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Features of the Electrical Conductivity Mechanisms of the New Semiconductor Thermoelectric Material $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$

The structural, thermodynamic, energetic, electrokinetic, and magnetic properties of the new semiconductor thermoelectric material $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$, $x=0-0.07$, obtained by introducing Sc atoms into the structure of the HfNiSn compound by replacing Hf atoms, were investigated. The features of the transformation of the crystal and electronic structures, as well as the nature of the generated energy states and mechanisms of electrical conductivity, were established. Analysis of the electron density function based on Bader's quantum theory for the HfNiSn and $\text{Hf}_{0.75}\text{Sc}_{0.25}\text{NiSn}$ compounds confirmed the experimental conclusions regarding the generation in $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ of structural defects of acceptor nature only and the corresponding energy states. High values of the specific electrical conductivity and the thermopower coefficient correspond to the condition of maximum efficiency of thermal-to-electrical energy conversion, making $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ a promising thermoelectric material.

Keywords: thermoelectric material, semiconductor, electronic structure, electrical resistivity, thermopower coefficient.

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Introduction

One of the most studied classes of thermoelectric materials with high efficiency in converting thermal energy into electrical energy is substitutional-type solid solutions based on semiconductor phases, in particular n-TiNiSn, n-ZrNiSn, and n-HfNiSn [1]. They have high efficiency in converting thermal energy into electrical energy, and appropriate doping allows optimization of the value of the specific electrical conductivity σ , the thermopower coefficient α , and the thermal conductivity κ to obtain maximum values of thermoelectric figure of merit Z ($Z = \alpha^2 \cdot \sigma / \kappa$) [2, 3].

In this context, it is interesting to study the semiconductive thermoelectric material $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$, obtained by introducing Sc atoms ($5d^14s^2$) into the structure of the HfNiSn compound by substituting Hf atoms ($5d^26s^2$) at position 4a. Such substitution should generate structural defects of an acceptor nature since Hf has more *d*-electrons than Sc. It creates a precondition for changing the type of electrical conductivity of $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ from electronic to hole at certain concentrations of Sc atoms, which will make the semiconductor heavily doped and highly compensated (HDHCS) [4].

To determine the conditions for the synthesis of a material with the maximum efficiency of converting thermal energy into electrical energy, a comprehensive study of the structural, thermodynamic, energy, electrokinetic, and magnetic properties of the $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ solid solution was carried out, as well as an analysis of the electron density function based on the quantum theory of R. Bader [5]. The combination of experimental results with quantum-chemical calculations based on the theory of R. Bader allows us to describe the electronic structure and mechanisms of electrical conductivity of the thermoelectric material $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$. After all, instead of using electronic orbitals or complex wave functions, a physically observable quantity is analyzed – the topology of the scalar field of the electron density, which can be obtained both by quantum-chemical calculations and experimentally.

Research methods

Samples of $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$, where $x = 0\text{--}0.10$, were produced by the arc-melting of a batch of starting components, including hafnium (purity 99.95 wt. %), nickel (purity 99.99 wt. %), tin (purity 99.999 wt. %), scandium (purity 99.9 wt. %) in an atmosphere of purified argon (sponge titanium was used as a getter). To bring the alloys to an equilibrium state, homogenizing annealing was performed at 1073 K for 700 h, followed by quenching in cold water without prior breaking of the ampoules. X-ray phase and X-ray structural analyses were performed using diffraction patterns obtained on a PROTO AXRD Benchtop diffractometer (Cu K_α radiation). The chemical composition of the samples was controlled by the method of energy-dispersive X-ray spectroscopy (Tescan Vega 3 LMU electron microscope). The structural parameters of the samples were calculated using the WinCSD software package [6]. The full-potential linearized augmented plane wave (FLAPW) method, based on density functional theory (DFT) for the ordered variant of the $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ crystal structure was employed to simulate the structural, thermodynamic, energy, and electric transport properties,

as well as the electron localization function (ELF). The calculations within the framework of the DFT density functional theory were performed on licensed software using the Vienna Ab initio Simulation Package VASP v. 5.4.4 with PAW-type potentials [7]. The Perdew-Burke-Ernzerhof exchange-correlation functional [8] was applied in the generalized gradient approximation (GGA) Monkhorst-Pack [9] for the $11 \times 11 \times 11$ k -grid. In the calculations, the plane wave cutoff was set at 400 eV. The Exciting code (FLAPW method) was used to model the electrokinetic properties by solving the linear Boltzmann equation in the constant relaxation time approximation. The electric transport properties of $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$, $x = 0\text{--}0.07$, were studied using samples measuring $5 \times 1 \times 1$ mm³. The temperature and concentration dependences of the resistivity (ρ), the thermopower coefficient (α) relative to copper in the temperature range $T = 80\text{--}400$ K, and the specific magnetic susceptibility (χ) (Faraday method) at a temperature of 300 K were measured.

Study of structural and thermodynamic properties of $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$

X -ray structural studies of $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ samples ($x = 0\text{--}0.10$) showed that all powder diffraction patterns are indexed in the MgAgAs structure type (space group $F\bar{4}3m$). There are no traces of other phases in the powder diffraction patterns with Sc concentrations $x = 0\text{--}0.07$ (Fig. 1a). However, samples with Sc concentrations of $x > 0.07$ contained minor inclusions of the binary phase Hf_5Sn_4 (Ti_5Ga_4 -type), so they were excluded from further studies. Microprobe analysis of the chemical and phase compositions of the surface of $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ samples, $x = 0\text{--}0.07$, showed that they correspond to the composition of the charge of the initial components. Fig. 1b, for example, shows the elemental distribution in the sample $\text{Hf}_{0.97}\text{Sc}_{0.03}\text{NiSn}$, which fully corresponds to the initial composition of the charge.

