

## THERMODYNAMIC PARAMETERS OF LEAD SULFIDE CRYSTALS IN THE CUBIC PHASE

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Geometric and thermodynamic parameters of cubic PbS crystals were obtained using the computer calculations of the thermodynamic parameters within density functional theory method DFT. Cluster models for the calculation based on the analysis of the crystal and electronic structure. Temperature dependence of energy  $\Delta E$  and enthalpy  $\Delta H$ , Gibbs free energy  $\Delta G$ , heat capacity at constant pressure  $C_p$  and constant volume  $C_v$ , entropy  $\Delta S$  were determined on the basis of *ab initio* calculations of the crystal structure of molecular clusters. Analytical expressions of temperature dependences of thermodynamic parameters which were approximated with quantum-chemical calculation points have been presented. Experimental results compared with theoretically calculated data.

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### 1. Introduction

About the unique properties of lead sulfide was known long ago. Striking evidence of this can serve its first use in thermoelectric generators.

Effective use of this compound due to its low thermal conductivity at high temperatures [1], a lot ellipsoidal character of energy spectrum ( $N=4$ ), low lattice thermal conductivity ( $\sim 2.092 \text{ J/m}\cdot\text{K}$ ) at relatively high carrier mobility ( $\sim 0.1 \text{ m}^2/\text{V s}$ ), high values of permittivity, low values of the band gap (0.41 eV [2]) [3] and their positive change with temperature [4], which are factors that contribute the efficient use of the material in thermoelectricity. Also, it is important to note that the band gap of lead sulfide is the highest among other lead chalcogenide compounds. Widespread industrial use of this material contributes to its low cost and availability of natural compound (mineral of galena). The combination of lead chalcogenides in solid solutions allows to achieving of higher performance thermoelectric efficiency.

Actually this compound is used in thermoelectricity, optoelectronics and spintronics devices, especially in the long-wavelength range, for manufacturing of infrared diode lasers and termophotovoltaic power converters [3]. Such wide range of materials application requires in-depth study of their properties at different conditions and dependence of these crystals properties with changing of external factors. Interest in such studies is due to the fact that often data are ambiguous or completely absent.

First principle calculations are convenient and quite accurate approaches for modeling of structure and finding of thermodynamic properties of crystals which are widely used in modern research [1], [5], [6]. They permit to obtain reliable data about the properties of crystalline solids and implement their theoretical interpretation using a relatively minor cost of machine time and minimum set of input parameters.

In paper was using the computer quantum chemistry calculations that caused by the

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possibility of investigations of short-range order of the atoms in real crystals and analyzing of the properties caused by them. It is also important, that intensive research of atomic clusters as components of new nanostructured materials is caused by the perspective application in nanotechnology.

## 2. Method of calculation

Within the rigid molecule approximation [7] the enthalpy  $H$  of crystals is defined as:

$$H \approx H_{\text{elec}} + H_{\text{vib}}^0 + E_{\text{vib}}(T) + H_{\text{rot}}(T) + H_{\text{trans}}(T) + RT. \quad (1)$$

There  $H_{\text{elec}}$  is the electronic component of enthalpy,  $H_{\text{vib}}$  is the vibration component of enthalpy,  $H_{\text{vib}}^0$  is the enthalpy of the main state vibrations,  $H_{\text{rot}}$  is the rotational component of enthalpy,  $H_{\text{trans}}$  is the progressive component of enthalpy,  $R$  is the universal gas constant,  $T$  is the temperature. The energy  $E$  was calculated similarly.

Entropy of crystal generally determined as the sum of components:

$$\Delta S = S_{\text{trans}} + S_{\text{rot}} + S_{\text{vib}} + S_{\text{elec}} - nR[\ln(nN_0) - 1], \quad (2)$$

where  $N_0$  is the Avogadro constant,  $n$  is the number of moles in molecules,  $M$  is the molar mass.

