PARAMAGNERTIC SUSCEPTIBILITY AND ELECTRICAL CONDUCTION OF LAYERED MAGNETS $Tl(Cr,Mn,Co)S_2$

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The magnetic and electric investigations which show that $TlCrS_2$ is the semiconductor ferromagnetic, $TlMnS_2$ is semiconductor anti-ferromagnetic, $TlCoSe_2$ is ferrimagnetic having the conduction of half-metal type, have been carried out in temperature interval 77÷400K. The enough big inclination of value of experimentally effective magnetic moment $TlCrS_2$ ($3.26\mu_B$) from theoretical one ($3.85\mu_B$) is explained by the presence of two-dimensional magnetic ordering in paramagnetic region of strongly-layered ferromagnetic $TlCrS_2$.

Introduction.

The low symmetry of magnetic crystalline structure of $TlMeX_2$ (where Me is 3d-metal; X=S,Se,Te) [1-5] predermines the dependence of their magnetic properties on the main crystallographic directions, in some cases up to the appearance of low-dimension effect when magnetic spin system (magnetic structure) in paramagnetic region in the definite temperature interval is in "quasi-two-dimensional" or "quasi-one-dimensional" magnetic ordering (Izing-Geyzenberg model) [6-9]. Besides, the magnetic and semiconductor properties combine in these compounds [10-12].

According to Izing-Geyzenberg model the behavior of low-dimension systems in the region of high temperatures (paramagnetic region) near phase transition in magnetic-ordered state and has the specific peculiarities strongly differed from the behavior of three-dimension spin systems in the region of low temperatures. For example, the magnetic susceptibility in paramagnetic region is characterized by the presence of wide maximum which characterizes the strongly developed short-range magnetic order at $T>>T_N$ and the anomaly with essential inclination from λ-type [13,6-8] is observed on temperature dependence. Such magnetic structures in particular, semiconductor or half-metal two-dimension ferro- and ferrimagnetics can be base materials for nano-technology. That's why the search of layered magnets on the base of compounds $TlMeX_2$ (where Me is 3d-metal; X=S,Se,Te) in magnetic relation having the different types of magnetic ordering is the actual task in both from theoretical and practical points of view.

Taking under consideration the above mentioned the crystals $Tl(Cr,Mn,Co)S_2$ are synthesized by us and X-ray, magnetic and electrical investigations are carried out.

Synthesis and X-ray analysis.

The compounds $TlCrS_2$, $TlMnS_2$ and $TlCoS_2$ are synthesized in electric furnace in quartz ampoules evacuated up to residual pressure ~10^{-3}Pa at temperature ~1050K from chemical elements suspended in stoichiometric relations. Previously, the lame (Cr) with the help of globular discharge is treated in powdered state The synthesis is carried during 72 hours, further the reaction product is disintegrated and the synthesis repeats. After it the obtained compounds are transformed in powdered state, pressed and treated to homogenizing annealing at temperature ~600K during 480 hours in evacuated quartz ampoules.

X-ray analysis of $TlCrS_2$, $TlMnS_2$ and $TlCoS_2$ samples specially prepared after annealing is carried out at room temperature (~300K) on diffractometer ДРОН-3M(CuK_α is radiation, Ni is filter, λ=1.5418$\AA$, the mode is 35kV,10mA). The angular discrimination of the shooting is ~0.01°. The mode of continuous scanning is used. The diffraction angles are defined on intensity maximum. The error of definition of diffraction reflection angles doesn't exceed $\Delta\theta=\pm0.02°$.

In angle interval $10°\leq2\theta\leq70°$ the diffraction reflections from $TlCrS_2$, $TlMnS_2$ and $TlCoS_2$ samples which indicate on the base hexagonal, tetragonal and trigonal crystal systems with crystalline lattice parameters given in table 1, are fixed.

Table 1.

