
FEATURES OF DEFECT FORMATION AND ELECTROCONDUCTIVITY MECHANISMS IN $HfNi_{1-x}Co_xSn$ THERMOELECTRIC MATERIAL

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- *The crystalline and electronic structures, energy state and electrokinetic properties of $HfNi_{1-x}Co_xSn$ thermoelectric material in the $T = 80 \div 1620$ K and $N_A^{Co} \approx 9.5 \cdot 10^{20} \text{ cm}^{-3}$ ($x = 0.05$) ranges were investigated. It was established that in the process of doping n - $HfNiSn$ compound with Co atoms the type of majority carriers and the mechanism of electroconductivity were changed. It should be explained by variation of the compensation degree in the semiconductor caused by the simultaneous formation in the crystal of structural defects at the substitution of Ni atoms by Co atoms as acceptors and partial occupation of Ni atoms positions by Sn atoms as donors.*

Introduction

In this work, we start a research on a novel class of thermoelectric materials possessing high efficiency of thermal into electrical energy conversion, and n - $HfNiSn$ intermetallic semiconductor will serve the basis for getting such materials. The n - $HfNiSn$ semiconductor, just as previously studied n - $ZrNiSn$ and n - $TiNiSn$ [1, 2], are crystallized in cubic syngony (space group $F\bar{4}3m$), $MgAgAs$ structural type. Parameter optimization of thermoelectric materials based on n - $ZrNiSn$ and n - $TiNiSn$ with a view to attain maximum values of thermoelectric figure of merit (the efficiency of thermal into electrical energy conversion) [3] was realized by heavy doping of semiconductors [4].

Previous studies [5, 6] of the galvanomagnetic characteristics of n - $HfNiSn$ in the range of $T = 1.6 \div 300$ K have established that electrons are the majority carriers, and so donor-nature defects of unknown origin are prevalent in the semiconductor.

Research on heavy doping processes of similar semiconductors n - $ZrNiSn$ and n - $TiNiSn$ with the atoms of rare-earth metals, $3d$ - and $4d$ -transition metals, as well as with p -elements allowed establishing in each specific case the mechanism of generation of donor, acceptor or neutral nature defects [7]. As a matter of fact, the concentration and type of defects eventually govern the semiconductor properties [8]. Research has shown that the mechanism of formation of structural defects in a matrix of basic semiconductor governs considerably the mechanism of generation of new defects on its heavy doping. Thus, it was established that crystalline structure of $ZrNiSn$ and $TiNiSn$ compounds is disordered, i.e. crystalline positions of Zr ($4d^25s^2$) atoms are ~ 1 at.% occupied with Ni ($3d^84s^2$) atoms and ~ 0.5 at.% occupied with Ti ($3d^24s^2$) atoms, generating donor-nature structural defects in a crystal and explaining the mechanism of their "a priori heavy doping with donor impurities".

With regard to the background experience, it is logical to start studying conditions for fabrication of novel thermoelectric materials based on n - $HfNiSn$ semiconductor from the research on its structural, energy state and electrokinetic characteristics, which will simplify considerably our

understanding of semiconductor reaction to heavy doping, for instance, with *Co* atoms. The results of this research are given in the proposed work.

Research methods

The object to be investigated included crystalline structure, electron density distribution (DOS), kinetic and energy state characteristics of $HfNi_{1-x}Co_xSn$. The *X*-ray structural analysis method was used to obtain the values of $HfNi_{1-x}Co_xSn$ ($x = 0 \div 0.40$) crystal lattice periods and establish their parameters: atom coordinates, thermal parameters and occupancy of crystallographic positions. The data arrays obtained by powder method with a stepwise recording of Bragg reflections intensity were used (diffractometer Guinier-Huber image plate system, $CuK_{\alpha 1}$ -radiation, $8^\circ \leq 2\theta \leq 100^\circ$). Calculations relating to the interpretation and specification of $HfNi_{1-x}Co_xSn$ crystalline structure were made with the use of WinCSD program [9]. The phase and chemical compositions of samples were controlled by scanning electron microscope JEOL-840A. The DOS calculation was made by the Green function method (KKR-CPA-LDA, AkaiKKR [10] and Wien2k programs [11]). The temperature and concentration dependences of the electrical resistivity (ρ) and the Seebeck coefficient (α) of $HfNi_{1-x}Co_xSn$ were measured in the ranges of $T = 80 \div 1620$ K and $N_A^{Co} \approx 9.5 \cdot 10^{20} \text{ cm}^{-3}$ ($x = 0.05$) $\div 7.6 \cdot 10^{21} \text{ cm}^{-3}$ ($x = 0.40$).

