

Quantum chemical calculations of the polymorphic phase transition temperatures of ZnS, ZnSe, and ZnTe crystals

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Abstract: Molecular models of polymorphs modifications of zinc chalcogenides have been designed. Based on the results of ab initio quantum chemical calculations of the crystal structure of clusters the temperature dependences of the Gibbs energy of sphalerite and of wurtzite have been found. Phase transformations “sphalerite–wurtzite” temperatures have been evaluated.

Key words: Zinc chalcogenides, sphalerite, wurtzite, quantum chemical

1. Introduction

Zinc chalcogenides are advanced materials for light diodes and photoresistors, and sources of spontaneous and coherent radiation [1]. However, practical applications of ZnS, ZnSe, and ZnTe need reliable information about the crystal structure of these materials. Semiconductors are crystallized in such way that each atom of Zn(X) (X = S, Se, Te) is located in the center of a regular tetrahedron; the 4 vertices are the atoms of another element X (Zn). These tetrahedrons form 2 types of structures: sphalerite and wurtzite. Low-temperature modification 3C ZnX (sphalerite) refers to the cubic system, space group F43m. High-temperature modification 2H ZnX (wurtzite) refers to the hexagonal crystal system, space group P6mc. Sphalerite’s structure is more stable than wurtzite’s structure below the transition temperature, while wurtzite’s structure is much more stable above the transition temperature [2]. There are quite contradictory data about the polymorphism of zinc chalcogenides in the literature. According to [3], the polymorphic transition “sphalerite–wurtzite” for ZnS occurs at $T_m = 1250\text{--}1450$ K, and for ZnSe at 1420–1713 K [4–6]. We were unable to find this information for ZnTe. Therefore, the evaluation of the characteristics of the polymorphic phase transition for zinc chalcogenides remains relevant. According to the technological complexity of production and the investigation of these materials there are extremely useful quantum chemical calculation methods. In this work these methods are used and the phase transition temperatures of “sphalerite–wurtzite” for zinc chalcogenides crystals have been determined.

2. Calculation methods

For the calculation of the thermodynamic parameters we used the cluster approach [7]. The calculations were performed with the software package Firefly [8] within the limited Hartree–Fock approximation, using the

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valence basis set SBKJC, which includes an effective core potential [9]. Visualization of spatial structures was carried out using Chemcraft.

For the calculation of sphalerite we used 2 cluster models of zinc chalcogenides: clusters A and B. Model A includes a zinc atom surrounded by 2 ligands and has the general formula $ZnC_2H_2X_4$ (Figure 1a). The general formula of cluster B is $Zn_4C_6H_6X_{13}$, it contains a zinc atom surrounded by 4 chalcogen atoms, it can be corresponded to a real crystal, and all these atoms are 4-coordinated (Figure 1b). We used 6 HXC_2 -ligands, which had saturated dangling bonds.

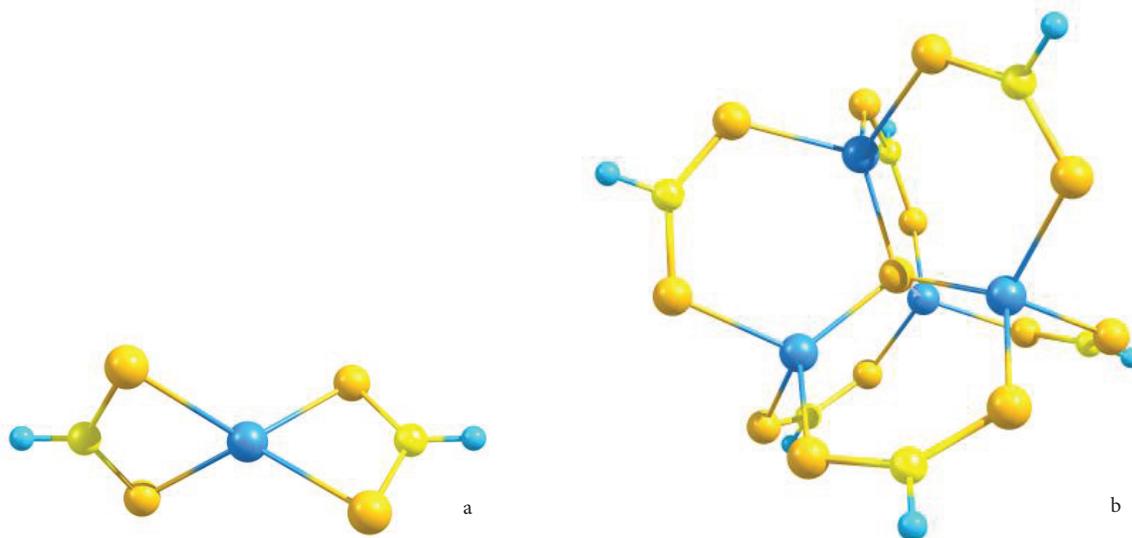


Figure 1. Cluster model A ($ZnC_2H_2X_4$) (a) and B ($Zn_4C_6H_6X_{13}$) (b) of sphalerite modifications of zinc chalcogenides crystals.

