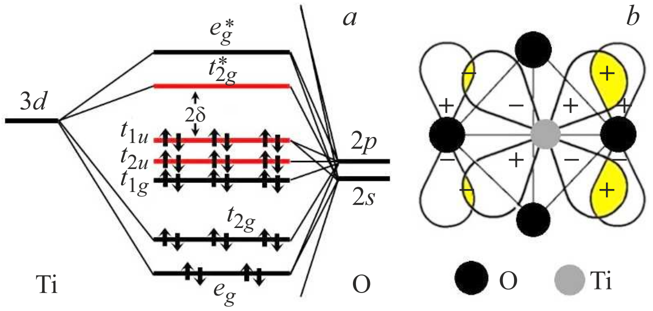

Figure 5. Correlation of energy levels of octahedral cluster $[TiO_6]$. Orbitals HOMO t_{1u} and t_{2u} (mainly oxygen) and LUMO t_{2g} (mainly titanium) are mixed as a result of JTPE (*a*) [27]. Added covalence due to distortions of low symmetry caused by JTPE. Yellow indicates closure of $3d$-orbital t_{2g}(Ti) with p-orbital t_{1u}(O) (*b*) [27].

Splitting of electron levels in the molecule in the Jahn-Teller effect causes structural phase transition with symmetry change, since symmetry damage reduces energy with partial or complete removal of degeneracy of electron orbitals. In $BaTiO_3$ energy clearance 2δ between electron p-orbital of oxygen O and d-orbital of titanium Ti may be determined, considering the bond Ti-O (with high degree of covalence) based on the Bersuker's article [27] (Figure 5).

The ferroelectric Hamiltonian in the vibron theory is as follows:

$$H = H_e + H_f + H_{e-f} + H_a, \tag{7}$$

where H_e is operator of electron energy in valence band and conduction band, H_f is harmonic phonon Hamiltonian, H_{e-f} is Hamiltonian of electron-phonon interaction, H_a is member describing intrinsic phononic anharmonicity [29]. We consider the part of the free energy of the system, which is active in phase transition, when the energy of phononic anharmonicity is subtracted (Figure 2, *b*):

$$F = \Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3, \tag{8}$$

or

$$F = \Delta H = \Delta H_1^* + \Delta H_2^* + \Delta H_3. \tag{9}$$

The produced values of free energy makes it possible to assess the fairness of theoretical description of the crystal thermodynamic properties. It should be taken into account that in the general case to calculate the free

Helmholtz energy for the real crystal (containing defects), it is necessary to take into account harmonic U_h and actual U potentials [30]:

$$A = kT\left[\sum_{i=1}^{3N-3}\ln\left(\frac{\hbar\omega_i}{kT}\right) - \ln\left\langle \exp\left(-\frac{U-U_h}{kT}\right)\right\rangle\right]. \quad (10)$$

In the application to a specific crystal it is necessary to separately consider a type of interatomic potential, which takes into account the nature of the chemical bond (ionic, covalent, metallic). Besides, the main difference of the strong covalent bond from the ionic interaction is the directional nature of the chemical bond and less significant role of the Coulomb interaction. Here we will consider the short-acting potentials, due to a more complicated description of interatomic interaction with account of long range [31]. It is rather justified that for the ionic crystals the most correct is the Buckingham potential (or Lennard-Jones potential), and for covalent interatomic interactions — Morse potential (or its combination with the harmonic potential) [32].

Buckingham potential U_B for the ionic bond is as follows:

$$U_B(r) = Ae^{-Br}\exp(-Br) - Cr^{-6}, \quad (11)$$

where A, B, C is constants, r is distance between atoms (ions) [33].

Morse potential U_M for the covalent bond is as follows:

$$U_M(r) = D(e^{-2a(r-r_0)} - 2e^{-a(r-r_0)}), \quad (12)$$

where D is depth of potential well, a is coefficient, r_0 is equilibrium interatomic distance (or equilibrium bond length) [34].

As it was noted above, for $BaTiO_3$ bond Ba-O is ionic, and bond Ti-O is covalent [13,14]. This causes the need to consider the effective interatomic potential U_{eff} with account of Morse potential U_M for bond Ti-O and Buckingham potential U_B for bond Ba-O in comparison of atomistic modeling results and experimental data. Such analysis is possible from calorimetric measurements. Temperature dependence of heat capacity in the proximity of the phase transition may be presented in the form of three summands, including heat capacity of Debye model $C_D(T)$, heat capacity of phonon anharmonicity (substantial at higher temperatures) $C_{\text{an}}(T)$ and heat capacity of phase transition $C_{\text{f.t.}}(T)$:

$$C_p(T) = C_D(T) + C_{\text{an}}(T) + C_{\text{f.t.}}(T). \quad (13)$$

As noted above, for $BaTiO_3$ the maximum heat capacity of Debye with account of Joule-Kopp law is equal to $C_D = 115$ J/mol. Heat capacity of phonon anharmonicity $C_{\text{an}}(T)$ rises steadily with rising temperature. Then, subtracting these two contributions from the measured heat capacity, one may obtain the heat capacity caused by the phase transition (Figure 2, *b*).