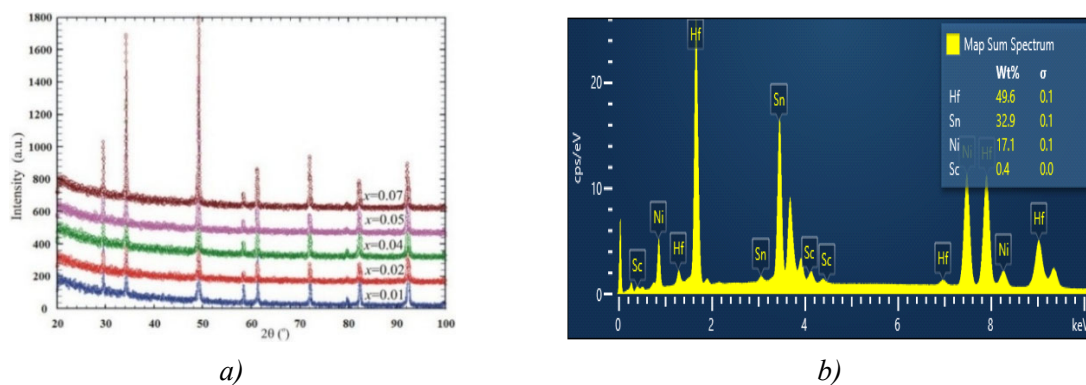


Fig. 1. Powder diffraction patterns of $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ samples (a)
 and elemental distribution in $\text{Hf}_{0.97}\text{Sc}_{0.03}\text{NiSn}$ (b)

At the beginning of the study, it was important to understand if replacing Hf atoms with Sc atoms in the 4a position of the HfNiSn compound is energetically feasible. In other words, does this form a substitutional-type $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ solid solution, and if so, in what concentration ranges, and are the samples we studied within these ranges?

Using the FLAPW method (VASP software package) within the framework of the DFT density functional theory, the mixing enthalpy $\Delta H_{\text{mix}}(x)$ was simulated in the approximation of

harmonic vibrations of atoms for a hypothetical solid solution $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$, $x = 0-1.0$, (Fig. 2a). The calculations show that at concentrations $x \approx 0-0.42$ and temperature $T = 1073$ K (temperature of homogenizing annealing of samples), the dependence $\Delta H_{\text{mix}}(x)$ decreases and has negative values. This behavior of $\Delta H_{\text{mix}}(x)$ is evidence of the energetic feasibility of substituting Hf atoms for Sc in position 4a and the existence of a solid solution $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ up to a limit concentration of Sc $x = 0.42$.

At higher concentrations $x > 0.42$ and $T = 1073$ K, the dependence $\Delta H_{\text{mix}}(x)$ increases, indicating the energetic inexpediency of such substitution; stratification occurs (spinoidal phase decomposition). Calculations also show that at lower temperatures, the region of existence of the solid solution decreases (the minimum of the dependence $\Delta H_{\text{mix}}(x)$ shifts to the region of lower Sc concentrations). Therefore, based on the results of modeling the mixing enthalpy $\Delta H_{\text{mix}}(x)$, it was established that the $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ samples at concentrations $x = 0-0.07$ belong to the region of existence of the substitutional-type solid solution.

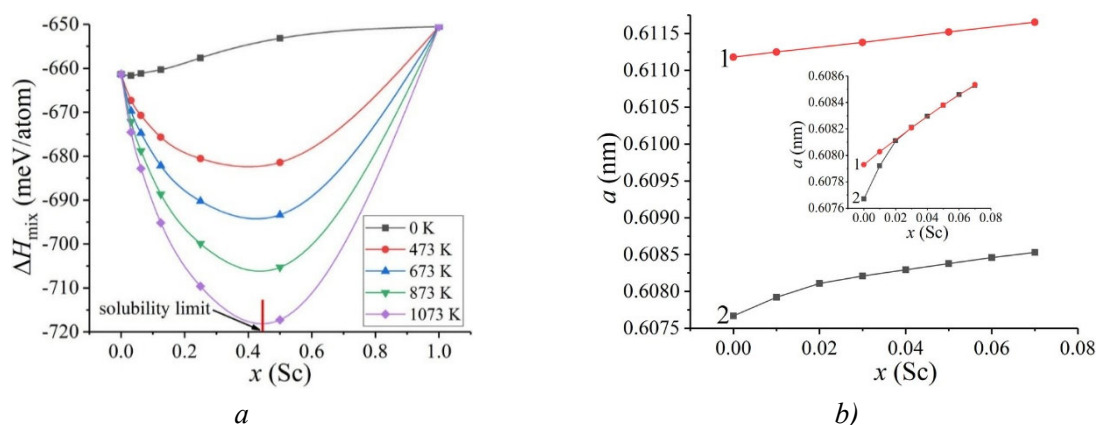


Fig. 2. Modeling of the mixing enthalpy $\Delta H_{\text{mix}}(x, T)$ (a) and the change in the unit cell parameter $a(x)$ based on the results of modeling (1) and experiment (2) (b) of the solid solution $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$

Modeling the change in the unit cell parameter $a(x)$ of $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ for the ordered variant of the crystal structure showed a linear increase at concentrations $x = 0-0.07$ (Fig. 2b). We considered the case when the Hf(Sc) atoms occupy the crystallographic position 4a (0, 0, 0), Ni – 4d ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$) and Sn – 4c ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$). Such a change in the unit cell parameter $a(x)$ is predicted, since the atomic radius of Sc ($r_{\text{Sc}} = 0.164$ nm) is larger than the atomic radius of Hf ($r_{\text{Hf}} = 0.158$ nm).

