THE ROENTGENOGRAPHIC, MAGNETIC AND ELECTRICAL INVESTIGATIONS OF $TlMnS_2$, $TlMnSe_2$ CRYSTALS

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The $TlMnS_2$, $TlMnSe_2$ crystals are synthesized by the method of solid reaction from chemical elements, suspended in stoichiometric ratio. The roentgenographic, magnetic and electrical investigations have been carried out. It is established, that $TlMnS_2$ crystallizes in tetragonal crystal system with parameters of elementary cell: a=7.74Å; c=30.60Å; z=20; ρ_x=6.40g/cm^3. The $TlMnSe_2$ crystallizes in hexagonal crystal system with parameters: a=6.53Å; c=23.96Å; z=8; ρ_x=6.71g/cm^3. The $TlMnS_2$, $TlMnSe_2$ compounds are semiconductors and have the antiferromagnetic character of exchange interaction.

1. Introduction

The low symmetry of crystal structure of magnets by $TlMeX_2$ type (where Me=3d-metal; *X*=S, Se, Te) [1-3] predestines the dependence of their magnetic properties on main crystallographic directions, in some cases, right up to appearance of low-dimensional effect, when spin system (magnetic structure) of magnet in paramagnetic region in definite temperature interval is in "quasi-two-dimensional " or quasi-one-dimensional" magnetic order (Izing-Geyzenberg model) [4]. Besides, the magnetic and semiconductor properties coincide in these compounds [5-8]. The given circumstances make the compound class by $TlMeX_2$ type (Me=3d-metal; X=S, Se, Te) the one from the perspective base material for nano-technology.

The magnetic structure of magnet is formed by its crystal structure, that's why the roentgenographic investigation get the supreme importance: the definition of type of crystal structure, crystal system and parameters of elementary cell of crystal lattice, which would allow to suppose in the aggregate to which layered system or chain structure the concrete synthesized crystal by $TlMeX_2$ type (Me=3d-metal; *X*=S, Se, Te) can be related to.

2. The sample obtaining and their roentgenographic analysis

The $TlMnS_2$ and $TlMnSe_2$ compounds had been synthesized by solid state method, in evacuated till residual pressure ~10^{-3} Pa in quartz ampoules at temperature ~1100K from chemical elements, suspended in stoichiometric ratio. The electric furnace temperature was increasing till melting point of sulfur (319 K), selenium (493 K) and was supporting during three hours for the prevention of ampoule explosion. Further, the furnace temperature was fluently increased till temperature ~1100 K, at which the ampoules were bearing during 72 hours. Later, the reaction product was degenerated and the synthesis was repeated. Further, $TlMnS_2$ and $TlMnSe_2$ were carried out in powder state, pressed and treated by homogenizing annealing at temperature ~600K during 480 hours in evacuated quartz ampoules.

The roentgenographic analysis of $TlMnS_2$ and $TlMnSe_2$ samples, specially prepared after annealing, was carried out at room temperature (~300 K) on DRON-3M diffractometer (CuK_α is radiation, λ=1.5418Å, Ni-filter, mode 35kV, 10mA). The angular discrimination of shooting was ~0,1°. The mode of continuous scan was used. The diffraction angles have been defined by measurement method on intensity maximum. The mistake of definition of reflection angles in experiments wasn't exceeded $\Delta\theta=\pm0.2°$. The diffractograms of $TlMnS_2$ (a) and $TlMnSe_2$ (b) crystals are presented on the fig.1.

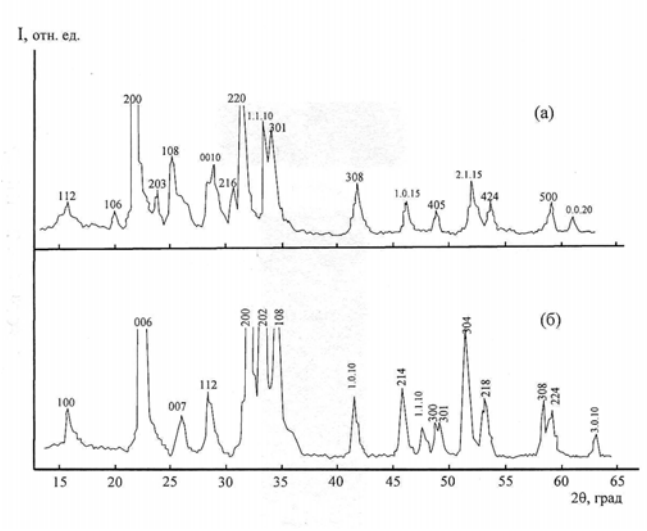

Fig.1. The diffractograms of $TlMnS_2$ (a) and $TlMnSe_2$ (b) crystals.

