The magneto-dielectric properties of compounds and alloys in the systems of TlInS$_2$–TlFeS$_2$, TlInS$_2$–TlFeSe$_2$

R.G. Veliyev [a,*], M.Yu. Seyidov [a,b], N.Z. Gasanov [a], F.M. Seyidov [a]

[a] Institute of Physics, Azerbaijan National Academy of Sciences, Az-1143, Baku, Azerbaijan
[b] Department of Physics, Gebze Institute of Technology, Gebze 41400, Kocaeli, Turkey

ARTICLE INFO

ABSTRACT

The research of dielectric properties of TlInS$_2$-layered compound shows that TlInS$_2$ is extrinsic ferroelectric ($T_c \approx 202.4$ K) with intermediate incommensurable phase ($T_i \approx 206.3$ K). Analysis of publications was carried out by us on magnetic properties of TlFeS$_2$ and TlFeSe$_2$ compounds, having chained crystalline structure, allows to draw a conclusion that these compounds are highly anisotropic (quasi-one-dimensional) antiferromagnets with Neel temperatures equal to $\sim$12 K and $\sim$14 K respectively (long-range magnetic order). Moreover, on the temperature dependence of reverse magnetic susceptibility TlFeS$_2$ and TlFeSe$_2$ in paramagnetic area at $\sim$196 K and $\sim$290 K respectively, wide minimums exist, which characterize short-range magnetic order in these quasi-one-dimensional antiferromagnets. Using method of differential-thermal analysis were founded regions of homogenous and heterogeneous co-existence of ferroelectric and antiferromagnetic orderings in the systems of TlInS$_2$–TlFeS$_2$ and TlInS$_2$–TlFeSe$_2$.

1. Introduction

The study of the co-existence in one alloy of electrical and magnetic orderings is of specific scientific interest, since it was historically formed so that entire existing set of the mechanisms of electrical ordering (ferroelectrics, antiferroelectric materials, extrinsic ferroelectrics, intrinsic and extrinsic ferroelectrics with the intermediate incommensurable phase, ferrielectrics) was predicted, and then realized in the concrete compounds, on the basis of the analogy of phenomenon with the mechanisms of magnetic ordering in the magnets. Such materials exhibit a magnetoelectric effect, which is characterized by the appearance of an electric polarization on applying a magnetic field and by the appearance of a magnetization when applying an electric field [2]. The study of the co-existence of electrical and magnetic orderings in both homogeneous and heterogeneous (composites) alloys, acquired an even larger urgency in connection with the development of the technical capabilities of nanotechnology [3].

In connection with accounted above the dielectric properties of layered compound TlInS$_2$ are investigated. Analysis of publications was carried out by us on magnetic properties of TlFeS$_2$ and TlFeSe$_2$ compounds. The molar relations in the systems of TlInS$_2$–TlFeS$_2$, TlInS$_2$–TlFeSe$_2$ were characterized by differential-thermal analysis (DTA).

2. The samples preparation and experimental techniques

For investigating the temperature dependence of dielectric permittivity ε (T) of the layered compound, TlInS$_2$ samples in the form of plates of polar shear, cut out from the single-crystal ingot of this compound were used. The single-crystal ingot of TlInS$_2$ was grown by Bridgman–Stockbarger method; in this case the rate of the movement of crystallization front was 2 mm/h.

Measurements of the real part of the dielectric permittivity were performed using HP4194A impedance gain/phase analyzer at the frequency of 5 kHz. A closed-cycle helium cryostat system and Lakeshore 340 temperature controller used in the measurements allowed the scanning of the temperature variation with a rate of about 0.2 K/min. Temperature was measured by GaAlAs diode sensor with an accuracy of 0.01 K. Fully computer controlled mea-