At the same time, the unit cell parameter $a(x)$ of $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$, calculated from the data of X-ray diffraction, also increases, but unlike the simulation results, contains two linear sections: $0 < x \leq 0.02$ and $x \geq 0.02$ (Fig. 2b). In addition, the unit cell parameter of the initial compound HfNiSn , obtained by simulation, is much larger than the unit cell parameter calculated from the experimental results. It is clear that for samples of the solid solution $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$, all subsequent values of the lattice parameter will also be larger than calculated from the experimental data.

In this context, it is important to note that a similar change in the unit cell parameter $a(x)$ was observed in previously studied solid solutions based on HfNiSn that included large atoms, specifically rare-earth metals (R), namely $\text{Hf}_{1-x}\text{R}_x\text{NiSn}$ [1]. The presence of two linear sections on the $a(x)$ dependence is due to the disorder of the crystal structure of the HfNiSn compound, while the simulation was performed for its ordered variant. The essence of the disorder lies in the partial, up to $\sim 1\%$, occupation of the crystallographic position $4a$ of Hf atoms by Ni atoms [10]. In this case, if in the structure of the HfNiSn compound the positions of large Hf atoms ($r_{\text{Hf}} = 0.158$ nm) are partially occupied by smaller Ni atoms ($r_{\text{Ni}} = 0.124$ nm), then the crystal structure of the compound is deformed. It is one of the reasons why, for the basic compound HfNiSn, the values of the lattice parameter $a(x)$ obtained by simulation are larger than those obtained from the experiment.

When larger Sc atoms ($r_{\text{Sc}} = 0.164$ nm) are introduced into the structure of the HfNiSn compound, they first displace the smaller Ni atoms from the crystallographic position $4a$. At Sc atom concentrations of $x \geq 0.02$, all Ni atoms will be displaced from the position of Hf atoms, and now only Hf atoms are substituted by Sc. In this case, the rate of change of the lattice parameter $a(x)$ of $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ in the concentration regions $0 < x \leq 0.02$ and $x \geq 0.02$ will be different. In the first case, this change will be greater, as indicated by the larger slope of the dependence $a(x)$, which is possible only when larger Sc atoms displace smaller Ni atoms from position $4a$. In this case, the ordering of the crystal structure of $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ also occurs. The overlay of the graphs of the changes in the lattice parameter $a(x)$ for $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ (inset Fig. 2b), calculated from the experiment and obtained by simulation, shows complete coincidence at concentrations $x \geq 0.02$.

The process of ordering of the crystal structure of $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ is also accompanied by a redistribution of the density of electronic states. Thus, if in the HfNiSn compound Ni atoms ($3d^8 4s^2$) partially occupy the $4a$ position of Hf atoms ($5d^2 6s^2$), this gives rise to structural defects of donor nature and the corresponding electronic states (Ni has more d -electrons than Hf). At the same time, vacancies appear in the crystallographic position $4c$ of Ni atoms, i.e., structural defects of acceptor nature and the corresponding acceptor states. The $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ semiconductor becomes heavily doped and highly compensated (HDHCS) of electronic conduction type [4].

The introduction of Sc ($3d^1 4s^2$) atoms into the structure of the HfNiSn compound and its ordering in the $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ solid solution leads to a simultaneous reduction of structural defects of donor and acceptor nature associated with Ni atoms (Ni atoms leave the $4a$ position and return to their own $4c$ position, and vacancies disappear). On the other hand, since Sc ($5d^1 4s^2$) contains one $5d$ -electron less than Hf, structural defects of acceptor nature and corresponding acceptor states are generated in $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$. The $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ semiconductor remains a HDHCS, but now of p -type conductivity. The presented results of the qualitative analysis of the redistribution of electron density in $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ are confirmed by the results of the quantitative analysis of the electron density function presented below, carried out based on the quantum theory of R. Bader [5].

Analysis of the electron density function of $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ according to R. Bader

The Bader atomic charge is calculated by integrating the electron density within an “electron pool”. In this approach, the continuous electron density is “cut” into individual atoms, which allows the determination of partial charges on the atoms. In other words, the real charge distribution is analyzed, rather than the mathematical analysis of complex wave functions (orbitals). The calculated Bader atomic charges for the compound HfNiSn show (Table 1) that the Hf atoms are positively charged, while the Ni and Sn atoms form the anionic sublattice $\text{Hf}^{n+}[\text{NiSn}]^{n-}$. In the compound $\text{Hf}_{0.75}\text{Sc}_{0.25}\text{NiSn}$, partial substitution of Hf atoms by Sc leads to an increase in the positive charge on both the Hf and Sc atoms and the negative charge on the Ni atoms. The charge of the Sn atoms becomes less negative, indicating a deficiency of electrons in the system.

This is also reflected in the visualization of the electron localization function ELF (Electron Localization Function) in the case of the HfNiSn and $\text{Hf}_{0.75}\text{Sc}_{0.25}\text{NiSn}$ phases (Fig. 3). Since the method of analyzing the electron density distribution using ELF determines the probabilities of finding an electron near another electron with the same spin (Fermi hole), the maximum ELF values of ~ 0.48 are characteristic of the electron gas of delocalized electrons (Fig. 3).

