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THE ROLE OF IMPURITIES IN THE MEMORY EFFECT IN FERROELECTRICS-SEMICONDUCTORS $TlInS_2$ AND $TlGaSe_2$

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The temperature dependences of the dielectric constant of ferroelectrics-semiconductors $TlInS_2$ and $TlGaSe_2$ have been studied after their annealing within the incommensurate phase. Unusual memory effects accompanied by both a remarkable inflection of the temperature dependence curves in the incommensurate phase, and various shifts of the incommensurate (T_i) and commensurate (T_c) phase transition temperatures have been revealed in both of crystals. Observed effects are explained on the basis of defect density wave (DDW) model taking into account the interaction of modulation wave with charge carriers localized at impurity states. Thermally activated population of these states during the heating or cooling processes is responsible for changes of phase transition temperatures

INTRODUCTION

The ternary compounds $TlInS_2$ and $TlGaSe_2$ belong to the group of semiconductors having layered crystalline structure. According to structural investigations [1], the crystals possess monoclinic structure with space symmetry group of C_{2h}^6. It has been established that both of the investigated crystals exhibit a sequence of structural phase transitions to an incommensurate (at T_i ~214K in $TlInS_2$ and ~113K in $TlGaSe_2$) and commensurate ferroelectric (at T_c ~196 K in $TlInS_2$ and ~105 K in $TlGaSe_2$) phases. According to existing data, the transition to incommensurate phase is associated with condensation of a soft mode at point **q**(δ, δ , 0.25) of the Brillouin zone, where δ is the incommensuration parameter. On subsequent cooling both crystals exhibit phase transition into the commensurate phase with quadrupling of the unit cell parameter along the direction perpendicular to the layers. In polar phase the spontaneous polarization vector lies in the plane of the layers [2,3].

As it is known, the presence of incommensurately modulated structure in crystals leads to occurrence of long-lived metastable states in the temperature interval of the successive incommensurate and commensurate phase transitions, which brings to the presence of thermal hysteresis and so-called memory effects [4,5], which were found to be observed after annealing of the crystals in the incommensurate phase. The fact is that when scanning the temperature after annealing, the crystals "remembered" the annealing temperature on subsequent heating or cooling cycle. According to widely accepted explanation existing in the literature [5], these effects are considered to be caused by mobile defects interacting with a modulated distortion. The mobile defects move to new positions during the long time annealing of the crystal within the incommensurate phase and create so called defect density wave (DDW). These defects still remain at their new positions on subsequent heating or cooling and, as a result, some changes in measuring parameters will be registered. Such "classic" memory effects, which include the influence of annealing on the shape of dielectric constant's temperature dependence, were observed in number of crystals with incommensurate phase [6-8]. In these cases the temperature dependence of $\nabla\varepsilon/\varepsilon$ has an "inflexion" point at annealing temperatures ($\nabla\varepsilon$ is the difference in ε values measured after and before the annealing). Besides, the low temperature shifts of the incommensurate-commensurate phase transition temperature can be observed after annealing the sample inside the incommensurate phase (a kind of memory effect) [9,10].

The present paper reports the results of measurements of temperature behavior of dielectric constants of $TlInS_2$ and $TlGaSe_2$ crystals on heating regime with different temperature scanning rates after annealing the crystals for some hours at some fixed temperatures within the incommensurate phase. Various shifts both to higher and lower temperatures for T_i and T_c, depending on the heating rate were observed for the first time together with the "classic" memory effect.Obtained results are discussed in the framework of the DDW model, which takes into account the role of charge carriers localized on the defects in commensurate-incommensurate and incommensurate – paraelectric phase transitions.

EXPERIMENTAL DETAILS

The crystals were grown by Bridgman method and oriented along the polar axis, which lies in the cleavage plane. The samples had rectangular form and the surfaces perpendicular to the layers plane were polished and covered with silver paste. The dimensions of the electrodes were 6×2 mm^2 with an inter electrode distance of 2 mm. Measurements of the real part of the dielectric susceptibility were performed using a capacitance bridge at the frequency of 1 kHz in the temperature range of 77-300 K. A cryostat and temperature controller allowed to scan the temperature with a rate between ~0.5 and ~3 K/min and to stabilize the temperature with accuracy better than 0.05 K.