Research on $HfNi_{1-x}Co_xSn$ crystalline structure

At the first stage of research we studied crystalline structure of $HfNiSn$ compound and the region of its possible existence. A series of samples was synthesized with their chemical compositions differing from $HfNiSn$ composition up to ~ 2 at.%. The microprobe analysis has shown that the compositions of samples correspond to the compositions of output batch components. The *X*-ray studies of $(Hf_{1-x}Ni_x)NiSn$ ($x \leq 0.01$) samples did not reveal traces of other phases, except for the basic one, indicating the presence of extensive (up to 1 at.%) region of $HfNiSn$ compound existence along *Ni* concentration ($(Hf_{1-x}Ni_x)NiSn$ interstitial solid solution). In the ordered variant of $HfNiSn$ structure *Hf* atoms occupy a correct system of points $4a$ (0, 0, 0), *Ni* – $4d$ ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$), and *Sn* – $4c$ ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) [7]. Specification of crystalline structure of $HfNiSn$ compound by the powder method with a simultaneous specification of the isotropic parameters of atomic substitution and occupancy of *Hf* crystallographic position ($4a$) has shown that the smallest factor of inconformity to model of crystalline structure and the array of Bragg reflections ($R_{Br} = 2.3\%$) was obtained for a model in which position of *Hf* atoms ($5d^26s^2$) up to ~ 1 at.% can be occupied with *Ni* atoms ($3d^84s^2$), which generates donor-nature structural defects in a semiconductor and explains the mechanism of its “a priori heavy doping with donor impurity”.

Taking into account the fact that the atomic radii of *Ni* ($r_{Ni} = 0.1246$ nm) and *Co* ($r_{Co} = 0.1252$ nm) are almost the same, we did not get an informative and consistent result from the *X*-ray investigations of *n*- $HfNiSn$ samples doped with *Co* atoms ($3d^74s^2$) by the substitution of *Ni* atoms. The investigations only unambiguously established their homogeneity and single-phase character. However, this analysis method, even with the use of up-to-date scientific equipment did not enable us to establish the mechanism of *Co* atoms entry into semiconductor structure, that is, to determine whether *Co* substitutes only *Ni* atoms in its crystallographic position or takes part in other structural rearrangements that generate structural defects. With regard to the fact that *Co* atom has one *3d*-electron less than *Ni* atom, the substitution of *Ni* atoms by *Co* atoms in $HfNiSn$ compound will generate acceptor-nature structural defects in the crystal. At the same time, for instance, *Sn* atoms ($4d^{10}5s^25p^2$) partially occupying the crystallographic position of *Ni*, generate donor-nature structural

defects. In so doing, it should be borne in mind that in the undoped n - $HfNiSn$ semiconductor the crystallographic position of Hf up to ~ 1 at.% can be occupied with Ni atoms, which also generates donor-nature structural defects.

Therefore, a direct method of studying the crystalline structure of $HfNi_{1-x}Co_xSn$ semiconductor did not allow establishing the nature of structural defects that govern its properties. To establish this nature, we will apply method for optimization of crystalline structure model based on the results of calculation of the electron spectrum and physical properties of semiconductor proposed in [7].

Research on $HfNi_{1-x}Co_xSn$ electrokinetic properties

The temperature dependences of electrical resistivity $\ln\rho(1/T)$ and the Seebeck coefficient $\alpha(1/T)$ for $HfNi_{1-x}Co_xSn$ ($x = 0 \div 0.40$) samples are given in Fig. 1. Prior to analyzing the results, let us note one feature of this class of semiconductors. Thus, repeated heating in vacuum of $HfNi_{1-x}Co_xSn$ ($x = 0 \div 0.40$) samples to $T = 1620$ K followed by their cooling to liquid nitrogen temperature did not bring into existence of irreversible processes. Such thermal stability of semiconductor characteristics is a guarantee of its further wide use as the basis for the formation of new thermoelectric materials.

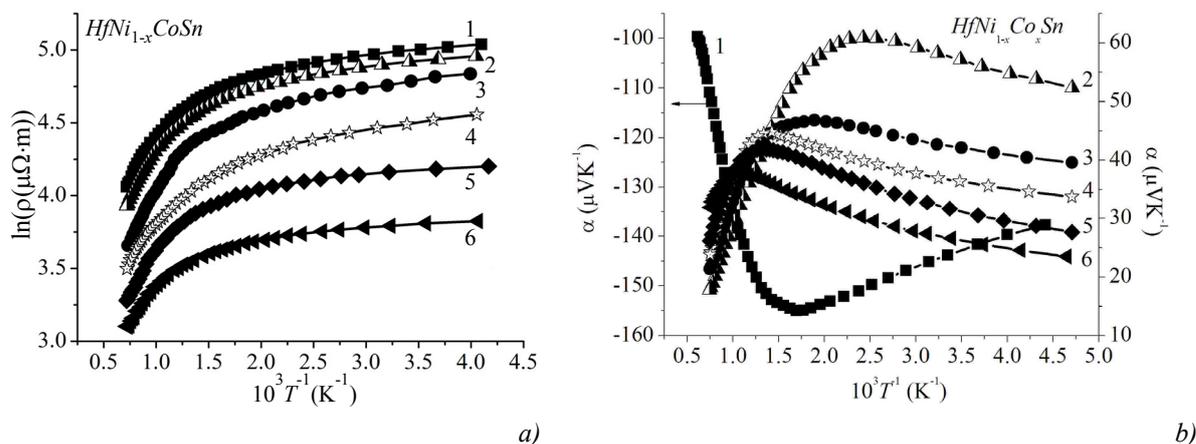


Fig. 1. Temperature dependences of electrical resistivity ρ (a) and the Seebeck coefficient α (b) in $HfNi_{1-x}Co_xSn$: 1 – $x = 0$; 2 – $x = 0.05$; 3 – $x = 0.15$; 4 – $x = 0.20$; 5 – $x = 0.25$; 6 – $x = 0.40$.

