Anomalous character of temperature dependences of some AgInSe₂ parameters AgInSe₂

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Abstract. Abstract – Based on the experimental and X-ray studies of the absorption spectra and the temperature dependence of the crystal lattice parameters of AgInSe₂ single crystals and the coefficients of thermal expansion along the corresponding crystallographic directions were calculated. It was found that the thermal expansion of AgInSe₂ crystals along the a and c axes changes its sign at a temperature of 142.31 and 135.14 K, respectively. The anomalous nature of the band gap width AgInSe₂ was established.

1. Introduction

The AgInSe₂ compound, which belongs to new classes of semiconductors type A\textsuperscript{III}B\textsuperscript{III}C\textsuperscript{VI} and A'B\textsuperscript{III}C\textsuperscript{VI} is of scientific interest for modern optoelectronics, is currently being intensively studied [1–8, 11–16]. The AgInSe₂ compound crystallizes into a chalcopyrite structure in which two types of cationic sublattices form an ordered sublattice. A unit cell containing 8 atoms (2Cu, 2In, 4Se) is characterized by the presence of a volume center and an axis ratio close to 2 [6].

The aim of this work is to study the temperature dependence of the thermal expansion coefficients and absorption spectra of AgInSe₂ single crystals. Investigations of the temperature dependence of lattice parameters up to low temperatures are of interest since they are closely related to lattice dynamics and therefore can lead to a deeper understanding of these properties in A'B\textsuperscript{III}C\textsuperscript{VI} crystals.

2. Methods and materials

The studied AgInSe₂ crystals were grown by the Bridgman-Stockbarger method. The starting materials were high purity elements: Ag-ultra high purity-4-11-4; In-000; Se-ultra high purity-17-4. The oxide film and other contaminants from the silver surface were removed by etching in a 5 % HNO₃ solution for 8–10 minutes, followed by washing in running distilled water. Ampoules for synthesis, made of thick-walled quartz with an inner diameter of 25 mm were first etched with a 40 % HF solution for 5 minutes, washed intensively with distilled water, and then annealed in a vacuum.
furnace at a temperature of 1300 K. To prevent contact of the molten substances with the quartz surface, the inner side of the ampoules was covered with a layer of graphite. After preliminary orientation on the RKOP installation in the (200) and (112) directions, plane-parallel plastics were cut off, which were subjected to grinding and polishing. The thermal expansion of AgInSe2 crystals was studied on a standard DRON-3 X-ray apparatus using a low-temperature attachment URNT-180. The rotation speed of the Dron-3 detector was 0.25 deg/min. An angular mark on the tape of the recording potentiometer was carried out every 0.1°. To improve the accuracy, the test sample was irradiated with characteristic radiation from a copper target, as a result of which the reflexes became sharper. Cooling of the sample was carried out by a low-temperature attachment URNT-180, working by the method of blowing.

The study of temperature dependences of the band gap width of AgInSe2 crystals was carried out on the SDL-2 installation. The error in determining the band gap width values from the absorption spectra was not more than 0.1 eV. The research samples were n-type AgInSe2 single-crystal plates with carrier concentrations of ~ 10^{18} cm^{-3} and mobilities of ~ 40–70 cm²/V·s, respectively, at 300 K. The surfaces of the samples were previously subjected to grinding, polishing, and then chemical etching.

3. Results
The chalcopyrite lattice has axial symmetry, therefore, the unit cell parameters a and c change independently with temperature.

To determine the temperature dependence of parameter a, the change in the interplane distance was measured d_{200}, since a = 2d_{200}.

The dependence c(T) was determined by the change in temperature d_{112}, where the lattice parameter c was found by the formula

\[ c = \frac{2ad_{112}}{a^2 - 2d_{112}^2} \]

The measured temperature dependences of the interplane distances d_{200}(T) and d_{112}(T) are presented in Fig. 1 a, b.

The temperature dependences a(T) and c(T), defined from d_{200}(T) and d_{112}(T), are shown in Fig. 2 a, b.

Dependences a(T) and c(T) were approximated by relations:

\[
\begin{align*}
    a(T) &= A_i + B_i + \frac{C_i}{T} \\
    c(T) &= A_i + B_i \frac{C_i}{T}
\end{align*}
\]

on an electronic computing machine in the entire temperature range, as a result of which the constants A_i, B_i, and C_i were determined, which amounted to 5.97 Å; 3.27·10^{-4} Å/K; 6.83 Å·K and 11.53 Å; 4.43·10^{-4} Å/K; 7.89 Å·K, respectively.

