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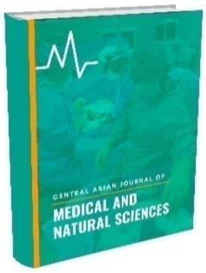

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Temperature Dependence of the Parameters of the Crystalline Lattice of A Single Crystal Tlgase

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Abstract: Objective. The aim is to study the temperature dependence of the crystal lattice parameters of a TlGaSe2 single crystal and, using these methods, to establish the homogeneity of a TlGaSe2 single crystal suitable for investigating electrophysical, photoelectric, optical, and other properties.

Methods. We studied the temperature dependence of the crystal lattice parameters in TlGaSe2 by X-ray diffraction. The measuring equipment was sensitive to a change in interplanar distance by □0.001 Å, which ensured a high accuracy of the results obtained. The calculations of the lattice parameters were carried out on a computer.

Results. When studying the temperature dependence of the crystal lattice parameters of TlGaSe2, we expected, strong anomalies were found in the temperature dependence a (T). In the entire investigated temperature range (90 - 300 K) $\Delta c / c > 0$. A sharp decrease in the parameter a with increasing temperature is observed at 105 K, and at ~ 120 K, the sign of Δa / a changes to positive (in a narrow temperature range) ...

Conclusion. На основании порошковых дифрактограмм, точечных электронограмм и рентгенограмм качания вокруг соответствующих кристаллографических осей установлена реальная пространственная группа и уточнены величины параметров решетки этих кристаллов.

Key words: parameters of the crystal lattice, by x-ray diffraction, sensitive, inter plane distance, spatial group.

Introduction: Crystals of $TlGaSe_2$ and solid solutions based on them are one of the promising little-studied semiconductor materials of the type $A^{III}B^{III}C_2^{VI}$. $TlGaSe_2$ are layered - chain semiconductor compounds characterized by a weak wander-waltz bond between layers and a covalent bond inside each layer $TlGaSe_2$. The specific features of the chemical bond of such compounds determine the inertness of the layer surface with respect to adsorption. The literature contains a large amount of data on the space symmetry group and unit cell parameters of TlGaSe2 due to the presence of various modifications of this crystal.

The crystal structure of $TlGaSe_2$ has been studied extensively by many authors. Below is a brief analysis of these studies. Table 1 shows some results of various authors on the crystal structure of $TlGaSe_2$. The first attempt to determine the structure of $TlGaSe_2$ was made in [1], the authors of which assumed that the unit cell of this compound has tetragonal symmetry with space groups of symmetries C^2_4 or C^4_4. Their later works [2], as well as those of other authors [3, 4], showed that $TlGaSe_2$ has a lower-symmetry monoclinic unit cell with the space group C^2_2 or C^2_{2h}. However, C22h was considered more probable due to the fact that in the infrared reflection and Raman spectra of $TlGaSe_2$ [5, 4, 6], different and non-coincident lines were found, which, in accordance with the alternative exclusion rule [7], contradicts the C^2_2 symmetry. In addition, the absence of the piezoelectric effect, according to the data of [4], was associated with the presence of a center of symmetry in $TlGaSe_2$.

Despite the fact that the primitive cell of this crystal contains 64 atoms, a small number of lines (24 maxima [8]) were observed in the Raman spectra of $TlGaSe_2$. In [9, 10], attempts were made to eliminate this contradiction by choosing the appropriate unit cell and space symmetry group for $TlGaSe_2$. One should be critical of the conclusions about the presence of symmetry centers in $TlGaSe_2$ crystals, made on the basis of an analysis of their vibrational spectra. Note that the structural imperfection of $TlGaSe_2$ crystals, namely the presence of twins, was the reason for the incorrect conclusion about the tetragonal symmetry of this crystal.

