SPECIFIC FEATURES OF DOPING THE p-TiCoSb INTERMETALLIC SEMICONDUCTOR WITH A Cu DONOR IMPURITY. 2. EXPERIMENTAL STUDIES

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Temperature and concentration dependences of the resistivity, magnetic susceptibility, Seebeck and thermoelectric power coefficients of the $TiCo_{1-x}Cu_xSb$ semiconductor solid solution in the temperature range from 80 to 380 K have been studied. A substantial difference between the activation energy values deduced from high-temperature sections of the conductivity versus temperature and the thermoelectric coefficient versus temperature dependences has been revealed and explained in the framework of the model which examines the heavily doped and strongly compensated semiconductor as the amorphous one. The theoretically predicted conductivity transition insulator–metal (the Anderson transition) stemming from crossing the percolation threshold level by the Fermi one has been discovered experimentally.

1. Introduction

This work continues our previous researches dealing with the influence of significant concentrations of a Cu donor impurity on the electrophysical properties of intermetallic semiconductor TiCoSb, which were started in work [1], where the calculations of the band structure and the distribution of the electron density of states (DOS) in $TiCo_{1-x}Cu_xSb$ have been carried out.

In this work, we studied the dependences of the electroconductivity σ, the thermoelectric (Seebeck) coefficient α, the magnetic susceptibility χ, and the thermoelectric power coefficient $Z^* = \alpha^2\sigma$ on the temperature and the concentration, as well as the spatial rearrangement of atoms in an elementary cell of doped intermetallic semiconductor p-TiCoSb. Doping was carried on by substituting Co($3d^74s^2$) atoms by Cu($3d^{10}4s^1$) ones and gave rise to the formation of a substitutional solid solution $TiCo_{1-x}Cu_xSb$. In so doing, the concentration of donor impurities in p-TiCoSb varied from $N_D = 1.9 \times 10^{19}$ cm^{-3} at $x = 0.001$ to $N_D = 7.6 \times 10^{21}$ cm^{-3} at $x = 0.4$.

The following remark will be used below, while discussing the experimental results. The technology of fabricating the intermetallic semiconductors comprises the fusion of a mixture of initial components followed by the uncontrollable cooling of the melt obtained. In so doing, one of the scenarios that give rise to the formation of disordered (amorphous) solids becomes partially realized [2], which results in the emergence of structural disordering, local deformations, and, as a consequence, stimulates the fluctuations of continuous energy bands. On the other hand, the distribution of energy levels, which appears owing to the fluctuation of considerable concentrations of charged impurities, in a heavily doped semiconductor has a similar structure [3]. Moreover, the authors of work [4] proposed that the energy model of a completely compensated crystalline semiconductor should be considered as that of an amorphous semiconductor.

Fluctuations of continuous energy bands in amorphous semiconductors manifest themselves in that the activation energies deduced from the temperature dependences of the electroresistance and the thermoelectric power coefficient are different from

each other within the same temperature intervals [2]. In slightly doped semiconductors, where the band fluctuations are absent, the energy barrier height is invariant with respect to the ways of its measurement.

The corresponding techniques for fabricating the specimens, the results of their structural researches, as well as the results of measurements of the specific electroresistance ρ, the thermoelectric power coefficient with respect to copper, and the magnetic susceptibility (the Faraday method) in the temperature interval $80 \div 380$ K, were reported in work [5].

2. Experimental Results and Their Discussion

X-ray phase and structural analyses of the specimens under investigation confirmed that all our $TiCo_{1-x}Cu_xSb$ specimens were composed of a single phase, and all X-ray reflections from the crystallographic planes of those specimens can be identified in the framework of the structural type MgAgAs (spatial group $F\bar{4}3m$): 4 Co atoms at $4(c)\frac{1}{4}\frac{1}{4}\frac{1}{4}$ sites, 4 Sb atoms at $4(a)000$ sites, and 4 Ti atoms at $4(b)\frac{1}{2}\frac{1}{2}\frac{1}{2}$ sites.

