TEMPERATURE DEPENDENCES OF ELECTRIC CONDUCTION AND THERMO-EMF IN CuFeS$_2$ AND (CuFeS$_2$)$_{0.7}$ (CuGaS$_2$)$_{0.3}$ SOLID SOLUTIONS

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The temperature dependences of electric conduction and thermo-emf of CuFeS$_2$ and solid solution (CuFeS$_2$)$_{0.7}$ (CuGaS$_2$)$_{0.3}$ in temperature interval 80-320K are investigated. The jump correlating with temperature dependence of thermo-emf is observed in σ-$f(T)$ dependence at 125K in CuFeS$_2$.

INTRODUCTION

The development of semiconductor instrumentation technology requires the widening of compound class with given parameters allowing us to control their physical characteristics.
The semiconductor compounds with impurities of magnetic elements or compounds containing Mn, Fe at alias take the especial place. Such compounds are of interest for creation of functional elements on their base, which are controlled by magnetic field. That's why the comprehensive research of their physical properties is the one of the important tasks of solid state physics.

The measurement results of electric conduction and thermo-emf in interval 80-320K of polycrystalline samples CuFeS$_2$ and (CuFeS$_2$)$_{0.7}$ (CuGaS$_2$)$_{0.3}$ are given in present work.

The investigations of structural properties CuFeS$_2$ [1] show that crystal lattice symmetry strongly depends on technology for its production. This compound crystallizes in several modifications:

1) cubic β-phase (lattice parameter a=5.328Å) crystallizes in sphalerite structure. Besides cubic β-phase the compound CuFeS$_2$ crystallizes in two tetragonal structures with different sizes of elementary cell.

2) tetragonal α-phase has chalcopyrite structure and following lattice parameters (a=5.292 Å, c=10.407Å). This phase is observed in stoichiometric compositions. Besides α-phase there is one more tetragonal γ-phase (a=10.598Å and c=5.380Å). In this phase Cu and Fe atoms take ordered positions in cation sublattice.

In A^{I}B^{II}C^{VI} compounds the forbidden band width changes in limits 0.8-3.5 eV. However, at replacement of trivalent cations in CuGaS$_2$ by Fe atom the obtained new compound becomes zero-gap semiconductor because additional d-band forms in forbidden one [2,3].

In CuFeS$_2$ at T=50K the magnetic phase transition, which is connected with antiferromagnetic ordering of Cu atom magnetic moments, is revealed [4]. In the same temperature region the anomalies of temperature dependence of kinetic parameters are also revealed.

The magnetic and thermal properties of CuFeS$_2$ at low temperatures are investigated in [5]. The observable anomalous increase of magnetic moment and magnetic susceptibility authors connect with formation of non-interacting magnetic clusters. The formation of such clusters is connected with disordering of Cu and Fe atoms in cation sublattice.

(CuFeS$_2$)$_{0.7}$ (CuGaS$_2$)$_{0.3}$ is investigated with the aim to study the influence on electrophysical properties at replacement of Fe magnetic element by Ga one.

THE SYNTHESIS OF POLYCRYSTALLINE SAMPLES AND EXPERIMENT TECHNIQUE

CuFeS$_2$ polycrystalline samples are synthesized by melting of initial components Cu, Fe and S in stoichiometric ratio. The temperature is increased with rate 3K/min up to temperature, which exceeds the melting point of CuFeS$_2$ on 30-50K (1148 K) and then the isothermal endurance during 2 hours is carried out. After finishing of this procedure the cooling up to room temperature with rate 3-5K/min is carried out. The isothermal annealing is carried out at 1073K during 550 hours.

The investigations of temperature dependences of electric conduction and thermo-emf of CuFeS$_2$ and (CuFeS$_2$)$_{0.7}$(CuGaS$_2$)$_{0.3}$ in temperature interval 80-320K are carried out.

The measurements are carried out by four-point probe method on direct current. The thermo-emf is measured by method of stationary heat flow. The observable samples have parallelepiped form with 18x2,5x1,5 mm^3 and 16x2,3x1,4 mm^3 sizes. The heating furnace in the form of diminutive cooper reel with size Φ=1,5mm and height 2mm is glued by silver paste on sample butt. The thin constantan wire bifilarly wound on reel serves as heater. The temperature registration in interval 77-300K is carried out with the help of cuprum-constantan thermo-couple.