The measurements were performed according to following procedure. Firstly the samples were cooled down to 77 K and the temperature dependence of the dielectric constant was measured on heating regime. After this measurement the samples were cooled down to 77 K and kept at this temperature during 20 min, then they heated and annealed at the some fixed temperature within the incommensurate phase during some hours. Then the samples were cooled again during the 15-30 minutes and the temperature dependences of the dielectric constant were measured on a heating cycle. After each measurement the sample was heated up to the room temperature then cooled, and the next cycle of measurement was performed.

EXPERIMENTAL RESULTS

The temperature dependences of the dielectric constant of $TlInS_2$ and $TlGaSe_2$ crystal without and after annealing the samples at 208 and 110 K respectively are shown in Figs. 1 and 2. All ε(T) curves are characterized by peaks, which correspond to phase transition points T_i and T_c. Thermal annealing within the incommensurate phase leads to two main effects: the classic memory effect, characterized by the change of ε(T) curve within the incommensurate phase and the shifting of phase transition points, which are discussed in details below. Figs. 3 and 4 demonstrate the memory effects in $TlInS_2$ and $TlGaSe_2$ crystals as they usually observed in other crystals with incommensurate phase, that is the changes of dielectric constant temperature behavior after and before annealing,$\nabla\varepsilon/\varepsilon$. In the case of experimental conditions realized during the registration of ε(T) curve, after annealing of the crystals during the 2-5 hours within the incommensurate phase the classic memory effect is observed with inflexion point at annealing temperature in both crystals. As it is seen from Figs. 2,3, the amplitude of the $\nabla\varepsilon/\varepsilon$ increases with annealing time, but the shape of $\nabla\varepsilon/\varepsilon$ curve depends on the annealing temperature also.

In both crystals the memory effect is not observed if the annealing temperature is choused within the commensurate phase. As in other crystals with memory effect, the amplitude of the $\nabla\varepsilon/\varepsilon$ function gradually decreases and memory effect is totally disappeared after the crystals heat to some temperature above the T_i. However, the obvious peculiarities of memory effect manifestation in investigated crystals also exist. First of all, the temperature interval in which anomalous behavior of dielectric constant is observed is very large comprising almost the whole incommensurate phase interval. Usually (see for ex. [4-6]), memory effect reveals itself in 1-3K temperature interval after 15-20 hours annealing within the incommensurate phase. Besides, the amplitude of deviation of dielectric constant in our case is almost twice larger in spite of much shorter annealing time. At last, when annealing temperature shifts to the lower temperatures, the $\nabla\varepsilon/\varepsilon$ curve becomes ''asymmetric'' (Fig.3a), proving once again that the memory effect comprises the whole incommensurate phase.

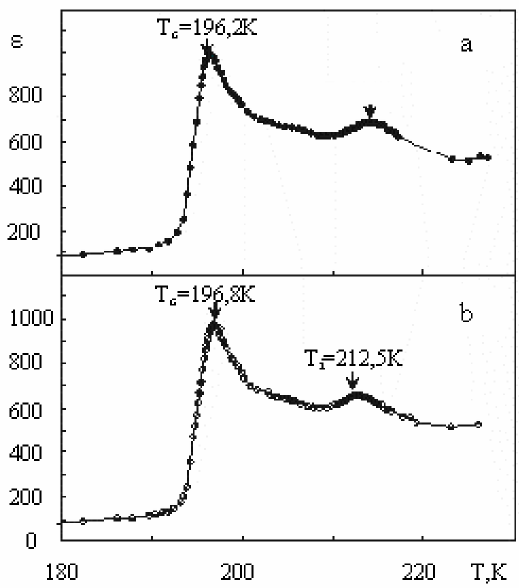

Fig.1. Temperature dependences of the real part of dielectric constant in $TlInS_2$ crystal measured on heating with rate- 1.11 K / min: a – without annealing, b – after annealing for 3 hours at 210 K.

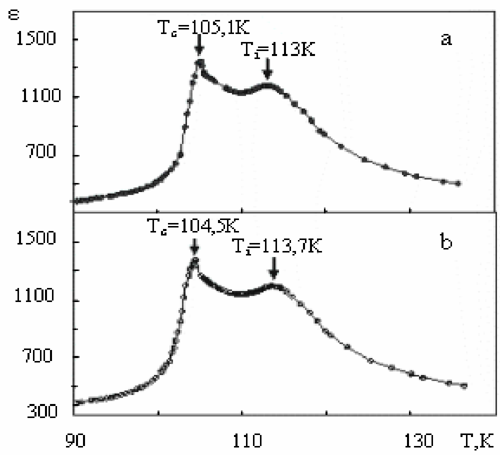

Fig.2. Temperature dependences of the real part of dielectric constant in $TlGaSe_2$ crystal measured on heating with rate - 0.4 K/min: a – without annealing, b – after the annealing for 3 hours at 110 K.

