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TIME RELAXATION OF METASTABLE CHAOTIC STATE IN $TlInS_2$

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The results of measurements of time dependences of the dielectric constant of $TlInS_2$ in the commensurate ferroelectric phase are presented. Observation of the decay of ε at different stabilized temperatures below the commensurate phase transition temperature after cooling from the incommensurate phase revealed a presence of two characteristic relaxational time constants with a different temperature behaviour. This peculiarity is considered as a result of occurance of a chaotic state accompanied by coexistence of different commensurate ferroelectric phase structures in the temperature range between 194 and 200K. As a result, the dielectric anomaly at about 195K is considered as a phase transition accompanying with destruction of the improper ferroelectric polarization.

INTRODUCTION

$TlInS_2$ belongs to a group of ternary layered chalcogenide semiconductors with a monoclinic structure [1]. On cooling it exhibits successive structural phase transitions into incommensurate (IC) and commensurate (C) ferroelectric phases. According to structural investigations [2], the transition from the paraelectric to the incommensurate phase occurs at T_{i1}~216K with condensation of a soft mode at a point in the Brillouin zone characterized by $q_i(\delta,\delta,0.25)$, where δ is the incommensuration parameter (δ=0.012), and the lock-in transition to the commensurate phase at T_{c1}~204K takes place with quadrupling of the unit cell volume along the direction of perpendicular to the layers. The presence of the ferroelectric soft mode with Curie temperature T_{c2}~201K and with the Curie constant of ~10^3 was discovered in a result of submillimeter spectra and dielectric constant measurements [3, 4]. The spontaneous polarization vector of the ferroelectric phase lies in the plane of layers. A set of anomalies in the temperature dependence of dielectric constant in $TlInS_2$ at about 216 K, 206 K, 204 K, 201 K and in the range of 190-195 K has been revealed after the detailed investigations of dielectric susceptibility and spontaneous polarization [5-8]. Some theoretical models have been suggested to explain the succession of the phase transitions in $TlInS_2$. According to [7], a weak disturbance (such as structural defects, impurities) can lead to splitting of IC-C phase transition in $TlInS_2$ into two closely spaced IC-C phase transitions at T_{c1}~204K and T_{c2}~201K. In a frame of this model the anomaly at T_{i2}~206 K is treated as an appearance of a new incommensurate structure. The presence of two modulated distortions in the crystal structure of $TlInS_2$ was also suggested in [8]. In a recent model [9], the coexistence of improper and proper ferroelectricity in the same crystal structure have been proposed according to the observed shifts of the phase transition points under the influence of the external bias electric field.

As it is known, the presence of incommensurately modulated structures in crystals leads to occurrence of long-lived metastable states in the temperature interval of the successive commensurate phase transitions. This brings to the presence of thermal hysteresis of the dielectric susceptibility, which has been observed for $TlInS_2$ [10]. Thermal hysteresis is usually attributed to defect-induced pinning of discommensurations, which prevents the crystal from reaching thermal equilibrium after the incommensurate-commensurate phase transition. A slow time evolution of the dielectric constant of $TlInS_2$ during approaching to the thermal equilibrium attracts much interest because of its importance for understanding the kinetics of the commensurate phase transitions.

The present paper reports the results of measurements of time dependencies of the dielectric constant of $TlInS_2$ in the commensurate ferroelectric phase after cooling the crystal.

EXPERIMENT

The crystals were grown in evacuated quartz tubes by using a modified Bridgman method. The samples, in rectangular form, were oriented along the polar axis which lies in the cleavage plane (the morphology of crystals permits cleavage to plane parallel plates with mirror-like surfaces). The plates were gently polished, cleaned and covered with silver paste. The dimensions of the electrodes were $5\times2mm^2$ with an inter-electrode distance of 1mm.

Measurements of the real part of the dielectric susceptibility ε' were performed using the capacitance bridge method at frequencies of 50kHz with instrument sensitivity of 0.1pF and with accuracy of 1%. A low-temperature cryostat system used in the measurements allowed to scan the temperature with a rate of about 0.1K/min and to stabilize the temperature with an accuracy better than 0.05K. The temperature was measured by a copper-constantan thermocouple placed close to the sample. The accuracy of the temperature measurements was better than 0.02K.

RESULTS AND DISCUSSION

As mentioned in [10], the dielectric constant of $TlInS_2$ along the ferroelectric axis exhibits the remarkable thermal hysteresis in both the incommensurate and commensurate phase. The temperature dependence of the dielectric constant of $TlInS_2$ measured during cooling and heating cycles is shown in Fig.1. Figure shows that the most prominent thermal hysteresis has been observed at around 195K, which is lower than the ferroelectric commensurate phase transition at T_{c2}~201K. The observed phenomenon is attributed to the formation of long-living metastable states caused by pinning effects of a domain-like soliton structure. According to [5], at thermocycling in the temperature interval of 194÷196K, the value of the thermal hysteresis of dielectric susceptibility was found to decrease with each successive cycle of cooling and heating.