The thermo-couples are glued by silver paste on sample edge on distance 8mm from each other. The signal registration from thermo-couples is carried out with the help of voltage comparator that allows us to totally compensate the background emf.

The type of conductivity in both samples corresponds to electron one. The obtained experimental results are shown in fig.1 and fig. 2.

As it is seen from fig.1 for $CuFeS_2$ the electric conduction value in interval 80-125K increases with temperature increasing. Further, the strong decrease of electric conduction value in narrow temperature interval ΔT=5-6K in 6-7 times is observed around 125K. The electric conduction increases with further temperature increasing. These peculiarities (fig.2) are also observed on temperature dependences of thermo-emf and electric conduction of solid solution $(CuFeS_2)_{0.7}(CuGaS_2)_{0.3}$ at 125K. Such behavior of electric conduction and thermo-emf can be explained by two approaches:

1. existence of structural-phase transition in this compound in given temperature region;

2. existence of additional phase in main composition.

According to first approach, we can note as follows. The kinetic coefficients unevenly change at structural phase transition because of lattice parameter changes and band parameters correspondingly. The observed temperature dependences of kinetic coefficients σ and S confirm on phase transitions in these samples. It is followed to suppose that phase transition in $CuFeS_2$ takes place in temperature interval 120-125K. It is possible that it is connected with disordering of Cu and Fe atoms in $CuFeS_2$ cation sublattice.

By other hand we note that such dependences aren't observed on temperature dependences of $CuFeS_2$ at electric property investigations by other authors [6-8]. The different dependences of magnetic susceptibility inverse value on temperaturre dependence above and below T=130K are observed in work [5]. The authors explains this peculiarity by revealing of cluster ferromagnetism at low temperatures. According to work [9] the peak at 120K is observed on temperature dependence of magnetic susceptibility. One can suppose that these changes are the result of magnetic structure changes of this material at this temperature. However, such strong influence of magnetic structure on electronic system is incredibly.

As it is seen from experimental data the decrease of S value correlating with of electric conduction value increasing is also observed on temperature dependence of thermo-emf in 100-150K interval. Further, the simultaneous growth of values both electric conduction and thermo-emf with temperature increasing can be explained by degeneracy eliminatiom.

Investigation of Hall effect is carried out to find the reason of such behaviour of electric conduction and thermo-emf. These investigations show that at 80K Hall coefficient value corresponds to electron concentration of $4.10^{16} cm^{-3}$ order. The strong magneto-field dependence at 80K (decrease of Hall coefficent value almost in 2 times) that confirms the high mobility of charge carriers. However, investigaion of Hall coefficient around 300K for both compositions show the high value of charge carrier concentration of $2.10^{20} cm^{-3}$ order. Such strong differences of concentration values at different temperatures, disagreement of sign of charge carriers obtained by Hall and thermo-emf measurements, the disagreement of temperature dependences of electric conduction and thermo-emf are observed in two-phase samples [10,11].

Indeed, it is difficult to imagine that charge carrier concentration increase on four orders in interval 200K. If it takes place then the other thermo-emf temperature dependence would observe.

Note that sulfur element including into observable sample compositions always make difficulties with obtaining of stable compositions [6,8]. It is probably, that especially this fact can lead to appearance of second phase.

Note, that if main and second phases have the different signs of charge carriers then the mutual compensation should take place and this affects on experimental data. However, the carried out roentgenostructural analyses don't reveal the tracks of any additional phases. Consequently, such temperature dependences are the result of structural phase transition in $CuFeS_2$.
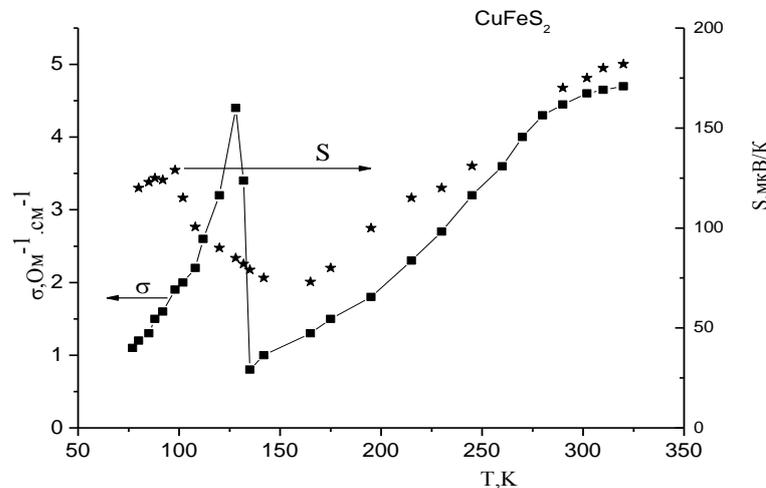