Table 1

Bader total atomic charges in HfNiSn and $\text{Hf}_{0.75}\text{Sc}_{0.25}\text{NiSn}$

HfNiSn		$\text{Hf}_{0.75}\text{Sc}_{0.25}\text{NiSn}$	
Atom	Bader charge (e^-)	Atom	Bader charge (e^-)
Hf	+1.408	Hf	+1.455
Ni	−1.028	Ni	−1.093
Sn	−0.380	Sn	−0.317
		Sc	+1.445

At the same time, ELF values of ~ 0 characterize regions with low electron density (interatomic space). As we can see from the results presented in Fig. 3, the localization of electrons around Sc atoms in the $\text{Hf}_{0.75}\text{Sc}_{0.25}\text{NiSn}$ phase becomes less pronounced compared to the HfNiSn compound.

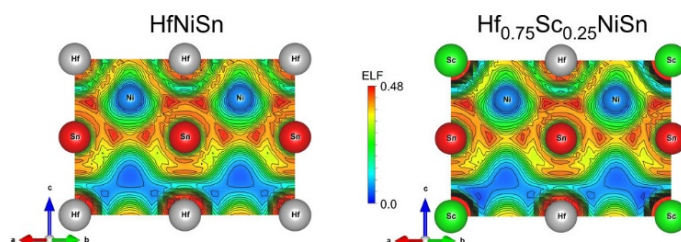


Fig. 3. Modeling of the localization of electrons (ELF) around atoms in the compound HfNiSn and $\text{Hf}_{0.75}\text{Sc}_{0.25}\text{NiSn}$ phase

Analysis of the electron density distribution of the HfNiSn compound shows (Fig. 4 a) that the average integral index of the COBI crystal orbitals below the Fermi level is bonding, while above it is antibonding, forming a band gap between them. Below the Fermi level, the interactions between Hf-Ni and Hf-Sn atoms are exclusively bonding.

On the other hand, the interaction between Ni-Sn atoms is bonding below -2 eV and antibonding above, which is caused by the filled antibonding d -states of Ni atoms. The strongest bonds are Hf-Sn, which are characterized by the highest -COHP values. The second strongest bonds are Hf-Ni, and the weakest are Ni-Sn. The analysis shows that there is a directed covalent bond between Hf-Ni and Hf-Sn atoms, which is reflected by the close COBI values.

In $\text{Hf}_{0.75}\text{Sc}_{0.25}\text{NiSn}$, the Fermi level is shifted into the valence band, and that creates unoccupied bonding states above E_F , which is clearly visible on pCOBI of Sc-Ni and Sc-Sn interactions and makes the compound less stable (Fig. 4 b). However, this partial depopulation of the valence band also has a positive effect, as the antibonding Ni-Sn interactions become less occupied. The ICOBI and -ICOHP (Table 2) of the Hf-Ni and Hf-Sn atom pairs are higher than the corresponding values for Sc-Ni and Sc-Sn, revealing that Sc creates local structural distortions and weaker bonding with neighboring Ni and Sn.

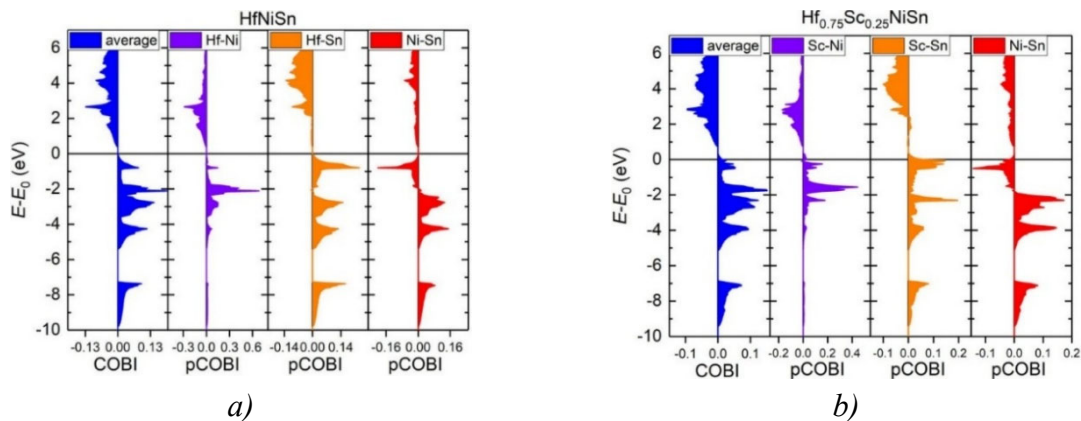


Fig. 4. Modeling of the electron density distribution of HfNiSn (a) and $\text{Hf}_{0.75}\text{Sc}_{0.25}\text{NiSn}$ (b)

Table 2

Calculated integrated crystal orbital bond index (ICOBI) and negative crystal orbital Hamilton population (-ICOHP) for atom pairs in HfNiSn and $\text{Hf}_{0.75}\text{Sc}_{0.25}\text{NiSn}$

HfNiSn	COBI	-COHP, eV	$\text{Hf}_{0.75}\text{Sc}_{0.25}\text{NiSn}$	COBI	-COHP, eV
Hf-Ni	0.382	1.211	Hf-Ni	0.385	1.197
Hf-Sn	0.360	1.656	Hf-Sn	0.368	1.642
Ni-Sn	0.176	1.051	Ni-Sn	0.190	1.106
			Sc-Ni	0.279	0.883
			Sc-Sn	0.255	1.207