The temperature dependence of the specific electroresistance of an undoped p-TiCoSb specimen (see Fig. 1) has an activation character: in the dependence $\ln\rho(1/T)$, there are several activation intervals, which can be associated, in the case of weakly doped semiconductors, with the activation of electrons from the Fermi level $E_{\rm F}$ into non-localized states in the conduction band (at high temperatures), the activation of electrons from the Fermi level onto the mobility edge of the conduction band (at intermediate temperatures), and the hopping conductivity (in the low-temperature range).

A conclusion about the semiconducting character of the p-TiCoSb conductivity is also confirmed by the temperature dependence of the thermoelectric coefficient (Fig. 1). The change of its sign at $T > 90$ K testifies that the specimen concerned was heavily doped and strongly compensated and contained a significant concentration of uncontrollable donor and acceptor impurities. Note that neither the x-ray phase analysis nor the structural one has revealed another phase in the specimen but the TiCoSb one.

By analyzing the high-temperature intervals of the $\ln\rho(1/T)$ and $\alpha(1/T)$ dependences for p-TiCoSb, we determined the magnitudes of activation energies ε_1^ρ and ε_1^α, respectively, which, for slightly doped semiconductors, evaluate the energy difference between the bottom of the conduction band and the Fermi level, the position of the latter being fixed by the Coulomb gap of the impurity band. For p-TiCoSb, calculations yield $\varepsilon_1^\rho \approx 106$ meV and $\varepsilon_1^\alpha \approx 196$ meV (see the Table). The result obtained, taking the aforesaid remark in consideration, testifies that both the partial disordering [2] and fluctuations of charged impurities [3,4] take place simultaneously in studied p-TiCoSb specimens; they give rise to the fluctuations of continuous energy bands, so that traditional approaches to the analysis of weakly doped semiconductors turn out inapplicable in our case.

Doping p-TiCoSb with donor impurities, which gives rise to $TiCo_{1-x}Cu_xSb$ compositions with $x \geq 0.001$, results in the disappearance of activation sections in the dependences $\ln\rho(1/T)$ (Fig. 1), so that we may assume that the conductivity of this semiconductor acquires a typically metallic character already at the lowest concentrations of the Cu donor impurity that were achieved in the experiment. On the other hand, for studied $TiCo_{1-x}Cu_xSb$ specimens, the dependences $\alpha(1/T)$ demonstrate strongly pronounced high-temperature activation sections.

The change of the Seebeck coefficient sign from the hole-related to electron-related one already at the lowest concentrations of donor impurities, which were introduced into p-TiCoSb, testifies that the compensation degree of a p-TiCoSb semiconductor undoped with Cu atoms was highest among the whole series of fabricated specimens. The point of complete compensation ($N_A = N_D$) falls within the content interval $0 < x < 0.001$. The result obtained qualitatively coincides with the results of calculations of the electron structure of $TiCo_{1-x}Cu_xSb$ [1], which also predict a drift of the Fermi level towards the conduction band, followed by its entry into the band. Using the Mott relation for the Seebeck coefficient [2],

$$\alpha = \frac{2\pi^2 k_{\rm B}^2 T}{3e}\frac{d}{dE}(\ln n(E_{\rm F})),$$

and the experimental dependences $\alpha(1/T)$, we determined the values of activation energies for various concentrations of donor impurities in $TiCo_{1-x}Cu_xSb$ (see the Table).

Energy and concentration characteristics of $TiCo_{1-x}Cu_xSb$

x	N_D, cm^{-3}	ε_1^ρ, meV	ε_3^ρ, meV	ε_1^α, meV	ε_3^α, meV
0	0	106	5.2	196	10.6
0.001	1.9×10^{19}	–	–	40.9	0.52
0.005	9.5×10^{19}	–	–	26.3	0.32
0.02	3.8×10^{20}	–	–	25.1	0.22
0.05	9.5×10^{20}	9.7	–	14.6	0.68
0.1	1.9×10^{21}	–	–	10.3	0.51
0.3	5.7×10^{21}	–	–	0.9	–
0.4	7.6×10^{21}	–	–	2.8	–

