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THERMAL EXPANSION OF ENVIRONMENTALLY FRIENDLY SEMICONDUCTOR MATERIALS

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Abstract

Multicomponent anisotropic semiconductors I-III-VI2 have ample opportunities for practical application in optoelectronics. The ternary compound CuInSe2 is used as an absorbing layer in high-efficiency solar cells. With a band gap Eg ≈ 1.05 eV, it is characterized by an exceptionally high absorption coefficient (α_L ≥ 105 cm–1). The basis for many photoconverters are heterojunctions created between CdS and CuInSe2, but the metal–CuInSe2 structure can also be a simple and cheap alternative. One of the main problems that arise when compounds I-III-VI2 are used in heterostructures is the negative coefficient of thermal expansion (TEC) αL at low temperatures. The article describes a physical model of thermal expansion of semiconductors I-III-VI2, which can calculate both negative and positive CTE and is in good agreement with the actual values and temperature behavior of the CTE of these materials. The model takes into account the temperature dependences of the band gap $E_G(T)$and the vibrational spectrum of the lattice. All calculations were carried out for the CuInSe2 compound based on the Mathcad 11 and Maple 9 computer mathematics systems. From a physical point of view, the observed negative CTE is explained by the contribution of the optical vibrational mode $G_5^6(T)$,, and the knowledge of the Grüneisen parameter makes it possible to calculate this negative CTE.

Keywords: Lattice, mathematics systems, physical model, semiconductors, thermal expansion, vibrational spectrum

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1. Introduction

Multicomponent anisotropic semiconductors I-III-VI2 have ample opportunities for practical application in optoelectronics (Coates & Meakin, 1988). The ternary compound $CuInSe_2$ is used as an absorbing layer in high-efficiency solar cells. With a band gap Eg ≈ 1.05 eV, it is characterized by an exceptionally high absorption coefficient ($\alpha_L \geq 105$ см–1). The basis for many photoconverters are heterojunctions created between CdS and $CuInSe_2$, but the metal–$CuInSe_2$ structure can also be a simple and cheap alternative (Kindyak et al., 1997; Kovalyuk et al., 2004). Thin-film structures based on chalcopyrite compounds $CuInS_2$ and $CuInTe_2$ also have a high absorption coefficient ($\alpha \approx 10^4 \ldots 10^5$ см$^{-1}$) and an optimal band gap for manufacturing efficient solar cells (Rincón et al., 1997).

Table 01 shows the structures made on the basis of the material as photocells and solar cells.

Of greatest interest among these structures are p-$CuInSe_2$/n-$Zn_{1-x}Cd_xS$ heterojunctions. They are characterized by similar values of the electronic affinity of the components, as a result of which there is no discontinuity of the edge of the conduction band. A small lattice constant mismatch contributes to the efficient separation of photogenerated carriers.

The efficiency of solar cells can be impoved by creating multilayer cascade structures that use photons of various energies of the incident radiation. Thus, the thin-film cascade structure $CuInSe_2$/CdS/CdTe/CdS with an efficiency of 3% at V_{xx} = 1.02 V was made. For this structure, an efficiency of more than 20% is expected, and in the case of replacing the upper CdS layer with $Zn_{1-x}Cd_xS$ solid solutions, its calculated value increases up to 30% [5].

An efficiency close to this can be achieved for $CuInSe_2$/CdS/$AgInSe_2$ structure, an integral cascade solar cell with heterojunctions having a common base of a wider gap semiconductor (Gashin & Simashkevich, 2020).

