MEASURING TRANSDUCERS

INVESTIGATION OF THERMOMETRIC MATERIAL Ti$_{1-x}$Sc$_x$CoSb. MODELING OF CHARACTERISTICS

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Abstract. The second part of the complex research of Ti$_{1-x}$Sc$_x$CoSb thermometric material for the sensitive elements of thermoelectric and electro resistant thermal converters is presented. Simulation of thermodynamic, electrotechnical, energetic and structural characteristics of Ti$_{1-x}$Sc$_x$CoSb semiconductor thermometric material for various options of atoms placement is performed. It is determined that under the orderly variant of the crystal structure Ti$_{1-x}$Sc$_x$CoSb the characteristic simulation results do not correspond to the experimental research results of temperature and concentration dependences of the resistivity, thermo-EMF coefficient of the Fermi ε_F level behavior character, etc. Thus, for the ordered structure of Ti$_{1-x}$Sc$_x$CoSb, the simulation showed that the substitution in the crystallographic position 4a of the TiCoSb compound of atoms Ti $(3d^24s^2)$ at Sc $(3d^14s^2)$ generates structural defects of the acceptor nature since the Sc atom has fewer 3 d-electrons. Adding to the TiCoSb the smallest in the experiment concentration of Sc atoms by replacing the Ti atoms radically changes the behavior of the resistivity ρ and the coefficient of thermo-EMF α Ti$_{0.995}$Sc$_{0.005}$CoSb. In the 80–350 K temperature range, the resistivity value ρ increases with temperature increasing, and the conductivity of Ti$_{0.995}$Sc$_{0.005}$CoSb is metallic. It means that the addition of the smallest in the experiment concentration of atoms Sc (x=0.005) which should generate acceptors changed the position of the Fermi level ε_F in a way that could only cause the appearance of donors in the semiconductor. Thus, if in TiCoSb the Fermi level ε_F laid in the restricted area, then the metallization of the conductivity Ti$_{0.995}$Sc$_{0.005}$CoSb indicates that it not only approached the conduction zone but also crossed its leakage level, and electrons remain the main carriers of electricity. This is indicated by the negative values of the thermo-EMF coefficient α Ti$_{0.995}$Sc$_{0.005}$CoSb, which is only possible if donors of unknown nature are generated. The metallization of the conductivity Ti$_{0.995}$Sc$_{0.005}$CoSb also does not match the results of the electronic structure simulation for the ordered structure variant. After all, the simulation demonstrates that at the smallest concentration of the Sc acceptor impurity, the Fermi level ε_F drifts from the conduction zone ε_C to the middle of the restricted zone ε_g. Therefore, in the high-temperature area of dependence $\ln(\rho(1/T))$, there must be an activation area associated with the thermal emission of electrons from the Fermi level ε_F into the conduction zone ε_C, and the value of the electron activation energy ε_1^ρ should be greater than in the case of TiCoSb. To clarify the crystalline and electronic structure of the TiCoSb compound, electronic state density distribution (DOS) simulations were performed for various options of occupying crystallographic positions by atoms, as well as occupying by atoms of tetrahedral voids of structure that make up ~24 % of the unit cell volume. It is shown that structural defects of the donor and acceptor nature are present in the TiCoSb base compound as a result of the location in the tetrahedral voids of the structure of additional Co * atoms and the presence of vacancies in the crystallographic position of 4a of the Ti atoms. Introduction to TiCoSb compound of impurity Sc atoms by substitution at position 4a of Ti atoms generates structural defects of acceptor nature, and the ratio of Ti$_{1-x}$Sc$_x$CoSb in the concentrations of available defects of donor and acceptor nature determines the location of the Fermi level ε_F and mechanisms of conductivity. The obtained results allow us to predictably simulate and obtain thermometric materials Ti$_{1-x}$Sc$_x$CoSb for the sensitive elements of thermotransducers.

Key words: Electronic structure, Resistivity, Thermo-EMF.

1. Introduction

Semiconductor thermometric materials based on the TiCoSb semi-Heissler phase have high and stable values in the wide temperature range of the resistivity ρ (T, x) and the coefficient of thermo-EMF α (T, x) [1], which is a necessary condition for the production of sensitive elements of thermal converters. Optimization of the parameters of thermoelectric materials to obtain the maximum values of the resistivity ρ (T, x) and the coefficient of thermo-EMF α (T, x) is carried out by doping the TiCoSb base semiconductor, as result – obtained materials became to doped semiconductors.