Wurtzite's structure was studied by using 3 models: C, D, and E. Cluster C (general formula $Zn_{15}X_{15}$, Figure 2a) was the base for the calculation of the spatial and electronic structure and the thermochemical quantities. This model consists of 30 atoms and contains 2 pairs of 4-coordinated, 8 pairs of 3-coordinated, and 5 pairs of 2-coordinated atoms. Cluster D (the general formula $Zn_{11}X_{11}$, Figure 2b) consists of 22 atoms. It contains 1 pair of 4-coordinated, 6 pairs of 3-coordinated, and 4 pairs of 2-coordinated atoms. Cluster E of wurtzite modification (with the general formula $Zn_{10}X_{10}$, Figure 2c) consists of 20 atoms. It contains 1 pair of 4-coordinated, 4 pairs of 3-coordinated, and 5 pairs of 2-coordinated atoms. During the calculation of the Gibbs energy ΔG_1 of sphalerite phase formation we used 2 clusters. For the first we calculated the Gibbs energy of cluster A, according to [10]:

$$\Delta G = G - \sum E_{el} + \sum \Delta H_{at}, \quad (1)$$

where G is the total Gibbs energy of the system, E_{el} is the electronic energy of the atoms that created the system, and ΔH_{at} is the atomization energy of the atoms. Total and electronic energies of the system derived from the results of the calculation, and all other values were taken from the literature [3]. Similarly, the formation enthalpy of cluster B was calculated. In the case of sphalerite, from the value of Gibbs energy of cluster B was taken away the triple value of Gibbs energy of cluster A. That means, from cluster ΔG , which consisted of a fragment of the crystal sphalerite and of 3 ligands, was deducted ΔG of 3 ligands. If you count

the number of atoms and their variety in the triple of cluster A and cluster B, cluster A has 1 more atom of zinc and 1 more chalcogen atom. That is why after using of this technique we obtain the value of the Gibbs energy, which can be attributed to the sphalerite crystal [11].

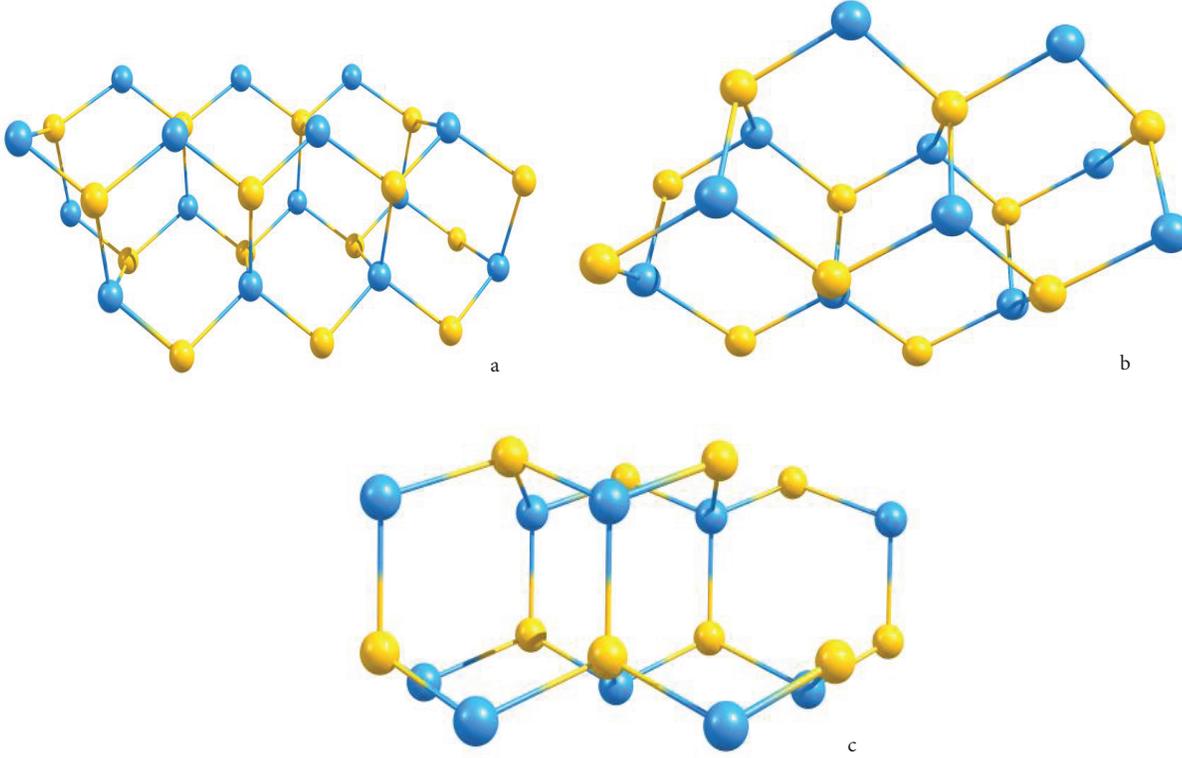


Figure 2. Cluster models C ($Zn_{15}X_{15}$) (a), D ($Zn_{11}X_{11}$) (b), and E ($Zn_{10}X_{10}$) (c) of wurtzite modifications of zinc chalcogenides crystals.

