THE ANOMALIES OF THE ELECTRIC AND DIELECTRIC PROPERTIES OF THE TIS IN THE PHASE TRANSITIONS AREA

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In the ref the results of experimental investigations of the electric and dielectric properties of the monoclinic TIS in the temperature interval 260-440K are given. The anomaly at 411K, connecting with the phase transition is registered firstly on the temperature curves of the electric conduction dependence, dielectric constant and tangent of the dielectric loss. The character of the anomaly is typical for the phase transition of II-type. The possible nature of the discovered phase transition is discussed.

I. Introduction

Моносульфид таллия TIS is the semiconductor connection, in respect of the binary connections of A^3B^6 type. By the TIS investigations it is established that this connection can be crystallized in the different crystal structures. The more populated type is the structure type of the chain crystal TIS of the tetragonal modifications with the space group (PG) of the symmetry D_{4h}^{18} (the structure prototype TISe) [1-3]. It was informed comparatively recent [4-8] about possibility of the obtaining of the single crystals TIS with the layer type of the crystal structure as monoclinic, so tetragonal modifications. The monoclinic crystal system of the layer TIS (the structure analog of the layer crystal $TIGaSe_2$) [4-6-8] is described at the room temperature PG C_2^3 (in the literature are also discussed thew variants PG C_s^3 and C_{2h}^3 [5,7]) and characterized by the period of the crystal grid: a=11,01Å, b=11,039Å, c=4+15,039Å and b=100,69°. The tetragonal cell of the layer TIS has the grid parameters at the room temperature: a=b=7,803Å and c=29,55Å. According to [7], PG of the layer crystals TIS of the tetragonal modification can be D_4^4 or D_4^8.

The polymorphic transformations of the layer TIS have physical properties. The layer crystals TIS of the monoclinic crystal system are interesting by that at the atmospheric pressure they are endured the successiveness of the structure phase transitions (FP): at T_i=341,1K from the high - temperature paraelectric phase into the incommensurable phase (NS) with the wave vector of the modulation $k_i = \left(\delta;0;\frac{1}{4}\right)$ where δ~0,04 incommensurable parameter; at T_c=318,6K in the unknown, ferroelectric, commensurable phase (S) with the quadrupling of the parameter of the elementar cell along crystal axis $\vec{c}$ [4,6]. The carried investigations in [4] show that lower than T_c dielectric hysteresis loops are observed and vector of the spontaneous polarization is situated in the layer plane. By the dates of the differential thermical analysis (DTA) and measurements of the temperature dependence of the dielectric constant (ε) TIS it is established that [4-6] FP at T_i is FP of II type, and at T_c is FP of I type. The pieces of information about FP realization in the structure of the layer TIS in the system TI-S. The carried investigations have been proved the existence in the structure TIS FP at 353K, in the result of which TIS transfers from the monoclinic phase into tetragonal phase with the totality of the diffraction pictures, which are completely suit to the structure TISe. We mention that in [9] on the TIS diffractograms the appearing of the satellite reflexes, proving the polar C phase existion in the crystal HC.

In the present paper the results of the experimental investigations of the electric and dielectric properties of the monoclynic TIS, obtained with the aim of the later elaboration pecularities of the structure FP in TIS and obtaining of the additional information about this crystal movement in the high-temperature paraelectric phase are informed.

II. The samples and experimental methodics

The investigated samples TIS of the black-grey color had the monoclinic structure, according to carried out x-ray pattern investigations at the room temperature. The especial character of the investigated monoclinic TIS as studied in [4-8,9] is the existing in its composition the superstichiometric sulfur quantity (TIS+4%S). The applicated technology of TIS monoclinic crystal obtaining, and also the dates of X-ray diffraction analysis will be given in [10] more in detail.

For the investigation the several especially picked up samples of the natural spalling of TIS in the form of plane-peralletl plates with the mutual perpendicular directions of the edges orientation, cutted out from the growed up ingot are used. All above mentioned measurements correspond to the sample with the line sizes 4+1,8+1,2mm^3.