It is possible to calculate the Gibbs free energy of the crystal at a given temperature  $T$  using contributions of zero-point energy and entropy of individual members of molecules reagents A (Pb) and B (S),.

$$\Delta G = H_A - H_B + \frac{1}{2} \sum_{i \in A} hv_i - \frac{1}{2} \sum_{j \in B} hv_j - T(S_{\text{vibr}}^A - S_{\text{vibr}}^B + S_{\text{rot}}^A - S_{\text{rot}}^B + S_{\text{trans}}^A - S_{\text{trans}}^B). \quad (3)$$

At calculations of  $\Delta E$ ,  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  we used the following method of the initial conditions consideration as shown at the calculations of energy  $\Delta E$ . Initially, the energy  $\Delta E_A$  of cluster A (fig. 1,A) was calculated according to [8] using formula:

$$\Delta E_A = E - \sum E_{\text{el}} + \sum E_{\text{at}}. \quad (4)$$

There  $E$  is the total energy of system;  $E_{\text{el}}$  is the energy of electrons in atoms that constitute the system (in atomic state);  $E_{\text{at}}$  is the atomization energy. Total energy and electron energy of system we were taken from the calculation results, all other values - from reference [9]. The energies  $\Delta E_B$ ,  $\Delta E_C$  and  $\Delta E_D$  of clusters B, C and D, accordingly (Fig. 3 B, C, D) have been calculated similarly.

The thermodynamic properties of PbTe crystals were calculated at different temperatures (Fig.2-4) on the base of calculations of the vibrational spectra.

As a result of quantum- chemical calculations we obtained the system of equations, which is as follows:

$$\begin{cases} 8x_3 + 24x_4 + 24x_6 = A, \\ 24x_3 + 24x_5 + 8x_6 = B, \\ 8x_3 + 12x_4 + 6x_5 + x_6 = C, \\ 8x_3 = D. \end{cases} \quad (5)$$

In (5)  $x_3$ ,  $x_4$ ,  $x_5$ ,  $x_6$  are the values of quantities for two -, four-, five- and six coordinated atoms, respectively.

The solution of this system relatively to  $x_6$  was obtained by the following ratio:

$$x_6 = \frac{2A-B}{4} + \frac{5D}{4} - C. \quad (6)$$

There  $A, B, C, D$  are the thermodynamic values for the respective clusters.

Heat capacity at constant volume  $C_V$  (similarly for  $C_P$ ), according to these approximations are determined by the following formula:

$$C_V = C_{V(\text{trans})} + C_{V(\text{rot})} + C_{V(\text{vib})}. \quad (7)$$

Contributions of translational degrees of freedom calculated without data of quantum-chemical calculations because they depend on external factors ( $T, P$ ) and mass of the molecule  $m$ .

Symmetrical relative equilibrium displacement of nuclei leads to a symmetric potential energy changes according to the contribution of vibrational component in the harmonic approximation and defined by the equation:

$$C_{V(\text{vibr})} = R \left( \frac{hc}{kT} \right)^2 \sum_i \frac{g_i v_i^2 e^{-\frac{hcv_i}{kT}}}{\left[ 1 - e^{-\frac{hcv_i}{kT}} \right]^2}. \quad (8)$$

There  $g_i$  is the degeneration degree of  $i^{\text{th}}$  vibration.

According to [10] the temperature dependence of the specific heat capacity of crystal structures determined by the following function:

$$C = a + b \cdot 10^{-3} T - c \cdot 10^5 T^{-2}, \quad (9)$$

where  $a, b, c$  are the constants depend on the lattice type of crystal and type of chemical compound.

