MEASURING TRANDUCERS

RESEARCH OF SENSITIVE ELEMENTS OF THERMOELECTRIC CONVERTERS BASED ON $Hf_{1-x}Nb_xNiSn$

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Abstract. The results of modeling and experimental studies of the structural, magnetic, electrokinetic and energy properties of the thermometric material $Hf_{1-x}Nb_xNiSn$, as well as the conversion functions of the sensitive elements of a thermoelectric thermometer based on it at temperatures of 4.2–1000 K are presented. For the case of an ordered variant of the crystal structure of the thermometric material, the simultaneous generation of donor and acceptor states in the forbidden band ε_g of the semiconductor is established. The dependence between the spatial arrangement of atoms in the nodes of the $Hf_{1-x}Nb_xNiSn$ unit cell and the mechanisms of electrical conductivity is revealed, which allows us to determine the conditions for the synthesis of materials with the maximum efficiency of converting thermal energy into electrical energy. It is shown that at $Hf_{1-x}Nb_xNiSn$ concentrations, x=0–0.02, the substitution of Hf atoms ($5d^26s^2$) by Nb atoms ($4d^45s^1$) in position 4*a* mainly occurs, which generates donor states. In the concentration range $Hf_{1-x}Nb_xNiSn$, x=0.02–0.05, the substitution of Ni atoms ($3d^84s^2$) in position 4*a* by Nb atoms mainly occurs, which generates acceptor states, and at concentrations $0.05<x$, the substitution of Hf atoms by Ni atoms generates additional donor states. The studied thermometric material $Hf_{1-x}Nb_xNiSn$ is promising for the manufacture of sensitive elements of thermoelectric thermometers. The transformation functions of the thermoelectric pair $Hf_{0.99}Nb_{0.01}NiSn$-(PtRh 13), the thermoelectrodes of which are made of the studied thermometric material and platinoid (PtRh 13) (positive branch), were simulated.

Thermometric materials $Hf_{1-x}Nb_xNiSn$, x=0.01–0.10, for the manufacture of sensitive elements of temperature transducers were obtained by fusing the charge of components in an electric arc furnace with a tungsten electrode (cathode) in an atmosphere of purified argon under a pressure of 0.1 kPa on a copper cooled bottom (anode). Pre-fused sponge titanium was used as a getter. Heat treatment of $Hf_{1-x}Nb_xNiSn$ alloys consisted of homogenizing annealing at a temperature of 1073 K. Annealing of samples was carried out for 720 h in evacuated quartz ampoules (up to 1.0 Pa) in muffle electric furnaces with temperature control with an accuracy of ±10 K. Arrays of diffraction data were obtained on a STOE STADI-P powder *X*-ray diffractometer Cu $K\alpha_1$-radiation). The structural characteristics of the $Hf_{1-x}Nb_xNiSn$ samples were calculated using the Fullprof software package. The chemical and phase compositions of the samples were monitored using metallographic analysis (Tescan Vega 3 LMU scanning electron microscope).

To optimize the parameters of the crystal and electronic structures, energy and kinetic properties of thermometric materials $Hf_{1-x}Nb_xNiSn$, calculations were performed within the framework of the density functional theory (DFT) using the Vienna Ab initio Simulation Package VASP v. 5.4.4 with PAW-type potentials. The calculation of electronic kinetic coefficients was performed using the Exciting code (FLAPW method – Full Potential Linearized Augmented Plane Waves) by solving the linearized Boltzmann equation in the constant relaxation time approximation. The distribution of the density of electronic states (DOS) was simulated using the Korringa – Kohn – Rostoker (KKR) method. The transformation functions of the thermoelectric thermometer at temperatures of 4.2–1000 K were simulated using the FLAPW methodмand the results of experimental measurements served as reference currents.

X-ray structural studies of the crystal structure of samples of the thermometric material $Hf_{1-x}Nb_xNiSn$, x=0–0.10, established that the diffractograms are indexed in the structural type MgAgAs and there are no reflections of other phases on them. Based on the obtained diffraction patterns, the change in the period of the unit cell $a(x)$ $Hf_{1-x}Nb_xNiSn$, x=0–0.10 was calculated. It was expected that the period of the cell $a(x)$ would decrease with increasing concentration of Nb atoms (r_{Nb}=0.146 nm), since its atomic radius is smaller than that of the Hf atom (r_{Hf}=0.158 nm). However, the change in the period of the cell $a(x)$ $Hf_{1-x}Nb_xNiSn$, x=0–0.10, is far from the expected and is of a complex nature. Thus, at concentrations of Nb atoms, x=0–0.02, the values of the cell period $a(x)$, as predicted, rapidly decrease. However, at concentrations x=0.02–0.05, we observe the same rapid growth of the dependence $a(x)$, which in the region of concentration $x\approx0.05$ passes through a maximum and then decreases again. The obtained results of the change in the cell period $a(x)$ $Hf_{1-x}Nb_xNiSn$, x=0–0.10, indicate complex structural transformations, which are a consequence of simultaneous changes in several crystallographic positions of the semiconductor thermometric material, which will cause a redistribution of the density of electronic states.