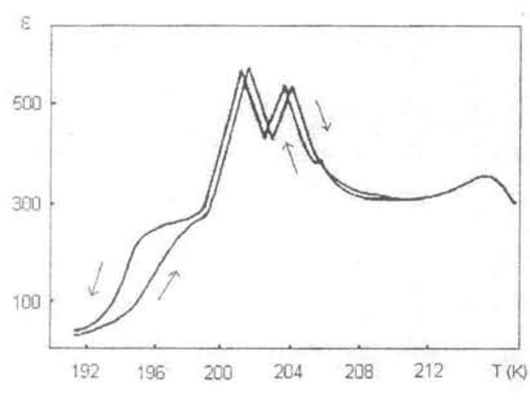

Fig.1.
Temperature dependences of the dielectric constant ε of $TlInS_2$ near the phase transitions on cooling and heating regimes.

Such an unstable behaviour is characteristic indication of a chaotic state. The presence of this state is an evidence of the coexistence of at least two different phases in the mentioned temperature range. The existence of the metastable chaotic state in the commensurate ferroelectric phase of $TlInS_2$ has been proposed from Raman lineshape analysis in [11]. Besides, the studies of dielectric hysteresis loops [8], sound velocity and absorption [12-14] in a wide temperature range revealed some peculiarities around 195K, which are regarded as independent confirmations of the occurence of the chaotic state at T<201K which is, in our opinion, characterized by the coexistence of improper and proper ferroelectric phases appeared at T_{c1}~204K and T_{c2}~201K respectively [9].

In order to check the relaxational behaviour of the metastable states and the kinetics of the phase transformations in the chaotic state, the time variations of the dielectric constant at different fixed temperatures in the range of 194-200K have been investigated. Measurements were performed at eight different temperatures. The sample was cooled from paraelectric phase down than 200K, then the temperature was stabilized and the time dependencies were measured. The results are presented in Fig.2. The equilibrium values of the dielectric constant ε_∞ at fixed temperatures have been chosen as the averages between the values of ε(T) measured during heating and cooling. It is evident that the time evolution of ε can be best fitted with:

$$\varepsilon_t = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty) \exp(-t/\tau)$$

where ε_0 and ε_∞ are the dielectric constant values at t=0 and t=∞ respectively, τ is a relaxation time constant.

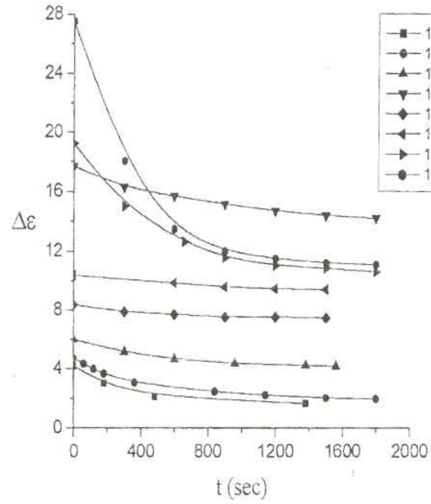

Fig.2.
Time dependences of the dielectric constant $\Delta\varepsilon=\varepsilon_t-\varepsilon_\infty$ of $TlInS_2$ at fixed temperatures inside the temperature interval 194-200K after cooling the sample from the paraelectric state.

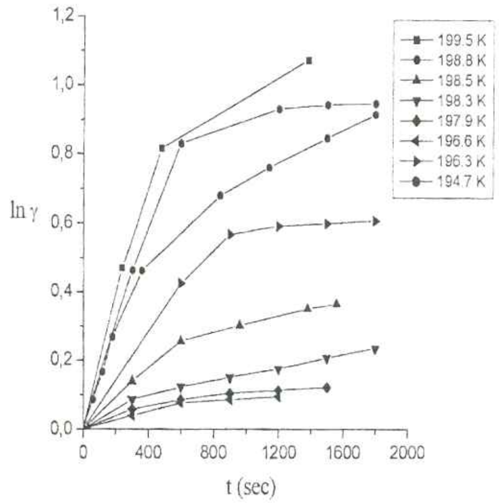

Fig.3.
Time dependences of ln γ ($\gamma=[(\varepsilon_0-\varepsilon_\infty)/(\varepsilon_t-\varepsilon_\infty]$) in $TlInS_2$.

In order to evaluate the characteristic relaxation time constants, the $\ln[(\varepsilon_0-\varepsilon_\infty)/(\varepsilon_t-\varepsilon_\infty)]$ versus t curves have been constructed. The results are depicted in Fig.3. All curves are seen to be linear functions of time. It is evident that the relaxation times can be obtained by determining the reciprocal values of the slope ratios of these lines. As is seen from the figure, there are two different relaxational behaviours for each of time dependencies. Naturally, these relaxation times are connected with different phases coexisting in the mentioned temperature interval. Thus, it is possible to study the kinetics of the phase transformations by changing the temperature during the chaotic state using the temperature dependencies of relaxation times. Finally, we can obtain information about the temperature evolution of the chaotic state.

The temperature dependencies of the relaxation times τ_1 and τ_2 are presented in Fig.4.