Electrokinetic, energetic and magnetic properties of $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$

Fig. 5 shows the temperature dependences of the electrical resistivity $\ln(\rho(1/T, x))$ and the thermopower coefficient $\alpha(1/T, x)$ for several samples of $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$, $x = 0-0.07$. The temperature dependences $\ln(\rho(1/T, x))$ of $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ (Fig. 5) are described by equation (1) [4]:

$$\rho^{-1}(T) = \rho_1^{-1} \exp\left(-\frac{\varepsilon_1^p}{k_B T}\right) + \rho_3^{-1} \exp\left(-\frac{\varepsilon_3^p}{k_B T}\right), \quad (1)$$

where the first high-temperature term describes the activation of current carriers $\varepsilon_1^p(x)$ from the Fermi level ε_F to the percolation level of the continuous energy band, and the second, low-temperature, term describes the jump conductivity $\varepsilon_3^p(x)$ along localized states with energies close to the Fermi energy ε_F . The presence of high- and low-temperature activation regions on the $\ln(\rho(1/T, x))$ and $\alpha(1/T, x)$ dependences indicates the location of the Fermi level ε_F in the band gap ε_g , from which the activation of current carriers to the percolation level of the continuous energy band occurs. In turn, the presence of activation regions on the $\ln(\rho(1/T, x))$ dependences at low temperatures indicates the existence of jump ε_3^p -conductivity, which is possible only in the presence of electronic states of different nature [4, 11]. Therefore, the studied $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ samples are heavily doped and compensated semiconductors.

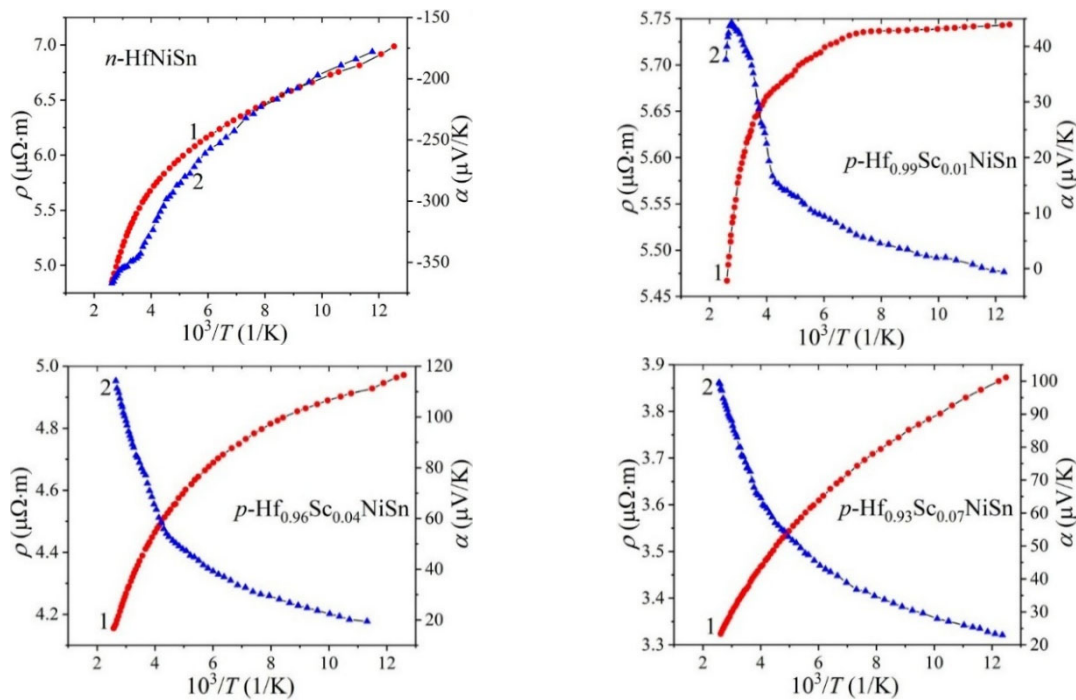


Fig. 5. Temperature dependences of the resistivity $\ln(\rho(1/T, x))$ (1) and the thermopower coefficient $\alpha(1/T, x)$ (2) of $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$

In the case of the HfNiSn compound ($x = 0$), negative values of the thermopower coefficient α indicate the location of the Fermi level ε_F near the percolation level of the conduction band ε_C of the semiconductor and the electronic type of conductivity. On the other hand, in the $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ samples at concentrations of $x > 0.01$, the Fermi level ε_F lies closer to the valence band ε_V (positive values of the thermopower coefficient α), and holes are the

main current carriers. For the sample with the lowest Sc concentration, $\text{Hf}_{0.99}\text{Sc}_{0.01}\text{NiSn}$, the values of the thermopower coefficient α are negative at low temperatures ($T \leq 82$ K), and become positive at higher temperatures (Fig. 6 a).

This behavior of the thermopower coefficient α indicates a state close to full compensation of the semiconductor, when the concentrations of ionized acceptor and donor states are close. This conclusion is confirmed by the behavior of the thermopower coefficient $\alpha(1/T)$ at high temperatures (Fig. 6 b), at which the values of the thermopower coefficient are positive, and an increase in temperature should increase the concentration of ionized acceptor states. However, the appearance of an extremum in the $\alpha(1/T)$ dependence at $T \approx 360$ is a manifestation of the ionization of still existing donor states, which compensate for the acceptor states.

