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Thermodynamic properties of II-VI chalcogenide crystals: modeling and calculation

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Thesis for the Doctor degree
in Physics and Mathematics

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CONTENT

Introduction

Relevance of the topic. The main reasons for the increased interest in ZnX and CdX (X=S, Se, Te) semiconductors are their impressive range of practical applications. Moreover, due to their unique physical and chemical properties, they are excellent objects for fundamental investigations. In particular, zinc chalcogenides are used in semiconductor and quantum electronics - solar batteries and detectors of X- and γ-radiation, lasers, infrared receivers. Cadmium chalcogenides are interesting for various fields of solar energy applications, solid-state electronics, and radiation engineering. In particular, CdTe, due to its unique set of physical properties, is used for the manufacture of a number of highly efficient devices of nuclear energy, solar engineering, optic and acoustic electronics, X- and γ -detectors, substrates for epitaxial growth. In addition to the above, cadmium sulfide and selenide have been used, for a long time, to form thin-film transistors, elements for solar cells and photoelectronic, lines for injection lasers, etc.

The effective implementation of the aforementioned applications requires the information about physical and chemical properties of crystals. Particularly, the information about the thermodynamic parameters, as well as the defect subsystem, are essential for potential practical applications. The investigations of these parameters are important for understanding the processes of electronica and phonon heat transfer in solids.

Despite the long-term practical use of the materials studied in the thesis, the urgent tasks were to determine the thermodynamic parameters, their temperature dependences, obtain reliable experimental and theoretical data about the energy characteristics of point defects, and their impact on the thermodynamic parameters. Moreover, the information about the link between the concentration of point defects and the concentration of charge carriers was still limited.

Connection of work with scientific projects and grants

The Ph.D. thesis was performed in the scientific laboratories of the Physical-Chemical Institute and on the Department of Physics and Chemistry of Solid State at Vasyl Stefanyk Precarpathian National University, Ivano-Frankivsk, Ukraine; and was a part of the projects of the Ministry of Education and Science of Ukraine: "Nanoscale systems based on semiconductor materials of II and IV subgroups” (State registration number 0106U000221) and "Dominant point defects and mechanisms of formation of solid solutions based on compounds $A^{IV}B^{VI}$ and $A^{II}B^{VI}$" (state registration number 0107U006768), as well as the project "Thermoelectric materials and devices for energy saving and safety "of the NATO science program for peace and security ”(NATO SPS 984536, state registration number 0114U007021). The author of the thesis participated in the above works as a young researcher from 2011 up to 2015. His work was related to the theoretical calculations of thermodynamic parameters and energetical characteristics of point

defects for the investigated crystals. He also performed the synthesis, sample preparation, and characterization of the studied materials.

The aim and objectives of the study. For the proposed structural cluster models, from the first principles, to determine the temperature dependences of thermodynamic parameters and temperatures of polymorphic phase transitions in stoichiometric II-VI crystals; depending on the particularities of the fabrication procedure and using thermodynamic and crystal-chemical approaches, to determine the type and charge state of dominant point defects.

To achieve this aim, the following tasks were outlined:

– to propose the cluster models, which can help to perform the calculations of the crystal structure and vibrational spectrum for the cubic modification of sphalerite and hexagonal modification of wurtzite of II-VI crystals;

- to calculate the temperature dependences of thermodynamic parameters for ZnX, CdX (X = S, Se, Te) stoichiometric crystals and to determine the temperatures of the polymorphic phase transition "sphalerite-wurtzite";

- based on the calculated values of the molar heat capacities C_p and C_v for the proposed clusters, to determine the Debye temperatures Θ_D for the investigated materials;

- to analyze the dependencies between the calculated thermodynamic parameters (ΔE, ΔH, ΔG, ΔS, C_v, C_p, Θ_D) and the chemical compositions of ZnX, CdX compounds;

- using the methods of thermodynamic potentials and crystal-chemical approaches, to determine the dominant point defects for nonstoichiometric ZnTe, CdTe crystals, calculate their temperature and pressure dependences, and determine the additional contributions of the defective subsystem on the values of thermodynamic parameters;

- based on the analysis of the obtained experimental and calculated data, to determine the influence of chemical composition and conditions of two-temperature annealing on the formation of the defect structure and complex physical-chemical properties of ZnX, CdX materials.

The object of research: thermodynamic properties and energy characteristics of point defects as functions of temperature and composition.

The subject of research: stoichiometric and non-stoichiometric II-VI crystals (ZnX, CdX (X=S, Se, Te)).