The least squares in the definition of a and c experimentally and according to the above formula are:

\[ a_{\text{theor}} - a_{\text{exp}} = \sum (a_{\text{theor}} - a_{\text{exp}})^2 = 1.70 \cdot 10^{-5}; \]

\[ c_{\text{theor}} - c_{\text{exp}} = \sum (c_{\text{theor}} - c_{\text{exp}})^2 = 3.63 \cdot 10^{-4}. \]
The standard deviation \( \sigma = \frac{f}{\sqrt{N-1}} \) was also \( \sigma^a = 8,99 \cdot 10^{-3} \) and \( \sigma^c = 4,15 \cdot 10^{-3} \). From the dependences \( a(T) \) and \( c(T) \) it follows that at a certain temperature value, the thermal expansion of the lattice changes sign.

It can be seen that at a certain temperature value, the thermal expansion changes its sign. From the dependencies \( a(T) \) and \( c(T) \) we counted the values of the coefficients of thermal expansion along the corresponding crystallographic directions by the formula

\[
\alpha_a = \frac{1}{a_o} \frac{da_o}{dT}, \quad \alpha_c = \frac{1}{c_o} \frac{dc_o}{dT}.
\]

Fig. 3 represents the temperature dependences of the thermal expansion coefficients of AgInSe2 crystals. The anisotropy of thermal expansion in these crystals is weakly expressed; however, in the low temperature range \( T < 120 \text{ K} \), the ratio \( \frac{\alpha_c}{\alpha_a} \) increases with decreasing temperature and amounts to 1.91 and 1.41 at 80 and 300 K, respectively.

![Figure 1. Temperature dependences of parameters of elementary cells of AgInSe2 single crystal](image1)

![Figure 2. Temperature dependences \( d_{200}, d_{112} \) of interplane distances](image2)

The thermal expansion of AgInSe2 crystals along the axes \( a \) and \( c \) changes its sign at a temperature of 142.31 and 135.14 K, respectively.

The values of the volume coefficient of thermal expansion calculated by the formula \( \alpha_v = \left(2\alpha_a + \alpha_c\right) \) showed that \( \alpha_v \) changes its sign at a temperature of \( T_o = 139.44 \text{ K} \).

The value of the characteristic temperature of the sign \( \alpha_v \) change is very close in value to the Debye temperature \( \theta = 138 \text{ K} \) for AgInSe2 crystals.
Comparing the obtained results with our results on the study of the temperature dependence $E_g(T)$ on the absorption spectra [4, 6], we conclude that the volume thermal expansion in AgInSe2 to the change $E_g(T)$ seems to dominate in the entire studied temperature range. However, the ratio between the relative change in volume $\frac{\Delta V}{V}$ and $\frac{\Delta E_g}{E_g}$ in the temperature ranges $90 < T < 120 \text{ K}$ and $140 < T < 300 \text{ K}$ is very different, which suggests the existence of a competing mechanism that gives a positive change $\Delta E_g$.

At $T > 120 \text{ K}$, we observed [4, 6] a clear anomaly in behavior $\Delta E_g$ in the sense that some "positive" mechanism almost completely compensates for the narrowing caused by the volume effect.

Usually, the thermal expansion of solids is described using the Grüneisen parameters.

In the case of AgInSe2, which crystallizes in a uniaxial chalcopyrite structure, it is necessary to introduce two independent Grüneisen parameters $\gamma_a$ and $\gamma_c$, which are related to the thermal expansion coefficients $(\alpha_a, \alpha_c)$ by the relations:

$$\gamma_a = \frac{V_m}{C_p} \left[ (C_{11}^S + C_{12}^S)\alpha_a + C_{13}^S \alpha_c \right]$$

$$\gamma_c = \frac{V_m}{C_p} \left[ 2C_{13}^S \alpha_a + C_{33}^S \alpha_c \right],$$

where $V_m$ – the molar volume, $C_p$ – the specific molar heat capacity at constant pressure, $C_{ij}^S$ – the adiabatic stiffness constant. Currently, there is no information about the experimental values $C_{ij}^S$ and $C_p(T)$ in AgInSe in the temperature range of interest to us and this creates difficulties in conducting the quantitative analysis of temperature dependences $\gamma_a$ and $\gamma_c$.
However, not excluding other explanations, it is possible to assume the existence of low-energy vibrations of the lattice modes with a negative mode of the Grüneisen parameters in AgInSe2. Unfortunately, information about the low-energy branches of the phonon spectrum is not sufficient.