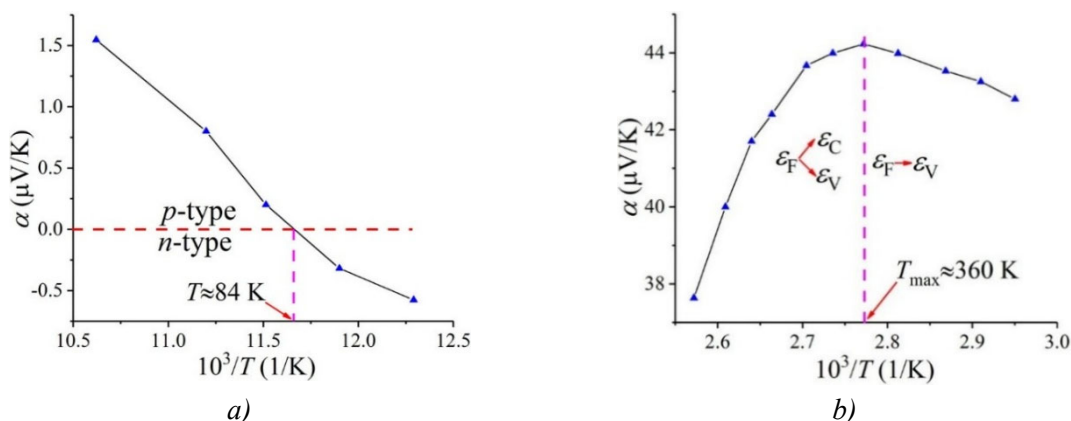


Fig. 6. Temperature dependences of the thermopower coefficient $\alpha(1/T, x)$ at low (a) and high (b) temperatures of the semiconductor $\text{Hf}_{0.99}\text{Sc}_{0.01}\text{NiSn}$

The proof of the generation of acceptor states when doping the n- HfNiSn semiconductor with a Sc impurity is the behavior of the Fermi level ϵ_F (Fig. 7 a). Thus, in n- HfNiSn , the energy $\epsilon_1^p(x=0) = 81.3$ meV was calculated from (1), which shows the energy gap between the percolation level of the conduction band ϵ_C and the impurity donor state (band), which fixes the Fermi level ϵ_F . Doping n- HfNiSn with Sc impurities at the lowest concentration ($x = 0.01$) radically changes the type of conductivity of $\text{Hf}_{0.99}\text{Sc}_{0.01}\text{NiSn}$, such that at temperatures above 82 K, holes become the main current carriers. The calculated activation energy $\epsilon_1^p(x = 0.01)$ is 27.1 meV, now indicating the energy gap between the valence band level ϵ_V and the acceptor state (band) where the Fermi level ϵ_F is located. Increasing the acceptor concentration in $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ leads to an almost linear decrease in the activation energy from $\epsilon_1^p(x = 0.03) = 24.3$ meV to $\epsilon_1^p(x = 0.05) = 17.91$ meV and $\epsilon_1^p(x = 0.07) = 10.2$ meV (Fig. 7 a). The obtained dependence $\epsilon_1^p(x)$ at concentrations $x = 0.01$ – 0.07 reflects the process of approaching the Fermi level ϵ_F to the level of the valence band ϵ_V , which allows us to determine the rate of its motion: $\Delta\epsilon_F/\Delta x \approx 3.9$ meB/%Sc. We did not obtain single-phase samples of $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ with concentrations $x \geq 0.10$, at which the Fermi level ϵ_F would cross the valence band ϵ_V , which would have caused the dielectric-metal transition of conductivity and metallization of electrical conductivity.

From the results presented, we can state that the semiconductor $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ contains significant concentrations of electronic states of various types and is a HDHCS [1, 4]. On the

other hand, the presence in the semiconductor of a significant number of different charged defects, the location of which is of a fluctuating nature, radically changes its electronic structure. It leads to fluctuations in potential relief with the amplitude of large-scale fluctuations and the modulation of continuous energy bands (small-scale fluctuations). At low temperatures, a heavily doped crystalline semiconductor is a partially disordered system. The electron in such a system is considered not in the periodic field of the crystal, but in the chaotic field of defects [4].

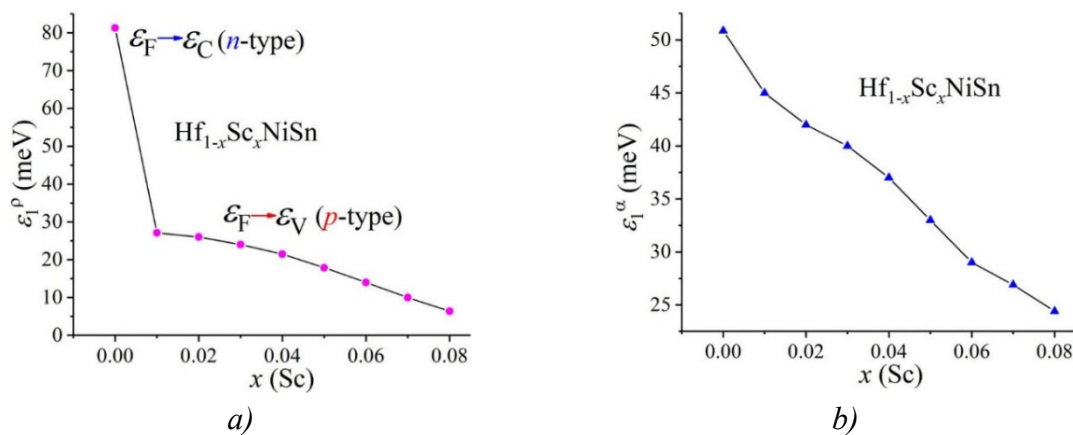


Fig. 7. Change in activation energies $\varepsilon_I^p(x)$ (a) and $\varepsilon_I^\alpha(x)$ (b) of $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$