Methods. A number of theoretical approaches and experimental methods were used for the investigation of crystal structure, thermodynamic, electrical, and thermal properties. In particular, the DFT and Hartree-Fock calculations, the crystal-chemical approach, and the thermodynamic

method based on the minimization of Gibbs free energy were used. To create cluster models of the crystal structure, the Chemcraft visualizer was utilized. The geometrical optimization of the proposed clusters and the calculations of the vibrational spectra were carried out using the DFT method in the quantum chemical software package FireFly (PCGamess). The cluster models for the calculations, as well as boundary conditions, were developed in this work. Computer simulation of the defect subsystem and calculation of the Debye temperatures were performed in Maple software. Materials were synthesized in quartz ampoules evacuated to a residual pressure of 10^{-5} mbar. The crystals were grown using the vertical Bridgman method, high-temperature treatment of the crystals was performed by the two-temperature annealing method. The phase composition was controlled by X-ray diffraction methods. Specific heat was measured using the differential scanning calorimeter DSC 404 F3, NETZSCH. The Hall effect was investigated using the four-probe method in constant electrical and magnetic fields with magnetic field induction of 1.4-1.5 T, and current through a sample of 400-500 mA. The uncertainty of the Hall measurements was ~10 %.

The scientific novelty of the obtained results

1. The models of clusters for sphalerite and wurtzite polymorphic modifications of stoichiometric nondefect II-VI (ZnX, CdX; X = S, Se, Te) crystals were developed. For sphalerite modification, aiming to compensate for the effect of the broken atomic bonds, it is suggested to use carbon and hydrogen atomic ligands. The wurtzite model is developed using clusters of the original crystal structure with the different number of atoms, and a system of equations formed on their basis. In such a way, the effect of the broken atomic bonds was eliminated.
2. The developed cluster models were used for the calculations of the thermodynamic parameters (formation energy ΔE, formation enthalpy ΔH, Gibbs free energy ΔG, and entropy ΔS) of zinc and cadmium chalcogenide crystals.
3. The obtained (by DFT method) values of the heat capacities C_p were used for the calculations of the Debye temperatures Θ_D of zinc and cadmium chalcogenides.
4. Equating the calculated Gibbs free energies for the sphalerite $\Delta G_1(T)$ and wurtzite $\Delta G_2(T)$ phases, the polymorphic phase transition temperatures were determined for stoichiometric crystals of zinc chalcogenides.
5. The correlation of the calculated thermodynamic parameters (ΔE, ΔH, ΔG, ΔS, C_v, C_p, Θ_D) of ideal ZnX, CdX crystals with their basic characteristics (bandgap E_g, degree of ionization δ, electronegativity ΔX, bond energy D, and compression module B) were established. All the aforementioned characteristics show the decreasing tendency in the series ZnS → ZnSe → ZnTe and CdS → CdSe → CdTe.

6. The homogeneity region of ZnTe and CdTe compounds under metal (and chalcogen) excess conditions are specified. The effect of the defect subsystem on the Gibbs free energy for ZnTe and CdTe nonstoichiometric crystals was estimated. This gives the essential information for controlling the growth of crystals with pre-determined electrical and thermal properties.

The practical significance of the obtained results

1. The cluster models of sphalerite and wurtzite polymorphic modifications of II-VI crystals for the calculation of thermodynamic parameters are developed. It is shown that these models can be used to analyze the electrical and elastic properties, as well as to calculate the energy characteristics of point defects of these crystals, which confirms their universal applicability.
2. The temperature-dependent thermodynamic parameters (ΔE, ΔH, ΔG, ΔS, C_v, C_p, Θ_D) for zinc and cadmium chalcogenides are calculated using the DFT approach. The offered dependences can play a role in standards for ideal nondefect stoichiometric II-VI crystals. Moreover, they determine the technological conditions for growing materials with predetermined physical and chemical properties.
3. The transition temperatures between polymorphic modifications of sphalerite and wurtzite phases of zinc chalcogenides are estimated, which is important for the practical use of the investigated materials.
4. Technological factors of two-temperature annealing (temperature T, vapor pressure of Zn (P_{Zn}), vapor pressure of Cd (P_{Cd})), which determine the point defect concentration, free charge concentration, and conductivity type for ZnTe, and CdTe crystals, are established.
5. Methods and computer programs for calculation of thermodynamic parameters and description of defect formation energies of II-VI semiconductor crystals are used in the teaching course "Physical and chemical fundamentals of semiconductor materials science" at Vasyl Stefanyk Precarpathian National University, Ivano-Frankivsk, Ukraine.