We will first discuss an undoped semiconductor n - $HfNiSn$. Several years apart, two series of n - $HfNiSn$ samples (№1 and №2) were synthesized, and the results of research on one of them (№1) are shown in Fig. 1. The temperature dependences $\ln\rho(1/T)$ and $\alpha(1/T)$ n - $HfNiSn$ are typical for doped semiconductors with high- and low-temperature activation regions testifying to the existence of several activation conduction mechanisms. Taking into account the negative sign of the Seebeck coefficient over the entire temperature range, we can assert that there is activation of electrons from the Fermi level (ϵ_F) to the percolation level of conduction band (ϵ_1^p) and electron jumps (ϵ_3^p) along the states with the energies close to the Fermi level [8]. The values of activation energy ϵ_1^p for both samples calculated from the high-temperature activation regions of dependences $\ln\rho(1/T)$ turned out to be close: $\epsilon_1^p(\text{№1}) = 145.9$ meV and $\epsilon_1^p(\text{№2}) = 148.6$ meV. The proximity of ϵ_1^p values, as well as the fact that n - $HfNiSn$ samples were synthesized at an interval of several years and different precursor components were used for their preparation can testify that the nature of semiconductor donor level (band) is not related to the energy level created by impurity atoms but is a manifestation of intrinsic structural defects.

At the same time, from the high- and low-temperature activation regions of $\alpha(1/T)$ dependences

for both samples there were calculated the values of activation energy ε_1^α which, as is shown in [12], are proportional to the amplitude of continuous energy bands of heavily doped and compensated semiconductor: $\varepsilon_1^\alpha(N\textcircled{1}) = 94.1$ meV and $\varepsilon_1^\alpha(N\textcircled{2}) = 49.7$ meV. The results obtained suggest some conclusions. First, the negative sign of the Seebeck coefficient values for both samples points to prevailing concentration of donor-nature structural defects over acceptor-nature ones. Second, since the values of activation energy ε_1^α for both samples are considerably lower than the values of activation energy ε_1^p , it is fair to say that in n - $HfNiSn$ the modulation amplitude of continuous energy bands is several times smaller than in the case of n - $ZrNiSn$ and n - $TiNiSn$ semiconductors [1, 2]. Taking into account that in sample $N\textcircled{1}$ the values of activation energy ε_1^α are almost twice those in sample $N\textcircled{2}$, as well as the proximity of values of activation energy ε_1^p , we can make a conclusion that concentration of ionized acceptors in sample $N\textcircled{1}$ is twice that in sample $N\textcircled{2}$. Apropos we recall that in a fully compensated semiconductor the modulation amplitude of continuous energy bands is equal to $\varepsilon_g/2$, and the Fermi level is located in the middle of the energy gap [8].

At low temperatures in n - $HfNiSn$ there exists hopping mechanism of charge transfer. From the low-temperature regions of $\ln\rho(1/T)$ there was calculated the value of hopping activation energy: $\varepsilon_3^p(N\textcircled{1}) = 5.2$ meV and $\varepsilon_3^p(N\textcircled{2}) = 2.9$ meV, and from the activation regions of $\alpha(1/T)$ – the value of activation energy: $\varepsilon_3^\alpha(N\textcircled{1}) = 4.9$ meV and $\varepsilon_3^\alpha(N\textcircled{2}) = 1.9$ meV, which (see [12]) are proportional to the depth of potential well of small-scale heavily doped and compensated semiconductor. As long as the value of activation energy ε_3^p is governed by the degree of compensation of semiconductor [8], the larger values of hopping energy in sample $N\textcircled{1}$ point to a larger content of compensating acceptors than in sample $N\textcircled{2}$. This is suggested by comparing the values of activation energy ε_3^α , i.e. the larger is the compensation degree, the larger is the depth of potential well.

The introduction into n - $HfNiSn$ of the smallest in the experiment concentrations of impurity atoms Co is followed by a change in semiconductor conductivity type, and holes become the majority carriers over the entire temperature range (Fig. 1, 2). At first glance, as was predicted at the beginning of the investigations, doping of n - $HfNiSn$ with Co atoms by the substitution of Ni atoms is attended with formation of only acceptor-nature structural defects, and the behaviour of kinetic characteristics seems to support the admitted assumption.