To comparison the obtained results the proposed models [1], [3], [10] and experimental data [11] were discussed. Theoretical calculation of heat capacity in [1] was realized by direct force-constant method. Calculations of heats in [3] were performed using WIEN2K program developed by Blaha [12]. This program uses the full potential linearized associated plane waves (FP-LAPW) based on density functional theory. Calculations in [10] carried out within density functional theory too. Molar heat capacity measurement in [11] carried out on 0.034 kg samples of PbS in calorimeter at a high vacuum under the hood, the temperature was maintained constant. Calorimeter is a 0.03 m length and 0.03 m diameter cylinder soldered with a domed bottom. The upper part was sealed by Wood's metal with a thin-walled copper-nickel tube with 0.001 m outer diameter and 0.2 m length attached. Constantan wire was used as heaters and thermometer is a platinum wire. Temperature drift recorded before and after the establishment of internal equilibrium. Measurements carried out in the temperature range from 20 to 260 K. In reference [13] values of isobaric molar heat capacity measured on analyzing of thermal installation (Dupont 1090B, USA) were listed. These results are also in good agreement with values obtained by us.

### 3. Cluster models

High level of modern scientific and technological progress is largely due to the development of theoretical research methods. However, these achievements would be impossible without the latest computer technology advances. First of all, they contribute to the improvement of model studies and are extremely convenient for expansion and deepening of information about the structure and properties of matter.

Rock salt structure was selected for modeling studies because lead chalcogenides crystallize in the face-centered cubic lattice NaCl (structural type B1) with the lattice parameter  $a=5,936 \text{ \AA}$  [13] for PbS compound, space group was  $Fm\bar{3}m-O_h^5$ . These atom locations can be explained by the fact that lead chalcogenides belonging to polar semiconductors, characterized by ion-covalent type of bond.

This structure allows build clusters without additional atoms that are introduced for compensation of dangling bonds. Crystal structures of lead sulfide were investigated using four models with 64, 56, 27 and 8 atoms accordingly. In constructing of clusters the most attention was paying to symmetry and electric charge of clusters for elimination of the structure distortion due to the action of surface forces. This approach has been successfully used for the construction of cluster models in II-VI compounds [14], [15].

The first cluster model (with general formula  $Pb_{32}S_{32}$ , fig. 1, A) is basic for calculation of the spatial and electronic structure and thermodynamic quantities. This model consists of 64 atoms and contain 4 pairs of six coordinated atoms, 12 pairs of five coordinated, 12 pairs of four coordinated and 4 pairs of three coordinated atoms.

The second cluster has a general formula  $Pb_{28}S_{28}$  (fig. 1, B) and consists of 56 atoms. It includes 4 pairs of six coordinated atoms, 12 pairs of five coordinated and 12 pairs of three coordinated atoms.

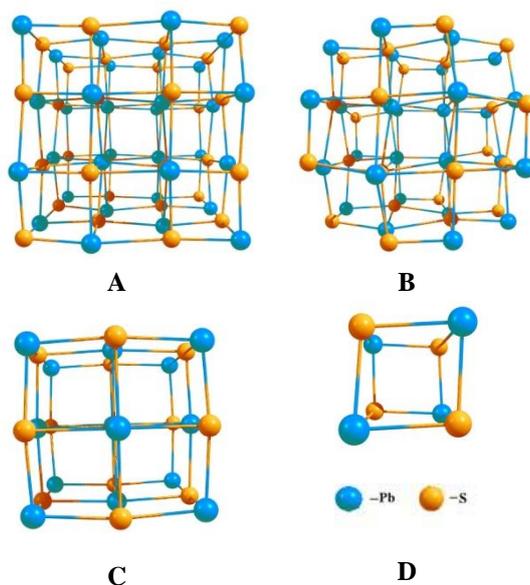


Fig. 1. Cluster models A ( $Pb_{32}S_{32}$ ), B ( $Pb_{28}S_{28}$ ), C ( $Pb_{14}S_{13}$ ) and D ( $Pb_4S_4$ ) for cubic phase of PbS.

The third cluster model constructed of 27 atoms and has the chemical formula  $Pb_{14}S_{13}$  (fig. 1, C). This structure includes one six coordinated atom, 6 pairs of five coordinated, 12 pairs of four coordinated and 8 pairs of three coordinated atoms.

The fourth cluster with the  $Pb_4S_4$  formula (fig. 1, D) composed of 8 three coordinated atoms.

