

## TlGaSe<sub>2</sub> IS PEIERLS DIELECTRIC

M.Yu. SEYIDOV<sup>1,2</sup>, R.A. SULEYMANOV<sup>1,2</sup>, T.G. MAMEDOV<sup>2</sup>, R.A. KHAMOYEV<sup>2</sup>

<sup>1</sup>*Department of Physics, Gebze Institute of Technology,  
41400, Kocaeli, Turkey*

<sup>2</sup>*G.M.Abdullayev Institute of Physics of National Academy of Sciences of Azerbaijan,  
AZ-1143 Baku, Azerbaijan*

The investigation results of temperature dependences of dielectric constants ( $\epsilon$ ), dark and pyroelectric currents and also VAC and dark current time evolutions of layered ferroelectric-semiconductor TlGaSe<sub>2</sub>, obtained at fixed temperatures in 77K÷ 300K interval are presented in the present work. The pronounced anomaly in the “pit” form with visually noticeable temperature boundaries ~150K and ~200K is firstly revealed on  $\epsilon(T)$  curve measured in the direction which perpendicular to the layers in the region of low frequencies. Also the development of electric instabilities revealing in the form of low-frequency current quasiperiodic vibrations on sample VAC in strongly limited temperature interval 145K – 205K is firstly experimentally fixed. The time character of current instabilities is established. It is shown that it is important for observance of the given instabilities that electric field should be given to the sample by the means of contact-free master potential electrodes prepared in the form of thin mica separator. The instability nature and its influence on the different physical parameters of layered crystal TlGaSe<sub>2</sub> are discussed.

### 1. Introduction

Thallium-gallium diselenide (TlGaSe<sub>2</sub>) relating to the family of low-dimension (layered and open-chain) triple chalcogenide semiconductor compounds with general formula  $Tl^+(M^{3+}X_2)^-$  where M = In, Ga; X = Se, S, Te is the interest example of ferroelectric-semiconductor in the scientific relation and important in the practical one the properties of which are actively investigated during long time. The significant volume of experimental material dedicated to systematic study of structural properties and physicochemical peculiarities TlGaSe<sub>2</sub>, synthesis condition development of these compounds and preparation technology of high-qualitative single crystals [1-7] has accumulated in the scientific works in the result of long-term investigations. Thus, for example, by rentgenodiffraction investigations it is established that TlGaSe<sub>2</sub> layered crystals have the monoclinic type of crystal structure with  $C_{2h}^6$  symmetry space group and  $a = 10,77\text{\AA}$ ,  $b = 10,771\text{\AA}$ ,  $c = 15,636\text{\AA}$  and  $\beta = 100,06^\circ$  lattice spacings. The two-dimensional-periodic double layer alternating parallel to crystallographic plane (001) (or perpendicular to c axis) is the main structural crystal unit. Each “sublayer” consists of group consistency of Ga<sub>4</sub>Se<sub>10</sub>-pyramids being the main structural reason which are constructed from combination of four elementary gallium-selenium GaSe<sub>4</sub> tetrahedrons. Two layers access to each other by vertexes of pyramids and are relatively shifted by such way that trigonal spaces form in which Tl atoms locate. The elementary cell contains 16 formula units (64 atoms) [1-7].

The interest to TlGaSe<sub>2</sub> is caused by the presence of temperature phase transition (PhT) consistency at atmosphere pressure in its structure. The three structural PhT: two in the volume and the one on the surface are explicitly identified by the structural [5,8], heat [9-14], acoustic [15-18], optical [19-22], dielectric [23-32], pyroelectric [33], NMR [34,35], EPR [36] and other investigations in TlGaSe<sub>2</sub> crystals. PhT realize in crystal volume: near  $T_f \sim 120\text{K}$  from high-temperature paraelectric phase into incommensurable (INC) phase and near  $T_c \sim 110\text{K}$  from INC-phase into improper, modulated, commensurable (C) ferroelectric phase with the spontaneous polarization vector lying in the layer plane. Note that PhT temperatures for TlGaSe<sub>2</sub> samples chosen from different technological sets can differ from above mentioned

ones on few degrees up or down on temperature scale. PhT in INC-phase is connected with stability loss of layered crystal lattice with respect to some degree of freedom corresponding to wave vector  $\vec{k}_i = (\delta; \delta; 0,25)$ , where  $\delta = 0,02$  is incommensurability parameter [5,8]. The parameter  $\delta$  at transforms into zero by the jump at  $T = T_c$  so ferroelectric properties of low-temperature C-phase are connected with “blocking” of modulation wave vector on rational value  $\vec{k}_i = (0; 0; 0,25)$  (soft mode on the boundary of Brillouin band). The symmetry space group of low-temperature polar phase and also temperature behavior of  $\delta$  incommensurability parameter haven't been revealed yet in spite of many attempts. PhT on the surface is observed near  $T \sim 135\text{K}$  according to [33,37]. The significant improvement in the understanding of surface PhT nature in TlGaSe<sub>2</sub> is absent in the present scientific works.

Meanwhile, enough many experimental facts obtained on the base of CSL and IR [19, 38-42] investigations and also by the methods of micro-wave and submillimetric dielectric spectroscopy [43, 44] which don't agree with above mentioned data and show on the TlGaSe<sub>2</sub> relation to the class of eigen ferroelectrics with intermediate INC-phase on temperature as the softening of some phonons in the middle of Brillouin band in commensurable ferroelectric phase is observed near PhT temperature. Nowadays the inconsistency reasons of above mentioned results can't be considered as finally determined ones in spite of the fact that there are several models [23-28, 45-47] in the scientific works which explain them.

Note that TlGaSe<sub>2</sub> crystals usually have the composition differing from stoichiometric one [48,49] because of the difference in steam tension of initial components. The stoichiometry failure in growing process or high-temperature thermal annealing of TlGaSe<sub>2</sub> samples leads to appearance of increased structural defect concentration in the form of Se volume inclusions the concentration and charge state of which significantly influence on semiconductor properties of TlGaSe<sub>2</sub> (double carrier injection, residual photoconductivity [48, 49] and etc.).

Besides regions close to temperatures of structural PhT, TlGaSe<sub>2</sub> single crystals reveal the series of unusual properties which don't have the proper explanation. Firts of all, it is

necessary to note the works [43,44] in which the dynamics non-trivial behavior of TlGaSe<sub>2</sub> crystal lattice consisting in splitting of soft ferroelectric mode on two components: low-frequency branch behaves itself normally and high-frequency one behaves itself anomalously with temperature change. Firstly its frequency monotonously decreases with temperature decrease, goes through minimum near ~180K and then it increases. The tractability of this singularity is given in [50] on the base of model of toroidal PhT. In [20,21] it is established that under study of temperature dependences of transmission spectrums of TlGaSe<sub>2</sub> samples chosen from different technologies sets and investigated in the direction perpendicular to layers, the intensity oscillations of monochromatic light (see fig.7, b) passing through the crystal are observed in TlGaSe<sub>2</sub> some samples aren't observed in the white light and their period doesn't depend on thickness of TlGaSe<sub>2</sub> investigated plates, they are defined only by sample temperature. With the help of control investigations authors establish that oscillations observable in the experiment aren't connected with multipath light interference in TlGaSe<sub>2</sub> parallel-sided plates and thermoluminescence of crystal impurity centers. By authors opinion [20, 21, 51] the above mentioned oscillations are connected with diffraction of monochromatic light on soliton lattice presenting itself the region alternation corresponding to commensurable ferroelectric phase on the structure and narrow domain-like walls which are phase solitons. By other words authors suppose that PhT into INS-phase in TlGaSe<sub>2</sub> takes place near  $T_I \sim 247$  K and into ferroelectric C-phase takes place near  $T_C \sim 140$  K, i.e. near temperatures not designated by structural investigations. It is need to note that theoretic estimations carried out in refs [52-55] make the realization in the experiment of above mentioned oscillation mechanism of transmission intensity in TlGaSe<sub>2</sub> unclear.

Besides the above mentioned unusual peculiarities, the one more is observed in the ref [22] at temperature investigations of conoscopic figures of TlGaSe<sub>2</sub> thin plates consisting in return of TlGaSe<sub>2</sub> optical axes beginning from the temperatures ~180K. The authors of ref [22] specially emphasize that observable phenomena can't be explained by even supposed PhT in TlGaSe<sub>2</sub> structure and is connected with appearance the internal electric fields directed perpendicular to TlGaSe<sub>2</sub> layers (the nature of which by the opinion of ref [22] authors is still unclear) and their influence on crystal refraction coefficients in the given temperature region in the crystal.

Finally let's mention the refs [10, 11, 16] in which the unusual temperature behavior of thermal-expansion coefficient and Yung module of TlGaSe<sub>2</sub> are observed in temperature interval ~140K÷~200K.

Taking into consideration the above mentioned the detail study of resistive and dielectric properties of TlGaSe<sub>2</sub> single crystal samples in temperature interval 140K÷200K with the aim of search and establishing of correlations between above represented unusual physical properties TlGaSe<sub>2</sub> in the given temperature region and measurements of dielectric and transport properties is the task of present paper. The experimental evidences of the fact that the given peculiarities present themselves the different forms of electric instability revealing realizing in the form of nonequilibrium PhT in TlGaSe<sub>2</sub> electronic subsystem are given in the work. Let's note that the data about similar investigations in the scientific work are absent in the moment of present work carrying out.

## 2. Sample preparation and measurement technique.

The specially chosed high-resistive samples TlGaSe<sub>2</sub> cutted from grown single crystal ingots modified by method Bridgmen-Stockbarger are used for investigations. X-ray micro-analysis carried out by the means of EDX (energy dispersive X-ray) attachment to scanning electron microscope proves the sample formula composition. According to EDX-analysis data the percent relation of initial components in the investigated sample differs from stoichiometric one to the side of tallium atom deficit and it is equal to (22,58 at %)Tl, (26,58 at %)Ga and (50,84 at %)Se. Let's also note that the control tests on TlGaSe<sub>2</sub> samples sawed out from other technological sets the stoichiometric composition of which either almost corresponds to above mentioned one or absolutely differs from it to the side of thallium atom excess and selenium atom deficit are carried by us with the aim of confirmation of obtained results.

The following electro-physical properties: VAC, dark current in the dependence on constant electric voltage applied to the sample and light intensity by the which the sample radiation is carried out up to measurements; the frequency dependence of complex dielectric constant; the current of short circuit passing through the sample (pyroelectric current near ferroelectric PhT) are studied in the prepared samples in wide temperature interval.