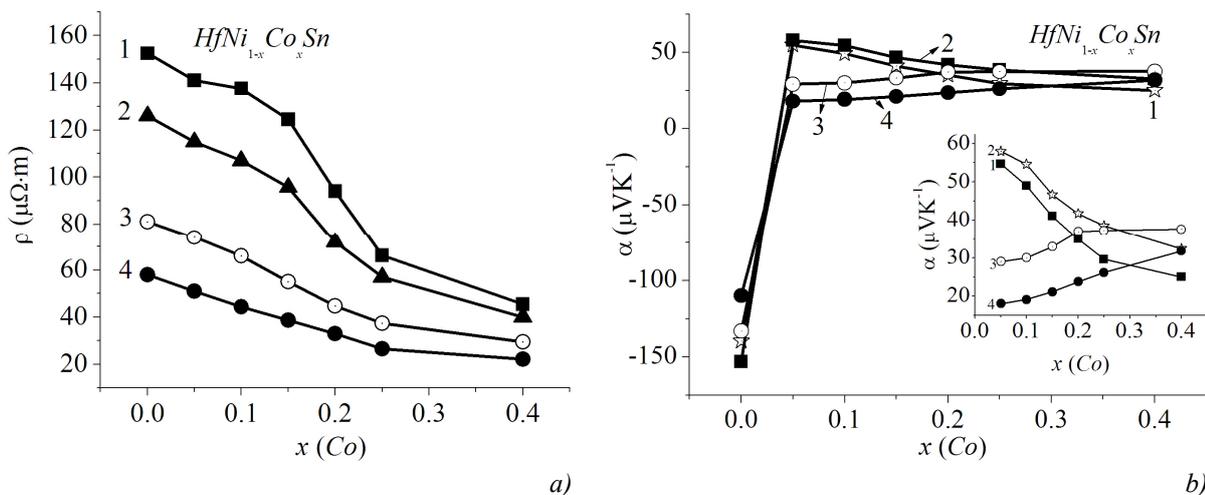


Fig. 2. Change in the values of electrical resistivity ρ (a) and the Seebeck coefficient α (b) in $HfNi_{1-x}Co_xSn$ at different temperatures: 1 – $T = 250$ K; 2 – $T = 500$ K; 3 – $T = 1000$ K; 4 – $T = 1330$ K.

It should be noted that in the process of samples synthesis technical reasons prevented from getting homogeneous samples of $HfNi_{1-x}Co_xSn$ ($0.005 \leq x \leq 0.03$) compositions, and we start the investigation from the impurity concentration $x = 0.05$. As a result, there is no maximum on the dependences $\rho(x)$ $HfNi_{1-x}Co_xSn$ (Fig. 2) and resistivity values are monotonously reduced, which is understandable, since on doping with acceptor impurity of already p -type semiconductor, the concentration of free holes is increased. At the same time, the calculation of DOS in $HfNi_{1-x}Co_xSn$ shows that the Fermi level will cross the middle of the energy gap in the concentration region $x \approx 0.02$ which is matched by the highest compensation degree, the largest resistivity value (maximum on $\rho(x)$), and the contribution of free electrons and holes will differ only in the values of their effective masses. In n - $HfNiSn$ the Fermi level is arranged closer to conduction band ($\varepsilon_1^p(N\approx 1) = 145.9$ meV), whereas in $HfNi_{1-x}Co_xSn$ it is closer to valence band. We have “jumped over” the concentration region of semiconductor maximum compensation and immediately obtained heavily doped and compensated semiconductor of p -type conductivity.

The activation energies mentioned above in the analysis of n - $HfNiSn$ were calculated from the high- and low-temperature areas of $\ln\rho(1/T)$ and $\alpha(1/T)$ dependences of $HfNi_{1-x}Co_xSn$ (Fig. 3). Taking into account the fact that the Seebeck coefficient of $HfNi_{1-x}Co_xSn$ ($x \geq 0.05$) has a positive sign, and reduction of $\varepsilon_1^p(x)$ values in the concentration range $x = 0.05 \div 0.4$ takes place almost in linear fashion, we can calculate the rate of the Fermi level motion toward the valence band: $\Delta\varepsilon_F/\Delta x \approx 1.7$ meV/at.% (Fig. 3 a). Such a change of the Fermi level position is possible, provided acceptors are generated in a semiconductor, which can take place with the substitution of Ni atoms by Co atoms. Note that in Fig. 3 a the value of activation energy ε_1^p for $x = 0$ is “torn” from dependence $\varepsilon_1^p(x)$ for the concentration range $x = 0.05 \div 0.40$, since in the former case there occurs activation of electrons from the Fermi level to the percolation level of conduction band, and in the latter case – activation of holes from the Fermi level to the percolation level of valence band.

As it follows from Fig. 3 a, a change in the values of hopping activation energy $\varepsilon_3^p(x)$ in $HfNi_{1-x}Co_xSn$, unlike a change in $\varepsilon_1^p(x)$ values, is not of a monotonous nature. Note at once that it is this, at first glance, minor difference in the behaviour of $\varepsilon_3^p(x)$ and $\varepsilon_1^p(x)$ dependences that allowed us understanding the mechanism of defect formation in $HfNi_{1-x}Co_xSn$. So, as long as the value of hopping activation energy ε_3^p is governed by the degree of compensation of $HfNi_{1-x}Co_xSn$ semiconductor, and the impurity Co atoms, as we at first expected, generate in the crystal the acceptor-nature structural defects, it is quite incomprehensible what is the reason for maximum on the dependence $\varepsilon_3^p(x)$ at $x = 0.20$ with subsequent fast reduction of values and reaching the plateau. In fact, all parameters of $HfNi_{1-x}Co_xSn$ semiconductor vary monotonously. We believe that such behaviour of $\varepsilon_3^p(x)$ dependence in a p -type semiconductor in the concentration range of acceptor impurity $0.05 \leq x \leq 0.20$ is possible only on condition of a simultaneous appearance of compensating donors.