Simulation of the density of states (DOS) distribution for the ordered variant of the crystal structure $Hf_{1-x}Nb_xNiSn$, x=0–0.10, shows the position of the Fermi level ε_F and the width of the band gap ε_g. Thus, if in *n*-HfNiSn the Fermi level ε_F is located in the band gap ε_g near the edge of the conduction band ε_C, then at the lowest concentration of Nb atoms, x=0.005, the Fermi level ε_F will cross the edge of the conduction band ε_C: a dielectric-metal transition of conductivity will occur.

Studies of the specific magnetic susceptibility $\chi(x)$ of the thermometric material $Hf_{1-x}Nb_xNiSn$, x=0–0.10, showed that the basic semiconductor n-HfNiSn is a weak diamagnet, as indicated by the negative values of the specific magnetic susceptibility χ at room temperature. Doping n-HfNiSn with Nb atoms makes the semiconductor $Hf_{1-x}Nb_xNiSn$ a Pauli paramagnet, in which the specific magnetic susceptibility is determined exclusively by the electron gas and is proportional to the density of states at the Fermi level $g(\varepsilon_F)(x)$. The studies established that in the concentration range x=0–0.02 there is a rapid increase in the values of $\chi(x)$ of $Hf_{1-x}Nb_xNiSn$, caused by the generation of donor states and an increase in the concentration of free electrons when replacing Hf atoms with Nb atoms. At higher concentrations of Nb atoms, the rate of change of the magnetic susceptibility $\chi(x)$ $Hf_{1-x}Nb_xNiSn$ decreases due to the appearance and increase in the concentration of acceptor states, which capture free electrons, reducing their concentration. The obtained results show that an external magnetic field with a strength of H≤10 kG does not affect the thermometric characteristics of thermal converters made of this material.

The nature of the change in the values of the specific electrical resistance ρ and the thermopower coefficient α of $Hf_{1-x}Nb_xNiSn$ with both temperature and concentration of Nb atoms is consistent with the conclusions made on the basis of structural studies and modeling of the electronic structure. Since the electrical resistance $\rho(T,x)$ of $Hf_{1-x}Nb_xNiSn$ increases almost linearly with increasing temperature, which is the result of metallization of electrical conductivity, this material is unsuitable for obtaining sensitive elements of resistance thermometers.

The temperature dependences of the thermopower coefficient $\alpha(T,x)$ $Hf_{1-x}Nb_xNiSn$ show that the main carriers of the electric current of the thermometric material at all temperatures are free electrons. This is indicated by the negative values of the thermopower coefficient α at all concentrations and studied temperatures. It is shown that with an increase in the concentration of Nb atoms, the absolute change in the values of the thermopower coefficient $\alpha(T,x)$ $Hf_{1-x}Nb_xNiSn$ decreases. The reason for this is the decrease in the width of the forbidden band ε_g of the thermometric material. According to the nature of the behavior of the thermopower coefficient $\alpha(T,x)$ $Hf_{1-x}Nb_xNiSn$, it is possible to establish the concentration of Nb atoms at which the change in the values of the thermopower coefficient $\alpha(T,x)$ will be the largest. In this case, this condition is achieved with the concentration of the semiconductor thermometric material $Hf_{0.99}Nb_{0.01}NiSn$, which became the basis for forming the electrode (negative leg) of the thermoelectric thermometer.

Keywords: Electric conductivity, thermopower coefficient, Fermi level.