The samples for electric measurements in constant electric field present themselves the rectangular plates with typical dimensions: thickness ~1,5mm and surface area ~8mm<sup>2</sup>. The two by two current-conducting contacts from silver paste, to which the thin copper wires are applied, are evaporated on basic mirror surfaces of TlGaSe<sub>2</sub> plates for the obtaining of low-resistance electric contacts with the sample. The width of interstice between contacts on each sample is ~2mm. Besides, the control measurements on the samples with electrodes from aurum evaporated on sample surfaces by the method of high-temperature thermal evaporation in vacuum are carried by us. The results obtained by the using of these electrodes are identical ones. From this it is followed that TlGaSe<sub>2</sub> sample contacts with electrodes have the resistance which is essentially less than the crystal volume resistance.

The nitric cryostat with optical windows and automatic regulation and temperature stabilization is used for investigations. The control of temperature and the rate of its change is carried with the help of Lake Shore 340 Temperature Controller. The measurements are carried in dynamic regime with different rates of linear temperature change in interval from 0,1K/min up to 20K/min. The sample temperature is measured by platinum resistance thermometer Pt-100 at the temperature stabilization level not less 0,01K. The sample radiation is carried by the light of quartz-halogen bulb with power 100W.

The current measurements are carried out with the help of peak-amperemeter Keithley 485 to the input of which the sample is connected off in resistance mode. The sensitivity lower limit of measured installation is 0,1pA with measurement error of current through crystal not more than ±0,01pA.

The pyrocurrent measurements are carried out by the common method of short-circuit sample at its uniform heating. The peak-amperemeter Keithley-485 is used in the capacity of registering device. The contacts from silver pasta

are coated on mirror surfaces TlGaSe<sub>2</sub> sample layers as along polar direction so perpendicular to one. The measurement procedure contains the following operations: firstly the sample is cooled up to melting point of liquid nitrogen in the darkness at the presence of external polarized current electric field the strength 400V/cm (which is essentially less than the coercive field one). Further the sample is heated up to room temperature in the dynamic regime with linear rate of temperature change 20K/min. Parallel to it the short-circuit current ( $i_p(T)$ ) passing through the sample (pyroelectric current near ferroelectric PhT) is registered in the regime of short-circuit sample.

VAC measurements are carried out with the help of electrometer Keithley 614 in isothermal conditions in the test current scanning regime. The current amplitude registered by the electrometer is  $\sim 0,1\text{pA}$ , the voltage applied to the sample is in interval  $-100\text{ V} \div +100\text{ V}$ .

The special investigations at which the electric contacts are removed from sample surface and electric field is applied by the means of non-contact, potential-retarding electrodes carried out in the form of thin mica separator (by thickness  $\sim 300\ \mu\text{m}$ ) hold on the sample surface with the help of vacuum lubrication are carried out with the aim of exclusion of electric contacts on TlGaSe<sub>2</sub> electrophysical properties. By other words the cycle of electric measurements is repeated on the sample putted between condenser armatures connected to closed circuit consisting of the direct current source, condenser and electrometer.

The investigations of complex dielectric constant are carried out in quasi-static temperature regime by the method of impedance spectroscopy in frequency range 50Hz – 13MHz with the help of HP 4192A LCR-meter. The measurements are carried out on TlGaSe<sub>2</sub> sample having the form of rectangular parallelepiped with parallel-sided ends with area 12mm<sup>2</sup> and 10mm<sup>2</sup> correspondingly in both perpendicular to the layers and along polar direction one. The sample surfaces which one perpendicular to polar direction are mechanically polished and burnished up to optical quality. The electric contact to the electrode formed by the evaporation of gold films on sample surface is carried out with the help of current contact devices. The sample during measurements is in thermostatically controlled chamber inside thin-walled glass Dewar. The temperature is controlled by cuprum-constant thermocouple. The accuracy of temperature maintenance is not less than 0,5K and sensitivity of its measurement is not less than 0,1K.

**3. Experimental results.**

The temperature dependences of dielectric constant real part ( $\epsilon'$ ) of TlGaSe<sub>2</sub> measured in heating regime at different fixed frequencies (200 Hz  $\div$  13 MHz) of measurement field in direction perpendicular to layers are presented on the fig.1. As it is seen from fig.1 the spectrums of dielectric constant real part show the significant frequency dispersion in the frequency range 200Hz $\div$ 10kHz (at frequencies bigger than 100kHz dielectric constant spectrum approbation and  $ac$  conductivity of TlGaSe<sub>2</sub> significantly becomes worse and corresponding curves on the fig.1 and 2 aren't shown in order to not fill the figure). The visually seen anomalies of  $\epsilon'(T)$  dependence in the form of small maximum near  $T_f \sim 120\text{K}$  and superficial hole in temperature interval  $\sim 150\text{K} \div \sim 200\text{K}$  with enough sleep low-temperature and tail high-temperature

slopes. The low-frequency anomalies in behavior  $\epsilon'(T)$  are gradually suppressed and practically aren't observed at frequency of measurement field 10KHz with alternative field frequency growth (see the inclusion on fig.1). The region of enough intensive  $\epsilon'(T)$  increase close to exponential one on the background of which the small bend is registered is observed at  $T > 190\text{K}$  in whole investigated frequency range 200Hz $\div$ 13 MHz.

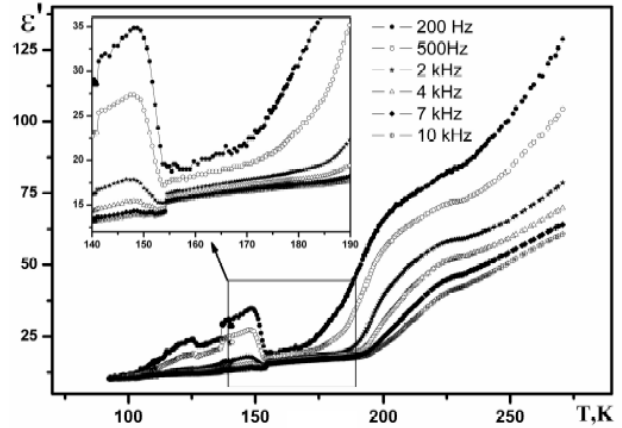


Fig.1. Temperature dependences of dielectric constant real component of TlGaSe<sub>2</sub> measured in heating regime in the direction perpendicular to layers at different frequencies. The anomalous behavior of  $\epsilon'(T)$  TlGaSe<sub>2</sub> in temperature interval 150 K  $\div$  200 K is shown on the attachment.

The spectrum temperature dependences of  $ac$  conductivity ( $\sigma$ ) of layered crystal TlGaSe<sub>2</sub> measured in the regime of sample heating in the direction perpendicular to the layers in frequency range 200Hz $\div$ 13 MHz are presented on the fig.2. From fig.2 it is seen that qualitatively temperature step of whole  $\sigma$  curves measured on different frequencies coincides with data of fig.1, moreover, the clearly expressed anomaly having “hole” form in temperature interval  $\sim 150\text{K} \div \sim 200\text{K}$  is also the main peculiarity of each from curves  $\sigma(T)$  in the investigated frequency range.

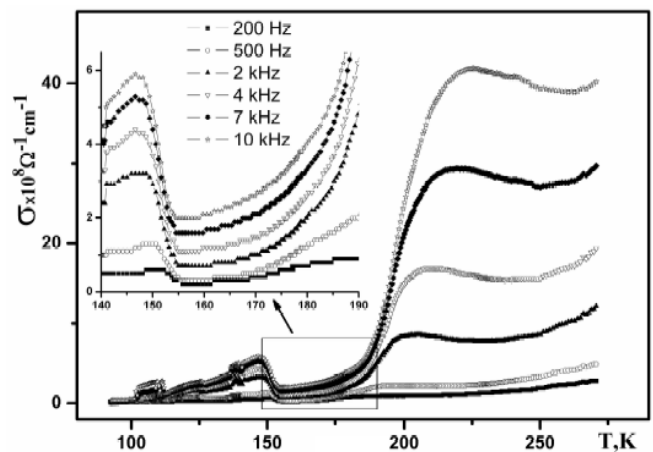


Fig.2. Spectrum temperature dependences of  $ac$  conductivity of TlGaSe<sub>2</sub> measured in the direction perpendicular to layers at different frequencies. The anomalous behavior of  $\epsilon'(T)$  TlGaSe<sub>2</sub> in temperature interval 150 K  $\div$  200 K is shown on the attachment.

The typical temperature dependences of complex dielectric constant real part of TlGaSe<sub>2</sub> measured in the

direction parallel to layer plane in frequency range 200Hz÷13MHz are shown on the fig.3. As it is seen from the fig.3 the curves  $\epsilon'(T)$  are essentially differed from the observable ones in the direction perpendicular to the layers. The measurements of  $\epsilon'(T)$  at different frequencies show that ferroelectric PhT in TlGaSe<sub>2</sub> takes place at  $T_c \sim 110$  K and has all peculiarities character for relaxation processes of Debye type: the peak  $\epsilon'(T)$  connected with ferroelectric PhT washes

out with decrease of dielectric constant maximum value and insignificant increase of PhT temperature with increase of frequency of alternative measurement field. Let's note that anomaly in the form of strong maximum character for ferroelectric PhT which is also suppressed with measurement field frequency increase (fig.3,b) is observed near  $T_c \sim 110$ K on temperature dependence  $\epsilon''$  (conductivity) studied in the direction parallel to TlGaSe<sub>2</sub> layers.

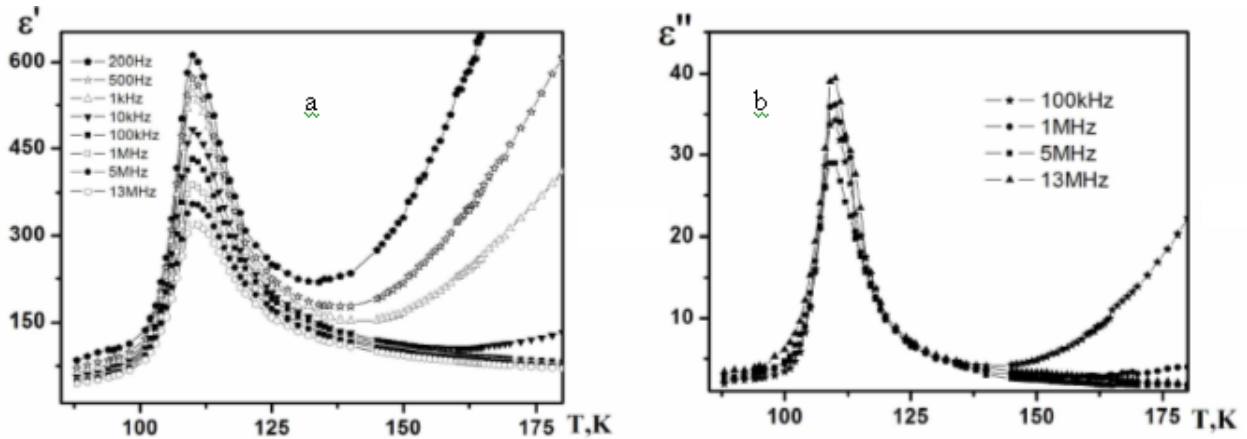


Fig.3. Temperature dependences of real (a) and imaginary (b) components of dielectric constants of TlGaSe<sub>2</sub> measured in heating regime in the direction perpendicular to layers at different frequencies.