This brings up the question as to the source of donors in $HfNi_{1-x}Co_xSn$. The same question arises in the analysis of behaviour of $\varepsilon_1^\alpha(x)$ and $\varepsilon_3^\alpha(x)$ dependences in $HfNi_{1-x}Co_xSn$ (Fig. 3 b). Thus, the character of change in $\varepsilon_1^\alpha(x)$ values in the concentration range $0.05 \leq x \leq 0.20$ testifies that the modulation amplitude of continuous energy bands in heavily doped and compensated semiconductor $HfNi_{1-x}Co_xSn$ is increased. Indeed, the values of activation energy $\varepsilon_1^\alpha(x)$ grow from $\varepsilon_1^\alpha(x = 0.05) = 38.3$ meV to $\varepsilon_1^\alpha(x = 0.20) = 59.2$ meV. As we mentioned before, this is possible only with the appearance in a p -type semiconductor of compensating electrons with the ionization of donors of unknown nature for us. In $HfNi_{1-x}Co_xSn$ ($x > 0.20$) samples, a reduction in $\varepsilon_1^\alpha(x)$ values points to a

decrease in modulation amplitude of continuous energy bands, which is possible only with a decrease of $HfNi_{1-x}Co_xSn$ compensation degree through a reduction or cease of generation of donor-nature structural defects.

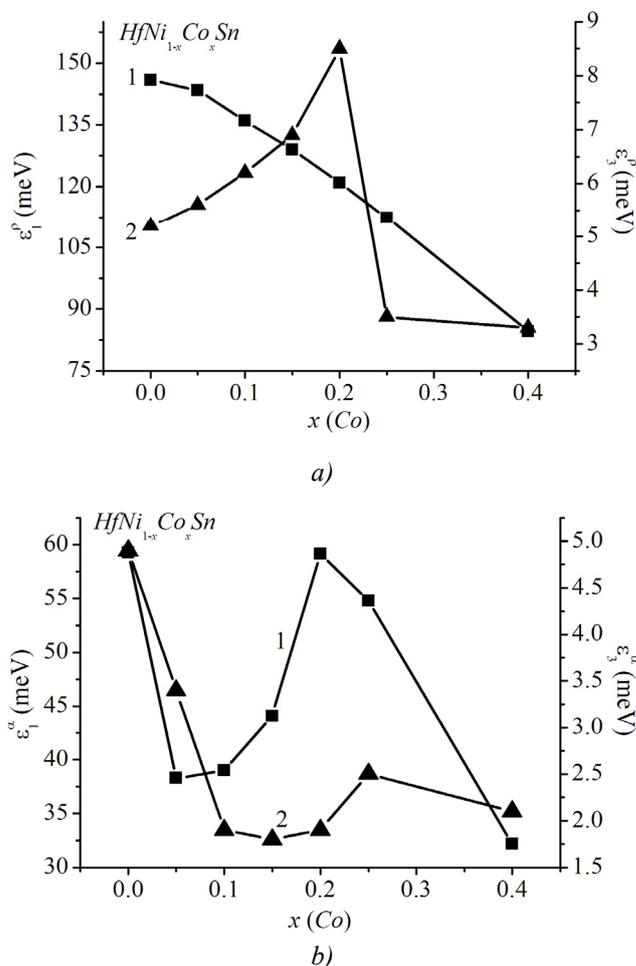


Fig. 3. Change in the values of activation energies $\epsilon_1^p(x)$ and $\epsilon_3^p(x)$ (a), $\epsilon_1^a(x)$ and $\epsilon_3^a(x)$ (b) in $HfNi_{1-x}Co_xSn$: 1 – ϵ_1^p and ϵ_1^a , 2 – ϵ_3^p and ϵ_3^a .

Thus, the initial assumption that doping of n - $HfNiSn$ with Co atoms by the substitution of Ni atoms is followed by generation of only acceptor-nature structural defects prevents from consistent explanation of the behaviour of energy characteristics in heavily doped and compensated semiconductor $HfNi_{1-x}Co_xSn$. The character of change in the values of hopping activation energy $\epsilon_3^p(x)$ and the modulation amplitude of continuous energy bands $\epsilon_1^a(x)$ unambiguously point to the existence of donor source in $HfNi_{1-x}Co_xSn$. Below we consider possible mechanism for the appearance of donors.