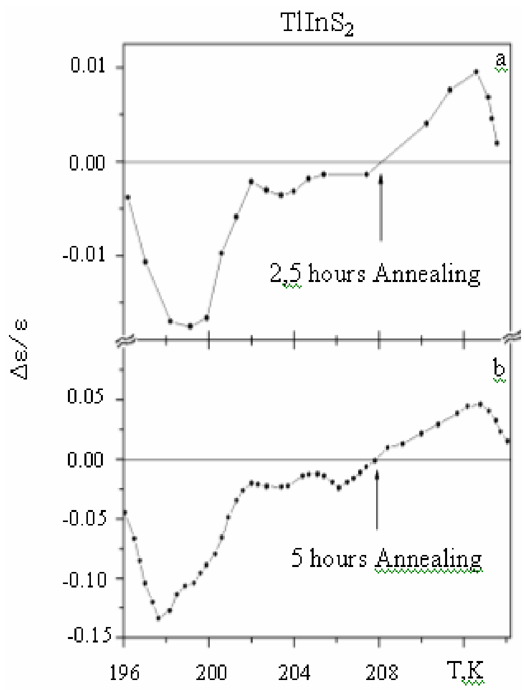

Fig. 3. The temperature dependencies of the deviations of the real part of dielectric constant, ∇ε/ε, in $TlInS_2$ crystals measured on heating cycle after the annealing at 208 K: a) for 2.5 hours; b) 5 hours

The second effect, which is of special interest, is the shifting of phase transitions temperatures T_i and T_c after the annealing, depending on the heating rate. Different types of shifts of phase transition points were obtained on heating the sample with various heating rates. The results of such experiments for $TlInS_2$ crystal are presented in Table 1 and Fig. 5.

As it can be seen from Table 1, and Fig.5, T_i and T_c in $TlInS_2$ can shift to lower and higher temperatures depending on heating rate. It is important to note that described effects can only be observed after thermal annealing of the crystals within the incommensurate phase. The following experimental details are of special interest. As it is clearly seen from Fig. 5, the positive saturation tendency is observed in T_i and T_c behavior at higher heating rates. The "usual", that is unshifted values of T_c =196 K and T_i =214 K are observed at a heating rates close to 1 K/min.

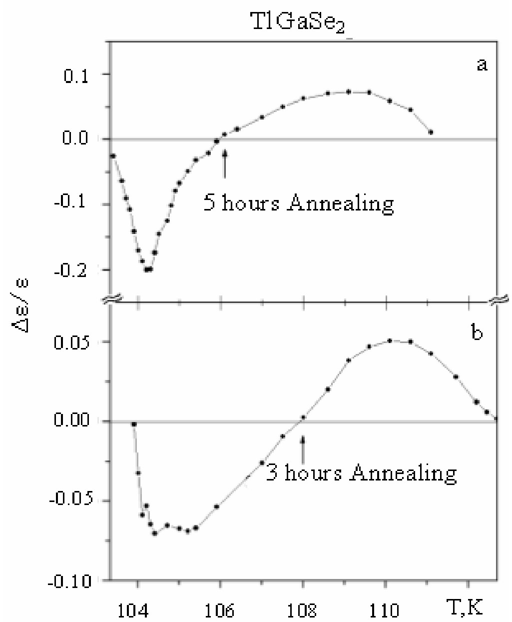

Fig. 4. The temperature dependencies of the deviations of the real part of dielectric constant, ∇ε/ε, in $TlGaSe_2$ crystals measured on heating cycle after the annealing for 5 hours at 106K-''a'', and 3 hours at 108K-''b''.

In $TlGaSe_2$ crystal the character of the phase transitions temperatures behavior with heating rate is the same as in the $TlInS_2$ crystal. But in contrast to $TlInS_2$ crystal, the values of shifting for T_i and T_c after annealing in $TlGaSe_2$ lead to the widening of the temperature interval in which incommensurate phase exists. Fig. 2b demonstrates the $\varepsilon(T)$ behavior for $TlGaSe_2$ crystal. As in the case of $TlInS_2$ crystal, thermal annealing within the incommensurate phase leads to the shifting of phase transition temperatures. After annealing the sample for 3 hours at the temperature 110 K, T_c shifts to lower temperatures, whereas T_i – to higher temperatures under experimental conditions realized in this case, that is at heating rate 0.4 K/min.