As it has been mentioned, the layered crystals TlGaSe<sub>2</sub> at normal conditions are semiconductors of p-type with width of forbidden band varying in the limits  $\Delta E \sim 2.03 \div 2.1$  eV ( $\Delta E$  values obtained by different authors can differ from each other as they significantly depend on the conditions and the method of sample growth, crude purity for growth, crystal high-temperature annealing in other mediums and other factors as other physical properties of TlGaSe<sub>2</sub> [23, 24, 56, 57]) and good sensitivity. TlGaSe<sub>2</sub> samples investigated in the present work have the specific resistance  $\sim 1.5 \cdot 10^7 \Omega$  cm and higher at temperatures close to room ones in the dependence on type and concentration of uncontrolled deep impurity. Their VAC obtained with the help of metallic contacts (silver pasta, aurum) are practically linear at room temperature, the polarity change of applied voltage doesn't almost change the contact resistance, temporary delay between applied voltage and electric current isn't also observed. Thus, the used electric contacts can be considered as ohmic ones.

The temperature dependence of electric current ( $i$ ) passing through TlGaSe<sub>2</sub> sample perpendicular to the layers at application to the crystal of constant external voltage 7V is shown on the fig.4. The curve  $i(T)$  is obtained in the heating regime at the rate of sample temperature scanning 1K/min. As it is seen from the fig.4 the dependence  $i(T)$  has semiconductor character moreover, beginning from  $T \sim 180$ K the current value strongly increases with temperature increase. The plot region  $i(T)$  is well described by activation law of arrenius type in temperature interval bigger than  $\sim 180$ K, moreover, activation energy of deep impurity defined on inclination of  $\ln i(T)$  dependence region on  $10^3/T$  is 0.31eV. The oscillating character of  $i(T)$  curve in temperature interval 117÷180K is shown in larger scale on the addition to fig.4. It is seen that  $i(T)$  curve after small increase in temperature interval 90K ÷ 117K on law close to exponential

one "drops" in quasi-periodic oscillation process the character of which changes at 138K and 168K at the achievement of temperature point 117K. The oscillation isn't observed in  $i(T)$  behavior at temperature than higher temperature 180K. The specially carried out investigations  $i(T)$  in interval 117K ÷ 180K in temperature stabilization regime show that current oscillations have temporary character with quasi-period  $\sim 1$ min.

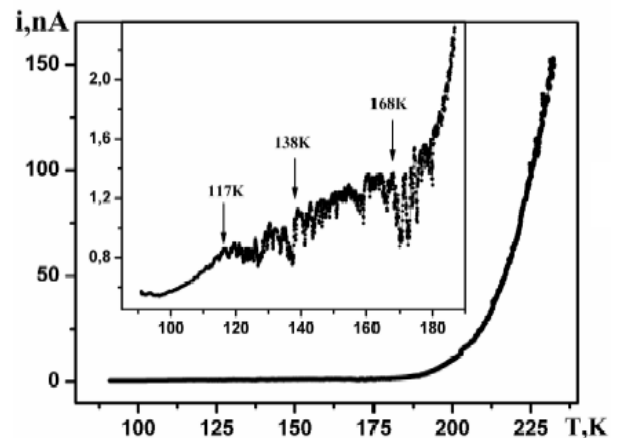


Fig.4. Temperature dependence of dark current passing through sample TlGaSe<sub>2</sub> perpendicular to layers at the application of external potential 7V. The curve  $i(T)$  is obtained in heating regime at sample temperature scanning rate 1K/min.

The curves on the figures 5, 6 and 7 give the visual illustration of  $i(T)$  dependence character changes of initial TlGaSe<sub>2</sub> at variation of experiment external conditions: rate change of sample temperature heating ( $dT/dt$ ) and applied to sample of constant voltage ( $U$ ).

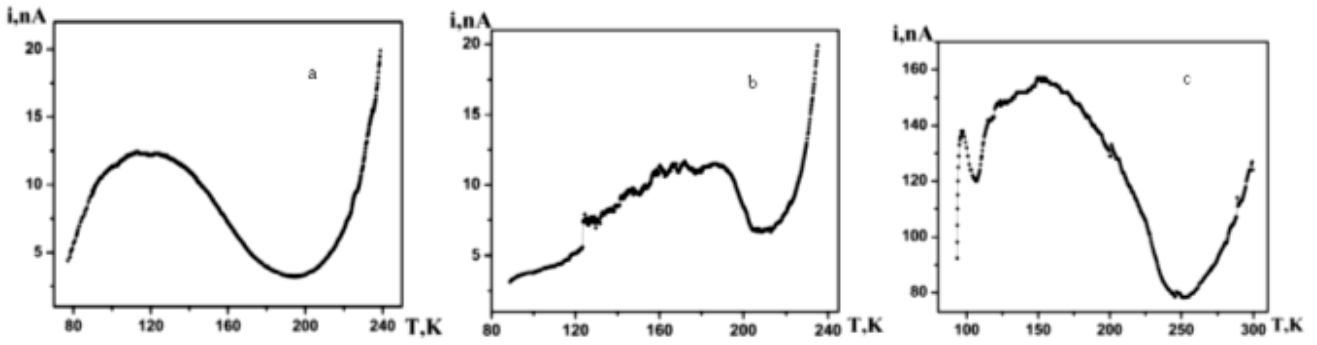


Fig.5. The same as on fig.4. Experimental dependences  $i(T)$  are obtained under following experiment conditions: a is  $dT/dt = 5$  K/min,  $U = 5$  V; b is  $dT/dt = 5$  K/min,  $U = 7$  V; c is  $dT/dt = 10$  K/min,  $U = 4$  V.

The curve  $i(T)$  obtained at the rate of sample temperature scanning 5K/min and external voltage 5V is presented on the fig.5a. It is seen that  $i(T)$  dependence in temperature interval 77K ÷ 200K has bell-shaped character with maximum corresponding to ~117K moreover beginning from ~117K up to ~200K the semiconductor sample resistance increases with temperature increase. The similar experimental dependences  $i(T)$  are obtained by us at other experiment conditions

(fig.5, b:  $dT/dt = 5$  K/min,  $U = 7$  V, fig.5 c:  $dT/dt = 10$  K/min,  $U = 4$  V). As it is seen from fig.5 the increase of temperature heating rate is accompanied: by essential increase of current value passing through the sample and expansion of bell form temperature interval in  $i(T)$  behavior which takes place up to ~250K at heating rate 10K/min.

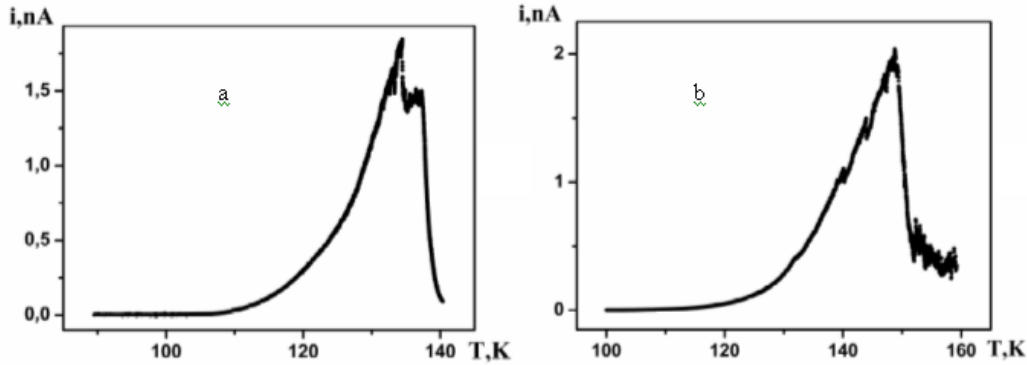


Fig.6. The same as on fig.4. Experimental curves  $i(T)$  curves are obtained at slow heating of initial sample with rates 0.1 K/min (a) and 0.2 K/min (b) at application of constant external potential 10V to the crystal.

The given experimental fact evidences about the fact that electro-transfer in TlGaSe<sub>2</sub> in the given “sensitive” temperature interval is defined not only by equilibrium electronic component, i.e. by carriers thermally activated from local levels in forbidden bands but by nonequilibrium component connected with formation of polarized state in crystal volume.

The experimental curves  $i(T)$  given on the fig.6 demonstrate the existence of relaxation effects more visually (of volume-charged polarization) in summary conductivity of TlGaSe<sub>2</sub>. From data of this figure it is seen that temperature dependences of current transfer in direction perpendicular to layers measured at super slow heating of initial sample with rates 0.1K/min and 0.2K/min endure the significant modifications in comparing with early presented data. The exponential growth of both curves of  $i(T)$  shown on the fig.6,a,b replaces by strong decrease of current value at achievement of temperature ~139K (fig.6,a) and ~148K (fig.6,b) that probably is caused by polarization processes (disappearance and/or formation of polarization charges) in the sample and their application on corresponding conductivity currents.

The current temperature dependence in the direction perpendicular to layers measured at initial crystal heating with rate 1K/min and application of small constant voltage

0,8V to the sample is presented on the fig.7,a. The intensity temperature dependence of monochromatic light passing through TlGaSe<sub>2</sub> crystal taken from publications [20, 21] is shown on the fig.7,b in the capacity of illustrations. The comparable analysis of these figures shows that  $i(T)$  curve up to small details makes the temperature dependence of transmission intensity. The detail consideration of fig.7,a allows us to emphasize some consistent temperature regions on  $i(T)$  curve: if current value in the interval ~ 80K ÷ 165K passing through the sample practically doesn't depend on temperature then interval ~ 165 K ÷ 200 K is characterized by the current value increase on the background of which the specific oscillations in  $i(T)$  behavior with quasi-period which is also equal to ~1min, are observed. The oscillating character  $i(T)$  is especially revealed in interval ~200K ÷ 220K which is characterized by the strong increase of amplitude of quasi-periodic current oscillations. The oscillating process isn't observed at temperatures higher than ~220K. The curve  $i(T)$  passes through maximum in this temperature interval, moreover maximal temperature corresponds to the point  $T \sim 242$ K.

The typical low-temperature VAC of initial sample obtained at direct (with increase of applied constant voltage) and reverse steps (with voltage decrease) with application of electric field along  $c$  axis is presented on the fig.8. It is seen



that the VAC ohmic region shifts to the region of lower voltages ( $\sim 10V$ ) with temperature decrease, moreover VAC curve is almost parallel to voltage axis in the region of critical voltage  $\sim 10 V \div 30 V$ , i.e it. has the form of *N*-shaped curve with the region of negative differential resistance (NDR). The

*N*-shaped characteristics are reversible ones, however the region of critical voltages at reverse step is less than at direct one. The current of VAC reverse branch is accompanied by hysteresis. VAC extrapolation to value  $i = 0$  gives the value of residual voltage  $\sim 30V$  on the sample.