The first step for the quantum-chemical calculation of the cluster properties was the determination of the lowest energy configuration. All calculations started with SCF convergence and geometry optimization; after obtaining a stable minimum, the frequencies were calculated. The calculations were carried out using density functional theory, on the basis of the Stevens–Basch–Krauss–Jasien–Cundari (SBKJC) [16] parameterization. In this basic set only the valence electrons which are directly involved in chemical bonding are considered. This basic set was chosen due to our previous experience with it in several vibrational studies carried out by group II-VI [17], [18]. DFT calculations were performed by using Becke's three parameter hybrid method

[19] with the Lee, Yang, and Parr (B3LYP) gradient corrected correlation functional [20] using the PC Gamess program packages [21]. The visualization of the spatial structures was carried out using Chemcraft.

This approach makes possible to create the equations system (5) for the thermodynamic variables of selected clusters. Solving it, we got the values of these parameters for six coordinated atoms that made up NaCl structure.

Comparing of calculated by us lattice constant value of  $a=5,92 \text{ \AA}$  is extremely close to obtained in paper [22] data  $a=5,938 \text{ \AA}$  calculated using the PBEsol exchange-correlation functional and presented there experimental result  $a=5,933 \text{ \AA}$ . Seeing the deviations within  $\sim 1\%$  indicate that DFT calculations reproduce the absolute values of the lattice constants reasonably well. Our results may be a good addition to the temperature dependences of lattice constants, volumetric expansion coefficients and bulk moduls were carried out using the Phonopy package, with VASP using the PBEsol exchange-correlation functional [22]. Small shifting of Pb atoms is associated with the softening of phonons at high temperatures within the quasi-harmonic approximation based on phonon-phonon interactions in many-body perturbation theory.

#### 4. Results and discussion

The dependences of energy  $\Delta E$ , enthalpy  $\Delta H$ , Gibbs free energy  $\Delta G$ , entropy  $\Delta S$  and heats capacities at constant volume  $C_V$  and constant pressure  $C_p$  for PbS crystals at temperatures from 20 K to 1000 K are presented on fig. 2-4. Their analytical expressions can be introduced by the next dependencies:

$$\Delta S(T) = 13.001 \cdot \ln T - 10.5 \quad (10)$$

$$\Delta G(T) = 100.17 + 0.0382 \cdot T \quad (11)$$

$$\Delta E(T) = 0.0158 \cdot T + 100.05 \quad (12)$$

$$\Delta H(T) = 0,0158 \cdot T + 100,05 \quad (13)$$

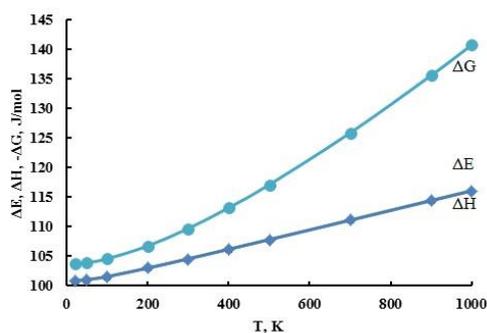


Fig. 2. The temperature dependence of energy  $\Delta E$ , enthalpy  $\Delta H$ , and Gibbs free energy  $\Delta G$  for cubic PbS crystals.

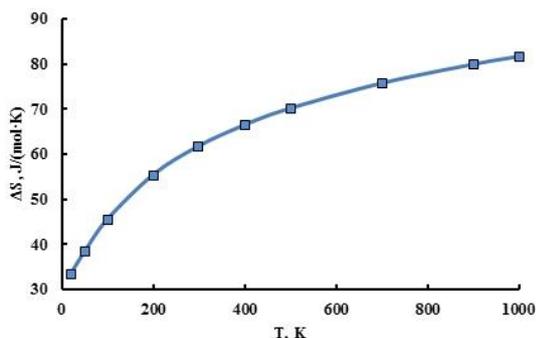


Fig. 3. The temperature dependence of entropy  $\Delta S$  for cubic PbS crystals.

