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THE STUDY OF STRUCTURAL, ENERGY AND KINETIC CHARACTERISTICS OF $Hf_{1-x}Y_xNiSn$ THERMOELECTRIC MATERIAL

The crystal and electronic structures, temperature and concentration dependencies of resistivity, the Seebeck coefficient and magnetic susceptibility of the $Hf_{1-x}Y_xNiSn$ thermoelectric material were studied in the ranges $T = 80 \div 400 K$ K, $x = 0.01 \div 0.30$. The mechanism of simultaneous generation of defects of acceptor nature was established. They change the compensation ratio of material and determine the mechanism of conduction.

Keywords: electronic structure, resistivity, Seebeck coefficient.

Introduction

Performance optimization of $Hf_{1-x}Lu_xNiSn$ thermoelectric material obtained by doping of *n-HfNiSn* intermetallic semiconductor with the atoms of rare-earth *Lu* metal [1], which will provide for high efficiency of thermal into electric energy conversion [2], revealed the non-reproducibility of material performance at high temperatures ($T \leq 1000$ K). It was established that in the process of doping there is a predictable generation of structural defects of acceptor nature in a crystal with substitution of $Hf (5d^2 6s^2)$ atoms by $Lu (5d^1 6s^2)$ atoms (*Lu* atoms possesses one $5d$ – electron less than *Hf*), and an uncontrolled generation of vacancies in the position of *Sn* (4*b*) atoms. Exactly uncontrolled generation of *Sn* structural defects (vacancies), apart from redistributing the electron density, accounts for the non-reproducibility of $Hf_{1-x}Lu_xNiSn$ performance, as long as at temperatures $T \leq 1000$ K vacancies are the cores of localization of uncontrolled defects. It was assumed that one of the reasons for generation of vacancies is deformation of $Hf_{1-x}Lu_xNiSn$ unit cell, caused by the difference in atomic radii of *Hf* ($r_{Hf} = 0.158$ nm) and *Lu* ($r_{Lu} = 0.173$ nm).

On the other hand, in the investigation of $Zr_{1-x}Y_xNiSn$ thermoelectric material [3] obtained by doping with *Y* atoms of *n-ZrNiSn* intermetallic semiconductor whose characteristics are close to *n-HfNiSn*, no mechanism of uncontrolled generation of vacancies in the position of *Sn* (4*b*) atoms was revealed. And this is despite the fact that the difference in atomic radii of *Zr* ($r_{Zr} = 0.1602$ nm) and *Y* ($r_Y = 0.180$ nm) is greater than in the case of *Hf* and *Lu* atoms, which causes even greater deformation of $Zr_{1-x}Y_xNiSn$ crystalline structure. And it means that generation of vacancies is not caused by deformation of $Hf_{1-x}Lu_xNiSn$ crystalline structure. This problem should be investigated further.

Based on the results of [3], an idea has started up to obtain a thermoelectric material with stable and reproducible characteristics by doping of *n-HfNiSn* intermetallic semiconductor with *Y* atoms. That is, like in the case of *Zr$_{1-x}$Y$_x$NiSn* [3], one can expect that in *Hf$_{1-x}$Y$_x$NiSn* crystal there will be also generated only structural defects of acceptor nature with a substitution of *Hf* atoms by *Y* ($4d^1 5s^2$) atoms (*Y* atom possesses one 5*d* – electron less than *Hf* atom). *The purpose* of the paper is to study conduction mechanisms of *Y*-doped *n-HfNiSn*, which will allow predicting the behaviour of the kinetic characteristics of *Hf$_{1-x}$Y$_x$NiSn* and study the conditions of obtaining a heat-resistant material with high efficiency of thermal into electrical energy conversion [1, 4].

Investigation procedures

The object to be investigated included crystalline structure, electron density distribution (DOS), the magnetic, electrokinetic and energy characteristics of *Hf$_{1-x}$Y$_x$NiSn*. The samples were synthesized in the laboratory of Institute for Physical Chemistry, Vienna University. The X-ray structural analysis (powder method) was used to obtain the data arrays (diffractometer Guinier-Huber image plate system, *CuKα_1*), and Fullprof program [5] was employed for the calculation of structural characteristics. The chemical and phase compositions of samples were controlled by microprobe analyzer (EPMA, energy-dispersive X-ray analyzer). The electronic structure calculations were performed by the Korringa-Kohn-Rostoker (KKR) method in coherent potential approximation (CPA) and local density approximation (LDA) [6] with the use of Moruzzi-Janak-Williams exchange-correlation potential [7]. The accuracy of calculating the position of the Fermi level ε_F is ± 8 meV. The temperature and concentration dependences of the electrical resistivity (ρ) and the Seebeck coefficient (α) were measured with respect to copper and magnetic susceptibility (χ) (Faraday method) of *Hf$_{1-x}$Y$_x$NiSn* samples in the ranges: $T = 80 \div 400$ K, $N_D^Y \approx 1.9 \cdot 10^{20}$ cm^{-3} ($x = 0.01$) ÷ $5.7 \cdot 10^{21}$ cm^{-3} ($x = 0.30$) and the magnetic field intensity $H \leq 10$ kE.