It is shown in ref. [12] that the amplitudes of modulation of the potential relief and small-scale fluctuations of the HDHCS can be quantitatively evaluated. The change in the thermopower coefficient with temperature $\alpha(1/T, x)$ of $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ (Fig. 5) is described by the well-known Mott formula (2) [13], using which the activation energies $\varepsilon_I^\alpha(x)$ and $\varepsilon_3^\alpha(x)$ can be determined from the high- and low-temperature activation regions of the thermopower coefficient $\alpha(1/T, x)$:

$$\alpha = \frac{k_B}{e} \left(\frac{\varepsilon_i^\alpha}{k_B T} - \gamma + 1 \right), \quad (2)$$

where γ is a parameter that depends on the nature of the scattering mechanism. It turned out that the activation energies $\varepsilon_I^\alpha(x)$ and $\varepsilon_3^\alpha(x)$ describe, respectively, the amplitudes of large- and small-scale fluctuations of continuous energy bands. Since the amplitude of large-scale fluctuations is in turn proportional to the compensation degree of the semiconductor, the nature of the change in $\varepsilon_I^\alpha(x)$ can be used to judge the ratio of ionized acceptor and donor states (degree of compensation).

According to formula (2), the activation energy $\varepsilon_I^\alpha(x)$ of n- HfNiSn was calculated as $\varepsilon_I^\alpha(x=0) = 50.8$ meV, which is consistent with the literature data (Fig. 7 b) [1, 10]. Doping n- HfNiSn with Sc impurity reduces the activation energy from $\varepsilon_I^\alpha(x=0.03) = 40.2$ meV to $\varepsilon_I^\alpha(x=0.05) = 33.1$ meV and $\varepsilon_I^\alpha(x=0.07) = 26.9$ meV. Considering that the activation energy $\varepsilon_I^\alpha(x)$ is proportional to the compensation degree, in a p -type semiconductor, the reduction of the degree of compensation is possible only if the concentration of acceptor states increases [4, 11]. Therefore, the decrease in the degree of compensation of the $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ experimentally proves the existence in the crystal of a mechanism for the generation of structural defects of an acceptor nature and the corresponding electronic states.

The behavior of the electrical resistivity $\rho(x, T)$ and the thermopower coefficient $\alpha(x, T)$ of $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ samples when changing the concentration of Sc atoms at different temperatures allows us to clarify the processes of restructuring the electronic structure of the semiconductor (Fig. 8). As seen from Fig. 8a, the resistivity $\rho(x, T)$ of $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ at concentrations of $x > 0.01$ monotonically decreases for all studied temperatures, which is due to an increase in the concentration of free holes during the ionization of acceptor states. It is indicated by the positive values of the thermopower coefficient $\alpha(x, T)$ (Fig. 8b).

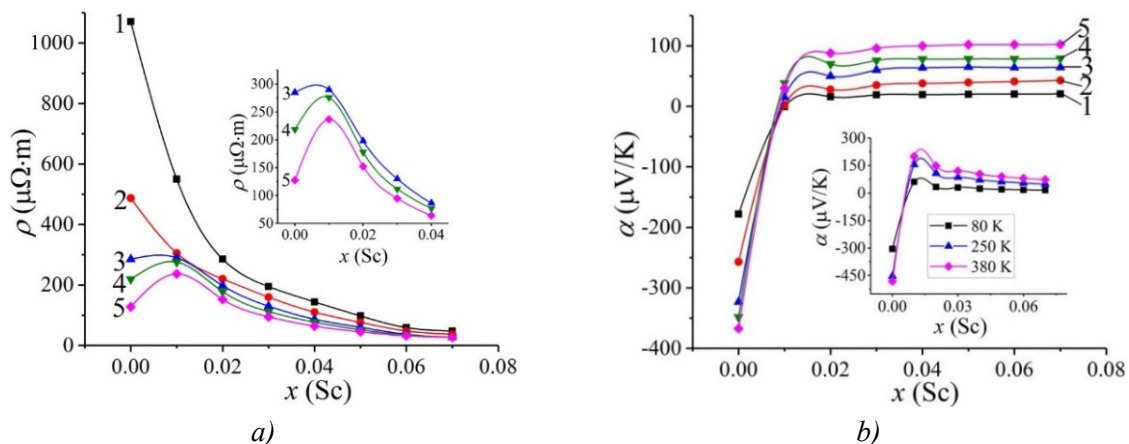


Fig. 8. Change in resistivity $\rho(x, T)$ (a) and thermopower coefficient $\alpha(x, T)$ (b) of $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ at temperatures: 1 – $T = 80$ K; 2 – $T = 160$ K; 3 – $T = 250$ K; 4 – $T = 300$ K; 5 – $T = 380$ K.