* Corresponding author. Tel.: +994 12 4383376.
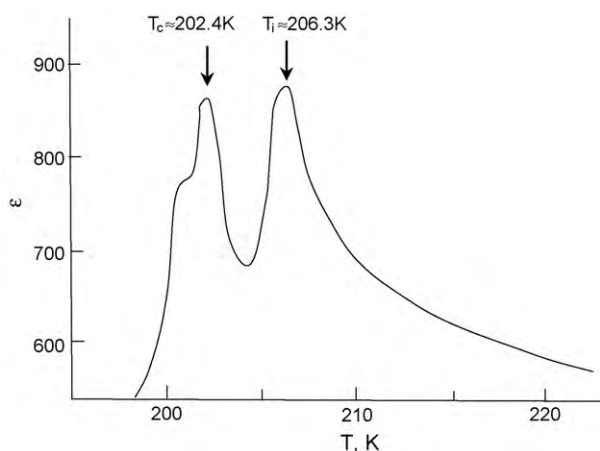 E-mail address: ramizveliyev@gmail.com (R.G. Veliyev).

Fig. 1. The temperature dependence of the dielectric permittivity of TlInS$_2$.

surements were performed in the temperature range of 5–300 K [1].

The DTA of compounds and alloys was carried out on the device NTR-73, which allowed identifying phase transition temperatures with precision of ±5 K. Heating rate was 2–4 K/min. Temperature was controlled by Pt–Pt/Rh thermocouple, graded according to fiducial elements in the interval of 430–1560 K.

3. Experimental results and discussion

In Fig. 1 the temperature dependence of the dielectric permittivity of TlInS$_2$ measured under the atmospheric pressure is given. As can be seen from figure, curve ε (T) is characterized by anomalies in the form of maximums at ~206.3 K and ~202.4 K, and also by the presence of small "bend" around 201 K. It is known that with a temperature decrease under the atmospheric pressure the layered crystal TlInS$_2$ experiences the complex sequence of structural phase transitions (PT), including PT in the incommensurate (IC) and commensurate (C) ferroelectric phases [4–7]. The initial paraelectric phase of TlInS$_2$ posseses monoclinic crystalline structure that is characterized by space group of symmetry C_{2h}^6 [8]. PT in IC-phase is related to the condensation (under $T_i \approx 216$ K) of soft mode at the point of Brillouin zone with the wave vector of $\vec{q}_i(\delta; \delta; 0.25)$, where δ the parameter of incommensurability [9]. At $T_c \approx 201$ K value δ abruptly becomes zero and crystal of TlInS$_2$ passes into the extrinsic ferroelectric (vector of spontaneous polarization is located in the plane of layer) C-phase with the wave vector $\vec{q}_c(0; 0; 0.25)$ [9–13].

Comparing our results with the data, represented in [4–7,13] it is possible to conclude that the curve ε (T) of the investigated sample sharply differs from the analogous curves, represented in the literature, both with the number of anomalies and their temperature positions. Let us note also that the color of the sample under investigation is characterized by orange nuance, whereas the crystals of TlInS$_2$, selected from the different parties and investigated in [4–7], possessed different nuances of yellow. Relying on data [11,12], in which strong sensitivity of the physical properties (including temperatures PT) of the layered compound TlInS$_2$ is determined to a quantity of admixtures in the sample and to the degree of the defectiveness of its crystal structure, it can be supposed that observed anomaly on the curve ε (T) under 206.3 K is related to PT in IC-phase, and under 202.4 K—with PT into the commensurate ferroelectric phase. Additionally, the "bend" around 201 K is the temperature interval of the co-existence of the remainders of the non-disintegrated solitons of IC-phase and domains of low-temperature commensurable ferroelectric phase [4].

In the work [14] in the range of temperatures of 1.5–400 K the reverse magnetic susceptibility $\chi^{-1}(T)$ of the semiconductor compounds of TlFeS$_2$ and TlFeSe$_2$ [15], having monoclinic crystalline structure, which contains chain crystal constructions [16–18] was investigated by Faraday's method. Dependence of $\chi^{-1}(T)$ was studied both in arbitrary crystallographic orientation and in basic crystallographic orientations across $\vec{c}$ and $\vec{a}$ axes. In magnets with low-symmetry crystallographic structure, which have plain or chain constructions, the peculiarities discovered following from Ising–Heisenberg model [19] are found during experiments. Crystallochemical formula of these magnets should contain at least three atoms.

