PHASE RELATIONS AND PHASE MAGNETODIELECTRICAL PROPERTIES IN $TlInS_2$-Tl(Cr, Mn, Co)S_2 SYSTEMS

R.G. VELIYEV

H.M. Abdullayev Institute of Physics of the NAS of Azerbaijan,
Az-1143, Baku, H. Javid ave., 33

The temperature dependence of the dielectric constant of $TlInS_2$ has revealed that this compound is ferroelectric one. The temperature dependence of the magnetic susceptibility of $TlCrS_2$, $TlMnS_2$, $TlCoS_2$ has ferro-, antiferro- and ferromagnetic structures correspondingly. The areas of homogeneous and heterogeneous coexistence of electric and magnetic orderings in $TlInS_2$-Tl(Cr, Mn, Co)S_2 systems have defined.

INTRODUCTION

The search of strong anisotropic ferro-magneto-active crystals (layered, chain) is the actual problem of solid state physics as besides the traditionally controlled factors such as temperature, electric and magnetic fields, their physical properties will depend on main crystallographic directions. The above mentioned circumstances suppose the variation by physic-chemical parameters of such crystals in wide range. Besides, the coexistence of electric and magnetic ordering in the one crystalline sample presents the scientific interest, i.e. history shows that whole existing complement of electric ordering mechanisms (for example: ferroelectrics, anti-ferroelectrics, non-intrinsic ferroelectrics, intrinsic and non-intrinsic ferroelectrics with intermediate phases) has been forecasted and so it is used in concrete crystals on the base of phenomenon analogy of magnetic ordering mechanisms in magnetic. The study of coexistence of electric and magnetic orderings in both crystals homogeneous and heterogeneous (composites) samples has the big actuality in the connection with development of technical properties of nano-technology [1].

EXPERIMENTAL PART

In connection with above mentioned we have synthesized the semi-crystalline ingots $TlInS_2$, $TlCrS_2$, $TlMnS_2$ and $TlCoS_2$ in electric furnace in quartz ampoules produced from melted quartz evacuated up to residual pressure ~10^{-3}Pa. Previously the chromium (Cr) is led to powder state with the help of ball mill. $TlCrS_2$, $TlMnS_2$ and $TlInS_2$, $TlCoS_2$ are synthesized by the melting of chemical elements suspended in stoichiometric state at temperatures ~1500*K* and ~1100*K* correspondingly. Moreover, the ampoules with $TlCrS_2$, $TlMnS_2$ are endured in the furnace during one hour and ampoules with $TlInS_2$, $TlCoS_2$ are endured during 3 hours. Further, the melts are led to fine-dispersed state and the synthesis repeats with further furnace cooling with velocity 100K/h up to temperature ~ 600*K*, at which the semi-crystalline ingots are annealed during 480 hours.

The *X*-ray analysis of the following samples: $TlInS_2$, $TlMnS_2$, $TlCrS_2$ and $TlCoS_2$ specially prepared after annealing is carried out at room temperature. (~300K) on diffractometer ДРОН-3М (CuK_α is radiation, λ=0.15418nm, Ni is filter, mode: 35кV, 10mA). The angular resolution is~0.01º. The regime of continuous scanning is used. The angles of diffraction reflections are defined by intension maximum and the error of definition of angles of reflection doesn't exceed $\Delta\theta$=±0.02º.

The diffraction reflections on samples $TlInS_2$, $TlCrS_2$, $TlMnS_2$ and $TlCoS_2$ which correspondingly are indicated on the base of monoclinic, hexagonal, tetragonal and trigonal syngonies with parameters of crystal lattice: *a*=1.095 *nm*, *b*=1.085 *nm*, *c*=1.514 *nm*, β=100º, *a*=0.3538 *nm*, *c*=2.1962 *nm*, *a*=0.774 *nm*, *c*=3.062 *nm* and *a*=0.3726 *nm*, *c*=2.251 *nm* are fixed in angle interval $10º \leq 2\theta \geq 70º$.