Parameters of crystalline lattice of $Tl(Cr,Mn,Co)S_2$

Compound	*a, Å*	*c, Å*	*c/a*	*Z*	$\rho_x, g/cm^3$
$TlCrS_2$	3.538	21.962	6.21	3	6.71
$TlMnS_2$	7.74	30.60	3.9	20	6.40
$TlCoS_2$	3.726	22.510	6.04	3	6.03

Sample preparation and investigation techniques.

The paramagnetic susceptibility (χ) of $Tl(Cr,Mn,Co)S_2$ compounds is investigated by Faraday method on magnitoelectric scale. The samples for measurements have the cylindrical form with sizes: $h\approx3$ мм, $d\approx2.5$мм.

The electrical conduction (σ_e) and thermoelectromotive force coefficient (S) $Tl(Cr,Mn,Co)S_2$ are investigated by four-probe compensation method. The samples for measurements have the form of parallelepiped with sizes: 7.15 × 4.57 ×2.53 мм ($TlCrS_2$), 4.20 × 5.84 × 1.37 мм ($TlMnS_2$) и 7.19 × 4.83 × 2.04 мм ($TlCoS_2$). The ohmic contacts are formed by the way of cuprum electrolytic precipitation on sample edges.

The investigation are carried out in temperature interval 77÷400K in quasi-static mode, moreover the rate of temperature change is 0,2 K/min. During measurements the samples are inside of nitrogen cryostat and the differential cuprum-constant thermo-couple the seal of which is stationary fixed on chip header near sample is used in the capacity of temperature gauge. The bucking seal of thermo-couple is stabilized at temperature of ice thawing temperature.

Experimental results and their discussion.

The temperature dependence of reversible paramagnetic susceptibility $\chi^{-1}(T)$ of $Tl(Cr,Mn,Co)S_2$ compounds is presented on the fig.1. It is seen that dependence $\chi^{-1}(T)$ is character for ferro-, antiferro- and ferromagnetic orderings, for $TlCrS_2$, $TlMnS_2$ and $TlCoS_2$ correspondingly.

Curie paramagnetic temperature (T_p) is defined by extrapolation of dependence $\chi^{-1}(T)$ on temperature axis and is equal to ~115K ($TlCrS_2$) and ~120K ($TlCoS_2$).

The effective magnetic moment ($\mu_{eff.}$) which is equal to $3.26\mu_B$ is considered from dependence $\chi^{-1}(T)$ (fig.1). The theoretical value calculated with taking under consideration the spin value of magnetic moment of Cr^{3+} is equal to 3.85 μ_B. The enough big inclination $\mu_{eff.}$ $TlCrS_2$ from theoretical value shows on the presence of quasi-two-dimensional magnetic ordering in paramagnetic region of layered ferromagnetic $TlCrS_2$. The low dimensionality of magnetic structure $TlCrS_2$ is shown in paper [6] on the investigation of low-temperature heat capacity (in adiabatic calorimeter) of layered compound $TlCrS_2$. The anomaly with significant inclination from λ-type is observed on temperature dependence of heat capacity at constant pressure $C_p(T)$ of this compound.

Also the experimental values of effective magnetic moment $TlMnS_2(4.5\mu_B)$ and $TlCoS_2(4.6\mu_B)$ are calculated from $\chi^{-1}(T)$ dependence (fig.1). The comparison of these values with theoretical ($4.9\mu_B$ for $TlMnS_2$ and $TlCoS_2$) calculated taking under consideration the spin values of magnetic moment of Mn^{3+} and Co^{3+}, shows the some difference for $TlMnS_2$ and $TlCoS_2$.

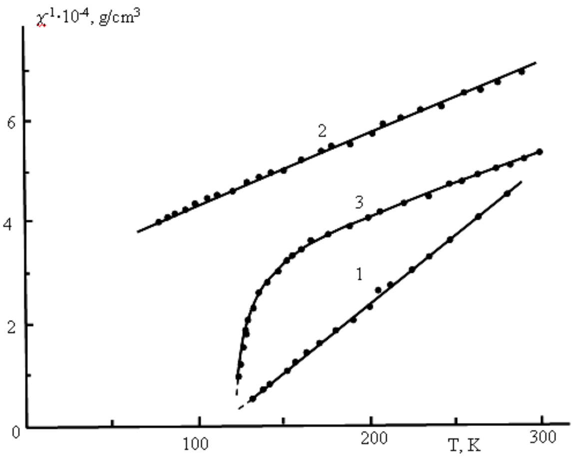

*Fig.1.*Temperature dependence of reversible magnetic susceptibility $TlCrS_2$ (1), $TlMnS_2$(2), $TlCoS_2$(3).