For the calculation of the Gibbs energy of the wurtzite crystal, first we calculated the Gibbs energy of clusters C, D, and E according to the method described above, and then created a system of equations:

$$\begin{cases} 2\Delta G_4^* + 8\Delta G_3^* + 5\Delta G_2^* = \Delta G_C \\ \Delta G_4^* + 6\Delta G_3^* + 4\Delta G_2^* = \Delta G_D \\ \Delta G_4^* + 4\Delta G_3^* + 5\Delta G_2^* = \Delta G_E, \end{cases} \quad (2)$$

where the coefficients before ΔG_i^* correspond to the number of pairs of bonds with the coordination number equal to the index $i = 2, 3, 4$ at ΔG_i^* ; ΔG_C , ΔG_D , and ΔG_E are the Gibbs energy of clusters C, D, and E, respectively, which have been obtained from the computer calculations. Then ΔG_4^* is the required value for the Gibbs energy of the crystal at the given temperature.

System (2) has been solved analytically by using the inverse matrix of Cramer's rule. As a result, the equation for determination of the Gibbs energy of the wurtzite crystal modification of zinc chalcogenides has been obtained:

$$\Delta G_4^* = \frac{7\Delta G_C - 10\Delta G_D + \Delta G_E}{5}. \quad (3)$$

3. Results and discussion

The temperature dependences of the Gibbs energy for sphalerite and for wurtzite are shown at Figure 3. Their analytical expressions are:

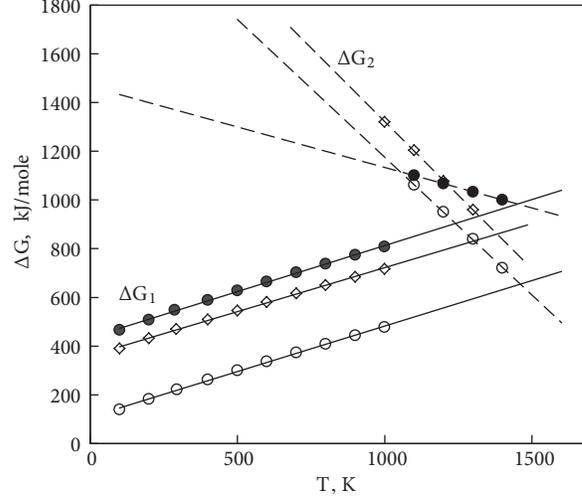


Figure 3. The temperature dependences of the Gibbs energy of sphalerite (solid lines) $\Delta G_1(T)$ and wurtzite (primed line) $\Delta G_2(T)$ structural modifications of ZnS (○), ZnSe (?), ZnTe (◇).

- For zinc sulfide (4):

$$\begin{aligned}\Delta G_1 &= 0,3736 \cdot T + 108,68, \\ \Delta G_2 &= -1,1384 \cdot T + 2307,1;\end{aligned}\quad (4)$$

- For zinc selenide (5):

$$\begin{aligned}\Delta G_1(T) &= 0,3786 \cdot T + 434,41, \\ \Delta G_2(T) &= -0,344 \cdot T + 1466;\end{aligned}\quad (5)$$

- For zinc telluride (6):

$$\begin{aligned}\Delta G_1(T) &= 0,3613 \cdot T + 360,75, \\ \Delta G_2(T) &= -1,21 \cdot T + 2531,5;\end{aligned}\quad (6)$$

In the solid–solid transition of the matter the Gibbs energy must be the same. In our case, the point of intersection of the dependencies $\Delta G_1(T)$ and $\Delta G_2(T)$ ($\Delta G_1(T) = \Delta G_2(T)$) will be the temperature of the phase transition from sphalerite to wurtzite. According to our data, for ZnS $T_c = 1454$ K; for ZnSe $T_c = 1427$ K; for ZnTe $T_c = 1382$ K.

We can see that the phase transition temperature increases as we move from a zinc telluride to selenide and to sulfide. This phenomenon was explained by the increase in the binding energy in a series of ZnS–ZnSe–ZnTe. Note that according to [4,5] the transition temperature of ZnSe is greater than the phase transition temperature for ZnS, which in our opinion is less regular.

It should be noted that energy of interactions between atoms is the largest energy characteristics of the crystalline state; that is why explaining the patterns in the phase transition temperature obtained from the analysis of these variables is logical. Besides other energy characteristics of the crystalline state, in particular vibrational energy is less than the relation energy and their effect on the result is less as well.

4. Conclusions

In this paper we propose the cluster models of sphalerite and wurtzite crystals of zinc chalcogenides and the technique of boundary conditions.

The temperature dependence of the Gibbs energies for zinc chalcogenides for polymorphic crystals and the phase transition temperature "sphalerite–wurtzite" have been found. These results are consistent with the experimental values of the other works, which have a significant variation interval [2–6].

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