The samples in the form of plates of polar section cutoff from single crystalline ingots of this compound are used for investigation of temperature dependence of dielectric constant – ε (*T*) of layered crystal $TlInS_2$. The single crystalline $TlInS_{2b}$ has grown up by Bridgman-Stockbarger method; moreover, the motion velocity of crystallization front is 2mm/h. The dielectric constant is measured with help of alternative current bridge on frequency 1 кHz. The silver paste is used as a electrodes.

The temperature dependence of reversal paramagnetic susceptibility $\chi^{-1}(T)$ of $TlCrS_2$, $TlMnS_2$ and $TlCoS_2$ is investigated by Faraday method on magneto-electric weigher. The samples for measurements have the cylindrical form with dimensions *h*≈3 *mm*, *d*≈2.5*mm*.

The investigations are carried out in temperature interval 77-300K in quazi-static regime; moreover rate of temperature change is 0.2 К/min. During measurements the samples are inside nitrogen cryostat and the differential cuprum-constant thermocouple the joint of which is stationary fixed on chip header near the sample is used as a temperature gauge. The support joint of thermocouple stabilizes at temperature of melting ice.

RESULTS AND DISCUSSIONS

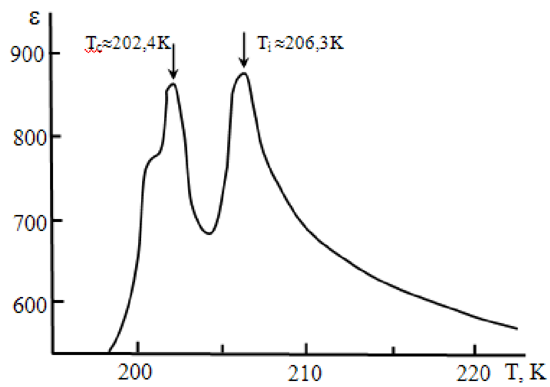

Fig.1. Temperature dependence of dielectric constant $TlInS_2$.

The temperature dependence of dielectric constant $TlInS_2$ measured at atmospheric pressure is given on fig.1. As it is seen from the figure the curve ε(*T*) is characterized by the set of anomalies in the form of maximums at ~206.3 *K* and ~202.4 *K* and also by the presence of some "bending" near 201K. As it is known the complex consistency of structural phases transitions (PhT), including PhT into incommensurable ferroelectric phase and commensurable one, [2-5] takes place in layered crystal $TlInS_2$ with temperature decrease at atmospheric pressure.

The initial paraelectric phase $TlInS_2$ is characterized by space symmetry group (SSG) C_{2h}^{6} [6]. PhT in incommensurable phase is connected with condensation (at T_i≈216 *K*) of soft water in the point of Brillouin zone with wave vector K_i= (*δ, δ*, 0.25), where *δ* is incommensurability parameter [7]. At $T_c \approx 201$ *K δ* value transforms into zero and $TlInS_2$ crystal transfers into nonintrinsic ferroelectric *C*-phase with wave vector K_c=(0, 0, 0.25) [7-11] (the vector of spontaneous polarization is situated in plane of field).

Comparing our results with data presented in [2-5, 11] we can conclude that curve *ε*(*T*) of investigated crystal differs from analogous curves presented in reference both by the number of anomalies and their temperature positions. Note that the color of investigated sample $TlInS_2$ differs by orange shadow whereas $TlInS_2$ crystals chosen from different sets and investigated in [2-5] have the different shadows of yellow color on color gamma. Basing on data [9,10] in which the strong sensitivity of physical properties (including PhT temperatures) of layered crystal $TlInS_2$ to impurity number in the sample and to defect degree of its crystal structure is set, so we can suppose that the anomaly observable by us on curve *ε*(*T*) at 206.3K is connected with PhT in incommensurable phase and at ~202.4 is connected with PhT in commensurable ferroelectric phase. Moreover, the "inflection" near 201K presents itself the temperature interval of residual coexistence of indecomposable solitons of incommensurable phase and domains of low-temperature *C*-phase [2].