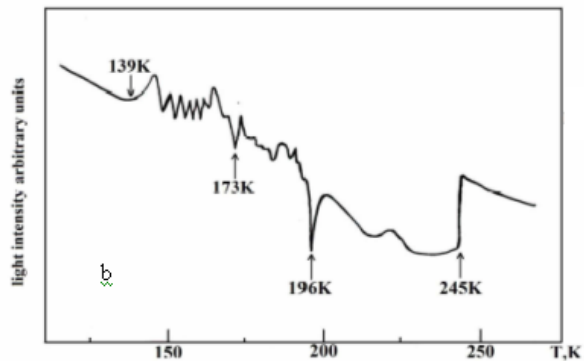
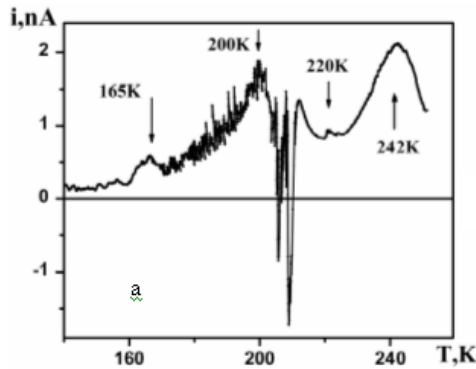


Fig.7. a: the same as on fig.4. Experimental curve  $i(T)$  is obtained at heating of initial sample with rate 0.1 K/min at application of small constant potential 8V to the crystal, b: intensity temperature dependence of monochromatic light passing through TlGaSe<sub>2</sub> crystal taken from publications [20, 21]

Besides the current value have the tendency not to transform into zero at reverse step in the region of small voltages. VAC hysteretic peculiarity connected probably with formation and kinetic changes of nonequilibrium processes (internal electric fields connected with polarized state) in the investigated sample reminds the ferroelectric hysteretic curves of polarization dependence on applied voltage if the net current passing through the sample is taken as the displacement current.

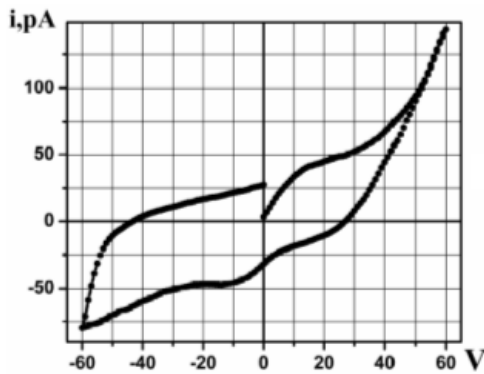


Fig.8. VAC obtained on initial sample with metallic contacts at temperature 113K. The change range of electric voltage  $-60 V \div +60 V$  applied to the sample changing with the step 1V for 1 second.

As it is known [58, 59] the relaxation effects in high-ohmic semiconductors connected with the presence of polarized charges in the crystal significantly depend on the influence of external effects of different types on the sample, sample pre-history before the measurements, temperature boundaries of sample heating in the previous measurement, cooling regime and etc. We carry out the investigation of dark current of TlGaSe<sub>2</sub> initial sample previously cooled by the lighting (the light of quartz-halogen bulb with power 100W) from room temperature up to 77K (see fig.9). As it is seen from this figure, the form of  $i(T)$  curve endures the significant modifications in "sensitive" temperature interval  $\sim 160K \div 220K$  that is also caused by the polarization processes in the sample and their application on the corresponding currents of equilibrium conductivity.

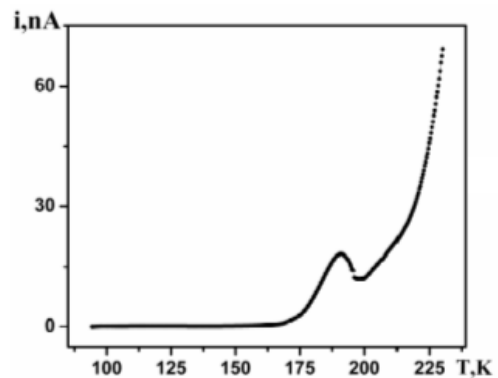


Fig.9. The same as on the fig.4. The curve  $i(T)$  is obtained in heating regime with rate 7K/min of initial sample TlGaSe<sub>2</sub> preliminary cooled under light (the light of halogen bulb by power 100W) from room temperature up to 77K at application of external constant potential 7V.

Let's note that initial characteristics of the investigated crystal are totally restored after its short temporary keeping at room temperature during 10÷20 min.

It is known that [60] transport properties of high-ohmic semiconductors are defined not only by material volume, but by its near-electrode regions. We try to reveal the connection of above mentioned resistometric investigation results of TlGaSe<sub>2</sub> processes with the ones on electrodes.

The curve form of dark current written in geometry which is perpendicular to the layers in the conditions when the external electric field on the sample is applied through block artificially created dielectric interstice carried out in the form of thin mica separator is shown on the fig.10. The given method allows us to avoid the undesirable surface and contact phenomenon presenting at conductivity measurements on usual technique with electrode application.

From the fig.10 it is seen that displacement current curve ( $i_{dis}(T)$ ) in the region of low temperatures reminds the temperature dependence of static dielectric constant of TlGaSe<sub>2</sub> given in [24-28]: the small anomaly is observed in the bend form near  $\sim 98K$  and further the curve passes through maximum moreover the biggest value  $i_{dis}(T)$  is

achieved at temperature ~117K in PhT point into INC phase. Besides, the anomaly on  $i_{dis}(T)$  curve in the spiked peak form is observed near 177K through “sandwich” mica - ample - mica, monotonously increases with temperature increase higher than ~180K that is probably caused by consistent inclusion of carriers from the corresponding deep levels in electric transition processes.

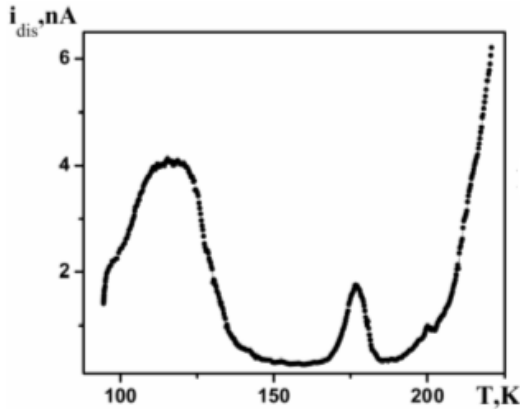


Fig.10. Temperature dependence of displacement current measured in the direction perpendicular to the layers of TlGaSe<sub>2</sub> sample with application of blocking mica separators. The data are obtained at temperature heating rate 5K/min and external potential 10V applied to crystal.

VAC are investigated on initial sample TlGaSe<sub>2</sub> isolated by mica separators in wide temperature interval (fig.11). We show many experimental data obtained by us (in spite of their variety) on the fig.11 as they are observed at first time.

Let's mention that there are the evidences of the fact that observable phenomena doesn't connect with any instrument phenomenon in measurement process.

VAC series obtained at two potential polarities in temperature interval 80K ÷ 140K is shown on the fig.11. It is seen that linear VAC curve and symmetric in relation to polarity of applied electric static voltage one measured at  $T=80K$  (VAC saves the same form up to ~106K) deforms at approximation to  $T_c$  and inside INC-phase. The position significantly changes in temperature interval 145K ÷ 205K (fig. 11 b, c, d): VAC has the form of specific oscillations with multiple increase of current amplitude and becomes even in respect to applied electric field (i.e. the polarity change of external voltage isn't accompanied by the change current direction). The oscillation process isn't observed higher the temperature 205K and at too high level of sample light (see fig.12,a).

Beginning from 210K the current amplitude values on VAC curves strongly decrease; VAC form begins to take the linearity contours; the reverse branch appears on VAC curve. VAC at 220K practically doesn't differ from VAC measured at 80K. During experiments we reveal that current oscillations observable in the given temperature interval have the temporary character with quasi-period ~1min. The example of compatible record of current oscillations and time is shown on the fig.12,b.

Finally, the temperature dependence of pyroelectric current ( $i_p$ ) measured at in heating regime on investigated sample TlGaSe<sub>2</sub> isolated by mica separators in the direction perpendicular to layers.

It is seen that there are two clearly expressed maximums on  $(i_p)T$  curve: the one near temperature ~98K, the second one at temperature ~150K, moreover the extreme value of  $(i_p)T$  in the given points differ from each other in more than 1,5 times that is probably evidences about their different nature. The measurements  $(i_p)T$  carried out on TlGaSe<sub>2</sub> crystals lead to the results which significantly differ from data of figure 13 with application of usual electric contacts in the directions both perpendicular to the layers and along plane layers. In particular, only one clearly expressed peak near  $T_c$  [33] is observed on  $(i_p)T$  curve.

#### 4. The discussion of obtained results.

Thus, the obtained experimental facts during of present investigations can be summed by the following way:

1. The current transfer differs by unique contribution combinations from equilibrium conductivity component (mobile carriers of band type) and nonequilibrium processes connected with formation and change of polarized state (the conductivity from nonmobile or localized charge carriers) in the direction perpendicular to TlGaSe<sub>2</sub> sample layers in temperature interval 120K ÷ 205K. The higher/lower the rate of sample temperature scanning or the less value of external electric field applied to the sample the stronger the deposit of volume-charged polarization in crystal sum electric conductivity reveals. Probably, the balance of the given contributions into kinetics electric charge transfer in TlGaSe<sub>2</sub> samples chosen from technological sets is very delicate and as the consequence the unusual form variety of temperature dependence resistivity curve [61-63] and its high sensitivity to the temperature change rate and value of external electric field are observed in practices instead expected Drude behavior.

2. The one more result obtained in the present work and enough rarely observed among different known semiconductor compounds [64] is connected with registration in TlGaSe<sub>2</sub> of current oscillations appearing probably because of electric instability taking place in crystal electron subsystem in temperature region 140K ÷ 205K. The direct experimental evidence of the fact that the given oscillations aren't connected with carrier injections through contacts but are caused by crystal volume properties is given by the method of blocking electrode. The joint analysis of the figures 1, 2, 5, 7, 11 and 13 and also data presented in [10, 11, 16, 20-22, 43, 44] allows us to make the conclusion that observable peculiarities in temperature interval 140K ÷ 205K have the one and the same nature and evidence the sample electric heterogeneity (conductivity heterogeneity in the volume) moreover the heterogeneity formation micro-mechanism and their topology are connected with nature of these layered compounds.