1. Introduction

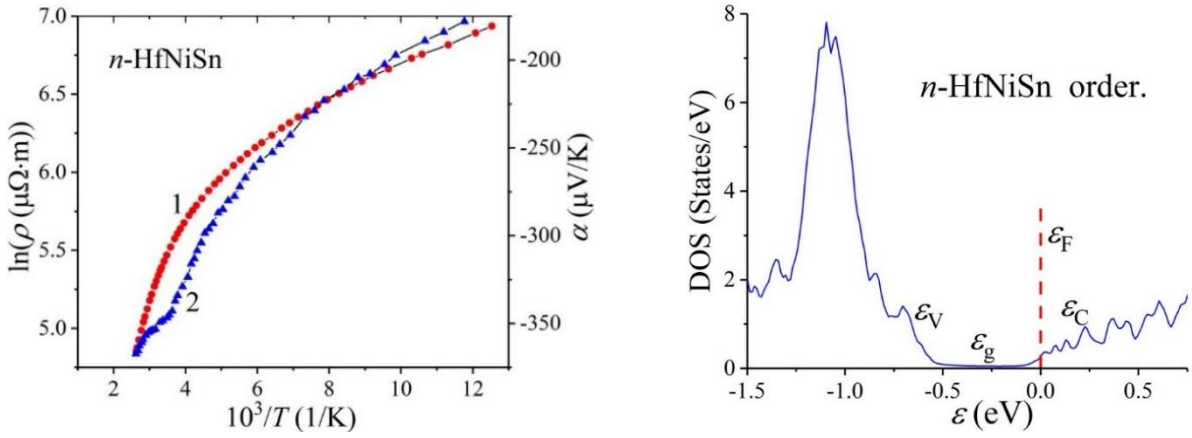
The presented work continues the program of creation of new sensitive elements of resistance thermometers and thermoelectric converters with improved metrological and operational characteristics from the investigated semiconductor materials obtained on the basis of half-Heusler phases (sp. Group $F43m$ [1]). The results of calculations and experimental studies of the structural, energy, electrokinetic and magnetic properties of the thermometric material $Hf_{1-x}Nb_xNiSn$, x=0–0.10, obtained by doping the basic semiconductor n-HfNiSn, are presented. The transformation function of the thermoelectric converter, the electrodes of which are conductors from the investigated thermometric material (negative leg) and platinum rhodium (positive leg), is simulated.

The use of new thermometric materials for the manufacture of sensitive elements of thermal converters and modern methods of modeling their properties allows to increase metrological characteristics in a wide temperature range. After all, the stability and reproducibility of the kinetic properties of thermal converters depends on the stability of the crystal and electronic structures of the materials from which they are made. Elimination and minimization of uncontrolled changes in thermometric characteristics is possible with the introduction of new semiconductor materials and physical principles of optimizing their properties using modern methods of modeling these properties.

Previous studies of the electrokinetic properties of the HfNiSn compound showed that it is a semiconductor of the electronic conduction type [2, 3]. This is indicated by the results of measurements of the temperature dependences of the resistivity ρ and thermopower coefficient α (Fig. 1, *a*). High-temperature activation regions are present on the temperature dependences $\ln(\rho(1/T))$ and $\alpha(1/T)$ of n-HfNiSn, indicating that the studied samples are doped and compensated semiconductors [4]. The presence of high-temperature activation on the dependence $\ln(\rho(1/T))$ of n-HfNiSn indicates the location of the Fermi level ε_F in the forbidden band ε_g of the semiconductor, and the negative values of the thermopower coefficient $\alpha(1/T)$ specify its position, at a distance of 81.3 meV from the edge of the conduction band ε_C. At the same time, the calculation of the density of electronic states distribution DOS by the KKR-CPA-LDA method for the ordered version of the structure of the HfNiSn compound showed that it is an n-type semiconductor, but the Fermi level ε_F is in the conduction band ε_C. The obtained results of DOS modeling (Fig. 1, *b*) do not agree with the results of kinetic studies (Fig. 1, *a*), according to which the Fermi level ε_F lies in the forbidden band ε_g of the semiconductor. Such a discrepancy shows that the crystal structure of the base semiconductor is not ordered [4].

In this context, the study of a new thermometric material $Hf_{1-x}Nb_xNiSn$, x=0–0.10, obtained by doping the basic semiconductor n-HfNiSn with Nb atoms ($4d^45s^1$) introduced into the crystal structure by replacing Hf atoms ($5d^26s^2$) in position 4*a* is of interest. Based on the fact that the Nb atom has more *d*-electrons than the Hf atom, it was planned to have structural defects of donor nature and donor states ε_D in the band gap ε_g in the semiconductor

$Hf_{1-x}Nb_xNiSn$. In turn, changing the concentration of Nb atoms allows you to smoothly change the ratio of donors and acceptors $Hf_{1-x}Nb_xNiSn$ (degree of compensation) and influence the mechanisms of electrical conductivity. This is the approach used to optimize the kinetic properties of a thermoelectric material to obtain sensitive elements of temperature transducers with improved metrological and operational characteristics.



a *b*

Fig. 1. Temperature dependences of the resistivity ln(ρ(1/T)) (1) and the thermopower coefficient α(1/T) (2) (a) and the distribution of the density of electronic states (DOS) (b) of n-HfNiSn for the ordered variant of the structure [3]

2. Disadvantages

Studies of sensitive elements of resistance thermometers and thermoelectric converters based on the basic semiconductor *n*-HfNiSn [2] have established their high sensitivity to heat treatment modes (temperature and duration of homogenizing annealing).

3. Research objective

To develop the physical principles of creating new sensitive elements of temperature converters based on the studied thermometric material $Hf_{1-x}Nb_xNiSn$ with improved metrological and operational characteristics, to establish the basic laws of the conversion functions of sensitive elements of thermal converters.