Personal contribution of the Ph.D. applicant

In all scientific works published in co-authorship, the Ph.D. applicant personally participated in the selection of research objects, setting tasks, discussing them, as well as in the final analysis and interpretation of the results. The Ph.D. applicant personally prepared drafts of the manuscripts of most published papers.

The Ph.D. applicant directly performed the theoretical investigation and modeling of the structure, compiled input and processed the output files of computer programs for calculating temperature dependences of thermodynamic parameters, performed modeling and analysis of polymorphic phase transitions "sphalerite-wurtzite", calculated the formation energy of defects and

performed the numerical calculations of the concentration of point defects as well as free charge carriers.

The Ph.D. applicant performed the main part of the experimental works related to the synthesis and growing of single crystals. He did the XRD analysis of the prepared materials. He did the DSC analysis and measured the Hall effect.

Presentation of the results shown in the Ph.D. thesis

The main results of the work were reported and discussed at many national and international conferences:

- XIII-th International Conference of Physics and Technology of Thin Films and Nanosystems. 2011, Ivano-Frankivsk, Ukraine.
- XIV-th International Conference of Physics and Technology of Thin Films and Nanosystems. 2013, Ivano-Frankivsk, Ukraine.
- Fourteenth open scientific and technical conference on electronics and infocommunication systems. 2011, Lviv, Ukraine.
- Fifteenth open scientific and technical conference on electronics and infocommunication systems. 2012, Lviv, Ukraine.
- The international scientific-practical conference "Semiconductor materials, information technology and photovoltaics". 2011, Kremenchuk, Ukraine.
- Conference of young scientists in semiconductor physics "Lashkarev readings - 2012". 2012, Kyiv, Ukraine.
- Conference of young scientists in semiconductor physics "Lashkarev readings - 2012". 2013, Kyiv, Ukraine.
- Ukrainian scientific conference "Actual problems of theoretical, experimental and applied physics". 2012, Ternopil, Ukraine.
- Materials of 6-th international conference on materials science and condensed matter physics. 2012, Chisinau, Moldova.
- VIII-th International School-Conference “Semiconductor Physics Urgent Problems”. 2013, Drohobych, Ukraine.
- VI-th International Conference “Physics of disordered systems”. 2013, Lviv, Ukraine.
- VI Ukrainian Scientific Conference on Semiconductor Physics (UNKFN-6). 2013, Chernivtsi, Ukraine.
- International Scientific Conference "Actual Problems of Solid State Physics". 2013, Minsk, Belarus.
- IX Rzeszowska konferencja młodych fizyków. 2014, Rzeszów, Poland.
- International Conference on Thermoelectricity ICT-2014. 2014, Nashville, TN, USA.

Publications

The Ph.D. thesis is presented in 20 papers, including 5 articles in peer-reviewed SCI/Scopus journals and materials of 19 national and international conferences.

1*. Localized states of electrons in semiconductors: Experimental research methods (review) / D.M. Freik, O.M. Vozniak, **T.O. Parashchuk,** V.M. Chobanyuk, I.V. Gorichok // **Physics and Chemistry of Solid State**. - 2011. - V. 12, № 2. - P. 445-454. (In Ukrainian).

2*. Localized states of electrons in semiconductors: Energy levels of point defects in zinc, cadmium and lead telluride (review) / D.M. Freik, V.M. Chobanyuk, O.M. Vozniak, I.V. Gorichok, **T.O. Parashchuk**, S.D. Bardashevska // **Physics and Chemistry of Solid State.** - 2011. - V. 12, № 4. - P. 545-560. (In Ukrainian).

3*. Own point defects and physicochemical properties of zinc telluride / V.M. Chobanyuk, **T.O. Parashchuk**, G.Ya. Gurgula, N.D. Freik // **Bulletin Of The Shevchenko Scientific Society Number.** - 2011. - V.1, № 9. - P. 144-153. (In Ukrainian).

4*. Ab initio calculation of thermodynamic parameters of phase transformations of zinc telluride / A.G. Grebenyuk, **T.O. Parashchuk**, V.M. Chobanyuk, D.M. Freik // **Physics and Chemistry of Solid State.** - 2012. - V. 13, № 2. - P. 346-350. (In Ukrainian).