Table 1

The calculation of $TlMnS_2$ crystal diffractograms

№	θ	I/I_0	$d_{exp.}$ (Å)	$d_{th.}$(Å)	*hkl*	Parameters of elementary cell (Å)
1	8°37′	10	5.1462	5.1427	112	
2	10°34′	8	4.2034	4.2058	106	
3	11°29′	100	3.8719	3.8700	200	
4	12°20′	13	3.6091	3.6101	203	Tetragonal
5	13°11′	26	3.3797	3.3802	108	
6	14°50′	24	3.0113	3.0060	00.10	a=7.74
7	15°47′	14	2.8342	2.8478	216	
8	16°17′	62	2.7493	2.7365	220	c=30.60
9	17°13′	42	2.6044	2.6347	11.10	
10	17°32′	40	2.5586	2.5705	301	z=20
11	21°15′	19	2.1272	2.1269	308	
12	23°25′	13	1.9399	1.9400	1.0.15	ρ_x=6.40 g/cm^3
13	24°44′	9	1.8425	1.8419	405	
14	26°24′	20	1.7339	1.7343	2.1.15	
15	27°12′	13	1.6865	1.6866	424	
16	29°52′	12	1.5480	1.5480	500	
17	30°49′	5	1.5048	1.5030	0.0.20	
18	32°09′	5	1.4488	1.4493	1.2.20	

The diffractional reflections from $TlMnS_2$ sample (table 1),

which indicate on the base of hexagonal crystal structure with parameters of crystalline lattice: a=7.74Å; c=30.60Å; c/a~ 3.9, number of atoms in elementary cell z=20; roentgen density ρ_x=6.40g/cm^3 were fixed in 10°≤2θ≤70° angle interval.

Table 2

The calculation of $TlMnSe_2$ crystal diffractograms

№	θ	I/I_0	$d_{exp..}$ (Å)	$d_{th.}$(Å)	hkl	Parameters of elementary cell (Å)
1	7°50′	10	5.6559	5.6552	100	
2	11°08′	100	3.9922	39933	006	
3	12°50′	10	3.4710	3.4229	007	
4	14°03′	30	3.1763	3.1501	112	Hexagonal
5	15°48′	100	2.8311	2.8276	200	
6	16°22′	90	2.7366	2.7520	202	a=6.53
7	17°04′	80	2.6275	2.6467	108	c=23.96
8	20°32′	40	2.1982	2.2062	1.0.10	
9	22°40′	40	2.0003	2.0131	214	z=8
10	23°32′	10	1.9311	1.9317	1.1.10	ρ_x=6.71 g/cm^3
11	24°08′	10	1.8858	1.8851	300	
12	24°19′	10	1.8720	1.8793	301	
13	25°28′	50	1.7928	1.7981	304	
14	26°22′	30	1.7359	1.7398	218	
15	28°56′	30	1.5934	1.5954	308	
16	29°18′	25	1.5752	1.5751	224	
17	31°18′	10	14839	1.4815	3.0.10	

The diffractional reflections from $TlMnSe_2$ sample (table 2), which indicate on the base of hexagonal crystal structure with parameters of elementary cell: a=6.53Å, c=23.96Å; c/a~ 3.7, z=8, ρ_x=6.71g/cm^3 were fixed in 10°≤2θ≤70° angle interval.

Probably, the layers situate in consecution Tl-S-Mn-S-Tl-S-Mn-S in $TlMnS_2$ structure. The layers of trigonal prisms from Mn and Tl, parallel planes (001) give such atom disposition. Se atoms in $TlMnSe_2$ structure create hexagons, situated under the tops of cell foundation in z=0 and 1/2 planes. Tl and Mn atoms separately create the triangular grids 6^3, packed on hexagonal law.

3. The sample preparation and experimental methods

The magnetization (σ) of $TlMnS_2$ and $TlMnSe_2$ has been measured on Domenicalli pendulum magnetometer, and magnetic susceptibility (χ) has been measured by Faraday method on magnetoelectric scales. The samples for the measurements had cylindrical form with dimensions h≈3mm, d≈2.5mm.

The electroconductivity (σ_e) of $TlMnS_2$ and $TlMnSe_2$ had been investigated by four-probe compensating method. The samples for measurements had parallelepiped form with dimensions 4.20mm×5.84mm×1.37 ($TlMnS_2$) and 12.47mm×5.65mm× 2.87mm ($TlMnSe_2$). The ohmic contacts had been created by the way of cuprum electrolytic precipitation on sample edges.

The investigations were carried out in temperature interval 77÷30K in quasi-static mode, moreover the velocity of temperature change was 0,2K/min. During the measurements, the samples were inside the nitric cryostat and the differential cuprum-constant thermocouple, the seam of which stationary fixed on chip carrier near the sample was used in the capacity of temperature gauge. The bearing seam of thermocouple stabilized at temperature of melting ice.