Studies [1] found that adding the smallest concentration of Sc atoms (used in the experiment) to the TiCoSb by replacing the Ti atoms radically alters the action system of the resistivity ρ and the coefficient of thermo-EMF α Ti$_{0.995}$Sc$_{0.005}$CoSb. In the temperature range of 80–350 K, the resistivity values ρ increase with increasing temperature and the electrical conductivity of Ti$_{0.995}$Sc$_{0.005}$CoSb has metallic character. It turns out that adding the smallest concentration of Sc atoms in the experiment ($x = 0.005$) which have to generate by the acceptors changed the position of the Fermi level ε_F in the way that could only cause the emerging of donor semiconductor. Thus, if in TiCoSb the Fermi level ε_F was in the prohibited zone, then the metallization of the conductivity Ti$_{0.995}$Sc$_{0.005}$CoSb indicates that it not only approached the conduction zone, but also crossed the leakage level, and electrons remained the main carriers of electricity. This is indicated by the negative

values of the coefficient of thermo-EMF α $Ti_{0.995}Sc_{0.005}$ CoSb, which is possible only if donors of unknown nature are generated. The metallization of the conductivity $Ti_{0.995}Sc_{0.005}$CoSb also does not correspond to the results of the modelling of electronic structure for the ordered structure variant. The discrepancy between the results of modeling the electronic structure of $Ti_{1-x}Sc_xCoSb$ and the experimental measurement of the change in the resistivity values and the thermo-EMF coefficient does not allow us to predict the characteristics of thermometric materials, which is a condition for their subsequent implementation. For this purpose, it is necessary to establish the nature of the structural defects of $Ti_{1-x}Sc_xCoSb$, which generate energy levels (zones) in the prohibited zone of the semiconductor material and determine the mechanisms of its electrical conductivity.

2. Limitations

Studies [1] have found that in thermometric material Ti1-xScxCoSb, structural defects of acceptor and donor nature are simultaneously generated, which makes an impossible prediction and receiving of sensitive elements of thermocouples with predetermined characteristics.

3. Research Objective

Determination of the nature of structural defects in thermometric material Ti1-xScxCoSb, that simultaneously generate in the prohibited zone energy levels of acceptor and donor nature, that permit to harmonize the results of experimental and theoretical studies of the material, and also making its kinetic characteristics predictable.

4. Research Methods

To model the electronic structure of $Ti_{1-x}Sc_xCoSb$, we used the Green's function method (Coring-Coon-Rostocker (KKR) method) in Coherent Potential Approximation (CPA) and Local Density Approximation (LDA) [2]. For the KKR calculations were used licensed software AkaiKKR and SPR-KKR in the LDA approximation for the exchange-correlation potential with Moruzzi-Janak-Williams (MJW) parameterization [3]. The Brillouin zone was broken down into 1000 k-points, which were used to model the energy characteristics by calculating DOS. The width of the energy window (22 eV) and was selected to capture all semi-core states of the p-elements. In the linear MT orbit calculations (Linear Muffin-Tin Orbital, LMTO), was used Full Potential (FP) represents plane waves. LDA approximation with MJW parameterization was also used as the exchange-correlation potential. The precision in the calculation of the position of the Fermi level ε_F ±6 meV. Crystallographic parameters were calculated using Fullprof [4].

5. Thermodynamic and Structural Characteristics of $Ti_{1-x}Sc_xCoSb$

Microprobe analysis of concentrations of atoms on the surface of samples of thermometric materials $Ti_{1x}Sc_xCoSb$ established their correspondence with the original charge compositions, and x-ray phase and structural analyses showed that the diffraction patterns of the samples including the composition $x=$ 0–0.15 are indexed in the structural type MgAgAs ($Fm43m$ group) and contain no trace of other phases.

To test the potential homogeneity region of $Ti_{1-x}Sc_xCoSb$ solid solution to a hypothetical ScCoSb compound with MgAgAs type structure, thermodynamic calculations were made in the approximation of harmonic oscillations of atoms in the framework of DFT density theory for the following concentrations of Sc atoms: $x=0$, $x=0.25$, $x=0.50$, $x=0.75$ and $x=1.0$ (Fig. 1, a). It can be seen that at low temperatures and all concentrations, the enthalpy of mixing is positive, indicating the absence of solubility of Sc atoms in the matrix of the TiCoSb compound ((Fig. 1, a, curves 1, 2, 3). However, at temperatures T>400 K, the solubility of Sc atoms increases, and the change in the free energy values ΔG (x) (Helmholtz potential) at a temperature $T = 800$ K passes through the minimum in the concentration range x≈0.35 (Fig. 1, a, curve 5). Therefore, the compositions of the samples $Ti_{1-x}Sc_xCoSb$, x=0–0.15, are within the solubility range, as evidenced by the absence of extraneous phases in them.