It should be noted that the article includes no calculation of separate contributions of heat capacity of the Debye model $C_D(T)$ and heat capacity of phononic anharmonicity $C_{\text{an}}(T)$. Only their sum is calculated in the temperature range of 350–420 K by construction of the approximating polynomial (2):

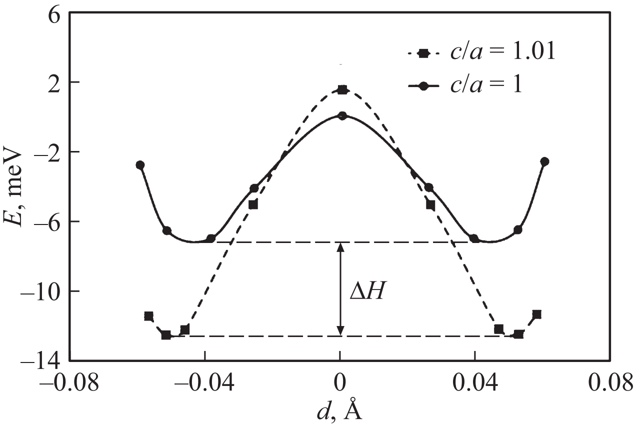

Figure 6. Energy E of Ti ion shift relative to Ba ion as a function of soft mode distortion in $BaTiO_3$ with different degree of tetragonality c/a [13]. ΔH is enthalpy of transition between two stages of crystalline lattice $BaTiO_3$.

$$C_p^{\text{approx}}(T) = C_D(T) + C_{\text{an}}(T), \quad (14)$$

which is sufficient to find the value of the heat capacity surge caused by the phase transition $C_{\text{f.t.}}(T)$.

Previously it was established that in the dependence $\Delta C_p(T)$ in the proximity of the phase transition (in T_C) one may identify two processes with different activation energies (0.99 and 2.46 eV) to T_C and one above T_C with activation energy 2.87 eV (Figure 2, *a*). Based on the above physical processes in ferroelectrics in the proximity of the phase transitions, one may assume that before temperature T_C the heat capacity grows due to appearance of additional degrees of freedom as a result of movement of oxygen vacancies. And starting from temperature $T_{\text{crit.}}$ also at the expense of the degeneracy of electron states at *d*-levels of transition metal ion (Ti in case of $BaTiO_3$) and activation of the process of crystalline lattice symmetry change from the tetragonal to the cubic one. Reduction of heat capacity, starting from temperature T_C to certain temperature (420 K for $BaTiO_3$), is explained, probably, by reduction in the quantity of the degrees of freedom in structural relaxation. The obtained value of the activation process enthalpy ΔH_2, occurring in the temperature area from $T_{\text{crit.}}$ to T_C (Table), must obviously be agreed with the effective interatomic potential U_{eff}, which is calculated, considering bonds Ba-O and Ti-O, and which is a function of interatomic potentials U_B (11) and U_M (12):

$$U_{\text{eff}}(r) = f\left(U_B(r), U_M(r)\right). \quad (15)$$

The produced values of enthalpy of the activation process ΔH make it possible to obtain new information on the phase transition process. This is done, for example, in analysis of the calculations of the potential energy of Ti ion shift relative to Ba ion, produced by calculations of energy as a function of soft mode distortion in $BaTiO_3$ at various degrees of tetragonality ($c/a = 1.01, 1$) [13]. In this case energy ΔH corresponds to enthalpy of transition between the two states of the crystalline lattice $BaTiO_3$ (Figure 6).

Such comparison of experimental and estimated results may be one of the criteria of proper choice and construction of interatomic potential for calculations from first principles (*ab initio*) in the crystalline systems with various types of chemical bond.

4. Conclusion

Identification of heat capacity surge from the temperature dependence of ferroelectric heat capacity $BaTiO_3$ caused by spontaneous polarization surge in the proximity of the phase transition, minus the Debye heat capacity and phononic anharmonicity heat capacity, made it possible to find the following peculiarities. It was found that in the ferroelectric phase when getting closer to the Curie temperature T_C in the temperature dependence of the heat capacity surge it is possible to identify two sections, which may be approximated by exponential equation with activation energy U. The first activation energy occurs in the temperature interval $350-389\,\mathrm{K}$ and is related to the movement of oxygen vacancies ($U_1 = 0.99\,\mathrm{eV}$). The second starts at the critical temperature $T_{\mathrm{crit.}}$ and occurs in the interval of $389-394\,\mathrm{K}$ (Curie temperature $T_C = 394\,\mathrm{K}$) and is related to the electron-phonon interaction in presence of electron orbital degeneracy and mixing of electron zones of $2p$-states O with d-states Ti ($U_2 = 2.46\,\mathrm{eV}$). The activation process in the paraelectric phase ($U_3 = 2.87\,\mathrm{eV}$) takes place with the decrease in heat capacity, which is related to decrease in the additional degrees of freedom due to structure relaxation after the change in the crystalline lattice symmetry. The enthalpy and entropy of the specified processes were calculated. The identified activation processes made it possible to receive the values of transition enthalpy between the two different states of the crystalline lattice $BaTiO_3$, arising as a result of Jahn-Teller effect (or pseudo-effect) in the proximity of the ferroelectric phase transition. Such consideration is possible within the vibron theory of ferroelectricity, where such effect is the only source of polar instability, which initiates the spontaneous polarization of crystal. The proposed comparison of experimental calorimetric and estimated atomistic results may be one of the criteria of proper choice and construction of interatomic potential for calculations from first principles (*ab initio*) in the crystalline systems with various types of chemical bond.

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Conflict of interest

The author declares no conflict of interest.

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