3. The data comparison of figures 1, 2, 4 ÷ 10 and 13 shows that direction of internal electric field of volume-charged polarization appearing in TlGaSe<sub>2</sub> samples in the direction perpendicular to layers is always reverse one to the external electric field applied to the crystal in the measurement process.

It is necessary to divide whole temperature interval of observable effects on three character regions for perception integrity of current transfer kinetics physical picture in the direction perpendicular to layers of layered crystals TlGaSe<sub>2</sub>:

the region of low temperatures up to  $\sim 140\text{K}$ , transition region  $\sim 140\text{K} < T < \sim 205\text{K}$  and high-temperature region  $T > \sim 205\text{K}$ .

The origin of current oscillations in temperature interval  $\sim 117\text{K} \div \sim 140\text{K}$  (see fig.4) can be connected with electron-thermal switching, i.e. with reverse sample switching from low-ohmic state into high-ohmic one the mechanism of which is considered in detail in [65, 66]. According to this theoretical model, any process accompanying by the conductivity decrease of semiconductor material with temperature increase should lead to non-linear VAC (of S- or N-type) and can cause the current instability.

Joule heating mechanism of semiconductor being near PhT on conductivity is considered in works [65, 66], however, it isn't excluded that increase of volume-charged polarization contribute into crystal electroconductivity (see fig. 5  $\div$  10) can be the alternative mechanism of NDR. The presence of strong electric field applied to semiconductor is the key point for realization of the given mechanism. Taking

into consideration the fact that current oscillations in the given temperature interval are observed only on  $\text{TlGaSe}_2$  sample with electric contacts from metal, then one can confirm that strong electric field concentrates in thin near-contact layer of investigated material. Such volume near-contact layer with significant distribution of near-electronic potential (more clearly with non-linear dependence of voltage drop along sample length) should influence on measurements of crystal capacity and electroconductivity (see fig.4-8).

Nowadays the detail quantitative analysis of instabilities (current oscillations on VAC) revealed by us in paraelectric temperature region far from PhT points  $\sim 140\text{K} < T < \sim 205\text{K}$  is difficult to carry out. By our opinion our results are the first experimental observation of such type effect in  $\text{TlGaSe}_2$ . Thus, here we give only some initial thoughts for future analysis of this phenomenon.

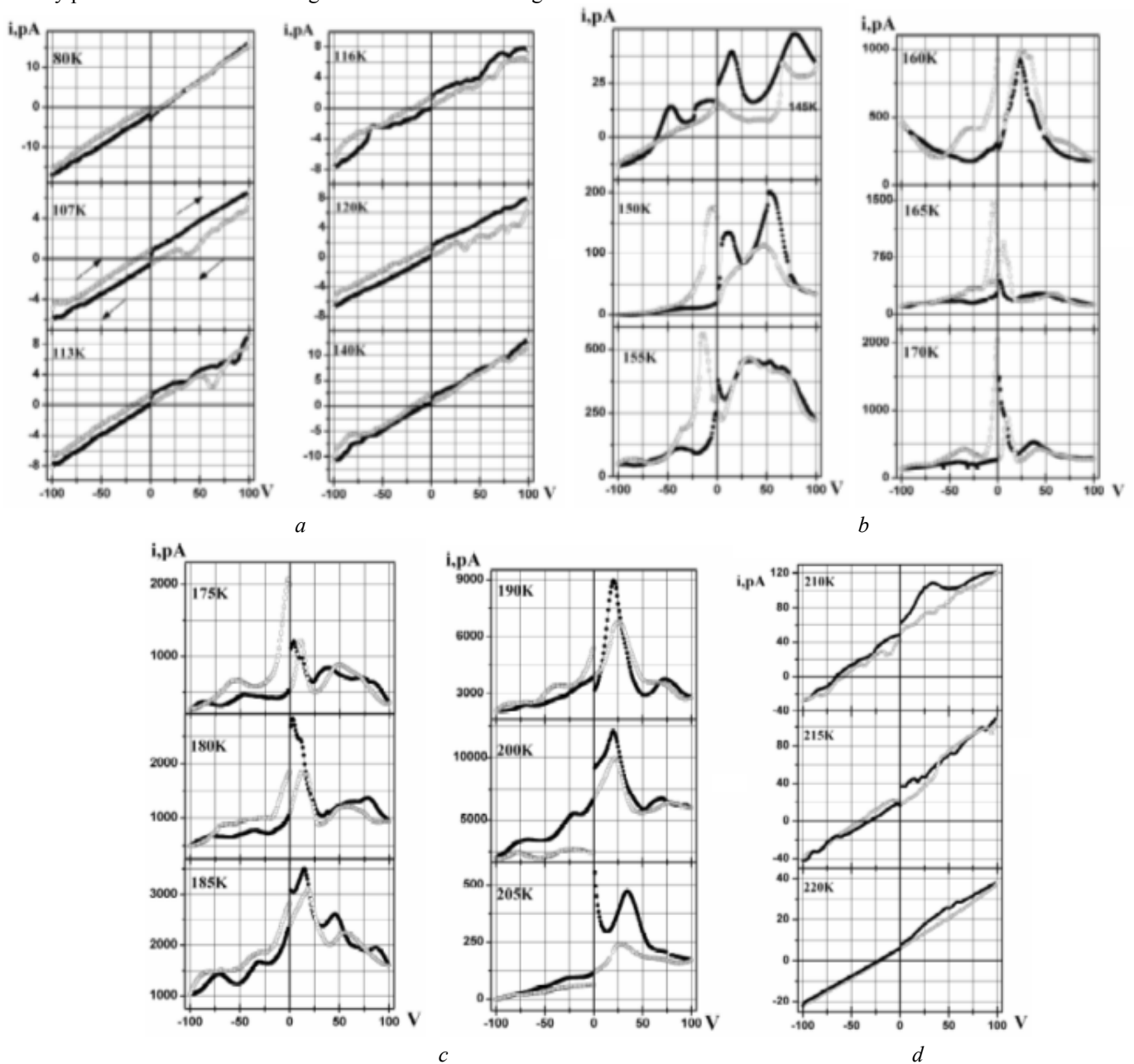


Fig. 11. VAC series obtained on  $\text{TlGaSe}_2$  sample isolated by mica separators in the direction perpendicular to the layers in temperature interval  $80\text{ K} \div 140\text{ K}$ . The change range of electric voltage applied to the sample is  $100\text{ V} \div +100\text{ V}$ , the step is  $1\text{ V}$  for  $1\text{ s}$ . The dark circles are  $0\text{ V} \div +100\text{ V}$ , light ones are  $+100\text{ V} \div 0\text{ V}$ , dark squares are  $0\text{ V} \div -100\text{ V}$ , light ones are  $100\text{ V} \div 0\text{ V}$ .



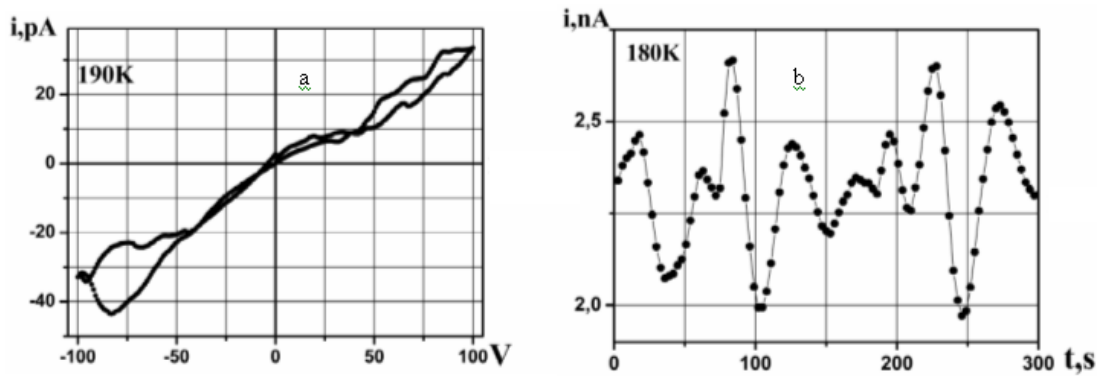


Fig.12. a) is VAC curve measured at sample light by the halogen bulb light by power 100W at temperature 190K; b) is example of recording of current oscillations in time. The curve is obtained at temperature 180K at constant potential 20V applied to sample.

The hypothesis of electronic PhT is the more logical one for interpretation of experimental data obtained by us. The investigated crystals TlGaSe<sub>2</sub> are resistively unstable in the above mentioned temperature interval, probably because of change (or dominance) of one conductivity regime by other one (or under other one). By this reason it is profitable that the system transits into electrically heterogeneous state, i.e. “splits” on macroscopic regions – electric domains periodically alternating in the direction perpendicular to layers [64]. In our case, i.e. in the system having the layered structure the domains present themselves the plane condensators on opposite plane of which (domain walls) the charge carriers of opposite signs concentrate. The voltage between domain walls in such condenser domain model is defined by surface charge density on domain walls and the current is defined by charge quantity forming on walls in time unit. The bias current registered by non-contact method through the sample surface presents itself the algebraic sum of currents in domains. It isn’t excluded that directions of displacement currents in domains of different dimensions and geometries can differ in external electric field by both the value and direction. The displacement current dependence on voltage, i.e. VAC (see fig.11) at change of external electric field applied to the sample is caused by temporary bursts of volume charge on microcondensator plates.

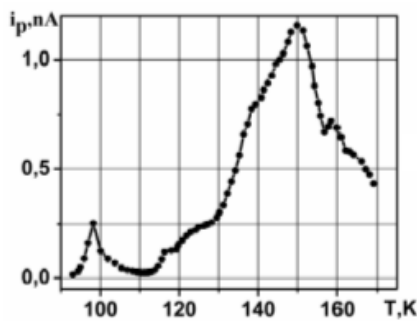


Fig.13. Temperature dependence of pyroelectric current measured in heating regime on investigated sample TlGaSe<sub>2</sub> isolated by mica separators in the direction perpendicular to layers.

The singular “dielectrization” of semiconductor system described above causes the many questions such as: the question about heterogeneity dimensions and typology of heterogeneous state; about nature and mechanisms leading

to heterogeneous state formation; about the role and interconnection of such state with low temperature structural PhT. However, it is important to note that electrically heterogeneous state or phase-splitting medium doesn’t lead to sample trivial chemical dividing of sample on phases. Under the phase we understand the homogeneous macroscopic regions (clusters) differing by carrier concentrations in the result of freezing (localization) of charge carrier part on distributed on impurity ions or defect accumulations. For example, according to [48] the peculiarity of technology of TlGaSe<sub>2</sub> layered crystal growth is the fact that there are always the defect accumulations in the form of volume inclusions of Se in their structure. In the case of investigated crystal the specific part of chargedly enriched phase (semiconductor) in the respect of chargedly depleted (dielectric) one depends on temperature and other external influences, that’s why current oscillations on VAC (see fig.11) have the strong temperature boundaries. It is obvious that the behavior of frequency dependences of dielectric constant and conductivity of TlGaSe<sub>2</sub> sample in temperature interval  $\sim 140K < T < \sim 205K$  ( see fig. 1 and 2) is the important argument for the benefit of the fact that the effect observed on fig.11 is caused by especially such scenario of electronic PhT semiconductor – dielectric type.