The accordance between the temperature dependences of the band gap width and the lattice parameters should be noted. The anomalous nature of dependence $E_g(T)$ is also inherent in dependence $a(T)$ and $c(T)$. This experimental fact testifies to the prevailing contribution of the volume effect to the temperature dependence of the band gap width of single crystals in AgInSe2.

As it was mentioned above, according to existing concepts, the temperature dependence $E_g(T)$ of semiconductors is due to thermal expansion of the lattice (volume effect) and electron-phonon interaction. The change in the sign of the temperature coefficient $\left( \frac{\partial E_g}{\partial T} \right)_p$ indicates the competition of the two effects. It is believed that the thermal expansion causes a positive temperature coefficient $E_g$, and the electron–phonon interaction – its negative sign. It is natural to assume that in AgInSe2 the contribution of thermal expansion predominates below 120 K, and the electron-phonon interaction – above 120 K.

It is known that the isochoric change can be caused by a nonlinear dependence $\left( \delta E_g \right)_V$ on interatomic distances. Generalizing the obtained result to the case of an anisotropic crystal, we write

$$\langle \delta E_g \rangle = \sum_{\mu} \left( \frac{\delta E_g}{\partial V} \right)_{\mu},$$

$$\left( \delta E_g \right)_{\mu} = \Xi_1^{(1)} \mu + \frac{1}{V} \sum_{f,\lambda} e_{f,\lambda} \chi_{\mu} \Xi_2^{(2)} \mu \lambda$$

where $\Delta_{\mu}$ – the expansion and compressibility $\chi_{\mu}$ corresponding to the main direction $\mu$.

For the temperature derivative of (1) we have

$$\left( \frac{\partial E_g}{\partial T} \right)_p = \left( \frac{\partial E_g}{\partial T} \right)_V + \alpha_V \left( \frac{\partial E_g}{\partial T} \right)_T;$$

$$\sum_{\mu} \alpha_{\mu} \Xi_1^{(1)} = \alpha_V \left( \frac{\partial E_g}{\partial \Delta_V} \right)_T$$

$$\left( \frac{\partial E_g}{\partial T} \right)_V = \frac{1}{V} \sum_{f,\lambda} \chi_{\mu} C_{f,\lambda} \Xi_2^{(2)} \mu \lambda \lambda$$

(2)

Here $\alpha_V$ – the temperature coefficient of volumetric expansion, $C_{f,\lambda} = \partial E_{f,\lambda} / \partial T$ – the heat capacity of the lattice oscillator ($f$ – wave vector, $\lambda$ – polarization).

Let us consider the contribution of longitudinal waves, at which

$$\langle \delta E_g \rangle = \sum_{\mu} \left( \left( \Delta_{\mu} \Xi_1^{(1)} \right) + \left. \left( \Delta_{\mu} \Xi_2^{(2)} \right) \right) \right; \sum_{\mu} \alpha_{\mu} \equiv \alpha_V$$

Using averaged parameters $E_1$ and $E_2$ defined by equalities,

$$\left( \frac{\partial \Delta}{\partial T} \right)_p \Xi_1^{(1)} + \left( \frac{\partial \Delta}{\partial T} \right)_c \Xi_2^{(1)} \equiv E_1 \Delta_V; \sum_{\mu} \chi_{\mu} \Xi_2^{(2)}$$

5
for the high \((T > \theta)\) range \(\theta = 138 \text{K}\) – temperature range – Debye temperature \([195,196]\) we get

\[
\left(\frac{\partial E_g}{\partial T}\right)_{\rho} = \left(E_1 + \frac{E_2}{3\gamma_G}\right)\alpha_v; \quad \alpha_v = \gamma_G \frac{K}{V} 3Nk_B
\]

where \(k_B\) – the Boltzmann constant, -the high-temperature value of the Grüneisen coefficient \((\gamma_G = 2)\).