A complete deciphering of the $TlGaSe_2$ structure and determination of the coordinates of atoms in the unit cell were carried out by Müller and Hahn in [13]. Crystals suitable for structure

Table 1. Crystallographic data for $TlGaSe_2$ (literature review)

№п\п	Syngonia	Space symmetry group	Lattice parameters	Note	Literature
1	Tetragonal	14⁄mcm	**a** = 7,62 Å; **c** = 30,50 Å	-	[1]
2	Monoclinic	$P2_1/m$	**a** ≈ **b** =7,60Å; **c**=31,36 Å; β = 90,33°	-	[3]
3	Monoclinic	C^4_S или C^2_{2h}	**a**≈**b**=10,77Å; **c**=15,62 Å, β = 100°	-	[2]
4	Tetragonal	14⁄mcm	**a**=7,62; **c**=30,50Å	film	[11]
5	Tetragonal	14⁄mcm	**a**=8,053; **c**=6,417Å	High press. phase	[12]
6	Monoclinic	C^4_S	**a**=10,772 Å; **b**=10,771 Å **c**=15,636Å, β=100,06°	-	[13]

Determination were obtained by vacuum sublimation. The main measurements were carried out in a four-circle “Syntex $P2_1$” diffractometer (M_o K_α -radiation).

According to [13], $TlGaSe_2$ is a monoclinic crystal with the space group C_c (according to Shepflies symbolism C^4_S) and unit cell parameters, a = 10.772 (3), b = 10.771 (5), c = 15.636 (8) Å, β=100,06(3)°. Analysis of the coordinates of atoms located in a separate layer showed that they are connected by a mirror-rotary axis of the fourth order (S_4). The $TlGaSe_2$ layer consists of seven atomic planes that are occupied by atoms in the SeTlGaSeGaTlSe sequence. The $TlGaSe_2$ unit cell, consisting of two layers, has a symmetry lower than that of one layer. A unit cell containing 64 atoms (z = 16) is formed by applying translation to (**a**+**b**)/2 to the coordinates of 16 of them and reflection in a slip plane perpendicular to the plane of the layers.

It was found that the $TlGaSe_2$ crystal is an indirect-gap semiconductor, in which the energies of direct and indirect transitions are approximately the same.

There is no detailed interpretation of the crystal structure of $TlGaS_2$ in the literature, but the available data [14, 15] suggest that, like $TlGaS_2$, this semiconductor compound has a monoclinic structure with parameters [16] a = b = 10.40 Å, c = 15 Å, β = 100°, space group $C_s{}^4$ or $C_{2h}{}^2$.

Thus, it is seen that the layered semiconductor compounds $TlGaSe_2$ and $TlGaS_2$ are isostructural crystals with rather similar unit cell parameters.

Relevance and research methods: The study of the relationships between the properties, composition and structure of multicomponent semiconductors today remains one of the most important tasks of modern solid state physics. It is the knowledge of such regularities that makes it possible to develop the scientific foundations for the search and creation of new, more efficient semiconductor materials with predetermined physical properties and, thereby, satisfy the increasing requirements of modern quantum physics and microelectronics. The creation of new semiconductor materials is of particular value if it is possible to obtain them in the form of perfect large single crystals. Among the large number of new semiconductor materials, semiconductors with a layered crystal structure occupy a special place. Interest in such semiconductors, both from a scientific and a practical point of view, is increasing every year. Therefore, the expansion of the class of layered semiconductors, the preparation of their perfect single crystals and the subsequent study of their complex of physical properties seem to be quite urgent problems in the field of modern physics of semiconductors.

The search for semiconductor materials with predetermined properties also requires studying the effect of various impurities on the physical parameters of promising compounds. For this reason, the doping of $TlGaS_2$ (Se_2) compounds, as well as the preparation of solid solutions based on them, is of great practical importance in terms of the possibility of controlling the physical parameters in a fairly wide range.

In this regard, the purpose of this study is to study the temperature dependence of the crystal lattice parameters of a $TlGaSe_2$ single crystal and, using these methods, to establish the homogeneity of a $TlGaSe_2$ single crystal suitable for studying electrophysical, photoelectric, optical, and other properties.