Inset b: modeling of the behavior of the thermopower coefficient $\alpha(x, T)$

However, in the concentration range $0 \leq x \leq 0.01$, the behavior of the dependence $\rho(x, T)$ at different temperatures differs. Thus, at low temperatures ($T = 80$ K and $T = 160$ K), the resistivity $\rho(x, T)$ of $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ monotonically decreases, and at higher temperatures, $160 \text{ K} < T \leq 380 \text{ K}$, it increases, passes through a maximum, and then monotonically decreases. This behavior of the dependence $\rho(x, T)$ of $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ is due to the presence of deep donor states in the band gap ε_g , which are ionized at $T > 160$ K and compensate for the acceptor states, reducing the concentration of free holes. It is what causes the increase in the resistivity $\rho(x, T)$ at concentrations $0 \leq x \leq 0.01$ (Fig. 8a). At the same time, for $x > 0.01$, the concentration of generated acceptor states significantly exceeds the concentration of donor states, and an increase in the concentration of free holes causes a decrease in the resistivity of $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$. It is important to note that the experimental studies of the electrokinetic properties of $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ align with the modeling results obtained using the FLAPW method. As evidence, the inset of Fig. 8b shows the calculated change in the thermopower coefficient $\alpha(x, T)$ of $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$.

Experimental measurements of the specific magnetic susceptibility $\chi(x)$ of $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ samples at room temperature showed that n- HfNiSn is a diamagnet, which is reflected by the negative values of the magnetic susceptibility ($\chi = -0.07 \cdot 10^{-6} \text{ emu/g}$) (Fig. 9). At the lowest Sc concentration in the experiment, the $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ semiconductor changes both the type of conductivity from electronic to hole and the magnetic state, becoming a Pauli paramagnet. Since in a Pauli paramagnet the magnetic susceptibility is determined by free carriers and is

proportional to the density of electronic states at the Fermi level $g(\epsilon_F)$, the plateau in the dependence $\chi(x)$ at concentrations $0.01 \leq x \leq 0.02$ indicates the invariance of the concentration of free holes with an increase in the content of acceptor states. It is possible if the holes capture the free electrons still present in the semiconductor, which rapidly reduces their concentration. It is the decrease in the concentration of free electrons when generating acceptor states in the $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ semiconductor that causes an increase in the resistivity $\rho(x)$ (Fig. 9).

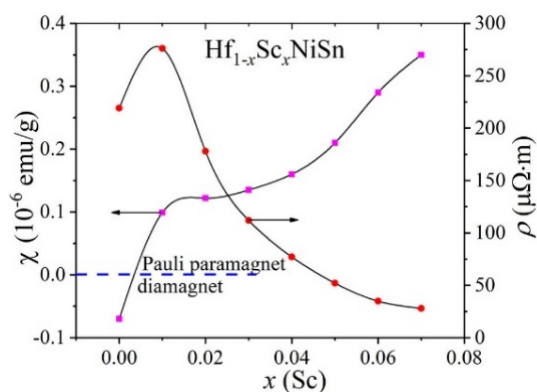


Fig. 9. Change in specific magnetic susceptibility $\chi(x)$ and electrical resistivity $\rho(x)$ $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ at $T = 300 \text{ K}$

Thus, as a result of a comprehensive study of the electrokinetic, energetic, and magnetic properties of the $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ solid solution, the features of the rearrangement of the crystal and electronic structures, as well as the nature of the generated energy states and mechanisms of electrical conductivity, have been established. It has been shown that structural defects of an acceptor nature and their corresponding energy states that determine the electrical conductivity of the semiconductor are generated in $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$.

Conclusions

The structural, thermodynamic, energetic, electrokinetic, and magnetic properties of the new semiconductor thermoelectric material $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$, $x = 0-0.07$, obtained by introducing Sc atoms ($5d^14s^2$) into the structure of the HfNiSn compound by replacing Hf atoms ($5d^26s^2$) in position $4a$, were investigated. The features of the transformation of the crystal and electronic structures, as well as the nature of the generated energy states and mechanisms of electrical conductivity, were established. Analysis of the electron density function based on the quantum theory of R. Bader for the compounds HfNiSn and $\text{Hf}_{0.75}\text{Sc}_{0.25}\text{NiSn}$ confirmed the experimental conclusions that only structural defects of acceptor nature and the corresponding energy states are generated in $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$. At the same time, the high values of the electrical conductivity and thermoelectric power coefficient of $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ meet the condition of maximum efficiency of converting thermal energy into electrical energy, which makes the semiconductor a promising thermoelectric material.

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Особливості механізмів електропровідності нового напівпровідникового термоелектричного матеріалу $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$

Досліджено структурні, термодинамічні, енергетичні, електрокінетичні та магнітні властивості нового напівпровідникового термоелектричного матеріалу $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$, $x = 0\text{--}0.07$, отриманого введенням у структуру сполуки HfNiSn атомів Sc шляхом заміщення атомів Hf . Встановлено особливості трансформації кристалічної та електронної структур, а також природу генерованих енергетичних станів та механізмів електропровідності. Аналіз функції електронної густини на основі квантової теорії Р. Бейдера для сполук HfNiSn та $\text{Hf}_{0.75}\text{Sc}_{0.25}\text{NiSn}$ підтвердив висновки експерименту щодо генерування в $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ лише структурних дефектів акцепторної природи та відповідних їм енергетичних станів. Високі значення питомої електропровідності та коефіцієнта термо-ерс відповідають умові максимальної ефективності перетворення теплової енергії в електричну, що робить $\text{Hf}_{1-x}\text{Sc}_x\text{NiSn}$ перспективним термоелектричним матеріалом.

Ключові слова: термоелектричний матеріал, напівпровідник, електронна структура, електроопір, коефіцієнт термо-ерс.