4. Research methods

Thermometric materials $Hf_{1-x}Nb_xNiSn$, x=0.01–0.10, for the manufacture of sensitive elements of temperature transducers were obtained by fusing the charge of components in an electric arc furnace with a tungsten electrode (cathode) in an atmosphere of purified argon under a pressure of 0.1 kPa on a copper cooled bottom (anode). Pre-fused sponge titanium was used as a getter. Heat treatment of $Hf_{1-x}Nb_xNiSn$ alloys consisted of homogenizing annealing at a temperature of 1073 K. Annealing of samples was carried out for 720 h in evacuated quartz ampoules (up to 1.0 Pa) in muffle electric furnaces with temperature control with an accuracy of ±10 K. Arrays of diffraction data were obtained on a STOE STADI-P powder *X*-ray diffractometer (Cu $K\alpha_1$-radiation). The structural characteristics of the $Hf_{1-x}Nb_xNiSn$ samples were calculated using the Fullprof software package [5]. The chemical and phase compositions of the samples were monitored using metallographic analysis (Tescan Vega 3 LMU scanning electron microscope). Measurements of the temperature dependences of the specific electrical resistance $\rho(T,x)$ and the thermopower coefficient $\alpha(x,T)$ of $Hf_{1-x}Nb_xNiSn$ samples, cut in the form of rectangular parallelepipeds of size ~1.0×1.0×5 mm^3.

To optimize the parameters of the crystal and electronic structures, energy and kinetic properties of thermometric materials $Hf_{1-x}Nb_xNiSn$, calculations were performed within the framework of the density functional theory (DFT) using the Vienna Ab initio Simulation Package VASP v. 5.4.4 with PAW-type potentials [6]. The Perdew – Burke – Enzerhoff exchange-correlation functional in the generalized gradient approximation (GGA) Monkhorst-Pack for the 11×11×11 *k*-grid was used [7]. In the calculations, the plane wave cutoff was set to 400 eV. For crystal structures with mixed atomic arrangements, the supercell approach was used. In this case, the lattice symmetry was reduced and all unique atomic distributions were generated using a combinatorial approach [8]. The lattice parameters for such structures were optimized by a variable lattice volume, which was then fitted by a universal equation of state. The calculation of the electronic kinetic coefficients was performed using the Exciting code [9] (FLAPW method – Full Potential Linearized Augmented Plane Waves) by solving the linearized Boltzmann equation in the constant relaxation

time approximation [10, 11]. The simulation of the electronic density of states (DOS) distribution was performed by the Korringa – Kohn – Rostoker (KKR) method (AkaiKKR software package [12]) in the coherent potential approximation (CPA) and local density approximation (LDA) for the exchange-correlation potential with the Moruzzi – Janak – Williams (MJW) parameterization [13]. The accuracy of the calculation of the Fermi level position ε_F was ±6 meV. The simulation of the transformation functions of a thermoelectric thermometer at temperatures of 4.2–1000 K was carried out using the FLAPW method, Elk software package [10, 11]). The results of experimental measurements served as reference currents in the simulation of properties.

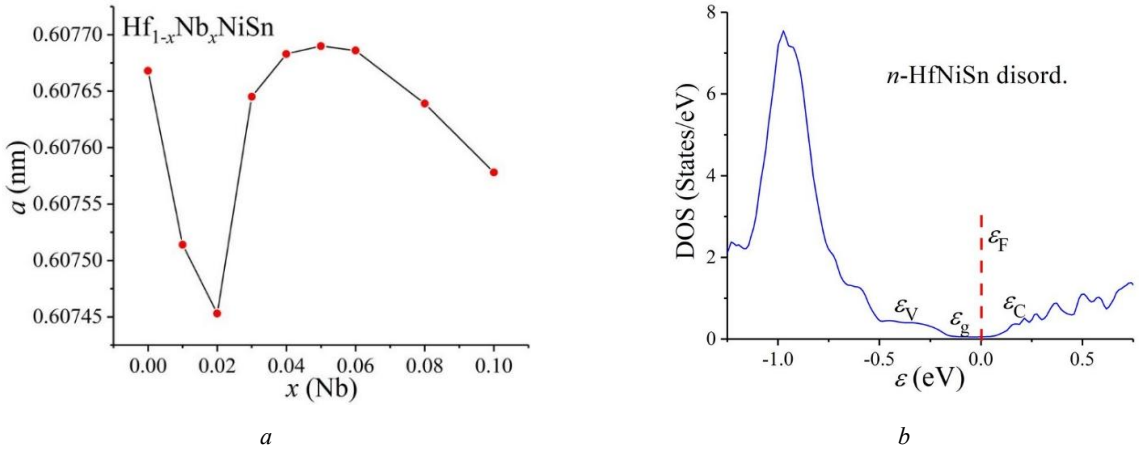
5. Study of structural and energy properties of thermometric material $Hf_{1-x}Nb_xNiSn$