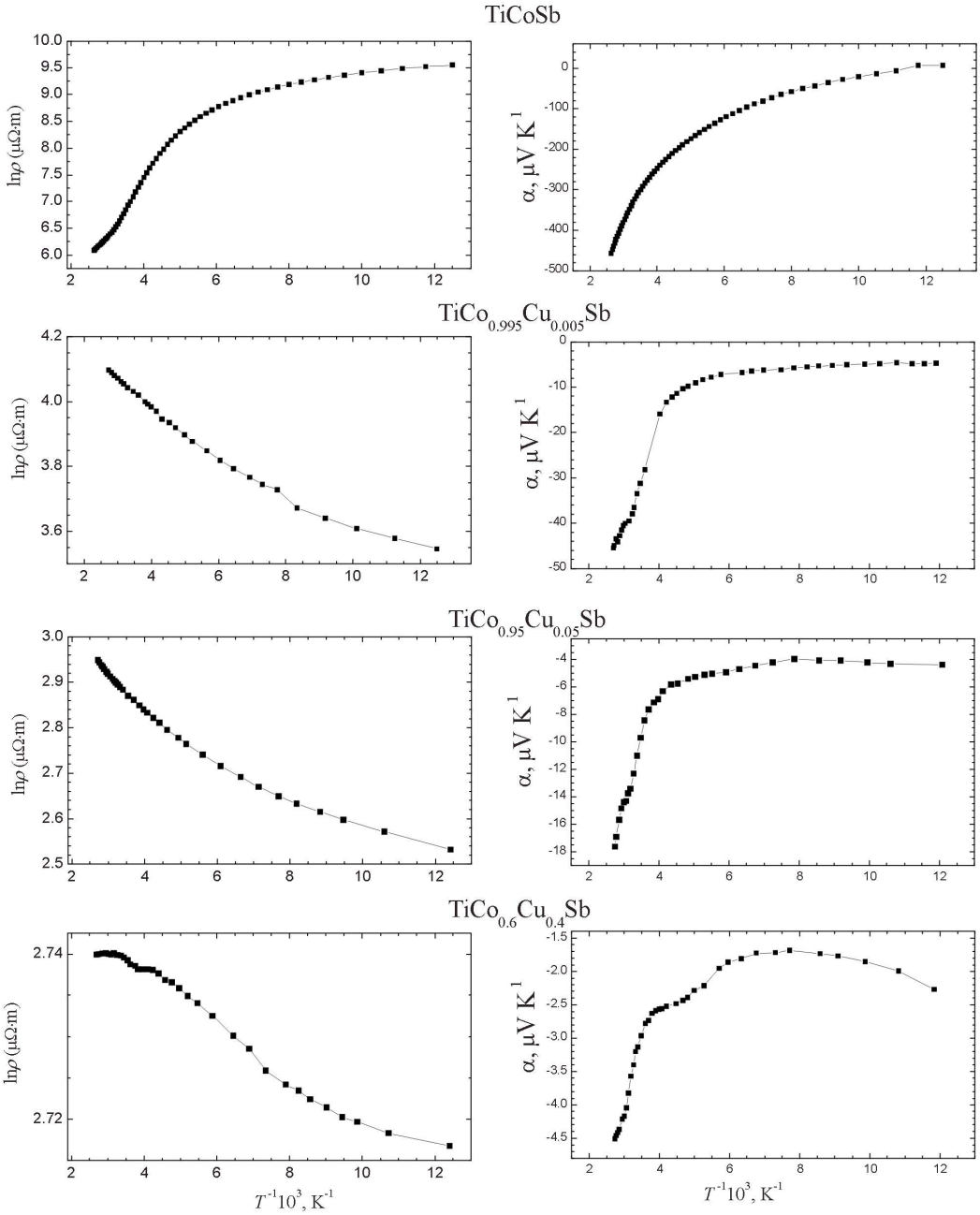

Fig. 1. Temperature dependences of the specific electroresistance ρ and the Seebeck coefficient α for $TiCo_{1-x}Cu_xSb$ with various x