Table 1. Heating rates and phase transitions temperatures, T_c and T_i in $TlInS_2$ crystal after annealing the sample at the temperature 210 K for 3 hours.

Heating rate, K/min	T_c, K	T_i, K	ΔT_c, K	ΔT_i, K
0.7	198.6	215.8	2.3	1.8
0.79	197.6	214.8	1.4	0.7
0.9	197.2	213.4	0.9	- 0.5
0.99	197.6	215.2	0.73	- 0.95
1.11	196.8	212.5	0.6	- 1.5
1.28	196.3	213.1	0.22	- 1.66
2.38	195.5	213	- 0.8	- 1.8

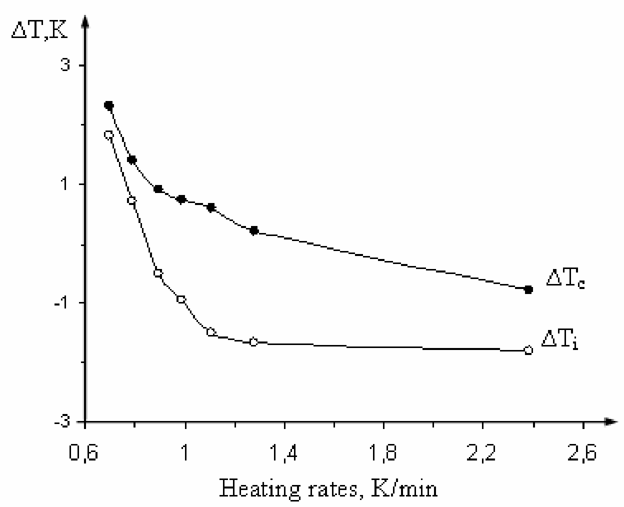

Fig. 5. Heating rate dependences of the phase transition temperature shifts (ΔT_c and ΔT_i) in $TlInS_2$ crystal (according to data given in Table 1)

DISCUSSION

As it is mentioned above, the mechanism of memory effect in crystals with incommensurate phase is based on the interaction of modulated wave with periodic potential created by DDW [4-6]. The modulation wave becomes locked at temperature interval close to annealing temperature leading to anomalies like shown in Figs. 2-3. Usually this type of artificial lock-in manifests itself in temperature interval which depends on some parameters which describe the modulation wave, defect subsystem and their interaction which each other, namely: modulation wave-defect interaction potential, concentration of mobile defects, their diffusion constant, annealing time, temperature variation of modulation wavelength, etc. In thiourea [5,6], for example, the artificial lock-in temperature interval does not exceed 1-2 K after annealing 10-15 hours. The same order of lock-in temperature interval is characteristic for memory effects in other crystals. Substantially wider temperature interval, which is typical for $TlInS_2$ and $TlGaSe_2$, needs special explanation and we think that this peculiarity of memory effect is due to peculiar character of mobile defects in layered crystals. Really, it is well known [11,12], that the most typical defects in layered crystals are interlayer defects which are very mobile and have very high concentration due to the weak interlayer bonding. The modulation wave in $TlInS_2$ and $TlGaSe_2$ is created in the direction perpendicular to the layers, so that it can be well distorted by interplanar defects. Thus, all the important parameters, which can lead to the widening of the artificial lock-in interval in layered crystals, are extremely large comparing with that in other crystals in which the memory effect is observed.

Usually the role of mobile defects is restricted to the creation of DDW and memory effects of the type described above. However, charge carriers localized at such defects may play an important role in phase transitions taking place in ferroelectrics-semiconductors.

As it was shown above, the annealing within the incommensurate phase in $TlInS_2$ and $TlGaSe_2$ crystals leads to the shifting of the phase transition temperatures. It seems natural to suppose that the model of extremely mobile defects with high concentration can help in understanding of these phenomena also. Below we propose the mechanism explaining the obtained results, based on the theoretical investigations of the role of charge carriers in memory effect and phase transitions in ferroelectrics-semiconductors [13-16].

It is well known that the incommensurate-commensurate phase transition temperature depends on the rate of temperature scanning even without any annealing: T_c shifts to the lower temperatures with increasing of heating rate. In this sense it must be emphasized that at least at heating rates realized in the present work no shifts of phase transition temperatures were observed without annealing. We think that the observed effects can be explained taking into account the role of charge carriers in these crystals.