The temperature dependence of reversal paramagnetic susceptibility $\chi^{-1}(T)$ of these compounds presented on fig.2 has been investigated for revealing of magnetic structure of $TlCrS_2$, $TlMnS_2$ and $TlCoS_2$ compounds in magnetic field with intensity 80A/m. From the figure it is seen that dependence $\chi^{-1}(T)$ is character for ferro-, anti-ferro and ferromagnetic orderings correspondingly for $TlCrS_2$, $TlMnS_2$ and $TlCoS_2$.

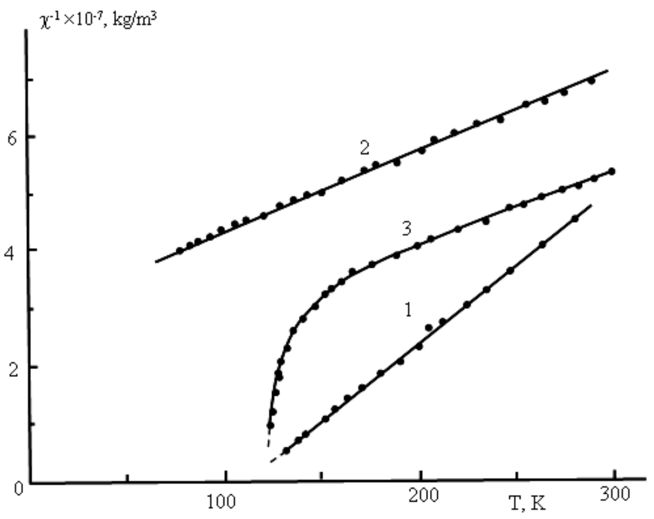

Fig.2. Temperature dependence of reversal paramagnetic susceptibility $TlCrS_2$ (1), $TlMnS_2$ (2), $TlCoS_2$ (3).

Curie paramagnetic temperature (T_p) is defined by extrapolation of $\chi^{-1}(T)$ dependence on temperature axis and is equal to ~115*K* ($TlCrS_2$) and ~120*K* ($TlCoS_2$). The effective magnetic moment which is equal 3.26 μ_B, is calculated from $\chi^{-1}(T)$ (fig.2) dependence. The theoretical value calculated with taking into consideration of spin value of magnetic moment of chromium ion (Cr^{3+}) is equal 3.85 μ_B.

The enough big deviation μ_{eff} $TlCrS_2$ from theoretical value (3.85μ_B) shows on the presence of quasi-two-dimensional magnetic ordering in paramagnetic area of strongly layered ferromagnetic $TlCrS_2$.

The low-dimensionality of magnetic structure $TlCrS_2$ is mentioned in work [12] on investigation of low-temperature heat capacity (in adiabatic calorimeter) of $TlCrS_2$.

The experimental values of effective magnetic moment $TlMnS_2$ (4.5μ_B) and $TlCoS_2$ (4.6μ_B) have been calculated from $\chi^{-1}(T)$ dependence (fig.2). The comparison of these values with theoretical ones (4.9μ_B for $TlMnS_2$ and $TlCoS_2$) calculated with taking into consideration of spin values of magnetic moment of (Mn^{3+}) manganese and cobalt (Co^{3+}) ions shows the some difference.

For solution of physical problem given in the article beginning, it is necessary to define the areas of homogeneous and heterogeneous coexistence of $TlInS_2$ of ferroelectric with $TlCrS_2$ ferromagnetic, $TlMnS_2$ antiferromagnetic, $TlCoS_2$ ferrimagnetic. The following systems $TlInS_2$-$TlCrS_2$, $TlInS_2$-$TlMnS_2$ и $TlInS_2$-$TlCoS_2$ have been investigated by method of differential-thermal analysis.

The state diagram of $TlInS_2$-$TlCrS_2$ system constructed on results of DTA is presented on fig.3.