Obtained by us the analytical expressions of the temperature dependences of heat capacity at constant volume  $C_V$  and constant pressure  $C_p$ , which were approximated by quantum-chemical calculation points using the mathematical package Maple14, are shown by the following equations:

$$C_V = 39,38 + 13,661 \cdot 10^{-3} T - 0,1312 \cdot 10^5 T^{-2}, \quad (14)$$

$$C_p = 41,315 + 13,910 \cdot 10^{-3} T - 0,1382 \cdot 10^5 T^{-2}. \quad (15)$$

As for crystal structure, the minor deviation from the perpendicular relative position of sides was observed also in structure modeling lead selenide by authors [23], who used calculation program GAUSSIAN 03 and SBKJC base set. These results do not contradict to experimental data given in [2], and to data of structural cards given in [24], where among compounds of lead chalcogenides are on the side of PbS cubic structure near the boundary between the cubic and orthorhombic modifications.

Received dependences are consistent with the theory of solid state physics. The increase of entropy with the increasing of temperature is reasonable, because of system energy increase and hardness of test material decrease. Since all thermodynamic parameters can be defined using other thermal characteristics, their direct dependence on the temperature increase can be totally explained by classical theory of solid state physics.

Also it is important that during calculation the temperature dependence of heat capacities were adjusted to 0 K. At calculations we use models that include the phonon contribution at the heat capacity which is a combination of Debye and Einstein functions, and the electronic component. The received values of heat capacity at constant volume  $C_V$  and constant pressure  $C_P$  at different temperatures are shown in Fig. 4. A good coincidence with theoretical data can be considered by obtained calculation data approach to the classic Dulong and Petit law. In low-temperature range the values are proportional to  $T^3$ , which corresponds to Debye theory. We also carried out the comparison of our results with the calculation results [1], [3], [10] and measured experimental values [11], [13]. During analysis of received data is observed coincidence of our results with previously obtained results within 2% error.

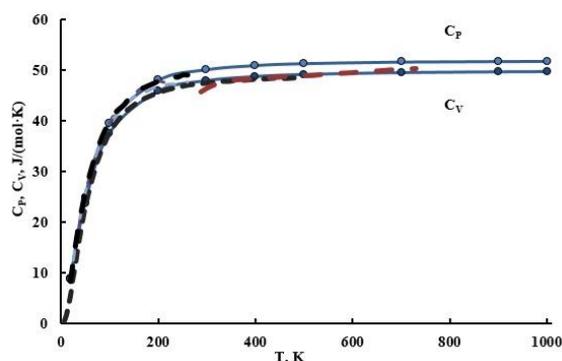


Fig. 4. Temperature dependence of isochoric  $C_V$  and isobaric  $C_P$  heat capacities:  $\circ$  - quantum-chemical calculation; line - approximation of analytical functions (14,15); intermittent lines - results of calculations [1], [3], [10].

The deviations of theoretically calculated equilibrium structure from values which are typical for rock salt lattice type can be explained by a significant deviation of the lattice spectrum from Debye theory [25]. Ionisity is an important factor that constrains phase transitions. Spin-orbital interaction is characterized by similar effect because it violates the congruence of the Fermi surface. The values for lead chalcogenides are large, which explains by the absence of transitions for these compounds [26].

## 5. Conclusion

Based on the crystal and electronic structures of cubic PbS and paying attention to their physical and chemical properties, cluster models for calculating the thermodynamic parameters of cadmium telluride have been proposed. A method of consideration of the boundary conditions for

cluster models of a PbS crystal at the cubic phase has been shown.

Temperature dependences of the thermodynamic parameters of the PbS crystals have been defined: energy  $\Delta E$ , enthalpy  $\Delta H$ , entropy  $\Delta S$  and Gibbs free energy  $\Delta G$ . These results can be used to predict properties of PbS crystals during annealing.

From the first principles' calculations we have been received the analytical expressions for the temperature dependences of the specific heat capacity of the PbS crystals in cubic phases at constant volume  $C_V$  and constant pressure  $C_P$ .

A good coincidence of the results with similar calculations and experimental data was received.

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