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INSTABILITY OF THE DIELECTRIC CONSTANT IN $TlInS_2$ NEAR THE PHASE TRANSITIONS

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Dielectric constant of $TlInS_2$ was measured in the temperature interval of successive incommensurate (IC) – commensurate (C) phase transitions. Considerable decrease of the dielectric constant was observed after annealing the sample at a fixed temperature in the ferroelectric state. Observed effect is qualitatively explained using phenomenological theory of IC systems containing discommensurations (DCs) undergoing nucleation and evolution processes.

INTRODUCTION

Ternary layered semiconductor $TlInS_2$ exhibits successive low temperature structural ferroelectric phase transitions. It belongs to monoclinic system (300 K) and may be described with C^6_{2h} space group containing two disordered layers per unit cell. Detailed investigations of the dielectric properties in a wide temperature range [1,2,3] showed that $TlInS_2$ undergoes a sequence of the phase transitions: at 216 K and 206 K - into two different IC phases; at 204 K - into the phase with antipolar ordering and at 201 K - into C ferroelectric phase.

Recently thermal memory effect related with IC phase was observed in $TlInS_2$ by analyzing the results of the piroelectric, photoelectric, thermally stimulated currents and the dielectric measurements [4,5,6,7]. The observed effect was explained assuming the pinning of IC modulation due to mobile defects in the crystal with layered structure.

In the present paper the temperature behavior of the dielectric susceptibility of $TlInS_2$ is investigated prior and after annealing the sample for a long time inside the C ferroelectric state.

EXPERIMENTAL

The crystals were grown in evacuated quartz ampoules with the modified Bridgman method. The samples were cleaved into plates parallel to the layers and oriented along the polar axis. Side faces of the samples were gently polished in the direction perpendicular to the direction of polar axis, cleaned and covered with silver paste. The thickness of the samples was typically of 1 mm, while the area was about 10 mm^2.

The measurements of the dielectric susceptibility were performed along the polar axis in the temperature range of 90-300 K in a low temperature cryostat system using bridge method. The measurements were performed at 1 kHz. The temperature was controlled with a copper-constantan thermocouple attached with Duco cement onto the sample. The temperature was measured with an accuracy not less than 0.05 K. The rate of the temperature scanning was 0.5 K/min.

RESULTS AND DISCUSSION

The experiments were performed in the following sequence: first the sample was cooled down to 90 K and the temperature dependence of the real part of the dielectric susceptibility $\varepsilon'(T)$ was measured on heating run up to the room temperature (Fig.:curve 1). Then the sample was cooled down to 90 K and annealed at this temperature during 10 hours. After annealing $\varepsilon'(T)$ dependence was measured again (Fig.:curve 2). No peculiarities of $\varepsilon'(T)$ were observed at the temperatures below 190 K that is why this temperature range is not shown in the figure. As it is seen after above mentioned treatments ε' decreased in the temperature range of the successive phase transitions. In addition the temperature points of C phase transitions at 201 K and 204 K shifted to higher temperatures to ~ 0.5 K. However, on subsequent thermocycling between the ferroelectric and paraelectric phases ε'(T) increased with increasing the number of cycles. Finally, after about 5-7 thermocycling the temperature dependence of ε' exhibited an initial behavior.

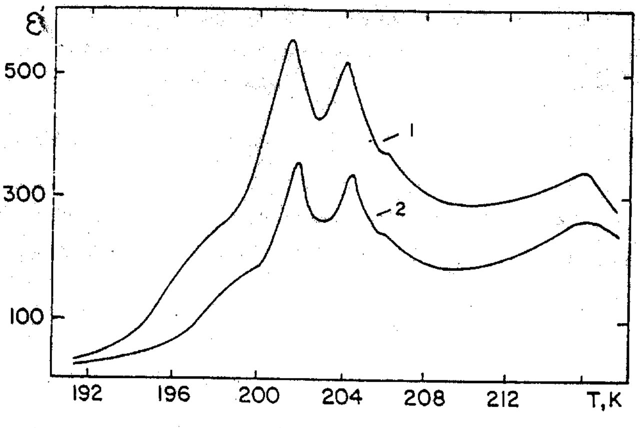

Fig. Temperature dependence of the dielectric susceptibility of $TlInS_2$ on heating process: 1 - normal behavior; 2 - after annealing the sample for 10 hours at 90 K.