Due to the lack of experimental data on \(E_I\), we assume that the change \(\delta E_g\) in the range \(T \leq 120\ \text{K}\) is caused only by a change in the lattice parameters \(a\) and \(c\), i.e.

\[
\left(\delta E_g\right)_{T<100} \approx E_I \Delta_v(T); \quad \Delta_v(T) = \frac{2}{a} \frac{\partial a}{\partial T} + \frac{\partial c}{\partial T}.
\]

from the course of the curves describing dependencies \(\delta E_g, a(T)\) and \(c(T)\) of the range \(T \leq 100\ \text{K}\) follows \(\delta E_g \approx 25\ \text{meV}; \quad \frac{\partial a}{\partial T} \approx -0.0033; \quad \frac{\partial c}{\partial T} \approx -0.0005;\)

For the parameter \(E_I\), this gives

\[
E_I = -(0.025/0.0038) = -6.6\ \text{eV}
\]

From high temperature dependences follows \(\alpha_v = 1.15 \cdot 10^{-4}\ \text{K}^{-1}\) and \(\left(\frac{\partial E_g}{\partial T}\right)_\rho = 1.5 \cdot 10^{-4}\ \text{eV/K}\)

Substituting these values gives \(\epsilon_2 \approx 32\ \text{eV}\). More accurate estimates require experimental data on pressure coefficients.

In addition, it can be seen from (1) that the influence of transverse waves of the lattice is not excluded.

At this stage, it follows from the above analysis that the isochoric part of the change \(\left(\delta E_g\right)_V\) in AgInSe2 single crystals has a positive sign, that is \(\left(\frac{\partial E_g}{\partial T}\right)_V > 0\), and at high temperatures \(\left(\delta E_g\right)_V\), apparently compensates for the negative contribution from the thermal expansion of the lattice.

We have suggested that at low temperatures the contribution of the volume effect (thermal expansion of the lattice) to the temperature dependence \(E_g\) is predominant.

The thermal expansion of the lattice at low temperatures is closely related to the dynamics of the lattice. The temperature dependences of the change in the band gap width of AgInSe2 are presented in Fig. 4.

An analysis of the temperature dependence of the change in the AgInSe2 band gap width shows that the band gap width increases with temperature in the range of \((80 \div 120)\ \text{K}\) (Fig. 4 and the temperature coefficient is \((4.0 \div 6.2) \cdot 10^{-4}\ \text{eV/K}\).

In the temperature range \((120 \div 300)\ \text{K}\), the width of the band gap decreases with increasing temperature and the temperature coefficient is \(-1.2 \div 1.9) \cdot 10^{-4}\ \text{eV/K}\.

The temperature dependence of the band gap width in semiconductors is caused by the thermal expansion of the lattice and the electron-phonon interaction.

Thermal expansion causes a positive temperature coefficient, and electron-phonon interaction – a negative sign [5].

In the studied temperature range, the role of each of the two mechanisms described above changes, which causes this behavior of temperature dependences of the band gap width in AgInSe2 crystals. In
particular, we believe that in AgInSe2 the thermal expansion prevails below 120 K and the electron-phonon interaction – above 120 K. Unfortunately, at the moment there are no data on low-energy branches of the phonon spectrum.

This does not allow for a detailed discussion of the role of electron-phonon interaction in the temperature dependences of the AgInSe2 width. This should be the subject of further research.

4. Conclusion
Based on the analysis of the temperature dependences of the absorption spectra and thermal expansion coefficients of AgInSe2 crystals, the following parameters are determined:

1) temperature dependences of band gap width and crystal lattice parameters;
2) It is shown that the experimentally discovered anomalous temperature dependence of the band gap width has a flat maximum at $T = 120$ K, which is a consequence of the anomalous behavior of the temperature dependences of the lattice parameters at this temperature;
3) having carried out a quantitative analysis on the basis of these dependencies and the corresponding theory, it was revealed that the isochoric part of the change $\langle \delta E_g \rangle_V$ in this case has a positive sign, that is,

$$\left( \frac{\partial \delta E}{\partial T} \right)_V > 0.$$

At high temperatures $\langle \delta E_g \rangle_V$ it is not decisive, but only partially compensates for the dominant negative contribution from thermal expansion.

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\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure4.png}
\caption{The temperature dependence of the band gap width in AgInSe2 single crystals}
\end{figure}
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