Taking into account that the atomic radius Sc (r_{Sc} = 0.164 nm) is larger than Ti (r_{Ti} = 0.146 nm), it is logical to increase the values of the unit cell period $a(x)$ $Ti_{1-x}Sc_xCoSb$ (Fig. 1, b). This behavior of the value of period $a(x)$ may indicate the realization of a solid $Ti_{1-x}Sc_xCoSb$ substitution solution and in the crystallographic position $4a$ of the Ti atoms, structural defects of the acceptor nature are generated. Also, in the prohibited zone ε_g of semiconductor thermometric material $Ti_{1-x}Sc_xCoSb$ an impurity acceptor zone ε_A^{Sc} is formed.

The refinement of the crystalline structure of the $Ti_{1-x}Sc_xCoSb$ phases studied allowed us to obtain the values of the Bragg discrepancy factor (R_{Br}) between the model view of the structure and the experimental results, which showed high accuracy and quality of the modelling process, in particular: $R_{Br} = 3$ % for $x = 0.005$, $R_{Br} = 1.5$ % for $x = 0.03$, $R_{Br} = 2.6$ % for $x = 0.05$, $R_{Br} = 3.5$ % for $x = 0.07$ and $R_{Br} = 3.7$ % for $x = 0.10$. Given the small amount of impurity Sc atoms dissolved in the TiCoSb compound matrix, as well as the low accuracy of the X-ray method, we were unable to detect any other structural changes in thermometric material in structural studies, such as the occupation of impurity atoms by other crystallographic positions.
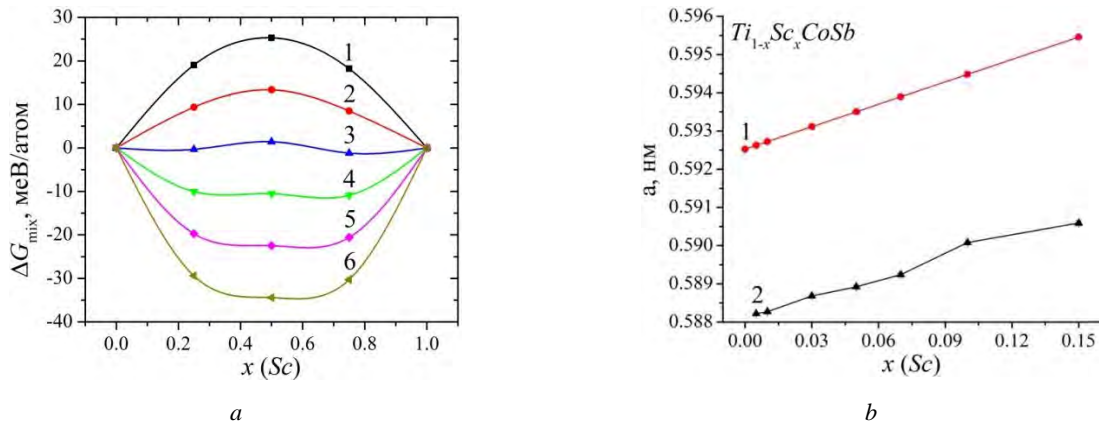
Fig. 1. Change of values of thermodynamic potential ΔG (x) at different temperatures (a):
1 – 0 K; 2 – 200 K; 3 – 400 K; 4 – 600 K; 5 – 800 T; 6 – 1000 K and unit cell period a (x) Ti$_{1-x}$Sc$_x$CoSb:
1 – modelling; 2 – experiment (b)

We also modeled a change in the period values of the unit cell $a(x)$ Ti$_{1-x}$Sc$_x$CoSb provided that all crystallographic positions of the TiCoSb compound are occupied by the structural type MgAgAs and impurity Sc atoms are displaced at the $4a$ positions by the Ti atoms. If we compare the experimentally obtained change in the values of the period $a(x)$ Ti$_{1-x}$Sc$_x$CoSb (Fig. 1, b, curve 2) with the course of dependence $a(x)$ obtained by calculations (Fig. 1, b, curve 1), then the curves are close to parallel. The result, at first glance, is extraordinary. If the course of the calculated and experimentally obtained dependences $a(x)$ Ti$_{1-x}$Sc$_x$CoSb do not coincide, then it can indicate an inability to take into account all the features of the structure by modeling. This is normal! However, the values of $a(x)$ periods for the TiCoSb base compound, to which the impurity Sc atoms are introduced, do not substantially coincide, forming the Ti$_{1-x}$Sc$_x$CoSb semiconductor solid solution.

What is it related to and why are the experimentally obtained values of $a(x)$ TiCoSb lower than calculated?