For the dielectric characteristics TIS measurement in the capacity of the electric contacts the silver paste was used. The electrodes from In were used at the temperature dependence of the electric conduction investigation. Before the electrods drifting the corresponding surfaces of the samples were polished. The samples were in the vacuum inside the thermostated camera with the aim of the averting the possibility of the TIS samples oxidation in time of their measurements. The sample's temperature was controlled by the copper-constantanal thermocouple with precision ±0,1°C. The investigations were carried out in the quazistatistical temperature mode, at this the temperature change velocity was 0,1K+min^{-1}. The dielectric constant (ε) and tangent of dielectric loss (*tgδ*) measurememts were on the frequency 9,8Hs with the help of the alternating-current bridge because of the high electric conduction of the TIS samplesin the investigated temperature interval 250-440K. The electric conduction measurements (σ) were carried out on the direct current on the standard methodics.

III. The experimental results and their discussion

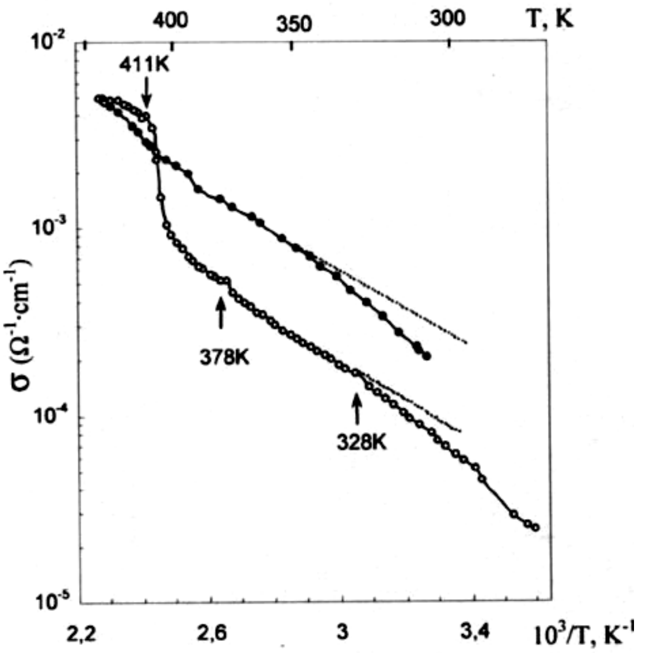

Fig.1. The temperature dependence of TlS electric conduction, measured in the heating (o) and cooling (•) modes of sample

The temperature electric conduction dependences TIS, measured in the mode of the heating and cooling of the sample are given in fig.1. It is need to note, that electrophysical characteristics of TIS, studied on the samples with the mutual perpendicular edge orientation, had practically the similar temperature dependences, but differed by the value strongly. So, for example, the ratio of the electric conduction values of the samples with the mutual perpendicular edge orientation ($3{,}571\cdot10^{-4}\Omega$ cm^{-1} and $5{,}11\cdot10^{-5}\Omega$ cm^{-1}) is ~7 at the room temperature. More over, by the absolute value the electric conduction of the investigated samples at the room temperature exceeds more than one degree the value σ of chained TIS [3] and 3-4 degree the value σ of the layer TIS of monoclinic modification, investigated in [8]. The heating curve σ from the opposite temperature has the line character in the temperature interval 255-401K. The existing of the following anomalies discover the more detailed heating curve analysis $\sigma(1/\text{-}T)$ (constructed in the logarithmic scale).

1) The change of the slope gradient $\sigma(1/T)$ at T=328K, obtained in the heating mode. The given anomaly is observed on the dependence $\sigma(T)$ and in the cooling mode.

2) The little anomaly in the form of the deflection from the line dependence is observed on the heating and cooling curves $\sigma(T)$ in the neighbourhood T~378K.