The temperature dependences of electrical conduction of $\sigma_e(T)$ and thermoelectromotive force coefficient S(T) of $TlCrS_2$ compound are given on the fig.2. As it is seen from the figure the temperature dependence of electrical conduction has the half-semiconductor type and the behavior of thermoelectromotive force coefficient on temperature proves on charge transfer by *p*-type carriers. Moreover, the anomaly (~340K) which is connected with delocalization of 3d-electrons in paramagnetic region and their participation in charge transfer is observed on *S(T)* $TlCrS_2$ dependence.

The temperature dependence of electrical conduction $\sigma_e(T)$ of $TlMnS_2$ compound is given on the fig.3. As it is seen from the figure σ_e increases with temperature increase, i.e. the strongly expressed the half-semiconductor character of co0nduction and strong increase of $\sigma_e(T)$ near T~300K connected with the fact that temperature achieves the self-conductance $TlMnS_2$ takes place.

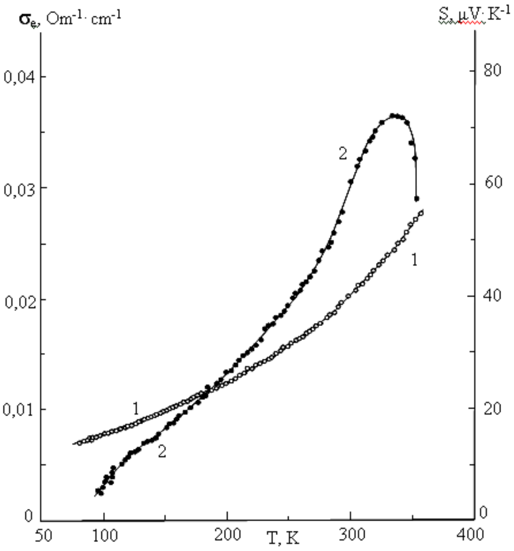

Fig.2. Temperature dependence of electrical conduction (1) and thermoelectromotive force coefficient (2) $TlCrS_2$.

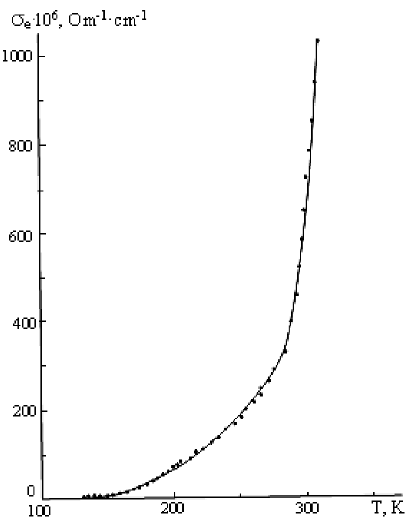

Fig.3. Temperature dependence of electrical conduction $TlMnS_2$.

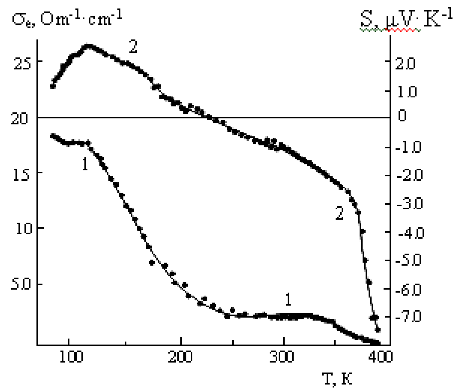

Fig.4. Temperature dependence of electrical conduction (1) and thermoelectromotive force coefficient (2) $TlCoS_2$.