4. The experimental results and their discussion

The dependence of specific magnetization σ of $TlMnS_2$ and $TlMnSe_2$ compounds on magnetic field at 77 K is given on the fig.2. As it is seen, the dependence $\sigma(H)$ at given temperature for both compounds has the form, which is character for paramagnetic state. However, the temperature dependence of reversible paramagnetic susceptibility of these compounds (fig.3) follows to Kurie-Weissa law with extrapolation in region of negative temperatures that evidences about existence of antiferromagnetic exchange interaction. From fig.3 it is followed, that temperature of magnetic transformation of both compounds is situated below 77 K. The experimental values of effective magnetic moment of investigated compounds, which were equal to 4.5μ_B ($TlMnS_2$) and 4.7μ_B ($TlMnSe_2$) are calculated from temperature dependence of reversible paramagnetic susceptibility. The calculation of theoretic value of effective magnetic moment (4.9μ_B) has been carried out with taking into consideration clearly spin value of magnetic moment of three-valency Mn ion. The comparison shows the well agreement of experimental and theoretic results.

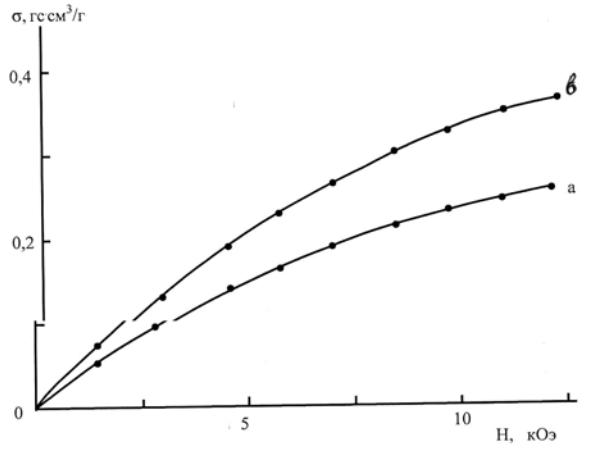

Fig.2. The dependence of specific magnetization of $TlMnS_2$ (a) and $TlMnSe_2$ (b) on magnetic field at 77 K.

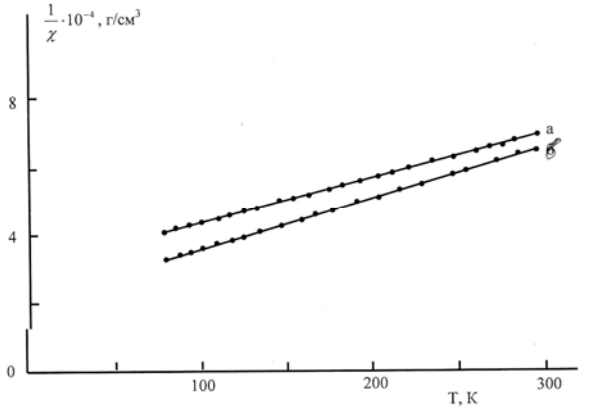

Fig.3. The temperature dependence of reversible paramagnetic susceptibility of $TlMnS_2$ (a) and $TlMnSe_2$ (b).

The interpretation of obtained experimental results, evidencing about antiferromagnetic interaction in $TlMnS_2$

and $TlMnSe_2$ can be carried out, basing on crystal structure of these compounds, which can be presented as in series altemating layers (grids) of Tl^{1+}, Mn^{3+} and S^{2-} (ore Se^{2-} ions, parallel to basis plane. The big enough ratio c/a (~4) evidences about layered structure of these compounds. In plane, consisting in itself Mn^{3+} ions the ferromagnetic order is carried out. The Tl^{1+} and S^{2-} (ore Se^{2-}) layers situate between nearest layers of Mn^{3+} ions, that's why the ferromagnetic layers are connected by more weak powers of antiferromagnetic type. The co-existence of two interactions: – ferromagnetic (inside layers) one and antiferromagnetic (between layers) one – leads to resulting antiferromagnetic interaction in $TlMnS_2$ and $TlMnSe_2$.

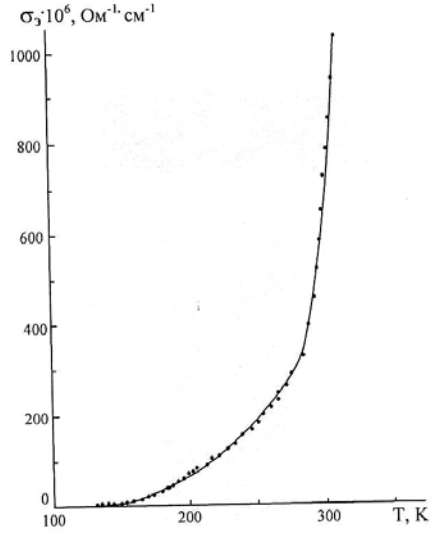

Fig.4. The temperature dependence of electroconductivity of $TlMnS_2$.