X-ray structural studies of the crystal structure of samples of the thermometric material $Hf_{1-x}Nb_xNiSn$, x=0–0.10, established that the diffractograms are indexed in the structural type MgAgAs [1] and there are no reflections of other phases on them. Based on the obtained diffraction patterns, the change in the period of the unit cell $a(x)$ $Hf_{1-x}Nb_xNiSn$, x=0–0.10, was calculated (Fig. 2, *a*). It was expected that the period of the cell $a(x)$ would decrease with increasing concentration of Nb atoms (r_{Nb}=0.146 nm), since its atomic radius is smaller than that of the Hf atom (r_{Hf}=0.158 nm). However, as can be seen from Fig. 2, *a*, the change in the period of the cell $a(x)$ $Hf_{1-x}Nb_xNiSn$, x=0–0.10, is far from the expected and is of a complex nature. Thus, at Nb atom concentrations, x=0–0.02, the values of the cell period $a(x)$, as predicted, rapidly decrease. However, at concentrations x=0.02–0.05, we observe the same rapid growth of the $a(x)$ dependence, which in the region of concentration $x\approx0.05$ passes through a maximum and then decreases again.

The obtained results of the change in the cell period $a(x)$ $Hf_{1-x}Nb_xNiSn$, x=0–0.10, indicate complex structural transformations, which are a consequence of simultaneous changes in several crystallographic positions of the semiconductor thermometric material, which will cause a redistribution of the density of electronic states. Thus, we associate the decrease in the period $a(x)$ $Hf_{1-x}Nb_xNiSn$ at concentrations x=0–0.02 with the substitution of Hf atoms in position 4*a* by smaller Nb atoms, which will generate impurity donor states in the forbidden band ε_g of the semiconductor (the Nb atom ($4d^45s^1$) has more *d*-electrons than the Hf atom ($5d^26s^2$)).

Since the crystal structure of the basic semiconductor *n*-HfNiSn is disordered due to partial, up to 1 %, occupation of the 4*a* position of Hf atoms by Ni atoms [2], the calculation of the distribution of the density of electronic states DOS was carried out for this variant of the structure (Fig. 2, *b*). It can be seen from Fig. 2, *b* that in this case the Fermi level ε_F lies in the forbidden band ε_g of the semiconductor near the edge of the conduction band ε_C of *n*-HfNiSn. Such an arrangement of the Fermi level ε_F will cause the appearance of activation regions on the temperature dependences of the resistivity $\ln(\rho(1/T))$ as a result of thermal injection of electrons from the donor level into the conduction band ε_C. And this is consistent with the results of electrokinetic studies of *n*-HfNiSn (Fig. 1, *a*).

In this case, the substitution of Ni atoms (r_{Ni}=0.125 nm) at position 4*a* by larger Nb atoms will lead to an increase in the period of the cell $a(x)$ $Hf_{1-x}Nb_xNiSn$ at concentrations x=0.02–0.05. At the same time, the crystal structure of $Hf_{1-x}Nb_xNiSn$ is ordered. Now such a substitution will be accompanied by the generation of acceptor states, because the Nb atom ($4d^45s^1$) has fewer *d*-electrons than the Ni atom ($3d^84s^2$). The decrease in the period of the cell $a(x)$ $Hf_{1-x}Nb_xNiSn$ at concentrations $0.05<x$ is due to the substitution of Hf atoms by Ni atoms, which will lead to the generation of additional donor states in the band gap ε_g of the semiconductor.



a *b*

Fig. 2. Change in the unit cell period a(x) $Hf_{1-x}Nb_xNiSn$ (a) and the distribution of the density of electronic states (DOS) for the disordered version of the structure (b) of the basic thermometric material n-HfNiSn

Simulation of the density of states (DOS) distribution for an ordered variant of the crystal structure of the thermometric material $Hf_{1-x}Nb_xNiSn$, x=0–0.10, shows the position of the Fermi level ε_F (Fig. 3) and the band gap ε_g of the semiconductor (Fig. 4, curve 1). Thus, if in n-HfNiSn the Fermi level ε_F (dashed line) is located in the forbidden band ε_g near the edge of the conduction band ε_C (Fig. 2*b*), then even at the lowest concentration of Nb atoms, x=0.005, the Fermi level ε_F will cross the edge of the conduction band ε_C: a dielectric-metal conduction transition will occur (Fig. 3). The substitution of Hf atoms for Nb atoms generates impurity donor states, which is accompanied by a rapid increase in the concentration of free electrons and the location of the Fermi level ε_F in the zone of continuous energies. In experimental studies of electrokinetic properties, we will obtain metallization of electrical conductivity even at the lowest concentration of impurity Nb atoms. In particular, in the temperature dependences of the resistivity $\ln(\rho(1/T))$ $Hf_{0.995}Nb_{0.005}NiSn$, activation regions will disappear, and the resistance values will increase with temperature due to the action of scattering mechanisms.