3) The strong increase of σ with the temperature growth in the interval 401411K. The relative change σ in the given temperature region is 3,36. The dependence $\sigma(1/T)$ is likely again higher than T=411K. The measurement of σ, carried out in cooling mode of TIS sample after its heating up to 438 showed the abscence of any anomaly in the б movement in the temperature interval 401-411K. The cooling curve $\sigma(1/T)$ has line character in the given temperature region (but no jumped).

The essential pecularity of the growed up TIS samples is the complete reconstruction of their initial electric (and dielectric also) properties after separate thermal maturing of the samples at the temperature 250K during three days are given in the fig.2. As it is seen from the fig. 2 the anomal movement of the electric conduction in the temperature interval 401÷411K doesn't re-create neither at the samples cooling, nor at its heating on the $\sigma(1/T)$ curve. At the same time the pecularities in the movement $\sigma(1/T)$ in the nieghbourhood 328K are clearly followed.

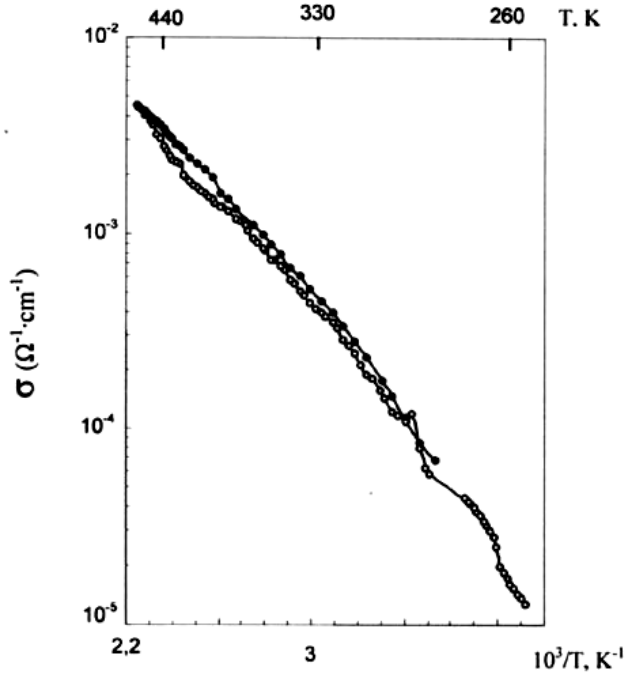

Fig.2. The temperature dependence of TlS electric conduction, measured in the heating (o) and cooling (•) modes after the temperature annealing of sample at 250Kduring of three days

The temperature dependences ε of TIS samples in the temperature interval 270÷425K, obtained in the heating and cooling modes are given the fig. 3. As it is seen from the fig.3, the heating curve $\varepsilon(T)$ is characterised by the anomalies in the nax forms at the temperatures 377,6 K and 411K. The given anomalies don't re-create at the $\varepsilon(T)$ measurements in the cooling mode of the sample. The complete re-creation of these anomalies on the dependence $\varepsilon(T)$ in the heating mode is observed after the ewak thermal maturing of TIS samples at temperature 250K. More over, the little anomaly is observed in the neighbourhood 328K, which also doesn't re-create at $\varepsilon(T)$ of the several TISsamples (see inset to fig.3).

At last, the temperature stroke *tgδ* TIS in the hearing and cooling modes of the samples is given in the fig.4. As it is seen from the fig.4 the essential growth tgб TIS takes place at the heating of the sample in the interval 380-410K. The big electric conduction of TIS samples at temperatures, higher than 410K complicates the $tg\delta$ measurement, that's why we couldn't registrate the max in $tg\delta(T)$ movement in the neighbourhood 411K.