Low symmetry of crystallographic structure of TlMeX$_2$ type magnets (where Me = 3d metal; X = S, Se, Te) [16–18,20–22] predefines dependence of their magnetic properties from basic crystallographic directions, in some cases (structure have plain or chain constructions)—up to occurrence of low-dimensional effect, when spin system (magnetic structure) of the magnet in paramagnetic area, in certain temperature interval, is in quasi-two-dimensional [19,23] or quasi-one-dimensional [19,24] magnetic ordering (Ising–Heisenberg model). According to this model, behavior of low-dimensional spin systems in the area of high temperatures (paramagnetic area), around phase transition to ordered magnetic state and in the area of low temperatures has specific peculiarities, which sharply differ them from behavior of three-dimensional spin systems. For example, temperature dependence of magnetic susceptibility of low-dimensional antiferromagnet in paramagnetic area of temperatures with $T \gg T_N$ (T_N—Neel point, below which three-dimensional antiferromagnetic ordering is possible), is characterized by the presence of wide maximum, which is bound with highly developed short-range magnetic order, and on the temperature dependence of thermal capacity of low-dimensional magnets anomaly with evident deviation from λ-type is observed [19,24–26].

In Fig. 2 the temperature dependence of reverse magnetic susceptibility $\chi^{-1}(T)$ of chain antiferromagnets TlFeS$_2$, TlFeSe$_2$ is represented (figure with our comments corresponds to publication [14]). It is seen on the figure, that magnetic properties of TlFeS$_2$ and TlFeSe$_2$ are dependent of crystallographic orientation. Authors of the work [14] consider wide minimum existing on the dependence of $\chi^{-1}(T)$ at ~196 K (TlFeS$_2$) and ~290 K (TlFeSe$_2$) to be Neel temperature T_N, below which has three-dimensional antiferromagnetic ordering. According to authors of [14], above these temperatures quasi-one-dimensional antiferromagnetic ordering in magnetic structure of TlFeS$_2$ and TlFeSe$_2$ is formed. We think that this conclusion is wrong, because authors of [14] did not take into account specifics of crystalline structure of TlFeS$_2$ and TlFeSe$_2$ compounds. It is known that spin system (magnetic structure) of magnet is formed by its crystalline structure.

TlFeS$_2$ and TlFeSe$_2$ compounds have monoclinic structure [16–18], which has chain constructions of FeX$_4$ tetrahedron (X-chalcogen) with joint edges. In the center of tetrahedrons Fe^{3+} ions are located, and chalcogen ions (S^{2-} or Se^{2-}) are placed in vertexes. Tl^{1+} ions are situated in prismatic voids of crystalline structures of TlFeS$_2$ and TlFeSe$_2$. FeX$_4$ tetrahedrons are connected into linear chains and are parallel to crystallographic axis $\vec{c}$. Exchanging magnetic interaction between iron ions along the chain are done along –Fe–X–Fe–atoms chain, forming a certain angle. Exchanging interaction between iron ions in the direction of crystallographic axis $\vec{a}$, perpendicular to FeX$_4$ tetrahedrons chain, is done along –Fe–X–Tl–X–Fe– atoms chain. It is known that if two magnetic ions are separated by two anions, then energy of this cation–anion–anion–cation interaction is smaller by an order of magnitude than energy of cation-anion-cation interaction [27]. It means that energy of super-exchange along the chain –Fe–X–Tl–X–Fe– should be two orders of magnitude smaller than
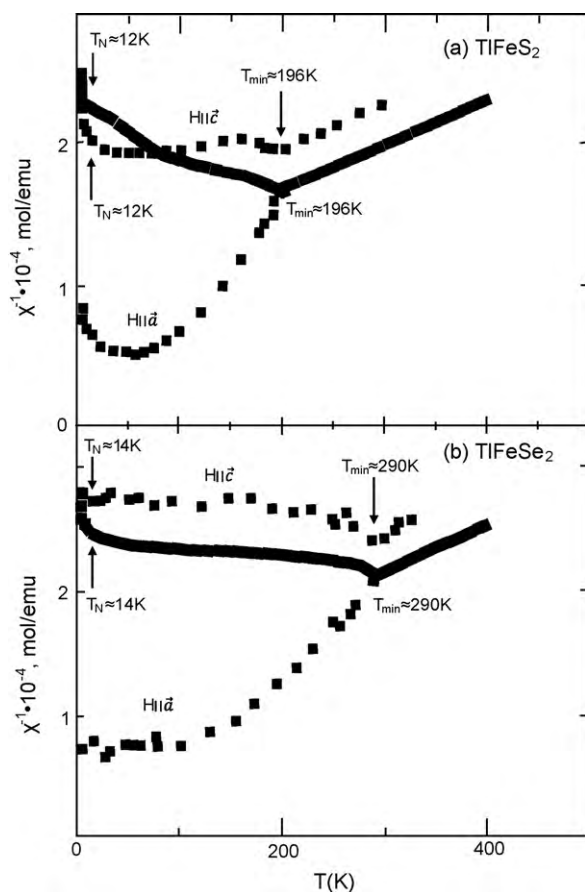
Fig. 2. The temperature dependence of the reverse magnetic susceptibility of TlFeS$_2$ (a) and TlFeSe$_2$ (b). (Figure with our comments corresponds to publication [14].)