We believe that the difference in the values of the period $a(x)$ is a manifestation of vacancies in the structure of the TiCoSb compound, which reduces its volume and, accordingly, the value of period $a(x)$. This conclusion is consistent with what was previously obtained [1]. If we conditionally combine the values of the period $a(x)$ of the TiCoSb compound obtained experimentally (Fig. 1b, curve 2) with the value obtained by the modeling (Fig. 1b, curve 1), then the dependences $a(x)$ of Ti$_{1-x}$Sc$_x$CoSb coincide within the accuracy range experiment.

Consequently, the thermodynamic and structural studies of the Ti$_{1-x}$Sc$_x$CoSb semiconductor thermometric material suggest that the crystalline structure is ordered, and the substitution at Sc $4a$ of the Ti atoms generates structural defects of the acceptor nature.

6. Modeling the Electronic Structure and Kinetic Characteristics of Ti$_{1-x}$Sc$_x$CoSb

To predict the behavior of the Fermi level ε_F, width of the prohibited zone ε_g, and kinetic characteristics of the thermometric material Ti$_{1-x}$Sc$_x$CoSb, the electron density (DOS) distribution was calculated (Figs. 2, 3) for an ordered variant of the structure in which the substitution takes place in position $4a$ atom Ti in Sc.

As it can be seen from Fig. 2, in the TiCoSb semi-Heissler phase, the Fermi level ε_F (dashed line) is located in the prohibited zone ε_g near its middle but is closer to the leakage level of the conduction zone ε_C. Since the replacement of Ti atoms by Sc generates structural defects in the acceptor nature, already at Ti$_{0.99}$Sc$_{0.01}$CoSb concentrations, the Fermi level ε_F drifts from the conduction zone ε_C and take a position in the middle of the prohibited zone ε_g.

At higher concentrations of the acceptor impurity, the concentration of acceptors increases, and the Fermi level ε_F approaches, and subsequently the intersection level of the valence zone ε_V Ti$_{1-x}$Sc$_x$CoSb: there is a dielectric-metal conductivity transition, that is the Anderson transition [1]. Approximation of the Fermi level ε_F to the level of the valence zone ε_V changes the sign of the coefficient of thermo-EMF $\alpha(T,x)$ from negative to positive, and the intersection of the Fermi levels ε_F and the flow of the valence zone ε_V changes the conductivity of the semiconductor Ti$_{1-x}$Sc$_x$CoSb to metallic [1]: the dependences of ln (ρ ($1/T$)) must be absent, and the resistance values of ρ increase with temperature. The change in the density of states at the Fermi level g (ε_F) is slower.

The distribution of the electron localization function (*elf*) in the Ti$_{1-x}$Sc$_x$CoSb solid solution (Fig. 3) indicates that there is strong localization in the TiCoSb

compound between the Co and Sb atoms, whereas it is a more closed spherical shell around the Ti atoms. Substitution at position 4*a* of Ti atoms in Sc reduces the localization of the electron density around the Co atoms in the direction of the Sc atoms and has little effect on the electron density distribution between the Co and Sb atoms.

The DOS electronic state density distribution for the ordered $Ti_{1-x}Sc_xCoSb$ structure allows us to model the