We commence the discussion of the obtained experimental results on a qualitative level by defining a basic difference between the electrokinetic and thermoelectric (the Seebeck coefficient) phenomena of conductivity in the case of a heavily doped semiconductor, in which the fluctuations of continuous energy bands are observed. In contrast to the case of a slightly doped semiconductor, where current carriers are subjected to the action of only one external force, the temperature gradient ∇T, the large-scale fluctuations of impurities in a heavily doped semiconductor create a potential [4] which considerably exceeds the potential difference between two points in the semiconductor, provided that a temperature gradient is maintained between them [2]. Therefore, the value of ε_1^{α} that is measured in a heavily

doped compensated semiconductor is comparable with the averaged amplitudes of continuous energy band fluctuations.

The electroconductivity of a semiconductor is mainly governed by the concentration and the mobility of current carriers ($\sigma(E) \sim n(E)\mu(E)$); it manifests itself only if an external electric field is applied. Hence, the measured quantity ε_1^ρ in a heavily doped compensated semiconductor is comparable with the energy gap value between the Fermi and percolation threshold levels.

Our conclusion is that the magnitude of ε_1^α in a heavily doped compensated semiconductor changes by the amplitude gain of band fluctuations, while the magnitude of ε_1^ρ by the energy distance between the Fermi level and the percolation threshold one.

In the framework of such a logic, the quantity ε_1^α must be larger than ε_1^ρ by value, which is really observed in experiments ($\varepsilon_1^\rho \approx 106$ meV and $\varepsilon_1^\alpha \approx 196$ meV). Again, if insignificant amounts of donor impurities are introduced into a semiconductor, so that the semiconductor does not become overcompensated, then the compensation degree becomes higher and the Fermi level becomes shifted proportionally to $n^{2/3}$, while the potential relief grows, because the electron screening becomes weaker [3]. In the experiment, we "jump" over such a concentration range owing to the specific features of the fabrication of specimens.

Provided that the semiconductor compensation is complete ($N_A \approx N_D$), the amplitude of continuous energy band fluctuations is maximal and equal to the semiconductor energy gap halfwidth, and the Fermi level is located in the middle of the energy gap (an analog of the intrinsic semiconductor) [4]. In such a situation, the energy of activation ε_1^ρ from the Fermi level onto the percolation threshold one is maximal and equal to the same energy gap halfwidth. The fact that the sign of the Seebeck coefficient of undoped p-TiCoSb semiconductor changes already at $T \geq 90$ K testifies that the acceptor and donor concentrations in the semiconductor are close by value, so that the compensation degree in such an undoped semiconductor must be as high as possible. In particular, this conclusion is evidenced for by both the largest amplitude of band fluctuations (of about 196 meV) and the largest distance between the Fermi level and the percolation threshold one (of about 106 meV).

If the semiconductor becomes overcompensated, a further increase of the donor impurity concentration n – now in the semiconductor with the electron type of conductivity – brings about a reduction of the compensation degree, an increase of the Fermi energy