5*. Quantum-chemical calculation of thermodynamic parameters of phase transformations in crystals of zinc sulfide / D.M. Freik, **T.O. Parashchuk**, V.M. Chobanyuk // **Bulletin of Vasyl Stefanyk Precarpathian National University. Chemistry series.** - 2012. - Ed. XIV. - P. 103-108. (In Ukrainian).

6*. Thermodynamic parameters and phase transformations of zinc selenide crystals: quantum-chemical calculations / Dmytro Freik, Taras Parashchuk, Nataliya Freik, Anatoliy Grebenyuk // **Chemistry of Metals and Alloys.** - 2012. - V.5, N 3-4. - C.123-128.

7*. Thermodynamic potentials of sphalerite crystals of zinc sulfide / **T.O. Parashchuk**, V.M. Chobanyuk, N.D. Freik, V.M. Boychuk // **Bulletin of Vasyl Stefanyk Precarpathian National University. Chemistry series.**- 2012. - Ed. XVI. - 2012. - P. 79-87. (In Ukrainian).

8*. Thermodynamic properties of zinc selenide crystals: quantum chemical calculation / T.O. Paraschuk, V.M. Chobanyuk, N.D. Freik // **Physics and Chemistry of Solid State.** - 2013. - V. 14, № 2. - P. 346-352. (In Ukrainian).

9*. Thermodynamic parameters of ZnTe sphalerite crystals: quantum chemical calculation (review) / D.M. Freik, **T.O. Parashchuk**, V.M. Chobanyuk // **Physics and Chemistry of Solid State.** - 2013. - V. 14, № 3. - P. 46-53. (In Ukrainian).

10*. Cluster models of ZnTe sphalerite crystals and ab initio calculation of thermodynamic properties (review) / **T.O. Parashchuk,** V.M. Chobanyuk, N.D. Freik, P.M. Fochuk // **Physics and Chemistry of Solid State.** - 2012. - V. 13, № 2. P. 46-58.

11*. Heat capacity and Debye temperature of ZnTe, ZnSe, ZnS crystals / T.O. Parashchuk // **Physics and Chemistry of Solid State.** - 2013. - V. 14. - № 4. - P. 721-725. (In Ukrainian).

12*. Quantum chemical calculations of the polymorphic phase transition temperatures of ZnS, ZnSe, and ZnTe crystal / R. Ahiska, D. Freik, **T. Parashchuk**, I. Gorichok // **Turkish Journal of Physics.** - 2014. - V.38. - P. 125 - 129.

13*. DFT-Calculations of Thermodynamic Parameters of ZnTe, ZnSe, ZnS Crystals / **T.O. Parashchuk,** N.D. Freik, P.M. Fochuk. // **Physics and Materials Chemistry.** - 2014. - V. 2, N. 1. - P. 14-19.

14*. Thermodynamic parameters of sphalerite CdS crystals in the representation of quantum chemistry / D.M. Freik, **T.O. Parashchuk**, B.P. Volochanska, M.A. Rekhteta, R.V. Dinzhos // **Physics and Chemistry of Solid State.** - 2014. - V. 15, № 1. - P. 48-53. (In Ukrainian).

15*. Thermodynamic parameters of CdTe crystals in the cubic phase / D.M. Freik, **T.O. Parashchuk**, B.P. Volochanska // **Journal of Crystal Growth, Elsevier.** - 2014. - V. 402, P. 90-93.

16*. Temperature dependences of thermodynamic parameters of CdTe and CdSe crystals / T.O. Parashchuk // **Physics and Chemistry of Solid State.** - 2014. - V. 15, № 2. - P. 276-281. (In Ukrainian).

17*. Heat capacity and Debye temperature of CdTe, CdSe crystals / D.M. Freik, **T.O. Parashchuk**, B.P. Volochanska // **Physics and Chemistry of Solid State.** - 2014. - V. 15, № 2. - P. 282-287. (In Ukrainian).

18*. Thermodynamic Properties of CdSe Crystals Using First Principles Calculations and Experiment / D.M. Freik, L.I. Nykyruy, **T.O. Parashchuk**, B.P. Volochanska // **International Journal of Engineering and Innovative Technology.** - 2014. - V. 4, N 2. - P. 99-104.

19*. Thermodynamics of the defective subsystem of crystals II-VI in the approximation of the Gibbs potential: modeling, calculation / I.V. Gorichok, **T.O. Parashchuk**, L.I. Nykyruy, D.M. Freik // **Physics and Chemistry of Solid State.** – 2014. – V. 15, № 3. – P. 552-558. (In Ukrainian).