behavior of the resistivity, the coefficient of thermo-EMF α (*x, T*), thermoelectric power Z^*, etc. (Fig. 4). Modeling the behavior of the coefficient of thermo-EMF (x, T) gives, as expected, positive values at all concentrations and temperatures, and maximum values α (*x, T*) are reached at concentrations $x\approx0.08$. In the range of concentrations of *Sc* atoms, $x\approx0.08–0.11$, the maximum values of the thermoelectric power factor Z^*_{calc} are predicted (Fig. 4*b*).
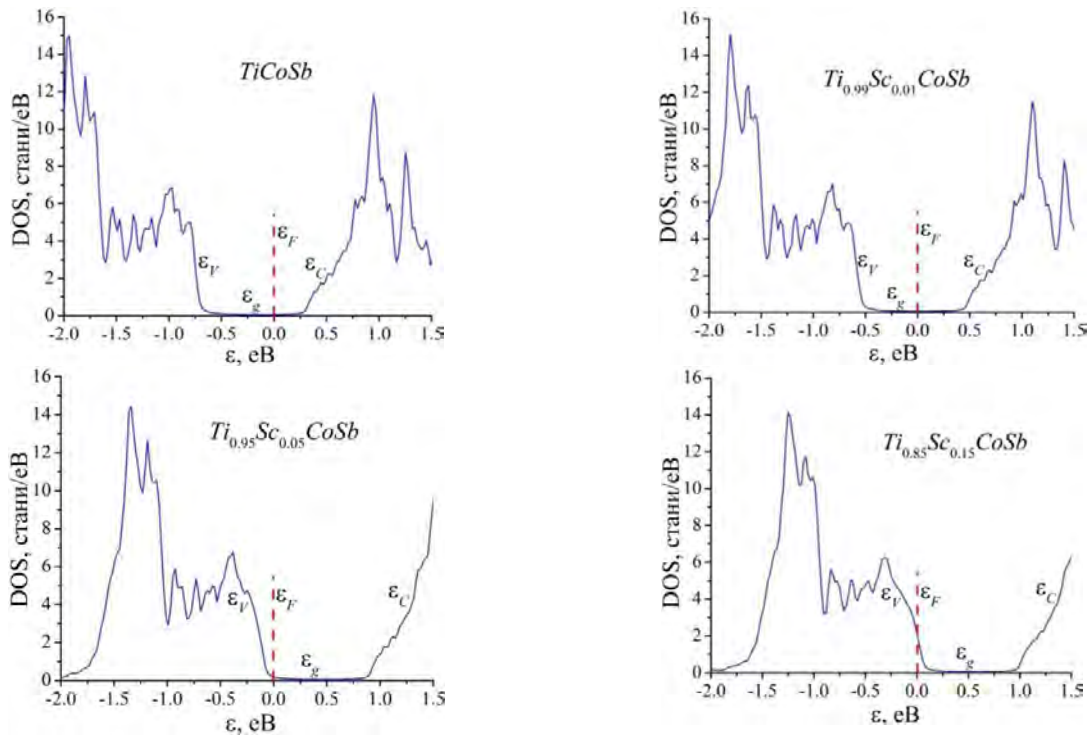

Fig. 2. DOS $Ti_{1-x}Sc_xCoSb$ electronic state density distribution for ordered structure
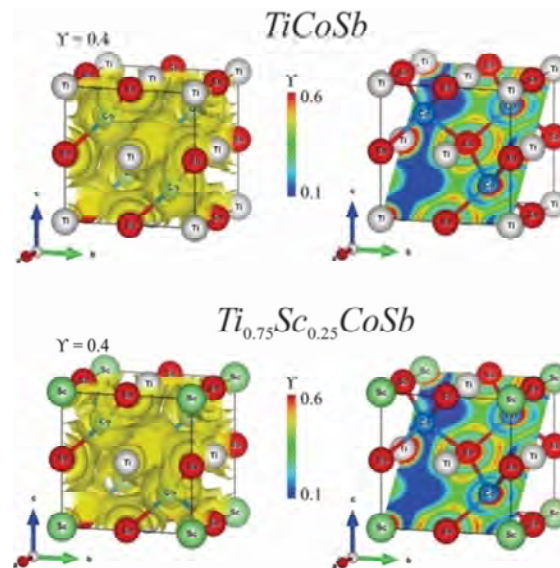

Fig. 3. Distribution of values of electron localization function ($\gamma = 0.4$)
in the plane [101] and isosurface of electron density
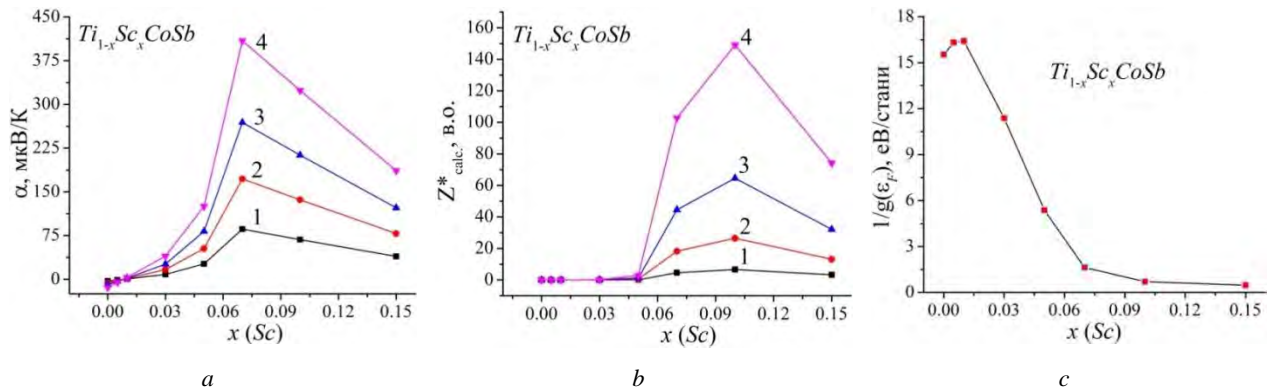(0.053 e / (103 nm³)) for TiCoSb and $Ti_{0.75}Sc_{0.25}C0Sb$