energy of –Fe–X–Fe– interaction, occurring along the chain of tetrahedrons. It can be assumed that magnetic properties of TlFeS$_2$ and TlFeSe$_2$ compounds will be mainly defined by exchanging interaction between iron ions, situated within tetrahedrons chain, i.e., TlFeS$_2$ and TlFeSe$_2$ can be viewed as quasi-one-dimensional magnetic systems.

The dependences of $\chi^{-1}(T)$ for TlFeS$_2$ and TlFeSe$_2$, measured both in arbitrary crystallographic orientation (filled squares) and in the direction of $\vec{c}$ axis, contains the anomalies at the temperature, ~12 K and ~14 K respectively, which indicate three-dimensional antiferromagnetic transition (long-range magnetic order). Neel temperatures, found in [24] from the temperature dependence of magnetic susceptibility of TlFeS$_2$ and TlFeSe$_2$, were equal to ~10 K and ~12 K respectively. Additionally, on the χ (T) dependence for TlFeS$_2$ [24] at ~200 K, wide maximum is present, which satisfies condition $T \gg T_N$, corresponding to the Ising–Heisenberg model [19].

In publication [28] neutron diffraction research found three-dimensional antiferromagnetic ordering for TlFeS$_2$ below 16 K (long-range magnetic order with $T_N \approx 16$ K), which are close to results of works [14,24]. Concerning broad minimums on $\chi^{-1}(T)$ dependence at $T_{min} \approx 196$ K (TlFeS$_2$) and $T_{min} \approx 290$ K (TlFeSe$_2$), which were observed in work [14], authors of [19] mention that magnetic susceptibility of strongly anisotropic antiferromagnet is characterized by the presence of wide maximum in the case of χ (T) or broad minimum-case of $\chi^{-1}(T)$, which is characterized by strongly developed short-range magnetic order with $T \gg T_N$, i.e., based on this assertion, it is possible to draw a conclusion that in the paramagnetic region of TlFeS$_2$ higher than the temperature of 12 K, quasi-one-dimensional magnetic ordering is formed, which

is retained up to ~196 K, after which begins the disordering of the magnetic structure of the strong-chained antiferromagnet of TlFeS$_2$, and for TlFeSe$_2$ higher than the temperature of 14 K quasi-one-dimensional magnetic ordering is formed, which is retained up to ~290 K, after which begins the disordering of the magnetic structure of the strong-chained antiferromagnet of TlFeSe$_2$.

Low-dimensional of magnetic structure of antiferromagnets TlFeS$_2$ and TlFeSe$_2$ is also shown by the fact that on the temperature dependence of thermal capacity, studied in adiabatic calorimeter under constant pressure C_p (T) in the temperature interval 4–300 K, anomaly with evident deviation from λ-type is seen [24].