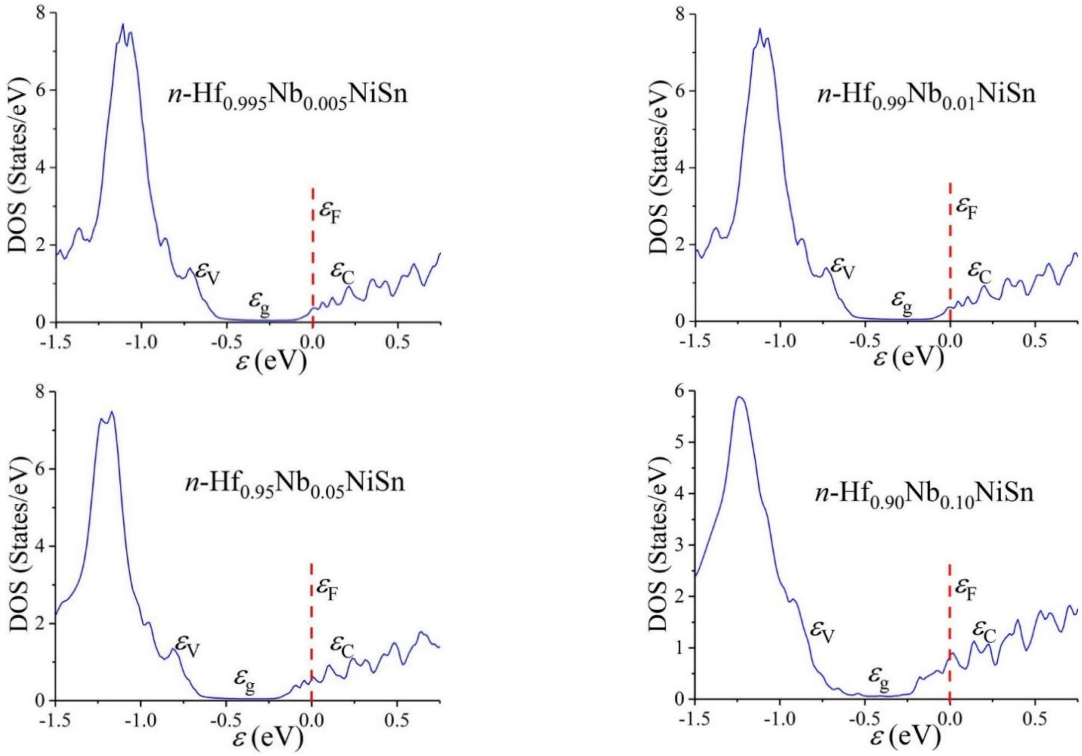


Fig. 3. Modeling of the distribution of the density of electronic states (DOS) of sensitive elements of thermal converters based on the thermometric material $Hf_{1-x}Nb_xNiSn$

At the same time, the forbidden band ε_g remains in the semiconductor $Hf_{1-x}Nb_xNiSn$, and its width decreases (Fig. 4, curve 1). It is clear that such a thermometric material is unsuitable for obtaining sensitive elements of resistance thermometers due to the insignificant change in resistance with temperature. Instead, preserving the band gap will contribute to high values of the thermoelectric power coefficient and the use of the thermometric material $Hf_{1-x}Nb_xNiSn$ to form one of the electrodes (negative leg) of the thermoelectric converter.

Thus, based on the results of structural studies and modeling of the electronic structure of the semiconductor thermometric material $Hf_{1-x}Nb_xNiSn$, the presence of donor and acceptor states in the band gap ε_g has been established, and their ratio will determine the main current carriers and the type of electrical conductivity (semiconductor or metallic).