Fig.4. Modeling of change of values of the coefficient of thermo-EMF α(x, T) at temperatures: 1 – 80 K;
2 – 160 K; 3 – 250 K; 4 – 380 K (a), thermoelectric power factor Z*calc. (b) and changes in values of 1/g(εF) (c) Ti₁₋ₓScₓCoSb
for an ordered structure

Fig. 4*c* represents a dependence inverse to the density of states at the Fermi level $g(\varepsilon_F)$, whose values are proportional to the electrical resistivity of the thermoelectric material $Ti_{1-x}Sc_xCoSb$. It can be seen that the dependence of $1/g(\varepsilon_F)$ passes through the maximum at the concentrations of Sc atoms, x≈.01, and then decreases rapidly to quasi-saturation at $x > 0.10$. This behavior $1/g(\varepsilon_F)$ is understandable since the increase in the dependence on the plot $x = 0–0.10$ is related to the intersection of the Fermi level ε_F in the middle of the prohibited zone, that causes the smallest values of $g(\varepsilon_F)$ and the maximum values of the semiconductor electrical resistance. At higher concentrations of Sc, $x > 0.01$, the Fermi level ε_F approaches the leakage level of the valence zone ε_V, leading to the appearance and increase of the concentration of free holes, as well as the density of states at the Fermi level $g(\varepsilon_F)$.

Therefore, with the orderly variant of the $Ti_{1-x}Sc_xCoSb$ crystalline structure, the simulation results do not correspond to the experimental results of the study of the temperature and concentration dependences of the resistivity, the thermo-EMF coefficient, the nature of the behavior of the Fermi ε_F level, etc. [1]. It can be assumed that the thermoelectric material $Ti_{1-x}Sc_xCoSb$ observed discrepancy in the results is due to an incomplete understanding of the spatial arrangement of the atoms and their impurity energy levels generated in the TiCoSb compound. We explore this in more detail below.

7. Modeling Ti₁₋ₓScₓCoSb electronic structure with different variants of its crystalline structure

To clarify the crystalline and electronic structure of the TiCoSb compound, electron density distribution (DOS) modeling were performed under different variants of occupying atoms of crystallographic positions, as well as occupying atoms of tetrahedral voids of the structure (Fig. 5), which make up ~ 24 % of the unit cell volume. After all, there is a causal relationship between crys-

talline and electronic structures. Thus, to calculate the energy of an electron in the first Brillouin zone, one must know the spatial location of the atoms or their absence (vacancies ([])) at the nodes of the unit cell. On the other hand, the smallest structural changes affect local symmetry and DOS values. Therefore, the adequacy of the results of modeling the electronic structure of a semiconductor and the results of experimental studies, for example, kinetic and/or energy characteristics implies that the model of its structure is the adequate spatial arrangement of atoms in the crystal. That is why the results of the calculation of the electronic structure in comparison with the results of the experiment [1], make it possible to obtain information about the structure of the crystal, which is not available to x-ray methods of research.

Let us analyze the DOS calculation results of the TiCoSb compound for several variants (Fig. 5).

a) In the case when the crystallographic position 4*a* of Ti atoms contains vacancies ([]) that makeup ~1 at. % of all Ti atoms, the compound formula looks like: $(Ti_{0.99}[]_{0.01})CoSb$. The structural defect formed is an acceptor in nature, and in the prohibited zone ε_g of the semiconductor near the valence zone ε_V, an impurity acceptor level (zone) ε_A appears, which fixes the position of the Fermi level ε_F (Fig. 5). We obtain a model of the electronic structure of a doped hole-type semiconductor. This conclusion coincides with the results of research [5]. Addition to the structure of a semiconductor $(Ti_{0.99}[]_{0.01})CoSb$ of CoSb impurity Sc atoms (3d14s2) by occupying the crystallographic position of 4*a* of the Ti atoms $(3d^1 4s^2)$ have the following consequences:

– generating structural defects in the acceptor nature as a result of the substitution of Ti atoms, since the Sc atom has fewer 3*d* electrons;