We studied the temperature dependence of the crystal lattice parameters in $TlGaSe_2$ by X-ray diffraction. The measuring equipment was sensitive to a change in the interplanar distance by ±0,001Å, which ensured a high accuracy of the results obtained. As is known, X-ray methods for studying the phase transition by measuring the temperature dependence of the lattice parameters (or thermal expansion) have a number of advantages [18] over dilatometric methods: a) for measurements, it is sufficient to have a small amount of the substance under study; b) the influence of cracks, pores, intercrystalline layers, etc. is excluded. thermal expansion; c) it is easier to study the anisotropy of thermal expansion, which can be carried out on polycrystalline samples.

The three most intense reflections with Bragg reflection angles of 23.15º were selected as calibration reflections; 23.50º and 31.10º. The intensity of the corresponding reflections at room temperature was 8600, 1200, and 3080 pulse / sec. The measurements were carried out with an interval of 5 K. The calculations of the lattice parameters were carried out on a computer.

Research results and discussion: Although structural phase transitions (PTs) were discovered and described as a result of studying macroscopic properties (heat capacity, thermal expansion, etc.), their understanding requires a more detailed study of microscopic properties. Structural phase transitions arise when the crystal structure of a substance changes. Therefore, naturally, the first step in solving the problem should be structural studies in the vicinity of PT temperatures. As already mentioned, the thermal expansion of $TlGaSe_2$ was studied in [17] by the interferometric method. The thermal expansion curve in the direction perpendicular to the layers ($\alpha_\perp$) has three anomalies at temperatures of 120 K, 111 K, and 102 K. In the entire investigated temperature range (50 - 200 K) $\alpha_\perp > 0$, in the range 50 - 140 K $\alpha_{\parallel} < 0$, and at T > 140 K $\alpha_{\parallel} > 0$.

In fig. 1 shows the temperature dependence of the crystal lattice parameters of $TlGaSe_2$. As we expected, strong anomalies were found in the temperature dependence **a** (T). In the entire investigated temperature range (90 - 300 K) Δ**c** / **c** > 0, which is consistent with the results of [17]. The **a** (T) curve is divided into three characteristic sections, for each of which Δ**a** / **a** < 0. A sharp decrease in the parameter **a** with increasing temperature is observed at 105 K, and at ~ 120 K the sign of Δ**a** / **a** changes to a positive one (in a narrow temperature range).

Plots with $\alpha_{\parallel}$ <0, i.e. where the layers are compressed with increasing temperature, are a consequence of strong expansion in the direction perpendicular to the layers. This was also observed in C, BN, $A^{III}B^{VI}$ layered crystals and was explained [19] by the dominant contribution of transverse acoustic waves with a displacement vector directed perpendicular to the plane of the layers.

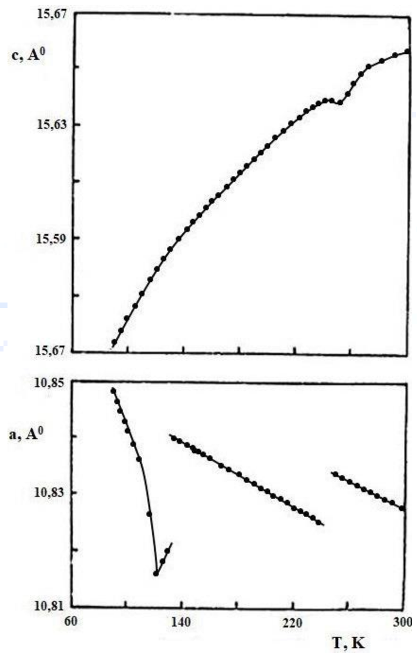

Figure1. Temperature dependence of the lattice parameters of $TlGaSe_2$ crystals

Noteworthy is the strong **a** (T) anomaly at 245 K, which, in contrast to the two previous ones (105 and 120 K), is also well manifested in the **c** (T) dependence. In previous studies of the phase transition in $TlGaSe_2$ [17, 20], the anomaly was not recorded in the mentioned temperature range. From this point of view, it was of considerable interest to study the temperature behavior of the intensity of the (004). Bragg reflection. Beginning with a temperature of 105 K, the intensity of the reflection increases (Fig. 2), reaches a maximum at 120 K, and drops sharply.