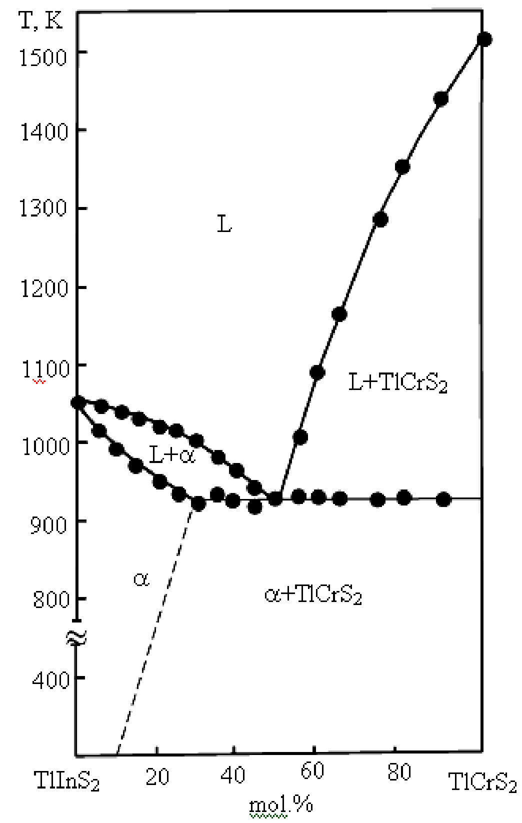

Fig.3. State diagram of $TlInS_2$-$TlCrS_2$ system.

This system is quasi-binary one of eutectic type with solid solutions on $TlInS_2$ base (homogeneous area of coexistence of ferroelectric and ferromagnetic orderings) achieving up to 10mol% $TlCrS_2$ at room temperature. The eutectic forms at component relation 1:1. The eutectic melts at 925K and has the composition $(TlInS_2)_{0.5}$ $(TlCrS_2)_{0.5}$, i.e. the electric and ferromagnetic orderings coexist heterogeneously (compositionally).

The state diagram of $TlInS_2$-$TlMnS_2$ system constructed on DTA results is presented on fig.4. This system is quasi-binary one of eutectic type with solid solutions on $TlMnS_2$ base achieving up to 8mol.% $TlInS_2$ (homogeneous area of coexistence of ferroelectric and ferromagnetic orderings). The eutectic forms at component relation 1:1. The eutectic melts at 820K and has the composition $(TlInS_2)_{0.5}$ $(TlCrS_2)_{0.5}$, i.e. the electric and ferromagnetic orderings coexist heterogeneously (compositionally).

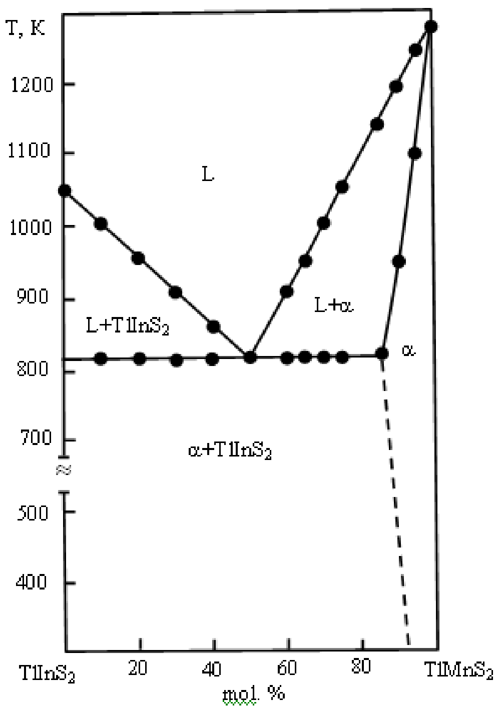

Fig.4. State diagram of $TlInS_2$-$TlMnS_2$ system.