Research on the structural peculiarities of *Hf$_{1-x}$Y$_x$NiSn*

The microprobe analysis of the concentration of atoms on the surface of *Hf$_{1-x}$Y$_x$NiSn* samples has shown their conformity to the initial charge compositions, which is one of the experimental proofs of the predicted substitution of *Hf* atoms by *Y*. In turn, X-ray phase and structural analyses have revealed no traces of other phases in all *Hf$_{1-x}$Y$_x$NiSn* samples up to and including $x = 0.30$. As was expected, replacement of smaller-size *Hf* atoms by larger-size *Y* atoms leads to increase in the values of unit cell period *a(x)* of *Hf$_{1-x}$Y$_x$NiSn* (Fig. 1). The fact that the values of *a(x)* in the concentration range *Hf$_{1-x}$Y$_x$NiSn*, $x = 0 \div 0.30$ practically coincide with the calculated ones points to realization of substitutional solid solution. A deviation of the values of unit cell period *a(x)* from the linear dependence at $x > 0.30$ fixes the limit for the existence of *Hf$_{1-x}$Y$_x$NiSn* solid solution. The *Hf$_{1-x}$Y$_x$NiSn* samples at $x > 0.30$ are two-phase.

Investigations have also confirmed the result of [8] as regards crystal structure disorder of base semiconductor *n-HfNiSn*, the key point of which lies in a partial, up to ~ 1%, occupancy by *Ni* ($3d^8 4s^2$) atoms of the crystallographic position 4*a* of *Hf* atoms (*Ni* atoms possesses a larger number of *d*-electrons than *Hf* atom), which creates structural defects of donor nature ("a priori" doping with donors [4]), and electrons are the majority carriers.

Refinement of *Hf$_{1-x}$Y$_x$NiSn* crystalline structure by powder method with a simultaneous refinement of the isotropic parameters of atomic substitution and occupancy of (4*a*) crystallographic

position of *Hf* has shown that the lowest value of coefficient of mismatch between a model of crystalline structure and an array of Bragg reflections was obtained for a model where the occupancy of position of *Hf(Y)* atoms for $x \geq 0.01$ is 100%. In other words, the introduced *Y* atoms put into order *Hf$_{1-x}$Y$_x$NiSn* crystalline structure ("heal" structural defects) by displacement of *Ni* atoms from the position of *Hf* (4*a*) atoms. In turn, ordering of *Hf$_{1-x}$Y$_x$NiSn* crystalline structure makes it resistant to temperature and time changes, which creates prerequisites for preparation of material with stable and reproducible characteristics.
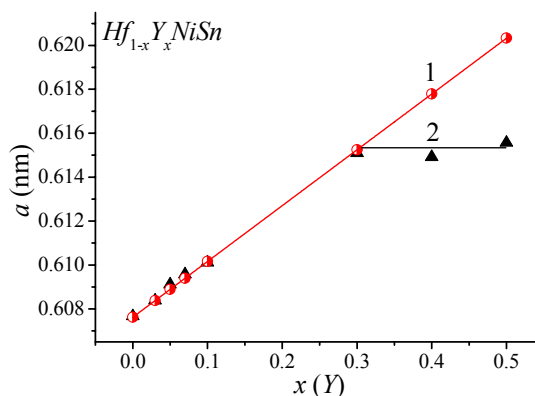

Fig. 1. Change in the values of unit cell period a(x) of Hf$_{1-x}$Y$_x$NiSn:
1 – calculation; 2 – experiment.

Apart from the structural peculiarities, ordering of *Hf$_{1-x}$Y$_x$NiSn* crystalline structure contributes essentially to the redistribution of the electron density of states. Thus, while in the initial *HfNiSn* compound there exist structural defects of donor nature as a result of displacement of up to ~1% of *Hf* atoms by *Ni* atoms [8], the process of semiconductor doping with *Y* atoms and ordering of crystalline structure is accompanied, on the one hand, by the reduction in the number of donors, as long as *Ni* atoms leave the position of *Hf* atoms. On the other hand, as long as *Y* atom has one 5*d* – electron less than *Hf* atom, structural defects of acceptor nature are generated in the crystal.

Therefore, in *Hf$_{1-x}$Y$_x$NiSn,* in the concentration range $x = 0 \div 0.01$ there is a simultaneous reduction of the number of donors (*Ni* atoms leave position 4*a* of *Hf* atoms) and increase in the number of acceptors (*Y* atoms occupy the position of *Hf* atoms). In this case, doping of *n-HfNiSn* semiconductor with lower concentrations of acceptor impurity will be accompanied, as expected, by increase in semiconductor compensation ratio (the ratio between donors and acceptors) [4]. With concentrations of $x > 0.01$, when *Ni* atoms will leave position 4*a* of *Hf* atoms, the concentration of acceptors in a crystal will increase, the type of majority carriers will change and the compensation ratio will decrease.