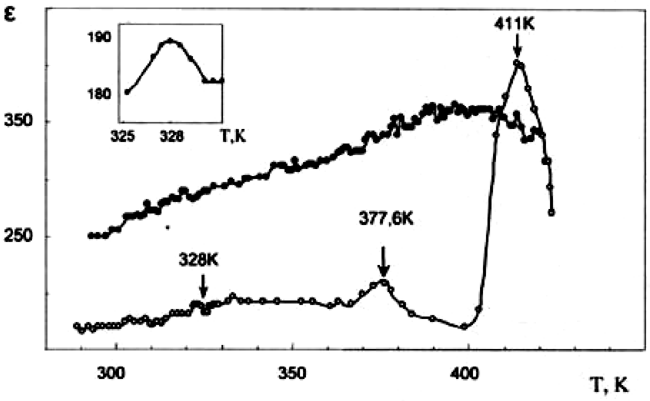

Fig.3. The temperature dependence of TlS dielectric constant, measured in the heating (o) and cooling (•) modes of sample. Insert to fig.3. The anomaly on the curve $\varepsilon(T)$, observed at the investigation of some samples of TlS in the neighbourhood of 328K.

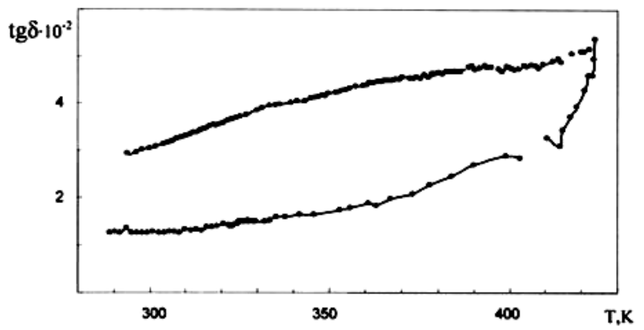

Fig.4. The temperature dependence of $tg\delta$ TlS, measured in heating heating (o) and cooling (•) modes of sample.

Summarizing the above mentioned dates about temperature dependences of electric and dielectric characteristics of the investigated crystal TIS in the temperature interval 250÷440K, we can make the definite conclusions about nature of the discovered anomalies. As it was given in the introduction, the layer TIS crystals of monoclinic modification combine the segnetoelectric and semiconductor properties at the same time [4, 6]. From the other side, according to the thermodynamic theory, the character pecularities on the temperature dependences of the wide of the prohiubited band have to be observed in the segnetoelectric-semiconductors [11] in the structure FP area: the jump at the FP of I type and temperature coefficient change at FP of II type. The registrated the change of the inclination of the curve $\sigma(1/T)$ and the existence of the little anomaly on the curve $\varepsilon(T)$ of the several TIS samples at T=328K could be connected with the discovered [4-6] FP of II type at T_i=341,1K. However, the nonconformity with the temperature of FP of II type, obtained in the given paper with the earlier published dates [4,6] and also the abscence the character anomalies on the dependences $\varepsilon(T)$ and $tg\delta(T)$ are possible connected with that the growed up TIS crystal of the monoclinic modification differs subsantially on its physical properties from layer TIS of the monoclinic crystal system, investigated in [4-6, 8]. It can be proposed that discovered pecularities of the electrophysical properties of the investigated TIS at 328K and in the neighbourhood 378K are connected with the structural FP between different TIS polymorphic transformations. The finding out of the mentioned above anomalies' nature in the temperature movement electric and dielectric properties growed up TIS needs the carrying out the additional structural investigations.

Let's stop on the possible nature of the anomalies at 411K. The combination of the experimental results allows to consider that near T~411K TIS endures FP, having the character traites FP of I type. The phase, appearing at T>411K is metastable. The relaxation time, needed for the complete re-creation of the initial physical properties of the sample is 160-170 hours at the thermal relieving at T=250K. We consider that in TIS in the temperature interval 401÷411K is FP in the state with the superion conductivity. The obvious analogy between pecularities of TIS electric and dielectric properties in the given temperature interval with the properties of the superion semiconductors [12, 13] is the argument in the benefit of this interpretation of the above mentioned experimental results.

As it is known [13-15] the ion currents in the superion semiconductors (solite electrolyties) are caused by the existence of the defects in their structures as vacancies and interstitial atoms (Frenkel and Shottki defects). At the same time the temperature dependence of ion conductivity is subject to thermoactivation law of the аррениусовского type [13-15]:

$$\sigma(T) = \frac{\sigma_0}{T} \cdot exp\left(-\frac{E_\alpha}{kT}\right) \qquad (1)$$

where σ_0 is the frequency factor; E_a is the activation energy, defined by the defect creation energy and ativation energy of its motion; k is Boltzmann constant.