Table 1. Semiconductor structures

Heterojunctions	**Schottky diodes**	***p-n*–transitions**
p-$CuInS_2$/*n*-CdS	*n*-$ZnSiP_2$/Cu	$CuInS_2$
p-$CuInSe_2$/*n*-CdS	*n*-$ZnSiAs_2$/Cu	$CuInSe_2$
p-$CuInTe_2$/*n*-CdS	*p*-$ZnGeP_2$/In	$CuInTe_2$
p-$CuInSe_2$/*n*-$Zn_{1-x}Cd_xS$	*p*-CuGaSe2/Cu	$CdGeP_2$
p-$CuInSe_2$/*n*-GaSe	*w*-$CuInSe_2$/Au	$CdSiAs_2$
p-$CuInSe_2$/*n*-$Zn_{1-x}Cd_xS$	*n*-CdGeP2/Cu	$ZnSiAs_2$
n-$Zn_{1-x}Cd_xS$/*p*-Cu_2S	*n*-CdSiP2/Cu	$ZnGeP_2$
n-$Zn_{1-x}Cd_xS$/*p*-CdTe	*n*-$CuInTe_2$/Cu	$ZnSiAs_2$

2. Problem Statement

One of the main problems that arise when compounds I-III-VI2 are used in heterostructures is the negative coefficient of thermal expansion (TEC) αL at low temperatures (Derollez et al., 2021; Deus et al., 2023; Neumann et al., 2019).

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3. Research Questions

In most studies on the thermal expansion of I-III-VI2 semiconductors (Kumar & Sastry, 2002; Kistaiah & Murthy, 2020; Kistaiah et al., 2021; Kistaiah et al., 2022; Sleight, 1998; Yelisseyev et al., 2019), there is no information about the physical nature of the negative CTE; only the authors (González et al., 1995; Gonzalez et al., 1996) indicate that the Grüneisen parameter of the vibrational mode is a possible reason for the formation of a negative CTE.

4. Purpose of the Study

The paper presents a physical model of thermal expansion of semiconductors I-III-VI2, allowing for the calculation of both negative and positive CTE. It is in line with the actual values and temperature behavior of the CTE of these materials. The model takes into account the temperature dependences of the band gap E_(G) (T) and the vibrational spectrum of the lattice (Mele, 2022; Nikulin, 2023; Rawel, 2022).

5. Research Methods

Single crystals of p-$CuInSe_2$ were grown using the modified Bridgman-Stockbarger method from initial elements taken in a stoichiometric ratio. The starting materials were the following grades: Se – 0SCh-17-4, Cu – 0SCh-11-4, In – 000. To remove the oxide film, copper was etched with a 5% solution of nitric acid, followed by washing it in running distilled water. Ampoules with initial elements weighed in a stoichiometric ratio were evacuated to a residual pressure of $1.3 \cdot 10^{-3}$ Pa. Rectangular plates with dimensions of 5x5x4 mm^3 were cut from single crystals, which, after grinding and polishing, were etched in a saturated solution of $7K_2Cr_2O_7 + 3H_2SO_4$ in distilled water (Collet-Sabé, 2023; Manakbayeva, 2023; Sheveleva, 2024).

The study of the thermal expansion coefficient (TEC) of p-$CuInSe_2$ single crystals was in line with the experimental in (Kistaiah & Murthy, 2020; Neumann et al., 2019) in a wide temperature range (Figure 01).

All calculations were carried out for the $CuInSe_2$ compound based on the Mathcad 11 and Maple 9 computer mathematics systems.

Ternary semiconductors I-III-VI_2 crystallize in a chalcopyrite structure, space group $1\bar{4}2$. Their crystal structure is characterized by lattice constants a and c, and tetragonal distortion $\Delta=2-c/a$ is observed with the transition to Ga-containing compounds.

Table 02 presents data on the crystal lattice constants a and c, tetragonal distortions, and the Debye temperature θ_D for the compound (Shay & Wernick, 1995) $CuInSe_2$.

The unit cell of anisotropic semiconductors I-III-VI_2 consists of 8 formula units (atoms) and two cubic lattices, with a Brillouin zone four times smaller than that of materials with a sphalerite structure.