The temperature dependence of electrical conduction of $\sigma_e(T)$ and thermoelectromotive force coefficient *S(T)* of $TlCoS_2$ ferromagnetic. As it is seen *S(T)* $TlCoS_2$ some increases in temperature interval 77÷115K achieving the maximum value at $T\approx 115$K. Further, the change of conduction type from *p*-type up to *n*-type is observed near $T\sim 225$K with temperature increase. From the fig.4 it is seen that σ_e $TlCoS_2$ decreases with temperature increase from 77K. Near $T\sim 115$K the break caused by fispersion of charge carriers of *p*-type on spin heterogeneities [14] forming at the transfer of spin system from magnetoordered state into paramagnetic one, is observed on $\sigma_e(T)$ dependence of $TlCoS_2$ compound.

Note, that temperature (~115K) at which the anomaly which well agrees with temperature of magnetic phase transition (~112K) of $TlCoS_2$ ferrimagnetic [15] takes place on $\sigma_e(T)$ and $S(T)$ $TlCoS_2$ dependences (fig.4).

The change of conduction type in $TlCoS_2$ from *p*-type up to *n*-type is connected with delocalization of 3d-electrons in paramagnetic region and their participation in charge transfer. The strong decrease is observed higher ~350K on $S(T)$ $TlCoS_2$ dependence to the side of negative values and this circumstance shows on half-metal character of conduction in $TlCoS_2$, i.e. the conduction decrease (fig.4) is observed up to $T\approx 250$K, further σ_e insignificantly increases in the interval 250-325K. The further decrease of conduction $TlCoS_2$ in temperature interval 325-400K is connected with the appearance self-conductance of half-metal $TlCoS_2$.

Conclusion.

Thus the investigation of paramagnetic susceptibility and electrical conduction of $Tl(Cr,Mn,Co)S_2$ compounds show that $TlCrS_2$ is the strongly layered (two-dimension) ferromagnetic of conduction half-semiconductor type, $TlMnS_2$ is half-semiconductor antiferromagnetics and $TlCoS_2$ is ferrimagnetics having the half-metal conduction type.

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$Tl(Cr,Mn,Co)S_2$ LAYLI MAQNETİKLƏRİN PARAMAQNİT QAVRAYICILIĞI VƏ ELEKTRİK KEÇİCİLİYİ

77÷400K temperatur intervalında aparılan maqnit və elektrik tədqiqatları göstərmişdir ki, $TlCrS_2$ - ferromaqnit yarımkeçirici, $TlMnS_2$ - antiferromaqnit yarımkeçirici, $TlCoS_2$ isə yarımmetalik keçirici gedişə malik ferrimaqnetikdir. $TlCrS_2$-nin eksperimental effektiv maqnit momentinin ($3.26\mu_B$) nəzəridən ($3.85\mu_B$) kifayət qədər böyük fərqi, güclü laylı $TlCrS_2$ ferromaqnetikinin paramaqnit oblastda ikiölçülü maqnit nizamlanmasının olması ilə izah edilir.

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ПАРАМАГНИТНАЯ ВОСПРИИМЧИВОСТЬ И ЭЛЕКТРОПРОВОДНОСТЬ СЛОИСТЫХ МАГНЕТИКОВ $Tl(Cr,Mn,Co)S_2$

В интервале температур 77÷400К проведены магнитные и электрические исследования, которые показали, что $TlCrS_2$ является полупроводниковым ферромагнетиком, $TlMnS_2$ - полупроводниковым антиферромагнетиком, а $TlCoSe_2$ - ферримагнетиком, обладающим полуметаллическим ходом проводимости. Достаточно большое отклонение значения экспериментального, эффективного магнитного момента $TlCrS_2$ ($3.26\mu_B$) от теоретического ($3.85\mu_B$) объясняется наличием двумерного магнитного упорядочения в парамагнитной области сильнослоистого ферромагнетика $TlCrS_2$.

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