– the decrease in the concentration of structural defects of acceptor nature in the crystal when occupying Sc atoms ([]).
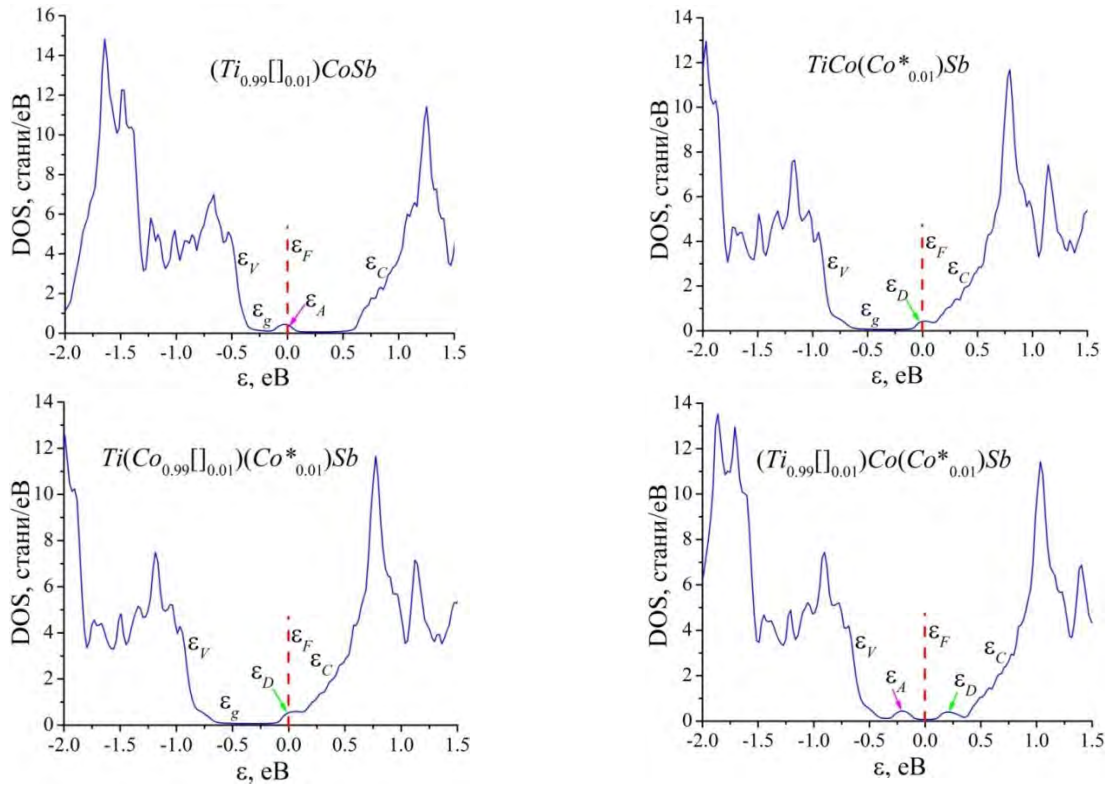
*Fig. 5. Calculation of the electronic state density distribution (DOS)
of a TiCoSb compound for different spatial arrangements of atoms*

As a result, we obtain a $Ti_{1-x}Sc_xCoSb$ semiconductor hole-type conductivity. This variant of the spatial arrangement of atoms does not correspond to the results of the experiment [1].

b) In the case of occupying additional atoms of Co* (~1 at. %) Tetrahedral voids of the structure (junction) of the TiCoSb compound, its formula takes the form of $TiCo(Co^*_{0.01})Sb$. We obtain a classical doped electronic conductor type semiconductor, in which the impurity donor level (zone) ε_D, appears, which fixes the position of the Fermi level ε_F (Fig. 5). Now the addition of Sc impurity atoms to the structure of the $TiCo(Co^*_{0.01})Sb$ semiconductor in the manner described above generates structural defects in the acceptor nature. As the concentration of impurity Sc atoms increases, the degree of compensation increases, and the Fermi level ε_F drifts from the conduction zone ε_C through the middle of the prohibited zone ε_g to the valence zone ε_V. This changes the conductivity type of the semiconductor from electron to hole.

This variant of the crystalline and electronic structures of the TiCoSb compound does not fully reflect the results of the experiment [1] because it does not answer the question of the absence of activation sites on the dependence of $\ln(\rho(1/T))$ at concentrations when the Fermi level ε_F departs from the zone conductivity ε_C and approaching the valence zone ε_V.

c) The presence of 1 % vacancies ([]) at position 4*c* of Co atoms and the location of 1 % additional Co* atoms in tetrahedral voids of the structure is described by the formula $Ti(Co_{0.99}[]_{0.01})(Co^*_{0.01})Sb$ (Fig. 5). In this case, structural defects of the donor nature are generated in the crystal due to the arrangement of Co atoms in the voids of the structure. Since Co atoms are involved in the formation of both the conduction zone and the valence zone of the semiconductor, in the presence of 1 % of vacancies ([]) in the position 4*c* of the Co atoms, there is a mutual compensation of the donor-acceptor energy levels, which explains their absence in the prohibited zone ε_g. That is why the energy scheme of such a spatial arrangement of atoms in their crystallographic positions (or their absence) contains only the impurity donor level and is identical to the previous case (***b***) and the conclusions drawn.