The study of the role of charge carrier subsystem on the memory effects in ferroelectric-semiconductors with incommensurate phase is of a great interest. In series of works [13-15] it was shown that these phenomena are greatly influenced by the charge carriers localized at defect states and interacted with modulation wave.

It is well known [16], that in ferroelectrics-semiconductors the phase transition temperature into the ferroelectric state shifts to lower temperatures due to the influence of electronic subsystem. In [17] the contribution of charge carriers on phase transition temperatures in semiconductors with incommensurate phase is considered within the framework of phenomenological theory of the structural phase transitions. According to this approach, both T_i and T_c will shift to lower temperatures when trapping centers will be full comparing with the case when they will be empty. However, it is worth to mention that the occupation of trapping levels and as a result the position of the phase transition temperatures will depend on interrelation between heating rate and relaxation time of electrons on the trapping levels, τ. Really, if heating time will be much higher than τ (slow heating rates) electrons will release from trapping centers and phase transition temperatures will correspond to the case of empty centers. In the case of fast heating when heating time much less than τ, trapping centers will be "overfilled" and phase transition temperatures will shift to lower temperatures in comparison with the previous case. It is clear that in the real experimental conditions both type of shifting for phase transition temperatures can be observed depending on heating rate. In this case the negative (to lower temperatures) shifts will be observed at higher heating rates and positive ones will be registered at smaller heating rates. Besides, increasing the heating rate the "saturation" of shifting values must be observed because all traps will be filled and no additional traps available. As it is seen from Fig. 5 and Table 1, all above-mentioned phenomena are observed experimentally in the case of $TlInS_2$ crystals. It becomes clear from obtained results that heating rates of 2.4 K/min are fast rates, whereas heating with rates of 0.5 K/min correspond to slow heating. The same tendency in phase transitions temperatures behavior is characteristic for $TlGaSe_2$ crystals also.

Two main problems arise from the considerations given above. The first problem is connected with the experimental investigations of trapping centers in $TlInS_2$ and $TlGaSe_2$ crystals. As a matter of fact, theoretical analysis requires the existence of trapping centers with appropriate parameters. First of all these traps must be activated in temperature region where phase transitions takes place, then the corresponding relaxation times for charge carriers must be comparable with the real experimental conditions during heating or cooling process. According to thermally stimulated current investigations in $TlInS_2$ crystals [18], the first and main requirement of theory is fulfilled: thermally activated current really exists in the temperature region of incommensurate and commensurate phase transitions in this crystal. Our recent investigations of thermally stimulated current in $TlGaSe_2$ showed that the same is true for this crystal. However, there is no information about the relaxation times of charge carriers in both crystals. The second problem that must be considered: theory described in [13,14,17] did not require the thermal annealing within the incommensurate phase to observe the shifts of phase transition points. However, the obtained results definitely show that only thermal annealing within the incommensurate phase gives the effects described above. According to [18], the incommensurate phase in $TlInS_2$ crystals greatly influences the parameters of impurity centers. As it was shown, above discussing the memory effect, these centers are very likely the defects placed between the layers. The interaction between modulation wave and impurity centers can be treated in the framework of memory effect mechanism. We think that the problem of modification of impurity centers parameters under the influence of modulation wave in the incommensurate phase is of special interest and must be considered separately. We can note here only, that the interaction between the mobile defects and modulation wave in ferroelectrics-semiconductors with layered crystalline structure may be very effective compared with other compounds with incommensurate phase, thus leading to specific manifestation of memory effect in formers due to specific type of mobile defects.

CONCLUSION

Thus, various shifts of the incommensurate and commensurate phase transition points both to higher and lower temperatures after the annealing within the incommensurate phase temperature interval depending on the heating rate were observed for the first time in $TlInS_2$ and $TlGaSe_2$ crystals together with the "classic" memory effect with "inflexion" point in the $\nabla\varepsilon/\varepsilon$ (T) curve. . The peculiarities of the giant "classic" memory effect in the investigated crystals can be considered in the frame of the model of defect density waves (DDW), so that such memory effect in layered crystals embraces the wide temperature interval due to the specific type of mobile defects in crystals with layered crystalline structure.

Widening and narrowing of the incommensurate phase temperature interval are considered in the framework of the model, which takes into account the role of charge carriers localized on the defects in commensurate-incommensurate and incommensurate – paraelectric phase transitions. Thermally activated population of these states is responsible for changes of phase transition temperatures.

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