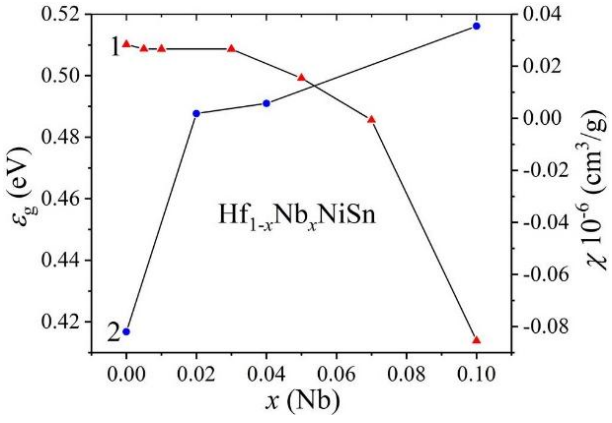


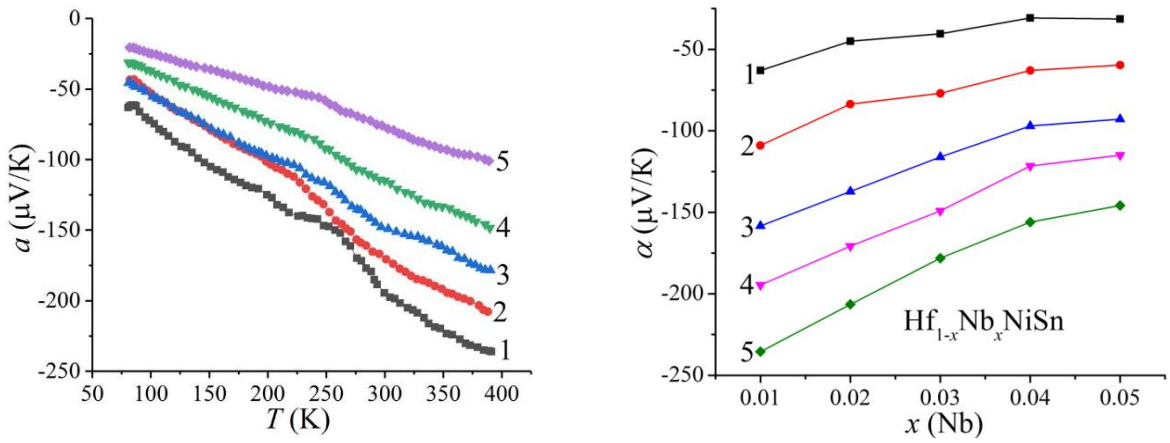
Fig. 4. Change in the band gap $\varepsilon_g(x)$ (1) and specific magnetic susceptibility $\chi(x)$ (2) at a magnetic field strength of H=10 kG of the thermometric material $Hf_{1-x}Nb_xNiSn$

6. Experimental studies of magnetic and electrokinetic properties of thermometric material Hf1-xNbxNiSn

The study of the specific magnetic susceptibility $\chi(x)$ of the thermometric material $Hf_{1-x}Nb_xNiSn$, x=0–0.10, allows us to identify the effect of an external magnetic field on the thermometric characteristics of thermal converters made of this material. The studies have shown that the basic semiconductor *n*-HfNiSn is a weak diamagnet, as indicated by the negative values of the specific magnetic susceptibility χ at room temperature (Fig. 4, curve 2). Doping *n*-HfNiSn with Nb atoms makes the semiconductor $Hf_{1-x}Nb_xNiSn$ a Pauli paramagnet, in which the specific magnetic susceptibility is determined exclusively by the electron gas and is proportional to the density of states at the Fermi level $g(\varepsilon_F)(x)$. From the results of Fig. 4, curve 2, it is seen that in the concentration range x=0–0.02 there is a rapid increase in the values of the specific magnetic susceptibility $\chi(x)$ $Hf_{1-x}Nb_xNiSn$, caused by the generation of donor states and an increase in the concentration of free electrons when replacing Hf atoms with Nb atoms. At higher concentrations of Nb atoms, the rate of change of the magnetic susceptibility $\chi(x)$ $Hf_{1-x}Nb_xNiSn$ decreases due to the appearance and increase in the concentration of acceptor states, which capture free electrons, reducing their concentration. The results obtained show that an external magnetic field with a strength of $H \leq 10$ kG will have practically no effect on the thermometric characteristics of thermal converters made of this material.

The nature of the change in the values of the specific electrical resistance ρ and the thermopower coefficient α (Fig. 5) of $Hf_{1-x}Nb_xNiSn$ with both temperature and concentration of Nb atoms is consistent with the conclusions drawn from structural studies of the semiconductor and modeling of its electronic structure. Since the electrical resistance $\rho(T,x)$ of $Hf_{1-x}Nb_xNiSn$ increases almost linearly with increasing temperature, which is the result of metallization of electrical conductivity, this material is unsuitable for obtaining sensitive elements of resistance thermometers due to the insignificant change in resistance with temperature. Therefore, let us focus on the analysis of the temperature and concentration dependences of the thermopower coefficient α of $Hf_{1-x}Nb_xNiSn$ (Fig. 5).

The temperature dependences of the thermopower coefficient $\alpha(T,x)$ $Hf_{1-x}Nb_xNiSn$ (Fig. 5, *a*) show that the main carriers of the electric current of the thermometric material at all temperatures are free electrons. This is indicated by the negative values of the thermopower coefficient α at all concentrations and studied temperatures. The results of Fig. 5, *a* also follow that with an increase in the concentration of Nb atoms, the absolute change in the values of the thermo-power coefficient $\alpha(T,x)$ $Hf_{1-x}Nb_xNiSn$ decreases, which is the reason for the decrease in the band gap ε_g of the thermometric material (Fig. 4, curve 1). According to the nature of the behavior of the concentration dependence of the thermopower coefficient $\alpha(x,T)$ $Hf_{1-x}Nb_xNiSn$, it is possible to establish the concentration of Nb atoms at which the change in the values of the thermopower coefficient α will be the largest. In this case, this condition is achieved with the concentration of the semiconductor thermometric material $Hf_{0.99}Nb_{0.01}NiSn$, which became the basis for forming the electrode (negative leg) of the thermoelectric temperature converter.