4. Phase diagrams of TlInS$_2$–TlFeS$_2$ and TlInS$_2$–TlFeSe$_2$ systems

For solving the physical task presented at the beginning of this article it is necessary to determine the regions of the homogeneous and heterogeneous co-existence of the layered ferroelectric TlInS$_2$ with the strongly chained (quasi-one-dimensional) antiferromagnets TlFeS$_2$ and TlFeSe$_2$ using DTA method. During the study of interaction in the system of TlInS$_2$–TlFeS$_2$ cation–cationic substitution occurs, i.e., the cation of indium (In^{3+}) is replaced by the cation of iron (Fe^{3+}), and in the case of the system of TlInS$_2$–TlFeSe$_2$ both cation–cationic and anion–anionic type of substitution occur.

For construction of the state diagram of the system TlInS$_2$–TlFeS$_2$, 17 compositions from initial compounds TlInS$_2$ and TlFeS$_2$ were prepared in equimolecular proportion. Preliminarily TlInS$_2$ and TlFeS$_2$ weighted in stoichiometrical proportion from the highly purity chemical elements, were placed in the quartz ampoules, which were evacuated until remaining pressure was ~10^{-3} Pa. After that TlInS$_2$ and TlFeS$_2$ were synthesized in electric furnace and using DTA method melting temperatures were identified to be TlInS$_2$ (1050 K) and TlFeS$_2$ (930 K). Regime for synthesizing of compositions, weighted in equimolecular proportion based on initial triple compounds TlInS$_2$ and TlFeS$_2$, preliminarily brought to low-dispersed state, was selected according to already defined melting temperatures. Quartz ampoules with compositions were evacuated until remaining pressure ~10^{-3} Pa, and then were put into electric furnace, heated above melting temperatures of the initial compounds, and were endured in this temperature for 7–9 h. Later furnace temperature was decreased to room temperature with the speed of 100 K/h. Synthesized alloys were annealed for homogenization for 25 days under ~700 K in case of alloys rich with indium, and around 28 days under ~620 K in case of alloys rich with iron. The annealed alloys were studied with DTA method.

Constructed according to the results of DTA diagram of state of the system of TlInS$_2$–TlFeS$_2$ is represented in Fig. 3. As follows from the diagram, the system of TlInS$_2$–TlFeS$_2$ is quasi-binary section. Continuous rows of solid solutions are formed in it with the minimum at a temperature of 640 K and 70 mol% of TlFeS$_2$; i.e. in alloys of TlInS$_2$–TlFeS$_2$ system ferroelectric and antiferromagnetic orderings for all changes of molar proportions of initial compounds homogeneously co-exist.

For construction of state diagram of TlInS$_2$–TlFeSe$_2$ system 14 compositions were prepared from initial compounds TlInS$_2$ and TlFeSe$_2$ in equimolecular proportion. Preliminarily compounds TlInS$_2$ and TlFeSe$_2$ were synthesized in quartz ampoules evacuated until remaining pressure ~10^{-3} Pa by melting chemical elements, which were weighted in stoichiometrical proportion. Regime for synthesizing compositions, weighted in equimolecular proportion on the basis of initial triple compounds TlInS$_2$ and TlFeSe$_2$, was selected according to melting temperatures TlInS$_2$ (1050 K) and TlFeSe$_2$ (875 K). Each alloy was heated above melting temperature of initial compounds and endured in this temperature for 5–6 h.
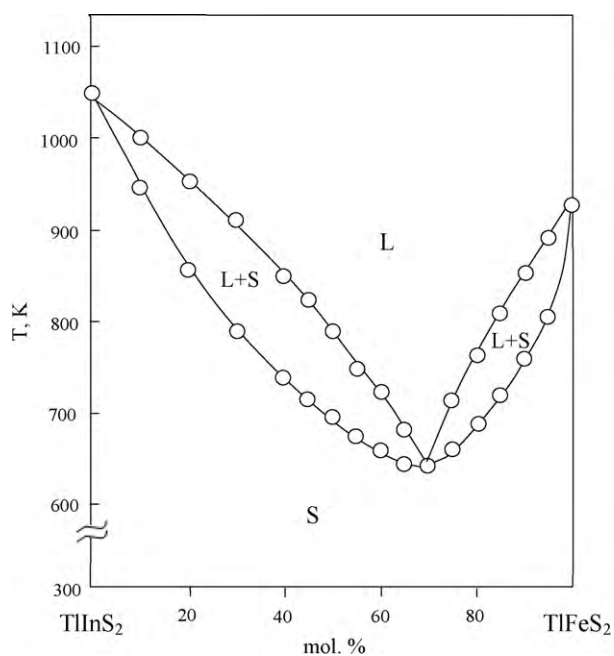
Fig. 3. TlInS$_2$–TlFeS$_2$ system state diagram.