d) The closest to the results of the experiment is the variant of the simultaneous presence of 1 % vacancies ([]) at position 4*a* of Ti atoms and 1 % of additional Co* atoms in tetrahedral voids of the structure, which can be described by the formula $(Ti_{0.99}[]_{0.01})Co(Co^*_{0.01})Sb$ (Fig. 5). In this case, vacancies in the position of the Ti atoms generate structural defects of the donor nature, and the corresponding acceptor level (zone) ε_A appears in the prohibited zone ε_g. In turn, the additional Co* atoms in the voids of the structure

generate a structural defect of the donor nature, and the corresponding donor level (zone) ε_D appears in the prohibited zone ε_g. It is quite logical to locate the Fermi level ε_F between the generated energy states of the donor and acceptor nature. The smallest changes in the ratio between defects in the acceptor and donor nature of the semiconductor, caused by, for example, different modes of thermal annealing of the samples and their cooling, the purity of the initial components during synthesis, etc., causes a change in the position of the Fermi level ε_F relative to energy levels in the prohibited zone ε_g. For this reason, in the temperature range T= 80–90 K, TiCoSb is a semiconductor of the hole-type conductivity [1], as evidenced by the positive values of the thermo-EMF coefficient α, and at higher temperatures, its sign changes and electrons are now the main carriers of current.

The addition of impurity Sc atoms to such a semiconductor by substitution at position $4a$ of the Ti atoms generates structural defects of the acceptor nature, which initially increase the degree of compensation and, as a consequence, lead to an increase in the resistivity ρ (x, T) [1]. And only at concentrations Sc, $x \geq 0.03$, the Fermi level ε_F is located in the acceptor zone ε_A^{Sc}, as indicated by the positive values of the coefficient of thermo-EMF α (x, T) by all temperatures, and by the presence at high temperatures of the activation region depending on ln $(\rho$ $(1/T))$ [1].

Thus, doping the TiCoSb semiconductor with the Sc acceptor impurities introduced into the structure by substitution at the $4a$ position of the Ti atoms made it possible to detect defects of the donor nature in the structure of the TiCoSb base compound as a result of the occupation of Co* tetrahedral voids in the structure zone) ε_D. The ratio of concentrations of donor and acceptor levels present in the TiCoSb compound structure determines the location of the Fermi ε_F level in a semiconductor, and doping with its acceptor impurities changes the mechanisms and conductivity type of the thermometric material Ti$_{1-x}$Sc$_x$CoSb.

8. Conclusions

The result of a comprehensive study of crystalline and electronic structures, kinetic, energy, and magnetic characteristics of the Ti$_{1-x}$Sc$_x$CoSb thermoelectric material is determining the nature of the structural defects of the donor and acceptor nature. It is shown that structural defects of the donor and acceptor nature are present in the TiCoSb base compound as a result of the location in the tetrahedral voids of the structure of additional Co* atoms and the presence of vacancies in the crystallographic position of $4a$ of the Ti atoms. The introduction into the structure of a TiCoSb compound of impurity Sc atoms by substitution at the $4a$ position of the Ti atoms generates structural defects of the acceptor nature, and the ratio of the existing defects of the donor and acceptor nature in Ti$_{1-x}$Sc$_x$CoSb determines the position of the Fermi level ε_F in the prohibited zone and conduction mechanisms.

9. Acknowledgment

10. Conflict of interests

The authors declare that there is no financial or other possible conflict related to this work.

References

[1] V. Ya. Krayovskyy, M. V. Rokomanyuk, V. A. Romaka, Yu. V. Stadnyk, L. P. Romaka, A. M. Horyn. "Investigation of thermometric material Ti$_{1-x}$Sc$_x$CoSb. Kinetic, energy and magnetic characteristics". *Measuring equipment and metrology*, vol. 8, No. 4, pp. 16–22, 2119.

[2] T. Roisnel, J. Rodriguez-Carvajal. WinPLOTR: a Windows Tool for Powder Diffraction Patterns analysis, in *Mater. Sci. Forum, Proc. EPDIC7*, vol. 378–381, pp. 118–123, 2001.

[3] M. Schruter, H. Ebert, H. Akai, P. Entel, E. Hoffmann, G.G. Reddy. "First-principles investigations of atomic disorder effects on magnetic and structural instabilities in transition-metal alloys". *Phys. Rev. B*, vol. 52, pp. 188–209, 1995.

[4] V. Moruzzi, J. Janak, A. Williams. *Calculated Electronic Properties of Metals*. NY, Pergamon Press, 1978.