Table 2. Crystal lattice constants p-$CuInSe_2$

$a, 10^{-10}$ m	$c, 10^{-10}$ m	c/a	θ_D, K
5.785	11.57	2.00	221.9

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6. Findings

The temperature change in the band gap $E_g(T)$ of semiconductors is due to the sum of the effects of lattice thermal expansion and electron-phonon interaction (Allen & Cardona, 1981).

$$\left(\frac{\partial E_G}{\partial T}\right)_P = \left(\frac{\partial E_G}{\partial T}\right)_V + \left(\frac{\partial E_G}{\partial lnV}\right)_T \cdot \left(\frac{\partial E_G}{\partial T}\right)_P = \left(\frac{\partial E_G}{\partial T}\right)_V + \left(\frac{\partial E_G}{\partial lnV}\right)_P \cdot \alpha, \quad (1)$$

where E – coefficient of thermal expansion, $\left(\frac{\partial E_G(T)}{\partial T}\right)_V$ – contribution of the electron-phonon interaction, $\left(\frac{\partial E_G(T)}{\partial lnV}\right)_P \cdot \alpha$ – thermal expansion contribution.

Based on (1), the following expression which describes ΔE_G (T) (Varshni, 1967) was obtained:

$$\Delta E_G\,(T) = \Delta E_G\,(0)\text{-}E_G\,(T) = \Delta E_G\,(T) = \frac{AT^2}{(T+\beta)}, \quad (2)$$

where $= \Delta E_G\,(0)$ is the band gap at 0 K, β is the constant (approximately equal to the Debye temperature θ_D , A is the empirical constant.

The temperature dependence of the band gap EG is also determined by the maximum frequency of acoustic and optical oscillations. Based on the above, the following expression was obtained for E_G (T) (Manoogian & Leclerc, 1979):

$$E_G\,(T) = E_D^0(1+ AT^X) + B[\theta_1 + \cosh(\frac{\theta_1}{2T}) + \theta_2 \cosh(\frac{\theta_2}{2T})], \quad (3)$$

where E_D^0, A, X, B, θ_1, θ_2 are parameters. In this expression, the first term is responsible for the contribution of thermal expansion, the second term – for the contribution of two modes, the constants θ_1,и θ_2 are characteristic temperatures of acoustic and optical oscillation modes, respectively.

Using the condition that ΔE(G) (0)=0, 0, we obtain the temperature dependence for ΔE(G) (T) (Manoogian & Woolley, 1984):

$$\Delta E_G\,(T) = E_G\,(0) - E_G\,(T) = UT^S + V\theta_E\left[\cosh(\frac{\theta_E}{2T}) - 1\right], \quad (4)$$

where $E_G\,(0)$ the band gap at 0 K, a U, S, V, θ_E are temperature independent parameters (Marín et al., 1997). The first component is the contribution of thermal expansion, and the second, which describes the contribution of the electron-phonon interaction, is proportional to the energy of the system of noninteracting harmonic oscillators

$$\langle E\rangle = h\omega\left\{\frac{1}{2} + \left(e^{h\omega/2k_BT} - 1\right)^{-1}\right\} = \left(\frac{h\omega}{2}\right)\cosh\left(\frac{h\omega}{2k_BT}\right) = \left(\frac{k_B\theta_E}{2}\right)\cosh\left(\frac{\theta_E}{2T}\right), \quad (5)$$

where $\theta_E = \frac{h\omega_{max}}{k_B}$ – Einstein temperature.

On the other hand, the contribution of thermal expansion to the temperature dependence

$E_G\,(T)$ is expressed in terms of the baric coefficient of change in the bandgap width (Gonzalez & Rincón, 1990), $\frac{\partial E_G(P)}{\partial P}$ compressibility K_T (Neumann, 2023) and linear coefficient of thermal expansion $\alpha_L = \frac{\alpha_{a+}\alpha_c}{3}$ (Quintero et al., 1991):

$$(\frac{\partial E_G(P)}{\partial P}) = \frac{\alpha_L}{K_T}\,\frac{\partial E_G(P)}{\partial P} \quad (6)$$

From here we obtain the expression for the CTE of ABC2 compounds:

$$\alpha_L = -\frac{\frac{\partial E_G(T)}{\partial T}\cdot K_T}{3\frac{\partial E_G(P)}{\partial P}}. \quad (7)$$

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The temperature dependence of the compressibility KT in formula (7) is determined on the basis of the ABC2 phonon spectrum. The vibrational spectrum of the ABC2 grating consists of 24 modes – 21 optical ones and 3 acoustic ones. The symmetry at the G, X, W points of the ZnS structure is transformed into G-points of compounds I-III-VI_2 (Gonzalez, Fernandez et al., 1996).