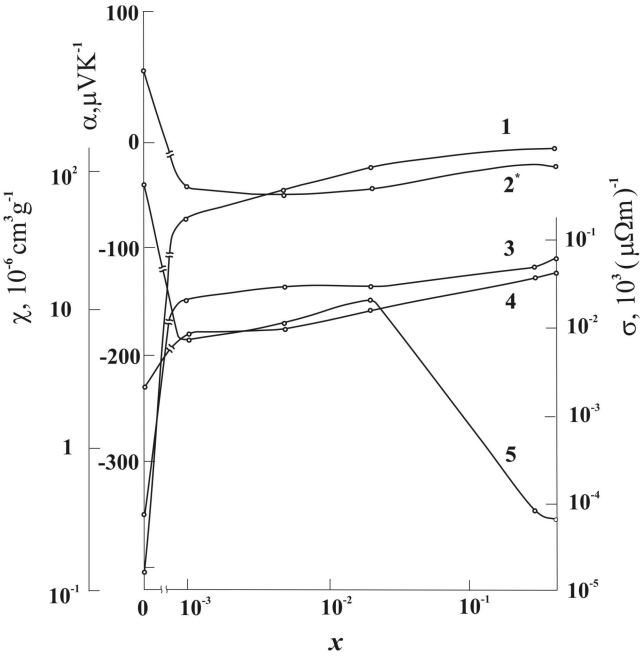

Fig. 2. Dependences of the Seebeck coefficient α at $T = 350$ (*1*) and 80 K (*2**), the electroconductivity σ at $T = 80$ (*3*) and 350 K (*4*), the magnetic susceptibility χ at $T = 300$ K (*5*), and the density of states at the Fermi level (the inset) on the $TiCo_{1-x}Cu_xSb$ content x; curve *2** is scaled up by an order of magnitude along the ordinate axis

(proportionally to $n^{2/3}$), and a reduction of the fluctuation amplitude [3, 4]. Just such a dynamics for the amplitude variation of continuous energy band fluctuations was observed in the experiment (see the Table).

The absence of activation sections from the dependences $\ln \rho(1/T)$ for all doped semiconductors (except for the case $x = 1$) testifies that the Fermi and the percolation threshold levels have swapped their places, and the insulator–metal conductivity transition (the Anderson transition) has happened. Such a transition was predicted theoretically, e.g., in work [1].

The dependence of the magnetic susceptibility χ on the Cu donor impurity concentration in p-TiCoSb (Fig. 2) has a complicated character. As was shown in work [6], there is a weak magnetic ordering in the specimens of undoped TiCoSb semiconductor; therefore, the Faraday method made it possible to determine the values of χ for them at magnetic field strengths $H \leq 2$ kGs only, whereas the χ-magnitudes for doped specimens were measured at $H = 10$ kGs. The

researches of the field and temperature dependences of the magnetic susceptibility showed that $TiCo_{1-x}Cu_xSb$ specimens with $x > 0.1$ are Pauli paramagnets. Whence it follows that the variation of χ with the temperature or composition in doped specimens must be adequate to the variation of the density of states at the Fermi level ($\chi \sim N(E_F)$).

The reduction of χ for $TiCo_{1-x}Cu_xSb$ within the content interval $0 < x < 0.1$ practically by an order of magnitude cannot be interpreted as that proportional to $N(E_F)$, because those alloys are not Pauli paramagnets. The calculations show that a sharp increase of $N(E_F)$ followed by the quasisaturation is observed at $x \leq 0.1$, which may be probably associated with the crossing of the percolation threshold level in the conduction band by the Fermi level. At the same time, at temperatures when the Fermi level is located below the percolation threshold one ($T = 80$ K), the character of the dependence $\alpha(x)$ in the $TiCo_{1-x}Cu_xSb$ content interval $0 \leq x \leq 0.001$ (curve *2* in Fig. 2) is similar to that of the density of states at the Fermi level ($S \sim 1/N(E_F)$). On the other hand, for x within the interval from 0 to 0.1, the reduction of $\chi(x)$ correlates with the growth of $N(E_F)$ and may be probably related to the destruction of a magnetic ordering. The further reduction of $\chi(x)$ at contents $0.1 \leq x \leq 0.2$ can be explained as that owing to the complete occupation of $3d$-states of Co atoms.

In works [5–10], we showed that the observable insulator–metal conductivity transition in intermetallic semiconductors of the structural type MgAgAs at their heavy doping is the Anderson transition. In the case of strong correlations in the metallic electron gas of amorphous semiconductors, the Anderson transition may be accompanied by the change of the Seebeck coefficient sign. In addition, on the nonmetallic side of transition, the crystalline substance is an amorphous antiferromagnet [2]. In addition to the reasons given above, two experimentally observable results – the change of the $\alpha(x)$-sign at the insulator–metal conductivity transition and the magnetic ordering in TiCoSb – provide an independent confirmation that the investigated intermetallic $TiCo_{1-x}Cu_xSb$ semiconductors are amorphous ones.