The consistent “switching” in electric transition processes of corresponding deep levels at  $T > \sim 205K$  is accompanied by destroy of electrically heterogeneous state in TlGaSe<sub>2</sub>. In the given temperature interval the contribution into sample electroconductivity gives only equilibrium impurity component and consequently, sample conductivity will have clear semiconductor behavior.

Let’s also note that similar fact on above mentioned process of phase splitting in TlGaSe<sub>2</sub> layered crystal in temperature interval  $\sim 150K > T < \sim 205K$  takes place in layered metal-oxide high-temperature supersemiconductors. As it is known, the superstructure and corresponding charge density modulation which is named charge density wave (CDW) [67, 68] form in many quasi-one-dimension supersemiconductors at temperature decrease in the result of Peierls instability in initial lattice. It is established that CDW fix on impurities and defects in real compounds, and conductivity in weak electric field is defined by electron-hole excitations through Peierls track. CDW influence on many thermodynamic parameters of superconducting materials in particular on thermal-expansion coefficient, heat capacity and etc because of strong electron-phonon bond (anomaly). In the next chapter it is shown that

temperature region  $\sim 140 \text{ K} < T < \sim 205 \text{ K}$  also characterizes by anomalous behavior of thermodynamic properties in  $\text{TlGaSe}_2$  layered crystal that is the evidence of electrically heterogeneous state deposit on crystal thermodynamic parameters.

**5. The anomalies of thermal-expansion coefficients and elastic properties of  $\text{TlGaSe}_2$  caused by nonequilibrium PhT in electron subsystem.**

The temperature dependences of thermal-expansion coefficients in both directions perpendicular ( $\alpha_{\perp}$ ) and parallel to layer plane ( $\alpha_{\parallel}$ ) [10, 11] are investigated on crystals of triple compounds  $\text{TlGaSe}_2$  in wide temperature interval including the points of structural PhT. The investigations are carried out on optical interferometer ( more detail see [10,11]). The corresponding curves  $\alpha_{\perp}(T)$  and  $\alpha_{\parallel}(T)$  are presented on fig.14. As it is seen from fig.14 the both curves have clearly expressed peculiarities in temperature interval  $\sim 120 \text{ K} \div \sim 240 \text{ K}$ . It is seen that monotonous step of  $\alpha_{\perp}(T)$  curve destroys at temperature  $\sim 240 \text{ K}$  where the small anomaly in the form of little step is observed in  $\alpha_{\perp}(T)$  behavior (the jump-like cancellation of sample length at its cooling takes place). Beginning from  $\sim 180 \text{ K}$  up to  $\sim 140 \text{ K}$   $\alpha_{\perp}(T)$  it anomalously increases with temperature decrease and below  $\sim 140 \text{ K}$  endures the significant changes moreover maximal value of  $\alpha_{\perp}(T)$  achieves in PhT point in INC-phase at  $T_i \sim 120 \text{ K}$ . From the fig.14 it is seen that  $\alpha_{\parallel}(T)$  dependence has the anomalous behavior in temperature interval  $\sim 120 \text{ K} \div 180 \text{ K}$ : beginning from  $\sim 180 \text{ K}$   $\alpha_{\parallel}(T)$  decreases with temperature decrease and below  $\sim 140 \text{ K}$   $\alpha_{\parallel}(T) = (dL/dT)/L < 0$  (the jump increase of sample length along layer plane takes place). The peak value of  $\alpha_{\parallel}(T)$  curve also falls on PhT point in INC-phase at  $T_i \sim 120 \text{ K}$  (as behavior of  $\alpha_{\perp}(T)$  and  $\alpha_{\parallel}(T)$  curves in the temperature region below  $T_i$  aren't shown on the fig.14, let's note only the fact that  $\alpha_{\perp}(T)$  and  $\alpha_{\parallel}(T)$  anomalies near  $T_i$  have  $\lambda$ -shaped character).

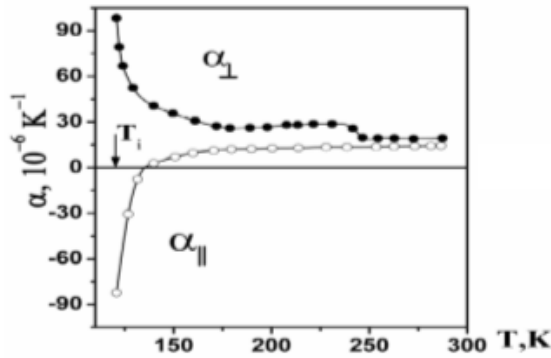


Fig.14. Temperature dependences of thermal-expansion coefficients in directions perpendicular ( $\alpha_{\perp}$ ) and parallel ( $\alpha_{\parallel}$ ) to  $\text{TlGaSe}_2$  layer plane. The data of figure corresponds to [10, 11, 16].

The temperature dependence of effective Young's module measured in ref [16] also endures the significant changes in the above mentioned temperature interval  $\sim 140 \text{ K} \div \sim 220 \text{ K}$ , i.e. in paraelectric phase far from structural PhT points, moreover the points of structural PhT on Young's module curve reveal in the form of character maximums at  $T_i \sim 120 \text{ K}$  and  $T_c \sim 110 \text{ K}$ . The nontrivial

character of temperature dependence of thermal-expansion coefficients  $\alpha_{\perp}(T)$  and  $\alpha_{\parallel}$  of  $\text{TlGaSe}_2$  described above is explained by the fact that PhT consistency exists in crystal structure. But many questions don't have the answers. For example, why the anomalous behavior of  $\alpha_{\perp}(T)$  and  $\alpha_{\parallel}(T)$  in cooling process begins in paraelectric phase far from structural PhT points or why the peak values of  $\alpha_{\perp}(T)$  and  $\alpha_{\parallel}(T)$  of investigated substance coincide with PhT point in INC-phase in spite of conclusions of conventional phenomenological theories [69, 70], though the given anomalies should take place near  $T_c$ ? Finally, the main question arises according to new experimental results above mentioned: what is interconnection of electric instabilities observed in temperature region  $\sim 140 \text{ K} \div \sim 205 \text{ K}$  with described peculiarities of thermal expansion.

Let's see on the fig.14. It is obvious that both curves  $\alpha_{\perp}(T)$  and  $\alpha_{\parallel}(T)$  endure the critical behavior at approach to  $\sim 120 \text{ K}$  that isn't expected in the experiment if point  $\sim 120 \text{ K}$  were only PhT temperature in INC-phase [69, 70]. Let's try to explain the anomalous behavior of  $\alpha_{\perp}(T)$  and  $\alpha_{\parallel}(T)$  in temperature interval  $\sim 120 \text{ K} \div \sim 220 \text{ K}$  on the base of other model. Let's base on quasi-harmonic model of crystal thermal expansion of hexagonal symmetry ( $\text{TlGaSe}_2$  structure with good approximation can be considered as quasi-hexagonal because of physical properties of  $\text{TlGaSe}_2$  don't reveal the anisotropy in layer plane [15, 16]). Besides, let's suppose the weak anisotropy of phonone spectrum and consider  $\gamma_{\perp} \approx \gamma_{\parallel}$  ( $\gamma$  are Grunaisen parameters) that is totally acceptable from the point of view of having data about phonon spectrums of these compounds [72, 73]. In this case the formulas for  $\alpha_{\perp}$  and  $\alpha_{\parallel}$  calculations [74] strongly simplify and have the form:

$$\alpha_{\perp} \approx \frac{C}{V} \gamma \frac{C_{11} + C_{12} - 2C_{13}}{(C_{11} + C_{12}) \cdot C_{33} - 2C_{13}^2}$$

and

$$\alpha_{\parallel} \approx \frac{C}{V} \gamma \frac{C_{33} - C_{13}}{(C_{11} + C_{12}) \cdot C_{33} - 2C_{13}^2}$$

Here,  $C$  is heat capacity,  $V$  is molar volume,  $C_{ik}$  are elastic constants. It is obvious that thermal expansion anomalies given on fig.14 can't be caused by specific behavior of heat capacity or  $\gamma$ . We suppose the temperature dependences of elastic modules  $\text{TlGaSe}_2$  in particular the nontrivial temperature behavior of elastic constant  $C_{13}$  are responsible for special behavior of  $\alpha_{\perp}(T)$  and  $\alpha_{\parallel}(T)$  in temperature interval  $\sim 120 \text{ K} \div \sim 220 \text{ K}$ . The joint analysis of experimental results obtained by investigation of temperature dependences of elastic constants  $C_{11}$ ,  $C_{12}$ ,  $C_{33}$  and effective Young's modulus [15, 16] of  $\text{TlGaSe}_2$  allows to authors of the present work to make conclusion about unusual strong temperature dependence of coefficient of elasticity  $C_{13}$  in temperature interval  $\sim 120 \text{ K} \div \sim 220 \text{ K}$ , moreover the enough strong increase with temperature decrease beginning from  $\sim 220 \text{ K}$  up to  $\sim 140 \text{ K}$  with small change of inclination  $\sim 180 \text{ K}$  should be observed in behavior of  $C_{13}(T)$  constant. The dependences of elastic compliances on value of coefficient of elasticity  $C_{13}$  are given on the fig.15 (taking into consideration the data [15, 16]).

$$S_{zz} = \frac{C_{11} + C_{12} - 2C_{13}}{(C_{11} + C_{12}) \cdot C_{33} - 2C_{13}^2}$$

and

$$S_{xx} = \frac{C_{33} - C_{13}}{(C_{11} + C_{12}) \cdot C_{33} - 2C_{13}^2}$$

As it is seen from this figure the behavior of elastic compliances  $S_{xx}$  and  $S_{zz}$  with increase of elastic constant  $C_{13}$  with accuracy corresponds to anomalous temperature behavior of  $\alpha_{\perp}(T)$  and  $\alpha_{\parallel}(T)$  curves in the interval  $\sim 120\text{K} \div \sim 220\text{K}$ .