Research on $HfNi_{1-x}Co_xSn$ electron density distribution

To predict the behaviour of the Fermi level, energy gap width, electrokinetic characteristics of n - $HfNiSn$ doped with Co atoms, a calculation of electron density distribution (DOS) was made. To fit the experimental investigation adequately, the results of calculations should be based on the comprehensive information on semiconductor crystalline structure. The smallest structural defects, for instance, different degree of crystallographic position occupancy both by the intrinsic atoms (the presence of vacancies) and interstitial atoms (for instance, Ni atoms in the position of Hf atoms), change the local symmetry of crystal (local amorphization [7]) which should be taken into account in

the calculations. On the other hand, the adequacy of DOS results to experimental results *a priori* stipulates that a model of semiconductor crystalline structure corresponds to its real state.

Thus, the authors of [13] based on the literary data on the energy characteristics of $TiNiSn$ and $ZrNiSn$, having compared them to the calculated energy parameters for different variants of atoms arrangement in the unit cell of compounds, without carrying out any structural studies, established their structural disorder. Adhering to this logic, however having the experimental results of our own, we shall study the mechanism of defect formation under heavy doping of n - $HfNiSn$ with Co atoms. First we present the results of DOS calculation for n - $HfNiSn$. Fig. 4 *a* shows such results for the ordered structure variant of $HfNiSn$ compound, whence it follows that the investigated compound is a semiconductor with the energy gap width $\varepsilon_g \approx 588$ meV, and the Fermi level enters the conduction band to a small extent. The fact that the Fermi level is arranged on the edge of conduction band agrees well with the results of galvanomagnetic studies of $HfNiSn$ [5, 6], and electrons are the majority carriers. However, it is contrary to the results of kinetic studies, since excludes the presence of activation mechanisms of charge transfer. Therefore, the obtained model of electronic structure is not adequate, hence the ordered model of crystalline structure of $HfNiSn$ compound is not adequate either, as we already mentioned above when analyzing the results of structural study.

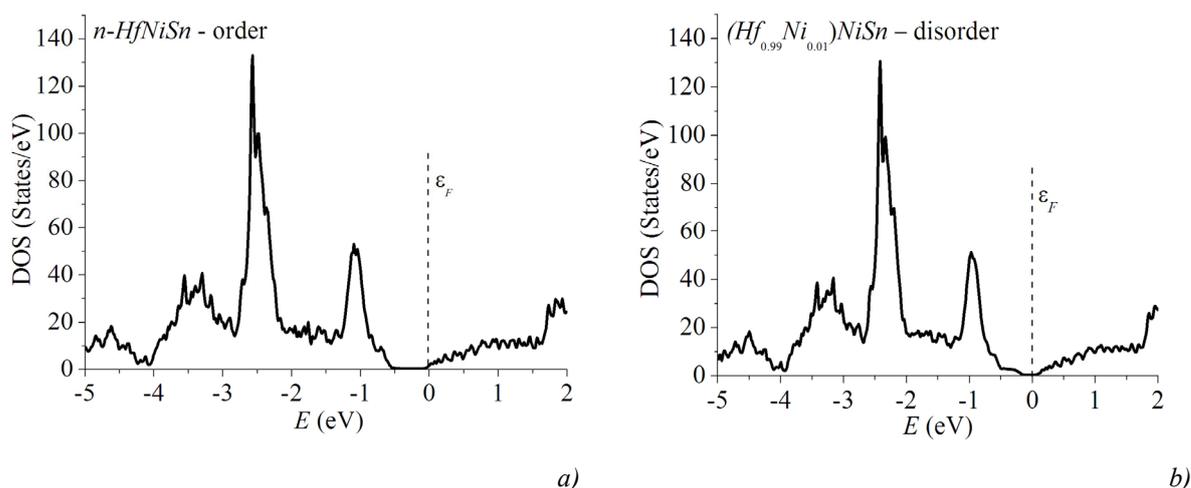


Fig. 4. Calculation of electron density distribution for the ordered (a) and disordered (b) variants of n - $HfNiSn$ crystalline structure.

To get more precise results, calculation of DOS was made practically for all possible cases of atoms substitution in the sites with the unit cell of $HfNiSn$ compound. Fig. 4 *b* shows a result which gives the best fit to the experimental results. It turned out that the most probable is a variant of disordered structure $(Hf_{1-x}Ni_x)NiSn$ ($x = 0.01$) of $HfNiSn$ compound. Note that the same result was obtained from the structural study of $HfNiSn$. Partial (up to 1 at.%) substitution of Hf atoms with Ni atoms generates donor-nature structural defects in the crystal, and the Fermi level is arranged in the energy gap the width of which is also reduced (Fig. 5 *a*). It also turned out that a minimum on the dependence of variation in the values of density of states on the Fermi level ($DOS_F(x)$) (Fig. 5 *b*) for the disordered variant of $(Hf_{1-x}Ni_x)NiSn$ structure of $HfNiSn$ compound corresponds to $(Hf_{0.99}Ni_{0.01})NiSn$ composition. In such a model of semiconductor the Fermi level lies in the energy gap, and its width is $\varepsilon_g \approx 282$ meV.