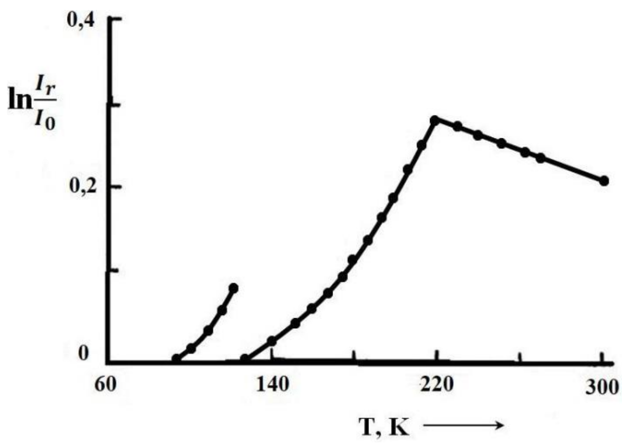

Figure 2. Temperature dependence of the intensity of the (004) reflection in $TlGaSe_2$

In the range 130 - 240 K, a uniform increase in intensity is observed, which then begins to decrease monotonically at T > 240 K. A change in the temperature behavior of ln (I_T / I_0) (I_0 and I_T are the intensities of the reflection at 90 K and TC, respectively) in the vicinity of 240 K indicates a phase transition in this region. An indication of the existence of a PT in $TlGaSe_2$ at T = 246 K is contained in [21], where the long-wavelength tail of the absorption edge of these crystals was analyzed. In the same work, proceeding from the anomalies in the temperature dependence of the heat capacity of $TlGaSe_2$, it is concluded that there is a phase transition also at T = 101 K.

It should be noted that when studying the temperature dependence of the specific heat C_p (T), the authors of [22] found features at 108.9 K and 118.4 K. At these temperatures, the C_p (T) curve showed finite jumps in the heat capacity (of the order of 10.5 % at T = 108.9 K and more than 3% at T = 118.4 K from its value near the jump).

However, no noticeable deviations of C_p (T) from the regular contribution at 240 K were recorded in [22]. Revealing the thermal effect during diffuse phase transitions strongly depends on the heating rate [23]. Therefore, in crystals of the $TlGaSe_2$ type, where there is a change with a small thermal effect, several series of measurements should be carried out, the average values of which are then presented in a graphical form, as was done, for example, for ZnP_2 in [24 - 26].

According to the above experimental results, the contributions of thermal expansion (TP) to the change in the band gap with temperature Eg (T) in $TlGaSe_2$ crystals are estimated. It is shown that these contributions lead to a decrease in Eg (T) in $TlGaSe_2$, a low-temperature structural-phase transition.

Conclusion: The results of a detailed X-ray study of the temperature behavior of the lattice parameters and the profiles of Bragg reflections in the range 90 - 300 K, as well as measurements of the electrical conductivity along the corresponding crystallographic directions in the range of 10 - 300 K.

On the basis of powder diffraction patterns, point electron diffraction patterns and rocking X-ray patterns around the corresponding crystallographic axes, the real space group was established and the values of the lattice parameters of these crystals were refined.

It was found that the $TlGaSe_2$ crystals under study belong to the space symmetry group C^4_s with the averaged values of the lattice parameters: a = 10.715 Ấ, b = 10.694 Ấ, c = 15.690 Å and β = 100,06° (z = 16).

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