The state diagram of $TlInS_2$- $TlCoS_2$ system constructed on DTA results is presented on fig.5. This system is quasi-binary one of eutectic type. The solid solutions achieving up to 15mol.% form on$TlInS_2$ base and solid solutions achieving up to 10mol.% $TlInS_2$ form on $TlCoS_2$ base (homogeneous area of coexistence of ferroelectric and ferromagnetic orderings). The eutectic forms at component relation 1:1. The eutectic melts at 525K and has the composition $(TlInS_2)_{0.5}$ $(TlCrS_2)_{0.5}$, i.e. the electric and ferromagnetic orderings coexist heterogeneously (compositionally).

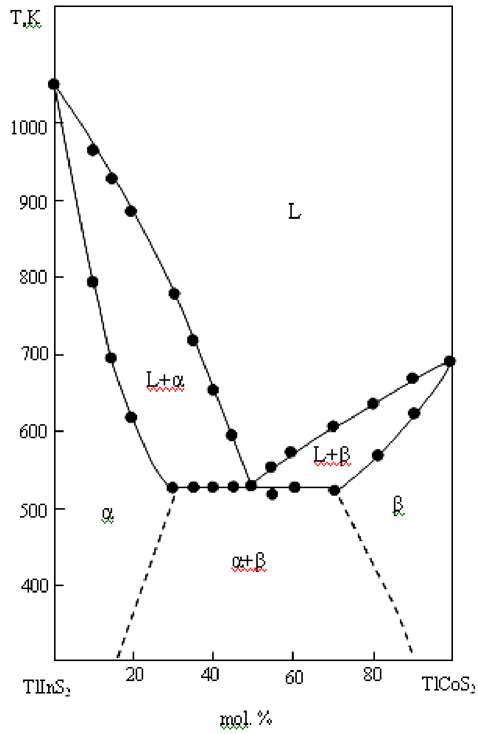

Fig.5. State diagram of $TlInS_2$-$TlCoS_2$ system.

CONCLUSION

The dielectric investigations of single crystalline sample $TlInS_2$ show that this compound is ferroelectric one. The investigation of magnetic susceptibility of semi-crystalline samples $TlCrS_2$, $TlMnS_2$ and $TlCoS_2$ reveals that these compounds have ferro-, antiferro- and ferri-magnetic properties structures correspondingly. The areas of homogeneous and heterogeneous coexistence of electric and magnetic orderings in $TlInS_2$-Tl (Cr, Mn, Co) S_2 systems are defined by DTA method.

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R.G. Vəliyev

$TlInS_2$ – $Tl(Cr, Mn, Co)S_2$ SİSTEMLƏRİNDƏ FAZA NİSBƏTLƏRİ VƏ FAZALARININ MAQNETODİELEKTRİK XASSƏLƏRİ

$TlInS_2$ –nin dielektrik nüfuzluluğunun temperatur asılılığı göstərdi ki, həmin birləşmə seqnetoelektrik xassəyə malik olur.$TlCrS_2$, $TlMnS_2$ və $TlCoS_2$ birləşmələrinin maqnitlənmə qabiliyyətinin temperatur asılılığı göstərdi ki, bu birləşmələr uyğun olaraq ferro-, antiferro- və ferrimaqnit struktura malik olurlar. Maqnit və elektrik nizamlanma varlığının $TlInS_2$-$Tl(Cr, Mn, Co)S_2$ sistemlərində homogen və heterogen sahələri təyin olunmuşdur.

Р.Г. Велиев

ФАЗОВЫЕ СООТНОШЕНИЯ И МАГНЕТОДИЭЛЕКТРИЧЕСКИЕ СВОЙСТВА ФАЗ В СИСТЕМАХ $TlInS_2$-$Tl(Cr, Mn, Co)S_2$

Температурная зависимость диэлектрической проницаемости $TlInS_2$ выявила, что это соединение является сегнетоэлектриком. Температурная зависимость магнитной восприимчивости показала, что соединения $TlCrS_2$, $TlMnS_2$ и $TlCoS_2$. обладают соответственно ферро-, антиферро-, и ферримагнитной структурами. В системах $TlInS_2$-$Tl(Cr, Mn, Co)S_2$ определены области гомогенного и гетерогенного сосуществования электрического и магнитного упорядочений

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