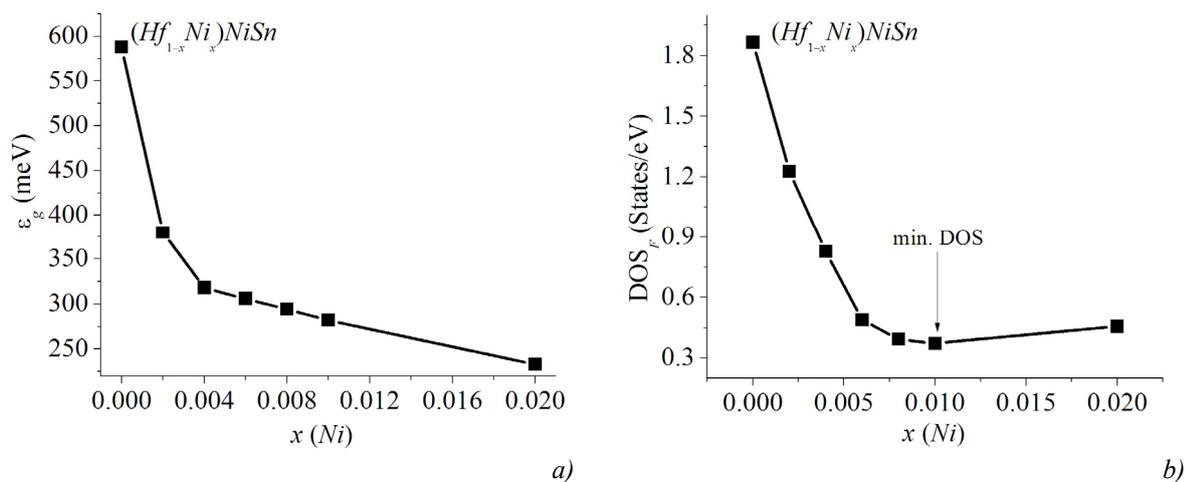


Fig. 5. Calculation of change in the values of energy gap ϵ_g (a) and the density of states at the Fermi level $DOS_F(x)$ (b) for the disordered variant of $(Hf_{1-x}Ni_x)NiSn$ structure of $HfNiSn$ compound.

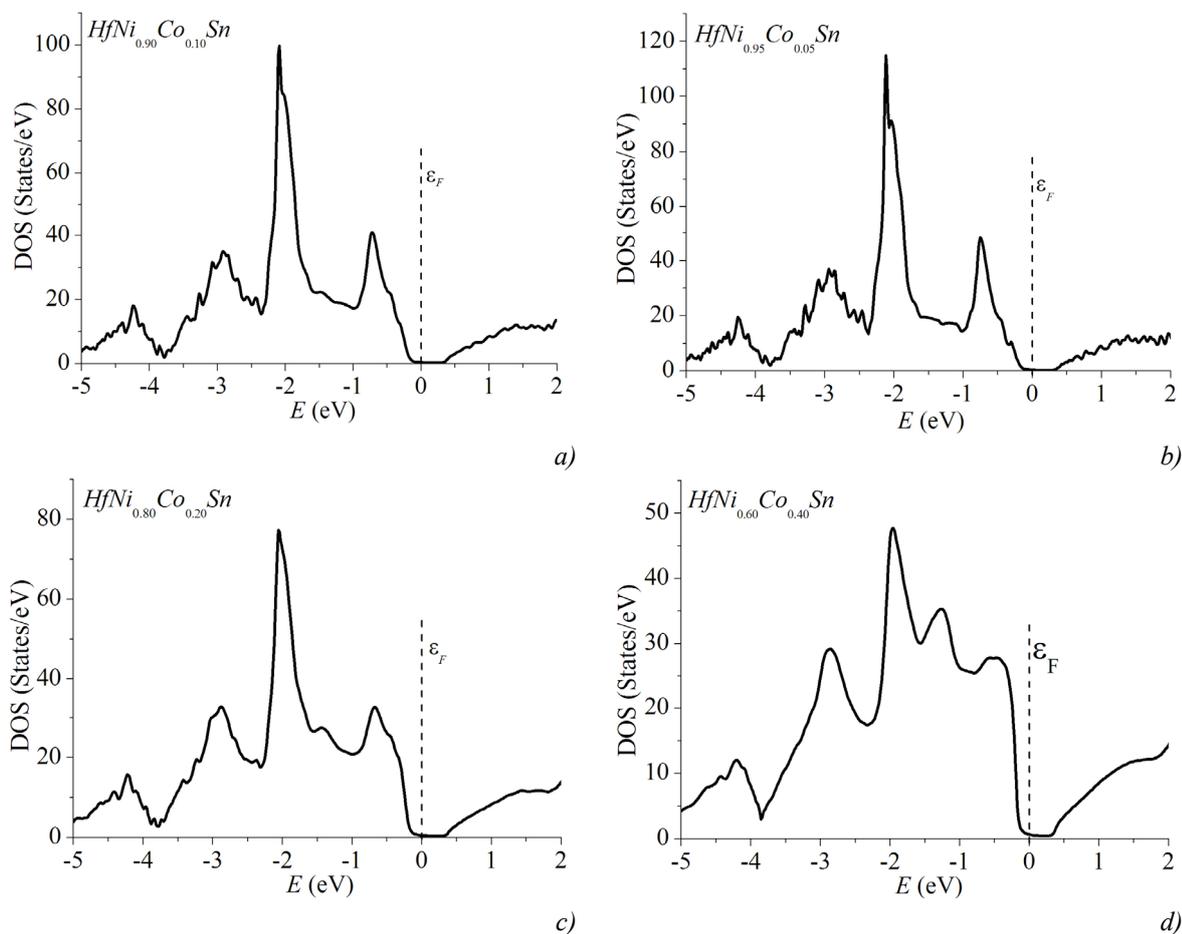


Fig. 6. Calculation of electron density distribution in $HfNi_{1-x}Co_xSn$.