Results obtained may be qualitatively explained on the base of phenomenological theory of IC systems assuming existence of DCs in $TlInS_2$ in the temperature interval of IC-C

phase transitions. As it was shown in [8], the dielectric susceptibility consists of normal and 'anomalous' part. 'Anomalous' part of the dielectric constant arises due to movements of DCs in response to applied electric field and this part determines mainly a magnitude of the dielectric susceptibility in the temperature range of $IC-C$ phase transitions. When cooling the crystal down to $IC-C$ phase transition point (T_c=204 K for $TlInS_2$) the distances between DCs increase leading to a weaker interaction between them. As a result applied electric field can easily induce larger domains, oriented in the direction of applied field. This will increase the total bulk polarization. Increased polarization will increase a magnitude of the 'anomalous' part of the dielectric susceptibility. According to phenomenological theory [9], in the vicinity of T_c the dielectric constant increases infinitely (as $T \to T_c$) explaining Curie Weiss behavior in a certain temperature range above T_c, which can be represented by the following expression:

$$\chi-\chi_o=[c'n_s/4\pi(T-T_c)]\exp(\pi/n_s) \ , \quad (1)$$

where n_s is the density of the DCs, χ_o is the dielectric susceptibility in the C phase, c' is a constant.

After C phase transition the dielectric susceptibility exhibits a slow decrease with decreasing the temperature below T_c. This may happen due to pinning of DCs by mobile defects in the crystal lattice. The expression for $\chi-\chi_o$ in the C phase was obtained in [10] and can be described as:

$$\chi-\chi_o=(P/\pi\sigma_E)n_S \quad , \quad (2)$$

where P is the spontaneous polarization below T_c and σ_E is the half width of the Gaussian distribution of the defects field.

As it is seen from above mentioned considerations, an 'anomalous' part of the dielectric constant in crystals with IC phases depends on the density of DCs (formula 1). Therefore we can suppose that observed peculiarities of $\varepsilon'(T)$ are associated with the processes of nucleation (annihilation), evolution and redistribution of DCs.

Taking into account above-mentioned comments the obtained results may be qualitatively explained as follows. After annealing the sample for a long time at 90 K the crystal will contain a minimum number of DCs. In this case the domain boarders are rigid and it is difficult to reorient the domains under applied electric field. Low value of induced polarization will result to a lower value of the dielectric susceptibility (Fig.:curve 1). Heating the crystal will result to formation and evolution of DCs. But this process has high activation energy and that is why is comparatively embarrassed. It will lead to a delay of crystal transformation into IC phase and we observe shift (0.5 K) of $\varepsilon'(T)$ maximum at 201 K and 204 K to higher temperatures (Fig.:curve 2).Subsequent thermocycling increases the density of DCs, which may act as a centre of nucleation for a new DCs. This process will require comparatively low activation energy. With each thermocycling a number of DCs increase, resulting to a higher value of the dielectric susceptibility. After 5-7 cycles the crystal will totally 'defreezed' (a uniformity of ICs will recover) and finally, an initial behavior of $\varepsilon'(T)$ dependence will take place (Fig.:curve 1). Relaxation processes in $TlInS_2$ have been also revealed when measuring the time-dependencies of the dielectric constant. The details will be presented in a separate paper.

CONCLUSION

Activation processes of nucleation (annihilation), evolution and redistribution of DCs play an important role in the relaxation of the dielectric susceptibility of $TlInS_2$ in the range of $IC-C$ phase transitions.

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FAZA KEÇİDLƏRİ YAXINLIĞINDA $TlInS_2$ KRİSTALININ DİELEKTRİK NÜFUZLUĞUNUN QEYRİ-STABİLLİYİ

Nisbətli-nisbətsiz faza keçidləri yaxınlığında $TlInS_2$ kristalının dielektrik nüfuzluğu (ε) ölçülmüşdür. Nümunəni seqnetoelektrik fazada uzun müddət saxladıqdan sonra ε-un qiymətinin böyük miqdarda azalması müəyyən edilmişdir. Göstərilmişdir ki, bu hadisə domenəbənzər solitonların yaranması və təkamül proseslərini nəzərə alan nisbətsiz faza keçidlərinin fenomenoloji; modeli əsasında izah oluna bilər.

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НЕСТАБИЛЬНОСТЬ ДИЭЛЕКТРИЧЕСКОЙ ПРОНИЦАЕМОСТИ $TlInS_2$ ВБЛИЗИ ФАЗОВЫХ ПЕРЕХОДОВ

Измерена диэлектрическая проницаемость (ε) слоистого кристалла $TlInS_2$ в окрестности фазового перехода несоизмеримая-соизмеримая фаза. Установлено значительное понижение ε после температурной выдержки образца в сегнетоэлектрической фазе. Показано, что наблюдаемое поведение ε можно объяснить на основе феноменологической модели несоизмеримых фазовых переходов, учитывающей процессы зарождения и эволюции доменоподобных солитонных образований.

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