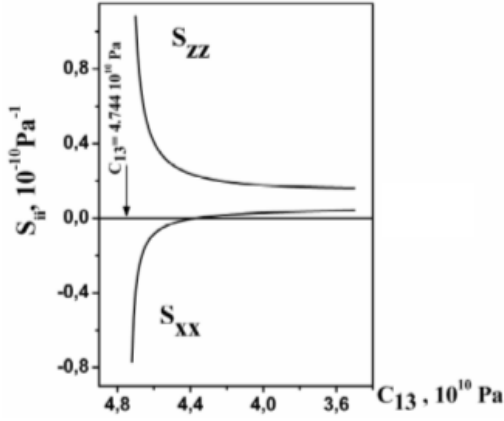


Fig.15. The dependences of elastic compliances  $S_{xx}$  and  $S_{zz}$  on the coefficient of elasticity value  $C_{13}$ . The arrow on the figure corresponds to numerical value  $C_{13} = 4,744 \cdot 10^{10}$  Pa defining the boundary of mechanical stability of TlGaSe<sub>2</sub> layered crystal.

As it is known [71] the mechanical stability of crystal lattice meaning its stability in relation to small homogeneous deformations is defined from generalized criterion of Born stability. According to this criterion at the given temperature all determinants of main matrix minors  $C_{ij}$  ( $i, j = 1, \dots, 6$ ) of isothermal modules of crystal elasticity in the Fogt designations should be positively defined. Born criterion of mechanical stability for hexagonal crystal includes the conditions:  $C_{44} > 0$ ;  $C_{11} > |C_{12}|$ ;  $(C_{11} + C_{12}) \cdot C_{33} > 2C_{13}^2$ ;  $C_{66} > 0$ . The theoretical estimations carried out by the attraction of experimental data [15, 16] show that the stability condition  $(C_{11} + C_{12}) \cdot C_{33} > 2C_{13}^2$  destroys at coefficient of elasticity module  $C_{13} = 4,744 \cdot 10^{10}$  Pa, consequently, this value  $C_{13}$  defines the boundary of mechanical stability of layered crystal TlGaSe<sub>2</sub> (the found boundary of crystal mechanical stability by Born is shown on fig.15 by the arrow). As it is seen from the fig.15 the numerical value of  $C_{13}$  corresponding to the boundary of crystal mechanical stability is such one that allows us to describe all main peculiarities in behavior of  $\alpha_{\perp}(T)$  and  $\alpha_{\parallel}(T)$ . Thus, the given circumstance shows on the fact that especially the increase of elastic constant  $C_{13}$  (but not PhT in INC-phase at  $T_i \sim 120$  K) with temperature decrease causes the anomalous temperature behavior of  $\alpha_{\perp}(T)$  and  $\alpha_{\parallel}(T)$  curves in paraelectric phase far from structural PhT points. The closeness of  $C_{13}$  to critical value at which the condition of crystal mechanical stability destroys is the precursor of low-temperature PhT in these compounds totally proving the earlier made conclusions [16]

about importance of coefficient of elasticity modulus role  $C_{13}$  in the nature of phase transformations in TlGaSe<sub>2</sub>.

The effects of negative thermal expansion similar to described above for TlGaSe<sub>2</sub> are observed in many layered metal-oxide high-temperature supersemiconductors [75]. The direct experiment evidence of the fact that anomalies of thermal expansion of high-temperature semiconductors have the electron nature and are connected with WCD (so-called charge on bonds) is given in present scientific works.

Taking into consideration the fact that temperature interval in which the peculiarities in the behavior of thermal-expansion coefficients of layered crystal TlGaSe<sub>2</sub> are observed, coincides with temperature region of electric instability appearance in this compound and also the absence of any macroscopic structural changes in this temperature interval, one can conclude that the instability in electronic subsystem of investigated crystal is the peculiarity of unusual transport, heat, elastic, spectroscopic [43, 44], optical [20-22] and other physical properties of TlGaSe<sub>2</sub> in temperature interval  $\sim 140\text{K} < T < \sim 205\text{K}$ . The last one means that anomalous increase of elastic constant  $C_{13}(T)$  and peculiarities in  $\alpha_{\perp}(T)$  and  $\alpha_{\parallel}(T)$  behaviors connected with it in the given temperature interval is defined by the contribution of electronic subsystem but not by crystal lattice anharmonicity. Let's note that as  $C_{13}$  is "interlayer elastic" constant, then it is the more sensitive to internal electric fields directed perpendicular to TlGaSe<sub>2</sub> crystal layers.

Thus, one can confirm that formation and dynamics of electric domains appearing because of electric instability considered as inequilibrium PhT in crystal electronic subsystem of TlGaSe<sub>2</sub> in temperature interval  $\sim 140\text{K} < T < \sim 205\text{K}$  because of strong interaction by crystal electron and elastic subsystem is accompanied by the appearance of internal fields of elastic deformations in TlGaSe<sub>2</sub> structure, moreover only such components of internal stress tensor are not equal to zero, which have non-zero projections in the direction perpendicular to plane of crystal layers. The long-distance field of elastic determinations formed by these fields are similar to electrostrictive fields in crystals. The electrostriction overlapping on  $T_c$  phonon part of thermal-expansion coefficient leads to anomalies in  $\alpha_{\perp}(T)$  and  $\alpha_{\parallel}(T)$  above described behaviors.

As the concurrence of two mechanisms of thermal-expansion coefficients, which are "charge" component and atomic anharmonicity, exists in real crystal TlGaSe<sub>2</sub> in temperature interval  $\sim 140\text{K} < T < \sim 205\text{K}$  then the unique possibility to strengthen or weaken "charge" component of thermal expansion appears in this crystal because of external influence on internal electric fields and to influence on lattice stability of TlGaSe<sub>2</sub> and anomaly form (suppress or strengthen) on  $\alpha_{\perp}(T)$  and  $\alpha_{\parallel}(T)$  curves. From this point of view, the layered crystal TlGaSe<sub>2</sub> is the fine model medium not only for study of appearance mechanisms, development of electric instabilities and their revealing in behavior of different crystal physical parameters, but for control of such crystal fundamental characteristics as thermal-expansion coefficients, transport and optical properties.

## 6. Conclusion.

Thus, in the present work the unusual transport properties of layered crystal of TlGaSe<sub>2</sub> in the direction perpendicular to the layers in temperature interval  $\sim 140\text{K} < T < \sim 205\text{K}$  are discussed in effective medium model appearing as the

consequence of PhT semiconductor – dielectric in crystal electronic subsystem and presenting itself the crystal inclusion regions with dielectric properties in semiconductor matrix (phase splitting). The electric instability observable in these samples because of strong electron-phonone bond

reveals by the anomalous behavior of thermal expansion and elastic properties of TlGaSe<sub>2</sub> in paraelectric phase, i.e. in temperature interval which are far from structural PhT points in this crystal.

- 
- [1] *V.D.Muller, H.Hahn. Z. Anorg.Allg.Chem.* 438, 258, 1978.
- [2] *H.Hahn, B.Wellmann. J.Naturwissenschaften* 54, 42, 1967.
- [3] *T.J.Isaacs, J.D.Feichtner. J.Solid State Chem.* 14, 260, 1975.
- [4] *T.J.Isaacs. J.Appl.Crystallogr.* 6, 413, 1973.
- [5] *S.Kashida, Y.Kobayashi. J. Korean Phys. Soc.* 32, S 40, 1998.
- [6] *G.D.Guseinov, A.M.Ramazanade, E.M.Kerimova, M.Z.Ismailov. Phys.Stat.Sol.* 22, K 117, 1967.
- [7] *G.E.Delgado, A.J.MoraI, F.V.Perez, J.Gonzalez. Cryst. Res. Technol.* 42, 663, 2007.
- [8] *D.F. Mc.Moorrow, R.A.Cowley, P.D.Hatton, J.Banys. J.Phys.: Condens. Matter* 2, 3699, 1990.
- [9] *E.S. Krupnikov, F.Yu. Aliyev. FTT.* 30, 3158, 1988. (in Russian).
- [10] *N.A. Abdullayev, T.G. Mamedov, R.A. Suleymanov. FNT,* 27, 915, 2001. (in Russian).
- [11] *N.A.Abdullayev, T.G. Mammadov, R.A. Suleymanov. Phys.Stat.Sol.(b)* 242, 983, 2005.
- [12] *S.G. Abdullayeva, A.M. Abdullayev, K.K. Mamedov, N.T. Mamedov. FTT,* 26, 618, 1984. (in Russian).
- [13] *M.A.Aldzhanov, N.G.Guseinov, Z.N.Mamedov. Phys. Stat. Sol.(a)* 100, K 145, 1987.
- [14] *O.B. Plyush, A.U. Sheleg. Kristallographiya.* 44, 873 1999. (in Russian).
- [15] *Yu.V. Ilisavskiy, V.M. Sternin, R.A. Suleymanov, F.M. Salayev, M.Yu. Seidov. FTT,* 33, 104, 1991. (in Russian).
- [16] *R.A. Suleymanov, M.Yu. Seyidov, F.M. Salayev. FTT,* 33, 1797, 1991. (in Russian).
- [17] *Yu.G. Gololobov, V.P. Perga, I.N. Salivonov, E.E. Shigol. FTT,* 34, 115, 1992. (in Russian).
- [18] *Yu.P. Gololobov, I.N. Salivonov. FTT,* 33, 298, 1991. (in Russian).
- [19] *H.D.Hochheimer, E.Gmelin, W.Bauhofer, Ch von Schnering-Schwarz, H.G.von Schnering, J.Ihringer. W. Appel, Zeitschrift fur Physik B-Condensed Matter* 73, 257 (1988)
- [20] *S.G. Abdullayeva, N.T. Mamedov, Sh.S. Mamedov, F.A. Mustafayev. Neorg. Mat.* 25, 35, 1989. (in Russian).
- [21] *S.G. Abdullayeva, N.T. Mamedov, Sh.S. Mamedov, F.A. Mustafayev. FTT,* 29, 3147, 1987. (in Russian).
- [22] *N.Yamamoto, N.Mamedov, T.Shinohara. J. Crystal Growth* 237, 2023, 2002.
- [23] *K.R. Allakhverdiyev, N.D. Akhmedzade, T.G. Mamedov, T.S. Mamedov, M.Yu. Seidov. FNT,* 26, 76 2000. (in Russian).
- [24] *V. P.Aliyev, S.S.Babayev, T.G.Mammadov, M.Yu.Seyidov, R.A.Suleymanov. Sol. St. Comm.* 128, 25, 2003.
- [25] *F.A.Mikhailov, E.Basaran, E.Senturk, L.Tumbek, T.G.Mammadov, V.P.Aliev. Phase Transitions* 76, 1057, 2003.
- [26] *F.A.Mikhailov, E.Basaran, E.Senturk, L.Tumbek, T.G.Mammadov, V.P.Aliev. Sol. St. Comm.* 129, 761, 2004.
- [27] *F.A.Mikhailov, E.Senturk, L.Tumbek, T.G.Mammadov, T.S.Mammadov. Phase Transitions* 78, 413. 2005.
- [28] *F.A.Mikhailov, E.Basaran, E.Senturk, L.Tumbek, T.G.Mammadov. Journal of Non-Crystalline Solids* 351, 2809, 2005.
- [29] *R.M.Sardarly, O.A.Samedov, I.Sh.Sadikov, E.I. Mordukhaeva, T.A.Gabibov. Sol. St. Comm.* 77, 453, 1991.
- [30] *Yu. Banis, A.Brilingas, I.Grigas, G. Guseynov. FTT* 29, 3324, 1987. (in Russian).
- [31] *A.K. Abiyev, N.A. Bakhishov, A.E. Bakhishov, M.S. Gadjiyev. Izvestiya vuzov. Fizika.* 12, 84, 1989. (in Russian).
- [32] *S.S.Babaev, E.Basaran, T.G.Mammadov, F.A.Mikhailov, F.M.Salehli, M-H.Yu. Seyidov, R.A.Suleymanov. J.Phys.: Condens. Matter* 17, 1985 (2005)
- [33] *M.Yu. Seyidov, R.A. Suleymanov, R.Khamoyev. FTT.* 48, 1270, 2006. (in Russian).
- [34] *S.P. Gabuda, S.G. Kozlova, N.T. Mamedov, N.K. Moroz. FTT,* 32, 1708, 1990. (in Russian).
- [35] *A.M. Panich, D.C. Ailion, S. Kashida, N. Gasanly. Phys. Rev. B* 69, 245319, 2004.
- [36] *F.A.Mikhailov, B.Z.Rameev, S.Kazan, F.Yildiz, T.G.Mammadov, B.Aktas. Sol. St. Comm.* 133, 389, 2005.
- [37] *N.I. Agladze, B.P. Antonyuk, V.M. Burlakov, E.A. Vinogradov, G.N. Jijin. FTT,* 23, 3289, 1981. (in Russian).
- [38] *Yu.I.Durnev, B.S.Kulbuzhev, A.U.Malsagov, L.M.Rabkin, V.I.Torgashev, Yu.I.Yuzyk. Phys. Stat. Sol. (b)* 153, 517, 1989.
- [39] *Yu.G.Goncharov, G.V.Kozlov, B.S.Kulbuzhev, V.B.Shirokov, V.I.Torgashev, A.A.Volkov, Yu.I.Yuzyk. Phys. Stat. Sol. (b)* 153, 529, 1989.
- [40] *V.M. Burlakov, S.Nurov, A.P. Ryabov. FTT,* 30, 3616, 1988. (in Russian).
- [41] *V.M.Burlakov, M.R. Yahkeev. Phys. Stat. Sol. (b),* 151, 337, 1989.
- [42] *A.A.Volkov, Yu.G.Goncharov, G.V.Kozlov, V.I.Torgashev, V.B. Shirokov. FTT,* 30, 3621, 1988. (in Russian).
- [43] *A.A. Volkov, Yu.G. Goncharov, G.V.Kozlov, S.P. Lebedev, A.M. Prokhorov, R.A. Aliyev, K.R. Allakhverdiyev. Pisma v JETF,* 37, 517, 1983. (in Russian).
- [44] *A.A. Volkov, Yu.G. Goncharov, G.V. Kozlov, R.M. Sardarli. Pisma v JETF,* 39, 293, 1984. (in Russian).
- [45] *B.R. Gadjiyev, Kh.M. Pashayev. FNT,* 17, 644, 1991. (in Russian).
- [46] *B.R. Gadjiyev. FNT,* 17, 889, 1991. (in Russian).
- [47] *F.A.Mikhailov, E.Basaran, T.G.Mammadov, M.Yu.Seyidov, E.Senturk. Physica B* 334, 13, 2003.
- [48] *S.G. Abdullayeva, V.A.Aliyev, N.T. Mamedov, M.K. Sheynmak. FTP.* 17, 1787, 1983. (in Russian).