Then the temperature of the electric furnace was decreased to room temperature with the speed of 100 K/h. Synthesized alloys were annealed during 25 days under ~670 K in case of alloys rich with indium, and for 27 days under ~580 K in case of alloys rich with iron for homogenization. Annealed alloys were studied using DTA method.

The diagram of state of the system of TlInS$_2$–TlFeSe$_2$ is represented in Fig. 4. This system is eutectic type quasi-binary
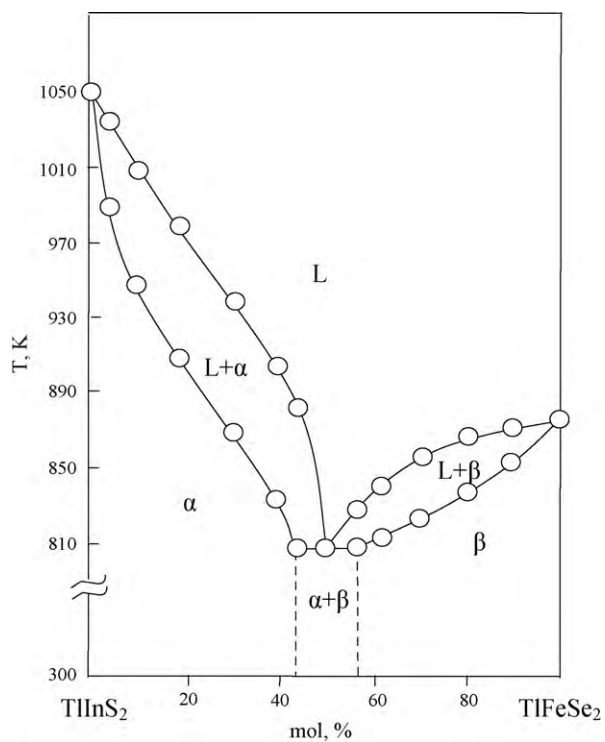

Fig. 4. TlInS$_2$–TlFeSe$_2$ system state diagram.

with the wide regions of solid solutions on the basis of TlInS$_2$ and TlFeSe$_2$, which reach up to 45 mol% (homogeneous regions of the co-existence of ferroelectric and antiferromagnetic orderings). Eutectic melts at 810 K and has a composition of (TlInS$_2$)$_{0.5}$(TlFeSe$_2$)$_{0.5}$, i.e., in this eutectic alloy heterogeneously (compositionally) co-exist ferroelectric and antiferromagnetic orderings.

5. Conclusion

A study of the temperature dependence of the dielectric permittivity of TlInS$_2$ showed that this compound it is extrinsic ferroelectric ($T_c \approx 202.4$ K) with intermediate incommensurable phase ($T_i \approx 206.3$ K). The analysis of publications, carried out by us, of the magnetic properties of TlFeS$_2$ and TlFeSe$_2$, revealed, that these compounds are strong-chained (quasi-one-dimensional) antiferromagnets with Neel temperatures equal to ~12 K and ~14 K respectively (long-range magnetic order). Additionally, on the temperature dependence of reverse magnetic susceptibility TlFeS$_2$ and TlFeSe$_2$ in paramagnetic area under ~196 K and ~290 K respectively, wide minimums exist, which characterize short-range magnetic order in these quasi-one-dimensional antiferromagnets. By the DTA method the regions of the homogeneous and heterogeneous co-existence of electrical and magnetic orderings in the systems TlInS$_2$–TlFeS$_2$, TlInS$_2$–TlFeSe$_2$ are determined.