For those specimens, whose $\ln \rho(1/T)$ and $\alpha(1/T)$ dependences reveal activation sections in the low-temperature interval, the activation energies ε_3^{ρ} and ε_3^{α}, respectively, were determined; we consider the values obtained to be comparable with the amplitude of small-scale fluctuations (the "fine structure" of fluctuations) in heavily doped semiconductors. In the case of the doping of p-TiCoSb with a Cu donor impurity, the dependence of ε_3 on the impurity concentration is descending (see the Table). While doping the intermetallic semiconductor n-ZrNiSn with a Cu donor impurity, a monotonous reduction of the hopping conduction ε_3 with the growth of the donor impurity concentration was also observed [10]. The reduction of the ε_3-value by almost an order of magnitude indicates that a substantial reduction of the small-scale fluctuation depth takes place if even the minimal concentrations of the donor impurity, which could be achieved in the experiment ($x = 0.001$), are introduced into the semiconductor of the p-type. As is evident from Figs. 1 and 2, at those concentrations of the donor impurity, there occurred the overcompensation of the semiconductor from the p- to n-type.

Semiconductors n-ZrNiSn and p-TiCoSb differ from each other basically by the type of their conductivity, so that the introduction of impurities – e.g., of the donor type – with certain concentrations into them might give rise to opposite results concerning the potential relief amplitude. If the concentration of uncontrollable acceptor and donor impurities in n-ZrNiSn and p-TiCoSb specimens is supposed constant, then, provided that the specimen fabrication conditions were also constant, the increase of the donor impurity concentration in heavily doped semiconductor n-ZrNiSn would result in an increase of the Fermi energy and a reduction of the potential relief (the fluctuation amplitude). In the case of p-TiCoSb semiconductor, the increase of the donor impurity concentration before the semiconductor having become overcompensated would give rise to an increase of the potential relief. At the donor impurity concentrations when the conductivity changes its type from p- to n-one, a further increase of the impurity concentration would result in a reduction of the potential relief and a diminishing of $\varepsilon_3(x)$, as it was in the case of n-ZrNiSn semiconductor.

As was pointed out above, the undoped semiconductor is characterized by the maximal degree of compensation, which manifests itself, in particular, in that the amplitude of fluctuations of the continuous energy bands and the amplitude of small-scale fluctuations are maximal (of about 196 and 5 meV, respectively). The lowest concentrations of donor impurities that were achieved in the experiment ($x = 0.001$), if being introduced into the semiconductor, recompensate the semiconductor conductivity from the p- to n-type drastically and at once; that is why we do not observe the expected increase of the amplitude of

fluctuations in the semiconductor of the p-type under its doping with donor impurities.

3. Thermoelectric Power Coefficient of $TiCo_{1-x}Cu_xSb$

In work [11], the thermoelectric power maximum in intermetallic semiconductors of the structural type MgAgAs was found to be reached at their heavy doping with acceptor and/or donor impurities up to the concentration, at which the Fermi level crosses the percolation threshold level in the corresponding continuous energy band. It was also found that, while doping intermetallic semiconductors by substituting the atoms of transition *3d*-metals by the nearest neighbor atoms of 3*d*-elements belonging to period IV, e.g., Cu or Nu, the Fermi level coincides with the percolation threshold one in the conduction band if the concentration of donor impurities corresponds to the composition with $x \approx 0.05$.

The results of the doping of p-TiCoSb by substituting Co atoms by Cu ones testify (Fig. 3) that the dependences *4* and *5* become quasisaturated at the donor impurity concentrations which are one order of magnitude lower than those in the cases of Ni → Co and Cu → Ni substitutions. We can assume that the influence of Cu donor impurities in p-TiCoSb on the potential relief reduction is one order of magnitude more substantial than it was in semiconductors considered earlier [5–10]. We cannot generalize this conclusion to all intermetallic semiconductors which are doped with transition 3*d*-metals that are not the nearest neighbors of atoms to be substituted, because this issue requires an additional study.