20*. Compensation mechanism of bromine dopants in cadmium telluride single crystals / I. V. Gorichok, P. M. Fochuk, Ye. V. Verzhak, **T. O. Parashchuk**, D. M. Freik, O. E. Panchuk, A. E. Bolotnikov, R. B.James // **Journal of Crystal Growth.** – 2015. – V. 415. – P. 146–151.

The structure and scope of the dissertation. The work consists of an introduction, five chapters, conclusions, and a list of references. The Ph.D. thesis consists of 176 pages, contains 62 figures, 15 tables, and 185 bibliographic references.

CHAPTER I. PHASE DIAGRAMS AND PHYSICAL-CHEMICAL PROPERTIES OF II-VI CRYSTALS

The available literature devoted to the features of P-T-X phase equilibrium diagrams in the systems of Zn - S, Zn - Se, Zn - Te, Cd - S, Cd - Se, Cd – Te was analyzed. The physical-chemical, thermodynamic and electrical properties of II-VI crystals were considered. Particular attention was paid to the crystal structure and possible polymorphic modifications of II-VI semiconductors. The analysis of literature data about the formation energies of point defects and thermodynamic parameters was made, the character of the change of atoms oscillations frequencies in the vicinity of defects was considered [1*-2*].

CHAPTER II. METHODS OF THE INVESTIGATION OF PROPERTIES AND TECHNOLOGY OF THE CRYSTALS PREPARATION

The basic aspects of the Hartry-Fock and Density Functional Theory methods were described. A procedure for the geometrical optimization through finding the minimum potential energy of the cluster model is presented. The difference between the cluster model approach and the supercell approach is discussed. The technology of material synthesis, single crystal growing, and details of the two-temperature annealing for precious control of stochiometry was described. The details of the X-ray diffraction, DSC, and Hall measurements, were shown [4* -19*].

CHAPTER III. THERMODYNAMIC PARAMETERS AND POLYMORPHIC PHASE TRANSITION TEMPERATURES FOR II-VICRYSTALS

Based on the crystallographic parameters and electronic structure of investigated crystals, the cluster models and new methods for the estimation of the thermodynamic properties and defect formation energies of II-VI crystals were proposed. The geometrically optimized clusters were used for the calculations of the temperature-dependent thermodynamic parameters for II-VI crystals. Taking into account the calculated data of heat capacities, the Debye temperatures for ZnX and CdX crystals were estimated. The temperatures of the polymorphic phase transition between the sphalerite and wurtzite modifications of ZnS, ZnSe, ZnTe crystals were estimated using the calculated Gibbs free energies. The results are represented in papers [4*-18*].

CHAPTER IV. CRYSTAL CHEMISTRY AND THERMODYNAMICS OF NONSTOICHIOMETRIC II-VI CRYSTALS

Using the available crystal structure data as well as the calculated thermodynamic parameters, the model describing the most favorable point defects in II-VI crystals was developed. The results of modeling and calculations of the dependence between the conductivity type, charge state, and concentration of point defects and the deviation from the stoichiometric composition are presented for ZnTe and CdTe crystals. Using thermodynamic analysis of crystals with intrinsic defects, the contribution of point defects on the thermodynamic properties of the investigated crystals were estimated [2^{*},3^{*},18^{*}-20^{*}].

Chapter V. THERMODYNAMICS OF EQUILIBRIUM POINT DEFECTS IN NONSTOICHIOMETRIC II-VI CRYSTALS

The formation energies of the most probable types of defects in zinc and cadmium telluride crystals were calculated. Possible positions of energy levels of defects in the band structure of crystals were analyzed. Using the calculated defect formation energies, the temperature and pressure dependences of concentration of point defects at conditions of the two-temperature annealing process were calculated [2^{*}, 3^{*}, 19^{*}, 20^{*}]. The condition for the growing of ZnTe and CdTe crystals with the predetermined conductivity type (n or p) and free charge carrier concentrations is established.