The temperature dependence of electroconductivity $\sigma_e(T)$ of $TlMnS_2$ is given on the fig.4. As it is seen from the figure, σ_e increases with temperature increase, i.e. it has the expressed semiconductor character of conductivity; and strict rise of $\sigma_e(T)$ in region T~300 K, probably is connected with temperature achievement of own conductivity of $TlMnS_2$ semiconductor.

The temperature dependence of conductivity $\sigma_e(T)$ of $TlMnSe_2$ is given on the fig.5. As it is seen from the figure, σ_e increases with temperature increase, i.e.the $\sigma_e(T)$ $TlMnSe_2$ dependence also has semiconductor character.

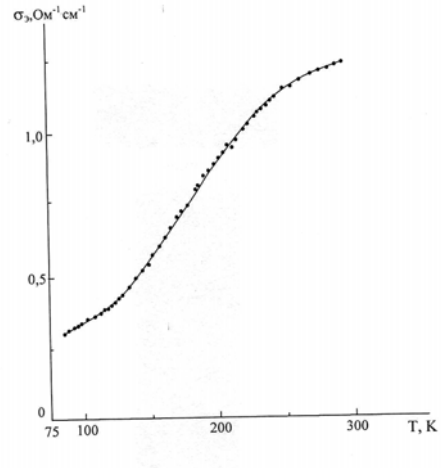

Fig.5. The temperature dependence of electroconductivity of $TlMnSe_2$.

5. Conclusion

The investigations of magnetic susceptibility and heat capacity (in adiabatic calorimeter) of layered antiferromagnetics $TlMnS_2$ and $TlMnSe_2$ is planned in temperature interval 5÷300 K in order to clarify whether their magnetic structure is strong-layered-quasi-two-dimensional (Izing-Geyzenberg model) or it is weak-layered-three-dimensional one. The behavior of quasi-two-dimensional spin systems in high-temperature region near phase transfer in magneto-ordered state and in region of low temperatures has the specific peculiarities, strongly differing from behavior of three-dimensional spin systems. For example, the magnetic susceptibility in paramagnetic region is characterized by the presence of wide maximum, which characterizes the strongly developed nearest magnetic order at $T>>T_N$, the anomaly with obvious inclination from λ-type is observed on temperature dependence.

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$TlMnS_2$, $TlMnSe_2$ KRİSTALLARININ RENTGENOQRAFİK, MAQNİT VƏ ELEKTRİK TƏDQİQATLARI

Bərk cisimli reaksiya metodu ilə stexiometrik nisbətdə kimyəvi elementlərdən çəkilmiş $TlMnS_2$, $TlMnSe_2$ kristalları sintez olunmuşdur. Rentgenoqrafik, maqnit və elektrik tədqiqatları aparılmışdır Müəyyən edilmişdir ki, $TlMnS_2$ elementar özəyinin paramətri: a=7,74Å; c=30,60Å; z=20; ρ_x=6,40 q/sm^3 olan tetraqonal sinqoniyada, $TlMnSe_2$ isə a=6,53Å; c=23,96Å; z=8; ρ_x=6,71q/sm^3 parametrli heksaqonal sinqoniyada kristallaşır. $TlMnS_2$, $TlMnSe_2$ birləşmələri antiferromaqnit qarşılıqlı təsirə və yarımkeçirici xarakterə malik olurlar.

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РЕНТГЕНОГРАФИЧЕСКИЕ, МАГНИТНЫЕ И ЭЛЕКТРИЧЕСКИЕ ИССЛЕДОВАНИЯ КРИСТАЛЛОВ $TlMnS_2$, $TlMnSe_2$

Методом твердотельной реакции из химических элементов, взвешенных в стехиометрическом соотношении, синтезированы кристаллы $TlMnS_2$, $TlMnSe_2$. Проведены рентгенографические, магнитные и электрические исследования. Установлено, что $TlMnS_2$ кристаллизуется в тетрагональной сингонии с параметрами элементарной ячейки: a=7,74Å; c=30,60Å; z=20; ρ_x=6,40 г/см^3. $TlMnSe_2$ - в гексагональной сингонии с параметрами: a=6,53Å; c=23,96Å; z=8; ρ_x=6,71 г/см^3. Соединения $TlMnS_2$, $TlMnSe_2$ являются полупроводниками и обладают антиферромагнитным характером обменного взаимодействия.

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