Again, it follows from Fig. 3 that, at $T \geq 150$ K, the Fermi level crosses the percolation threshold one in the conduction band of the undoped semiconductor. This fact confirms the assumption stated earlier that the influences of the temperature and the impurity concentration on the maximal values of the thermoelectric power coefficient Z^* are additive [11].

4. Final Conclusions

Thus, a correlation between the parameters of continuous energy band fluctuation – in particular, between its depth and the depth of the potential well (its small-scale fluctuation) – has been revealed experimentally for the first time, with intermetallic semiconductors serving as an example. The insulator–metal conductivity transition observed in the intermetallic p-TiCoSb semiconductor at its doping with a Cu donor impurity is the Anderson transition which takes place at much lower impurity concentrations than it was in the cases studied earlier [5–10]. This reduction of the impurity concentration threshold originates from a larger contribution of $Cu(3d^{10}4s^1)$ *3d*-electrons in comparison with $Ni(3d^8 4s^2)$ ones.

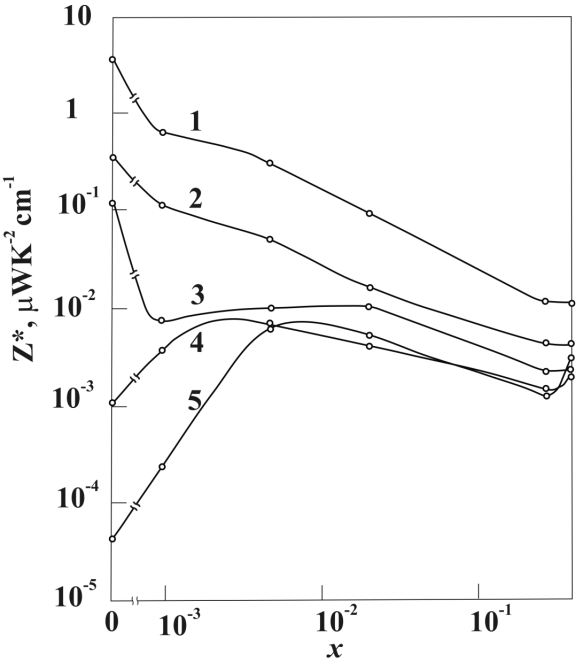

Fig. 3. Dependences of the thermoelectric power coefficient Z^* on the $TiCo_{1-x}Cu_xSb$ content x at various temperatures T = 350 (*1*), 250 (*2*), 150 (*3*), 80 (*4*), and 110 K (*5*)

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ОСОБЛИВОСТІ ЛЕГУВАННЯ ІНТЕРМЕТАЛІЧНОГО НАПІВПРОВІДНИКА *p*-TiCoSb ДОНОРНОЮ ДОМІШКОЮ Cu. 2. ЕКСПЕРИМЕНТАЛЬНІ ДОСЛІДЖЕННЯ

В.А. Ромака, Ю.В. Стадник, Д. Фрушарт, Я. Тобола, Ю. К. Гореленко, Л.П. Ромака, В.Ф. Чекурін, А.М. Горинь

Р е з ю м е

Досліджено температурні і концентраційні залежності питомого електроопору, магнітної сприйнятливості, коефіцієнтів термо-ерс та термоелектричної потужності напівпровідникового твердого розчину $TiCo_{1-x}Cu_xSb$ у температурному інтервалі 80 – 380 K. Встановлено значну розбіжність у величинах енергій активації, отриманих з високотемпературних ділянок залежностей електропровідності та коефіцієнта термо-ерс, яка пояснюється на прикладі моделі сильнолегованого і сильнокомпенсованого кристалічного напівпровідника як аморфного напівпровідника. Експериментально виявлено передбачений розрахунками [1] перехід провідності діелектрик–метал (перехід Андерсона), пов'язаний з перетином рівнів протікання та Фермі.