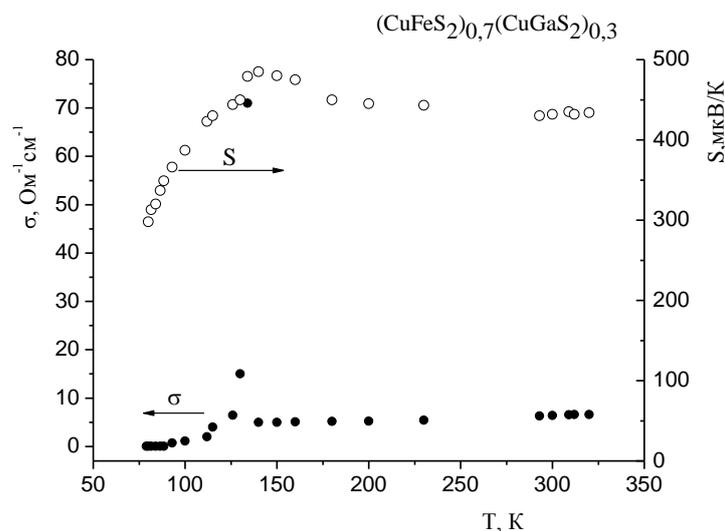*Fig.1.* Temperature dependences of electric conduction and thermo-emf of $CuFeS_2$.

Fig.2. Temperature dependences of electric conduction and thermo-emf of (CuFeS$_2$)$_{0.7}$(CuGaS$_2$)$_{0,.3}$.

CONCLUSION

The analysis of temperature dependences of electric conduction and thermo-emf and roentgen measurement results allow us to conclude that CuFeS$_2$ and (CuFeS$_2$)$_{0,7}$(CuGaS$_2$)$_{0,.3}$ solid solutions are two-phase systems.

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[1] *R. Adams, R. Beaulien, M. Vassiladis, A. Woid.* Mater.Res.Bull, 1972, **7**,87.

[2] *L.V. Kradinova, A.M. Polubotka, V.V. Popov, V.D. Prochuxan, Yu.V. Rud, V.K. Skoryutin.* FTT, 1987, **29**, 2209. (In Russian).

[3] *L.V. Kradinova, A.M. Polubotka, V.V. Popov, V.D. Prochuchan, V. Rud, V. Skorukin.* Semicond. Sci. Technol. 1993, **8,** 1616,.

[4] *Amarche, M. Quienero, J.R. Swalmason, T.M. Hobden.* J. Magn. Mater. 1990, **162**, 347,.

[5] *V.V. Popov, S.A. Kijaev, Yu.V. Rud.* FTT, 2011, **53**, 70. (In Russian).

[6] *V.V. Popov, P.P. Konstantinov, Yu.V. Rud.* JETF 2011, **140**, 783. (In Russian).

[7] *Naohito Tsujii and Takao Mori.* J.Applied Physics Express, 2013, **6**, 043001.

[8] *T. Teranishi, K. Sato.* J. Phys. (Paris) **36**, Coll. C3, Suppl. 1975, **9,** 149.

[9] *J. C. Woolley, A.-M. Lamarche, G. Lamarche* at al. J. Magn. And Magn. Mater. 1996, **164, 154**.

[10] *S.A. Aliev, S.S. Raqimov.* Neorqanicheskie Materiali. 1992, **28**, 329. (In Russian).

[11] *C. Herring.* J. of Applied Physics, 1960, **31,** 1939.

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