a *b*

Fig. 5. Change in thermopower coefficient α of $Hf_{1-x}Nb_xNiSn$ with temperature (a) and concentration (b)

7. Modeling of the conversion functions of a thermoelectric converter based on the thermometric material $Hf_{1-x}Nb_xNiSn$

In Fig. 6, as an example, the results of modeling the conversion function of the thermoelectric couple $Hf_{0.99}Nb_{0.01}NiSn$-(PtRh 13), the thermoelectrodes of which are made of the studied thermometric material and platinoid (PtRh 13) (positive leg) are presented. The modeling of conversion functions in the temperature range 4.2–1000 K was carried out using the FLAPW method, Elk program package [10, 11]. As can be seen from the presented results, the temperature dependence of the change in the thermopower values is a smooth curve, which ensures the unambiguity of temperature measurements. The stability of the operation of the obtained sensitive elements of thermoelectric thermometers based on thermometric materials $Hf_{1-x}Nb_xNiSn$ is ensured by the stability of their crystal structure in a wide temperature range. The lower limit of temperature measurements by sensitive elements is T=4.2 K, and the upper limit is 1300 K.

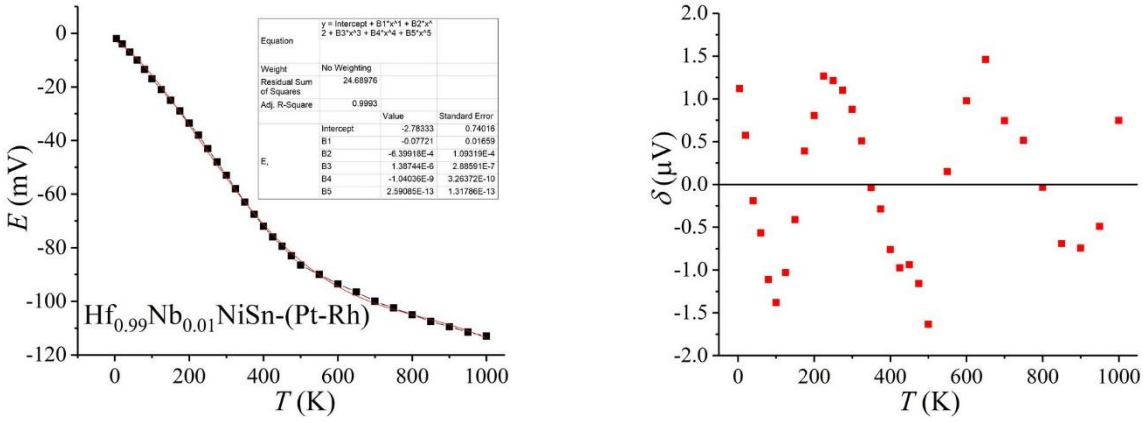


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Fig. 6. Conversion function E(T) of the thermoelectric converter $Hf_{0.99}Nb_{0.01}NiSn$-(PtRh 13) (a) and regular deviations δ(T) (b)

8. Conclusions

Modeling and experimental studies of the structural, magnetic, electrokinetic and energy properties of the thermometric material $Hf_{1-x}Nb_xNiSn$ for the case of an ordered variant of its crystal structure established the simultaneous generation of donor and acceptor states in the forbidden band ε_g of the semiconductor. The dependence between the spatial arrangement of atoms in the units of the unit cell (crystal structure) of the thermometric material $Hf_{1-x}Nb_xNiSn$ and the mechanisms of electrical conductivity was revealed, which allows us to determine the conditions for the synthesis of materials with the maximum efficiency of converting thermal energy into electrical energy. It was established that at concentrations of $Hf_{1-x}Nb_xNiSn$, x=0–0.02, the substitution of Hf atoms ($5d^26s^2$) by Nb atoms ($4d^45s^1$) in position 4*a* mainly occurs, which generates donor states. In the concentration range of $Hf_{1-x}Nb_xNiSn$, x=0.02–0.05, the substitution of Ni atoms ($3d^84s^2$) in position 4*a* by Nb atoms mainly occurs, which generates acceptor states, and at concentrations of 0.05<x, the substitution of Hf atoms by Ni atoms generates additional donor states. It is shown that the studied thermometric material $Hf_{1-x}Nb_xNiSn$ is promising for the manufacture of sensitive elements of thermoelectric thermometers. The regularities of the t conversion function of the thermoelectric couple $Hf_{0.99}Nb_{0.01}NiSn$-(PtRh 13), the thermoelectrodes of which are made of the studied thermometric material and platinoid (PtRh 13) (positive leg), are studied.

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Conflict of Interest

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

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