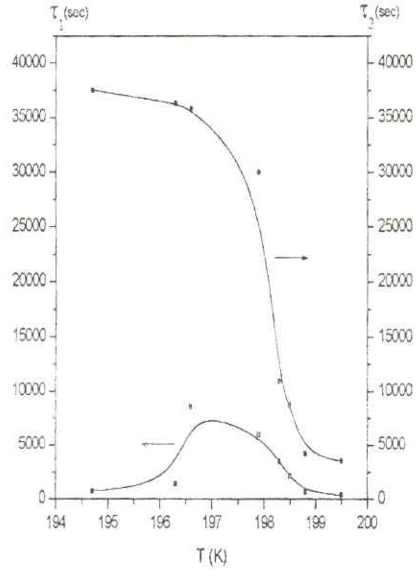

Fig.4.
Temperature dependences of the relaxation times τ_1 and τ_2 of the coexisting phases in the metastable chaotic state of $TlInS_2$.

It is seen that by reducing the temperature from 200K, τ_1 increases, reaches a maximum and then decreases. The other time constant τ_2 increases and then saturates. Such saturation is due to stabilizing of one of coexisting phases, while the decreasing of the other relaxation time τ_1 is attributed to destruction of the polar regions of the second coexisting state by decreasing the temperature.

As mentioned in [8], cooling the crystal below T_{c2}~201K is accompanied by a transformation of double dielectric hysteresis loop into a ternary loop stable in the range of about 195K. This phenomenon is attributed to coexistence of two polar phases. On subsequent cooling the loop obtains the common ferroelectric shapes and the usual symmetric saturated dielectric hysteresis loop is observed. This is a consequence of an increase of the proper ferroelectric polarization as a result of cooling.

Thus, we may conclude that the increasing and saturation of the relaxation time τ_2 on cooling are connected with the effect of stabilization of proper ferrolectric state. Meanwhile, the fast decay of τ_1 is the indication of destroying of the other coexisting state, which is attributed to improper ferroelectric one [9] appeared at T_{c1}~204K and which is characterized by double hysteresis loops [8]. So, the dielectric anomaly at about 195K observed in [5-8] can be qualitatively explained as follows: by decreasing the temperature, the sharp increasing of the proper ferroelectric polarization gives rise to destabilizing of the coexisting improper state and the phase transition to a singe ferroelectric state occurs.

CONCLUSION

The observation of the decay of ε at different temperatures revealed a presence of two characteristic relaxation time constants with a different temperature behaviour. This peculiarity is considered as a result of occurance of a chaotic state accompanied by coexistence of different commensurate ferroelectric phase structures in the temperature range of 190-200 K. The approximate values of the relaxation time constants are about 10^4 sec. According to the result of temperature dependencies of the relaxation times, the dielectric anomaly at 195K observed ealier can be interpreted as the destruction of improper ferroelectric state under influence of proper ferroelectric polarization.

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$TlInS_2$ KRİSTALINDA METASTABİN XAOTİK HALININ MÜDDƏTLİ RELAKSİYASI

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Məqalədə $TlInS_2$ kristalın nisbətli seqnetoelektrik fazasında dieletrik nüfuzluluğun zamandan asılılığı öyrənilmişdir. Nümunənin izotermik halını saxlamaqla müxtəlif fiksə olunmuş temperaturlarda $TlInS_2$-nin seqnetoelektrik fazasının T_c ətrafında nisbətsiz fazadan kristalı soyudan zaman ε qiymətinin azalması müşahidə edilmişdir. $TlInS_2$ kristallının seqnotofazasında müxtəlif temperatur asılılıqlı relaksiyaya xas olan iki zamanın mövçudluğu müəyyən edilmişdir. Alınmış təçrübi nətiçələr $TlInS_2$-də xaotik halın mövçudluğu fərziyyəsi əsasında 194÷200K temperatur intervalında müxtəlif nisbətli polyar fazaların yanaşı olmaqları ilə izah edilmişdir. Fərziyyənin nətiçəsi kimi 195K-də ε anomaliyasına faza kejidi kimi baxılır hansı ki, onun nətiçəsində qeyri məxsusi seqnetoelektrik polyarizasiya dağılır.

ВРЕМЕННАЯ РЕЛАКСАЦИЯ МЕТАСТАБИЛЬНОГО ХАОТИЧЕСКОГО СОСТОЯНИЯ В $TlInS_2$

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В работе представлены временные зависимости диэлектрической проницаемости (ε) кристалла $TlInS_2$ в соразмерной сегнетоэлектрической фазе. Обнаружено уменьшение величины ε при изотермической выдержке образца при различных фиксированных температурах в сегнетофазе $TlInS_2$ в окрестности T_c при охлаждении кристалла из несоизмеримой фазы. Вблизи T_c установлено наличие двух характерных времен релаксации с различными температурными зависимостями. Полученные экспериментальные результаты объяснены на основе предположения о наличии хаотического состояния в $TlInS_2$, обусловленного сосуществованием различных полярных соразмерных фаз в температурном интервале 194÷200K. Как следствие предположенного, аномалия ε при 195K рассматривается как фазовый переход, в результате которого разрушается несобственная сегнетоэлектрическая поляризация.

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