It was much more complicated to get an adequate model of $HfNi_{1-x}Co_xSn$ electronic structure, due to the lack of understanding about defect formation mechanism. To solve this problem, we have used an inverse problem. Using a strict tie-in to the numerical values of activation energy (ϵ_1^p) from the Fermi level to the percolation level of $HfNi_{1-x}Co_xSn$ valence band, we sought for the compensation degree in the semiconductor that would assure experimentally the established rate of the Fermi level movement:

$\Delta\varepsilon_F/\Delta x \approx 1.7$ meV/at.%. Under these conditions, calculation of DOS was made for different variants of atoms arrangement in the unit cell sites of $HfNi_{1-x}Co_xSn$, and the degree of occupation of crystallographic positions (Fig. 6). It turned out that the most acceptable is a model which provides for partial substitution of Ni atoms both by Co atoms that are introduced into n - $HfNiSn$ structure and by Sn atoms. The latter, occupying the crystallographic position of Ni atoms, generate donor-nature structural defects in a crystal. We have also succeeded in calculating the rate of generation of such structural defects (Fig. 7 a). Calculations show that introduction of one acceptor into n - $HfNiSn$ is followed by a simultaneous generation from ~ 0.1 (for $x = 0.05$) to ~ 0.23 (for $x = 0.40$) donors. Such defect formation pattern affects the rate of change in the energy gap of $HfNi_{1-x}Co_xSn$ (Fig. 7 a) and the density of states on the Fermi level (Fig. 7 b).

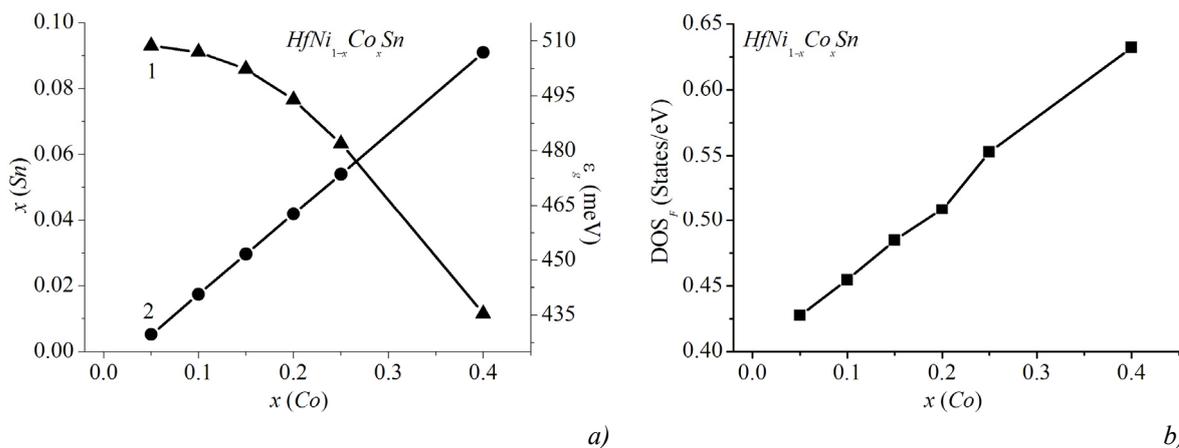


Fig. 7. Calculation of change in the values of energy gap ε_g (1), concentration of donor defects (2) (a) and density of states at the Fermi level $DOS_F(x)$ (b) in $HfNi_{1-x}Co_xSn$.

Conclusions

Thus, as a result of integrated research on the crystalline structure, energy spectrum and electrokinetic characteristics of n - $HfNiSn$ intermetallic semiconductor heavily doped with Co impurity, we have revealed a change in the type of majority carriers and electrical conductivity mechanisms. It should be explained by variation of the compensation degree in the semiconductor caused by the simultaneous formation in the crystal of structural defects at the substitution of Ni atoms by Co atoms as acceptors and partial occupation of Ni atoms positions by Sn atoms as donors. The crystalline structure of n - $HfNiSn$ is disordered, and position of Hf atoms up to ~ 1 at.% can be occupied with Ni atoms, which generates donor-nature structural defects in the semiconductor and explains the mechanism of its “a priori doping with donors”. From the results obtained one can predict conditions for the formation on the basis of n - $HfNiSn$ semiconductor of thermoelectric materials with high values of thermoelectric figure of merit.

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