Conclusions

1. Based on the crystallographic parameters and electronic structure of ideal stoichiometric crystals of zinc and cadmium chalcogenides ZnX, CdX (X = S, Se, Te), the cluster models for sphalerite and wurtzite phases were developed, which take into account their electroneutrality, charge stoichiometry, and stability conditions.
2. The formation energy ΔE, formation enthalpy ΔH, Gibbs free energy ΔG, and entropy ΔS of sphalerite phases of ZnS, ZnSe, ZnTe and CdS, CdSe, CdTe ideal stoichiometric crystals were calculated over the entire temperature range.
3. The specific heat capacities of stoichiometric crystals of zinc and cadmium chalcogenides were calculated and compared with the experimental data. The analytical expression for the fittin of the heat capacities as a function of temperature is suggested. A correlation between the values of the coefficient "a" ($c = a + b \cdot 10^{-3} \cdot T - c \cdot 10^{5} \cdot T^{-2}$, where a_i, b_i, c_i are the coefficients, which depends on the structure and type of the material) and ion substitution in the cationic and anionic sublattices were shown.
4. The Debye temperatures Θ_D for ZnX and CdX crystals were determined. It is shown that the value of Θ_D with temperature decreases with increasing ordinal number of chalcogen X in series of ZnS → ZnSe → ZnTe and CdS → CdSe → CdTe.
5. Considering the equality of Gibbs free energies of sphalerite $\Delta G_1(T)$ and wurtzite $\Delta G_2(T)$ phases, the transition temperatures between sphalerite and wurtzite phases were determined, which decreases in the series of ZnS → ZnSe → ZnTe and equal to 1454 K, 1427 K, and 1382 K, respectively for zinc chalcogenides stoichiometric crystals.
6. It is shown that the calculated thermodynamic parameters (ΔE, ΔH, ΔG, ΔS, the molar isochoric $C_{V,}$ and isobaric C_P heat capacities, and Debye temperatures Θ_D) well correlate with changes of bandgap E_g, degree of ionization δ, electronegativity ΔX, bond energy D, and compression module B, in the series of ZnS – ZnSe – ZnTe and CdS – CdSe – CdTe.
7. Based on a combination of crystal-chemical and thermodynamic approaches, a model of a defect subsystem for nonstoichiometric ZnTe and CdTe crystals is proposed. The model considers vacancies in cationic ([V_{Zn}], [V_{Cd}]), anionic [V_{Te}] sublattices, interstitial atoms [Zn_i], [Cd_i], [Te_i]) and antistructural point defects ([Zn_{Te}], [Te_{Zn}], [Cd_{Te}], [Te_{Cd}]) with different charge states. The concentrations of point defects and free charge carriers as a function of the deviation from stoichiometry have been calculated. Their temperature and pressure dependences have been estimated.

8. It is shown, that for the p-type ZnTe crystals, the dominant point defects are doubly charged zinc [V_{Zn}^{2-}] and tellurium [V_{Te}^{2+}] vacancies and interstitial tellurium atoms [Te_i^{2-}], whose concentration increases with increasing deviation from stoichiometry on the side of tellurium. The exceed of zinc causes growth of the interstitial zinc atoms [Zn_i^+]. In the conditions of the annealing of p-type ZnTe crystals in zinc vapors P_{Zn} = (10^3-10^5) Pa and annealing temperatures T = (1000-1250) K, the dominant point defects are double [V_{Zn}^{2-}] and single [V_{Zn}^-] ionized zinc vacancies. The annealing of the crystals in the tellurium pair P_{Te_2} leads to a domination of the [V_{Zn}^-] and [V_{Zn}^0], resulting in the shift of the chemical potential towards the valence band and an increase in the concentration of holes.
9. For n-type CdTe crystals with overstoichiometric Cd, at annealing temperatures T> 870 K, the dominant donor defect is a doubly charged interstitial cadmium atom [Cd_i^{2+}], and at T <870 K - a doubly ionized tellurium vacancy [V_{Te}^{2+}]. With an excess of Te in p-type CdTe, up to temperatures T ≈ 1200 K, a single ionized vacancy of cadmium [V_{Cd}^-] is dominated, and at higher temperatures, a single ionized interstitial tellurium [Te_i^-] would be the most possible defects. This observation is connected with the lowering of the position of the chemical potential below the second energy level of the vacancy of cadmium $(E_V + 0.512\ eV)$ and the second energy level of the interstitial tellurium $(E_V + 0.365\ eB)$.
10. The effect of intrinsic point defects [D] on the values of thermodynamic parameters are determined, and the homogeneity regions of ZnTe and CdTe compounds under conditions of maximum saturation with both metals (Zn, Cd) and tellurium Te, are specified. It was found that for cadmium telluride the maximum deviations from stoichiometry in the direction of cadmium excess is 3.5×10^5 (x_{Cd} - 0.5), and in the direction of tellurium excess is 13.8×10^5 (x_{Te} - 0.5). The one-sidedness shape of the homogeneity region of the zinc telluride phase diagram is confirmed, and the maximum deviation from stoichiometry towards the tellurium excess is determined (13.6×10^5 (x_{Te} - 0.5)).