Acoustic and optical vibration modes have the form.

$$G_{ac} = G_4 + G_5 \quad (8)$$

$$G_{opt} = G_1(R) + 2G_2 + 3G_3(R) + 3G_4(IR, R) + 6G_5(IR, R), \quad (9)$$

where R and IR are the Raman and infrared modes, respectively.

Use the scheme of correspondence of vibrational modes of gratings of sphalerite and chalcopyrite structures, taken from (Gonzalez et al., 1996).

When calculating KT in formula (7), the value of the Grüneisen parameter γi of the optical mode$G(T)$ (T) was used; for compounds I-III-VI_2, it is determined from the point G15 of the central zone (TO) of the ZnS structure.

For γi, the following expression is true (Gonzalez, Quintero, et al., 1992)

$$\gamma_i = \frac{\partial \ln \omega_i}{\partial \ln V} = \frac{1}{K_T \cdot \omega_i} \frac{\partial \omega_i}{\partial P}, \quad (10)$$

the compressibility KT in formula (7) has the form:

$$K_T = \frac{1}{\gamma_i} \omega_i \frac{\partial \omega_i}{\partial P}, \quad (11)$$

where ω_i is the frequency corresponding to the mode$G_5^6(T)$ (Koschel & Bettini, 1975; Tanino et al., 1992);

$\frac{\partial \omega_i}{\partial P}$ – pressure coefficient ω_i (Gonzalez, Fernandez, et al., 1992).

If $E_G(0)$ is unknown, it can be extrapolated using data $E_G(T)$ (Jaffe & Zunger, 2024).

The results of the CTE simulation for anisotropic I-III-VI_2 semiconductors demonstrate a qualitative agreement with the data of experimental studies (Kistaiah & Murthy, 2020; Neumann et al., 2019) in a wide temperature range (Figure 1). This demonstrates that this physical model based on the temperature dependence of the band gap $E_G(T)$ and the vibrational spectrum of the lattice are acceptable for calculating the thermal expansion anomalies of compounds I-III-VI_2.

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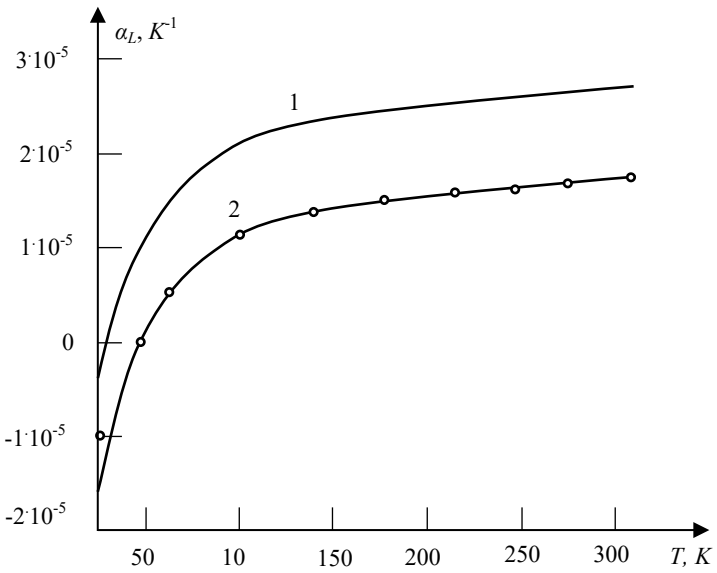

Figure 1. Calculated and experimental temperature dependences of the thermal expansion coefficient of $CuInSe_2$. 1 – calculated; 2 – experimental

7. Conclusion

From a physical point of view, the observed negative CTE is explained by the contribution of the optical vibrational mode $G_5^6(T)$,, and the knowledge of the Grüneisen parameter makes it possible to calculate this negative CTE.

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