References

[1] M.Yu. Seyidov, E.M. Kerimova, R.K. Veliyev, R.N. Kerimov, F.A. Mikailov, J. Alloys Compd. 453 (2008) 503.
[2] L.D. Landau, E.M. Lifshiz, Electrodynamics of Continuous Media, Pergamon, Oxford, 1960.
[3] N. Mamedov, K. Wakita, S. Akita, Y. Nakayama, Jpn. J. Appl. Phys. 44 (2005) 709.
[4] F.M. Salayev, K.R. Allakhverdiyev, F.A. Mikailov, Ferroelectrics 131 (1992) 163.
[5] R.A. Suleymanov, M.Yu. Seyidov, F.M. Salayev, F.A. Mikailov, FTT 35 (1993) 348 (in Russian).
[6] K.R. Allakhverdiyev, N.D. Akhmed-zade, T.G. Mamedov, T.S. Mamedov, M.Yu. Seyidov, FNT 26 (2000) 76 (in Russian).
[7] F.A. Mikailov, T. Basaran, T.G. Mammadov, M.Yu. Seyidov, E. Senturk, Physica B 334 (2003) 13.
[8] T. Isaaks, Zeitshrift für Crystallografic 141 (1971) 104.
[9] S.B. Vakhrushev, V.V. Zhdanova, B.E. Kviatkovsky, N.M. Okuneva, K.R. Allakhverdiyev, R.A. Aliyev, R.M. Sardarli, JETF Lett. 39 (1984) 245 (in Russian).
[10] K.R. Allakhverdiyev, A.I. Baranov, T.G. Mamedov, V.A. Sandler, Ya.N. Sharifov, FTT 30 (1988) 1751 (in Russian).
[11] S. Ozdemir, R.A. Suleymanov, E. Civan, Solid State Commun. 96 (1995) 757.
[12] S. Ozdemir, R.A. Suleymanov, E. Civan, T. Firat, Solid State Commun. 98 (1996) 385.
[13] R.A. Aliyev, K.R. Allakhverdiyev, A.I. Baranov, N.R. Ivanov, R.M. Sardarli, FTT 26 (1984) 1271.
[14] Z. Seidov, H.A. Krug von Nidda, J. Hemberger, A. Loidl, G. Sultanov, E. Kerimova, A. Panfilov, Phys. Rev. B 65 (2001) 014433.
[15] S.N. Mustafayeva, E.M. Kerimova, A.I. Jabbarli, FTT 42 (2000) 2132 (in Russian).
[16] K. Klepp, H. Boller, Monatsh. Chem. 110 (1979) 1045.
[17] M. Zabel, K. Range, Naturforsch. B 34 (1979) 1.
[18] G.I. Makovetskiy, E.I. Kasinskiy, Neorgan. Mater. 20 (1984) 1752 (in Russian).
[19] K.S. Aleksandrov, N.V. Fedoseyeva, I.P. Spevakova, Magnetic phase transitions in galoid crystals, Novosibirsk[nl]Science (1983) 193, in Russian.
[20] A. Kutoglu, Naturwissenchaften B 61 (1974) 125.
[21] M. Rosenberg, A. Knulle, H. Sabrowsky, C. Platte, Phys. Chem. Solids 43 (1982) 87.
[22] R.G. Veliyev, R.Z. Sadykhov, Yu.G. Asadov, E.M. Kerimova, A.I. Jabbarov, Crystallogr. Rep. 53 (2008) 130.
[23] R.G. Veliyev, R.Z. Sadykhov, E.M. Kerimova, Yu.G. Asadov, A.I. Jabbarov, FTP 43 (2009) 1175 (in Russian).
[24] M.A. Aldzhanov, N.G. Guseinov, G.D. Sultanov, M.D. Nadzhafzade, Phys. Stat. Sol. (b) 159 (1990) K107.
[25] M.A. Aldzhanov, A.A. Abdurragimov, S.G. Sultanova, M.D. Nadzhafzade, FTT 49 (2007) 309 (in Russian).
[26] M. Aldzhanov, M. Nadzhafzade, Z. Seidov, M. Gasumov, Tr. J. Phys. 20 (1996) 1071.
[27] D. Gudenaff, Magnetism and Chemical Bond, Metallurgy, Moscow, 1968, p. 325 (in Russian).
[28] H. Sabrowsky, M. Rosenberg, D. Welz, P. Deppe, W. Schafer, J. Magn. Magn. Mater. 54-57 (1986) 1497.