- [49] *S.G.Abdullaeva, V.A.Aliev.* Phys.Stat.Sol.(a) 69, K33, 1982.
- [50] *Yu.Yu. Kopayev, V.V. Tutushev.* Pisma v JETF, 41, 320, 1985. (in Russian).
- [51] *B. R.Gadjiev.* Ferroelectrics 291, 111, 2003.
- [52] *V.A. Golovko, A.P. Levanyuk.* JETF, 77, 1556, 1979. (in Russian).
- [53] *V.A. Golovko, A.P. Levanyuk.* JETF, 81, 2296, 1981. (in Russian).
- [54] *V.A. Golovko, A.P. Levanyuk.* Pisma v JETF, 32, 104, 1980. (in Russian).
- [55] *V.A.Golovko, A.P.Levanyuk.* Ferroelectrics 26, 699 (1980)
- [56] *M.Yu.Seyidov, Y.Sahin, M H.Aslan, R.A.Suleymanov.* Semicond. Sci. Technol. 21, 1633, 2006.
- [57] *M.Yu.Seyidov, Y.Sahin, D.Erbahar, R.A.Suleymanov.* Phys. Stat. Sol. (a) 203, 3781 (2006)
- [58] *V.M. Fridkin.* Segnetoelektriki-poluprovodniki. M. 1976. 408 c. (in Russian).
- [59] *V.M. Fridkin.* Fotosegnetoelektriki. M. 1979. 284 c. (in Russian).
- [60] *R. A.Smith.* Semiconductors. Cambridge. 1978. 561 p.
- [61] *I.A. Karpovech, A.A. Chernova, L.I. Demidova, E.I. Leonov, V.M. Orlov.* Neorg. Mater., 8, 70, 1972. (in Russian).
- [62] *V.A.Aliev,E.F.Bagirzade, N.Z.Gasanov, G.D.Guseinov.* Phys. Stat.Sol.(a) 102, K109 (1987)
- [63] *S.N. Mustafayeva, V.A. Aliyev, M.M. Asadov.* FTT, 40, 48, 1998. (in Russian).
- [64] *A.Neumann.* Appl. Phys. Rev. 90, 1 (2001)
- [65] *E.A. Lebedev, M.Ya. Goykhman, K.D. Cendin, I.V. Podeshvo, I.E. Terukov, V.V. Kudryavcev.* FTP. 38, 1115, 2004. (in Russian).
- [66] *K.D. Cendin, E.A. Lebedev, A.B. Shmelkin.* FTT, 47, 427, 2005. (in Russian).
- [67] *L.I. Bulayevskiy.* UFN, 115, 263, 1975. (in Russian).
- [68] *L.I. Bulayevskiy.* UFN, 116, 449, 1975. (in Russian).
- [69] *Incommensurate Phase in Dielectrics 1. Fundaments / R.Blinc, A.P.Levanyuk (ed.).* North Holland, Amsterdam, 1986.
- [70] *H.Z.Cummins.* Physics Reports 185, 211, 1990.
- [71] *M.Born, K.Huang.* Dynamical theory of crystal lattices. Oxford, 1964, 489 p.
- [72] *K.R.Allakhverdiev, T.G.Mammadov, R.A.Suleymanov, N. Z.Gasanov.* J. Phys. Condens. Matter 15, 1291, 2003.
- [73] *T.G. Mamedov, R.S. Suleymanov.* FTT, 45, 2141, 2003. (in Russian).
- [74] *N.A.Abdullaev, K.R.Allakhverdiev, G.L.Belenkii, T.G.Mamedov, R.A.Suleymanov, Y.N.Sharifov.* Sol.St.Comm. 53, 601, 1985.
- [75] *A.I. Golovashkin, A.P. Rusakov.* FTT, 49, 1363, 2007. (in Russian).

**M.Yu. Seyidov, R.A. Süleymanov, T.Q. Məmmədov, R.A. Xamoyev**

### **TiGaSe<sub>2</sub> – PAYERLS DIELEKTRİKİ**

Laylı TiGaSe<sub>2</sub> seqnetoelektrik-yarımkəçirici kristalda dielektrik nüfuzluğunun ( $\epsilon$ ), qaranlıq və piroelektrik cərəyanlarının temperatur asılılıqları və həmçinin 77-300K temperatur intervalında stabil temperaturalarda volt-ampere xarakteristikaları və qaranlıq cərəyanının zamana görə dəyişməsi tədqiq edilmişdir. Kiçik tezliklərdə laylara perpendikulyar istiqamətdə ölçülən  $\epsilon(T)$  əyrisində ilk dəfə olaraq 150K və 200K temperaturalarla sərhədlənən “çökük” formalı anomaliya müşahidə olunmuşdur. Həmçinin ilk dəfə təcrübə olaraq 145-205K temperatur intervalı ilə məhdudlanan nümunənin volt-ampere xarakteristikasında cərəyanın alçaq tezlikli kvaziperiodik rəqsləri şəklində müşahidə olunan elektrik qeyri-tarazlıqlarının təkamülü qeydə alınmışdır. Cərəyan qeyri-tarazlıqlarının zaman xarakteri müəyyən edilmişdir. Bu qeyri-tarazlıqların müşahidə olunması üçün elektrik sahəsinin nümunəyə verilməsi kontaktsız, nazik lövhə şəkilli slyüdadan hazırlanmış potensialötürən elektrodlar vasitəsilə verilməsinin vacibliyi göstərilmişdir. Qeyri-tarazlıqların təbiəti və onun laylı TiGaSe<sub>2</sub> kristalının müxtəlif fiziki parametrlərinə təsiri öyrənilmişdir.

**М.Ю. Сеидов, Р.А. Сулейманов, Т.Г. Мамедов, Р.А. Хамоев**

### **TiGaSe<sub>2</sub> – ПАЙЕРЛСОВСКИЙ ДИЭЛЕКТРИК**

В работе представлены результаты исследований температурных зависимостей диэлектрической проницаемости ( $\epsilon$ ), темнового и пироэлектрического токов, а также вольт-амперные характеристики и временные эволюции темнового тока слоистого сегнетоэлектрика-полупроводника TiGaSe<sub>2</sub>, полученные при фиксированных температурах в интервале 77K ÷ 300K. На кривой  $\epsilon(T)$ , измеренной в направлении перпендикулярном к слоям, в области низких часто впервые обнаружена ярко выраженная аномалия в виде “ямы”, с визуально заметными температурными границами ~ 150K и ~ 200K. Также впервые экспериментально зафиксировано развитие электрических неустойчивостей, проявляющихся в виде низкочастотных квазипериодических колебаний тока на вольт-амперных характеристиках образца в строго ограниченном температурном интервале 145K ÷ 205K. Установлен временной характер токовых неустойчивостей. Показано, что для наблюдения указанных неустойчивостей важно, чтобы электрическое поле к образцу подавалось посредством бесконтактных, потенциалоподающих электродов, выполненных в виде тонких прокладок из слюды. Обсуждается природа неустойчивости и её влияние на различные физические параметры слоистого кристалла TiGaSe<sub>2</sub>.

Received: 10.09.08