The character pecularity of the heating curve $\sigma(1/T)$ of our samples (as other superion semiconductors) is the existence of three like temperature areas with the different inclination angles.

1) The inclination angle of the like area of the heating curve $\sigma(1/T)$ in the temperature interval 330÷401K is characterized by activation energy E_a=0,224eV. ???

2) The inclination angle of the like area of the heating curve $\sigma(1/T)$ in the temperature interval 401-411K is characterized by E_a=2,66eV. The given temperature area, so-called the intrinsic conductivity area [13], is that type region, where the superion conductivity appears. The ion conductivity on this temperature area is defined by the defects, created in the crystal lattice because of the warmth [13,14]. The activation energy value on this area is more by the value, than in the temperature interval 330÷401K, as Ea is defined by the energies' sum, needed as for the defect creation so for the its motion along the crystal. In many superion conductors this area is finished by FP type order-disorder. The discovered the -------- anomaly on the curve $\varepsilon(T)$ TIS at 411K is connected with the existence of this FP.

3)The inclination angle of the area of the heating curve $\sigma(1/T)$ in the temperature interval 401÷411K corresponds to the activation energy E_a=0,226 eV. The given temperature area corresponds to conductivity in the strong разупорядочная crystal structure.

We note also, that in [3] the pecularities like above mentioned were discovered in the another temperature region 300÷350K at the investigation of the electric conduction temperature dependence and Hall coefficient of the chain TIS of the tetragonal transformation (structure analog TISe). By the sign of Hall constant in [3] it is established that the main role in the electric conduction of the chain TIS play the positive charge particles (holes according to [3]). Besides by the authors of [3] it is established that in the temperature interval 300÷350K Hall mobility m(n) is subject to law μ_H~$T^{8,33}$, ---------in 215÷300K the temperature dependence μ_H~$T^{6,78}$. In [3] it is noted that such temperature movement of Hall mobility of the chain TIS doesn't correspond to any from the famous carriers' scattering mechanisms in the semiconductors [16].

On our opinion the authors of [3] don't consider the FP possibilities in the state with the superion conductivity, which also takes place in the chain TIS structure of the tetragonal transformation. Using dates about Hall coefficient sign [1,3] it can be proposed that in TIS structure the transition in the state with the superion conductivity is caused by the разупорядочением in таллиевой sublattice because of potential barrier decrease between allowed тфллий cations' positions in the temperature interval 401÷411K.

Nevertheless, the authors of the given paper consider that the above mentioned experimental facts connect with the разупорядочением in the anionic sublattice of the investigated TIS, Because of the existence of the nonctoichiometric quantity of sera anions in TIS lattise, the last, situated in the interstices of the tetragonal elementary all TIS, promotes to the monoclinic distortion of the initial elementary cell. At the achieving of the temperatures, corresponding to the activation energy of the anionic defects is the wide ----- of the anionic sublattice and later the appearing of the pecularities in the temperature movement of TIS electrophysical properties in the temperature interval T>401K.

The authors are thankful to T.S.Mamedov and A.S.Nadjafov for the giving of the samples for the investigations.

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АНОМАЛИИ ЭЛЕКТРИЧЕСКИХ И ДИЭЛЕКТРИЧЕСКИХ СВОЙСТВ КРИСТАЛЛОВ TlS В ОБЛАСТИ ФАЗОВЫХ ПЕРЕХОДОВ

В работе представлены результаты экспериментальных исследований электрических и диэлектрических свойств моноклинного TlS в интервале температур 260÷440 К. На кривых температурной зависимости электропроводности, диэлектрической проницаемости и тангенса угла диэлектрических потерь впервые зарегистрирована аномалия при 411К, связываемая с фазовым переходом. Характер аномалии типичен для фазового перехода I- рода. Обсуждается возможная природа обнаруженного фазового перехода.