Research on the electron structure of *Hf$_{1-x}$Y$_x$NiSn*

To predict the behaviour of Fermi level ε_F, the energy gap ε_g and the kinetic characteristics of *n-HfNiSn* doped with *Y*, the electron density of states (DOS) of *Hf$_{1-x}$Y$_x$NiSn*, $0 \leq x \leq 0.10$ was calculated (Fig. 2*a*). Taking into account the results of structural investigations that introduction into *HfNiSn* compound of *Y* atoms puts into order its crystalline structure, calculation of DOS was performed for the case of ordered variant of *Hf$_{1-x}$Y$_x$NiSn* structure. As we can see from Fig. 2*a*, on introducing into *n-HfNiSn* of minimum attainable in experiment concentrations of acceptor impurity *Y*, Fermi level ε_F (dashed line in Fig.2*a*) starts drifting from conduction band ε_c, spaced ~81.3 meV from

it [8], to the midgap ε_g (shaded area in Fig. 2*a*), and then to the valence band ε_V which will be crossed by it at certain *Y* concentrations.

When crossing by Fermi level ε_F of the midgap ($x \approx 0.025$) and its further motion to valence band, the semiconductor changes its conductivity type, and holes become the majority carriers. Note that apart from the drift of Fermi level ε_F caused by a change in semiconductor compensation ratio, there is also a reduction in the energy gap ε_g from the values of $\varepsilon_g(x = 0) = 514.3$ meV to $\varepsilon_g(x = 0.10) = 426$ meV.
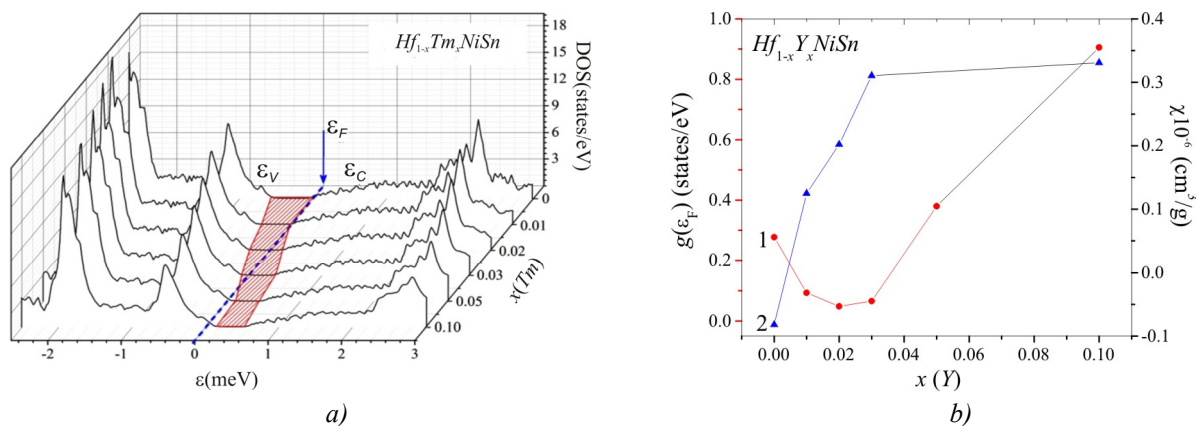

Fig. 2. Calculation of the electron density of states DOS (a) and density of states at Fermi level $g(\varepsilon_F)$
(curve 1) and change in the values of magnetic susceptibility χ (curve 2) (b) Hf₁₋ₓYₓNiSn.

The predicted behaviour of Fermi level ε_F is accompanied by interesting behavior of the density of states at Fermi level $g(\varepsilon_F)$ (Fig. 2*b*). Thus, doping of *n-HfNiSn* with acceptor impurity *Y* leads, as expected, to density of states reduction at Fermi level, and minimum dependence $g(\varepsilon_F)$ corresponds at ($x \approx 0.025$) to crossing by Fermi level ε_F of the midgap ε_g of *Hf₁₋ₓYₓNiSn*. At *Y* concentrations, when Fermi level ε_F will cross the midgap and will be approaching the valence band ε_V, the density of states at Fermi level will increase in a predictable fashion.

The above results of calculations of a change in the density of state at Fermi level $g(\varepsilon_F)$ agree with the results of experimental measurements of magnetic susceptibility of χ *Hf₁₋ₓYₓNiSn* (Fig. 2*b*, curve 2). The research has shown that samples of *Hf₁₋ₓYₓNiSn*, $x > 0.01$, are Pauli paramagnetics, where the magnetic susceptibility is defined exceptionally by electron gas in proportion to density of states at Fermi level. As can be seen from Fig. 2*b*, dependence $\chi(x)$ at $x > 0.03$ drastically changes the slope and achieves plateau, which we attribute, according to calculations, exactly to a change in the density of states at Fermi level $g(\varepsilon_F)$ when crossing of valence band by Fermi level. Note that *n-HfNiSn* semiconductor is not Pauli paramagnetic, but a weak diamagnetic, as testified by the negative values of magnetic susceptibility: $\chi(x = 0) = -0.082$ cm³/g [4]. So, supposedly, the growth of dependence $\chi(x)$ in the concentration area $x = 0 \div 0.01$ cannot be attributable to increase in the density of states at Fermi level.

Calculation of the electronic structure of *Hf₁₋ₓYₓNiSn* allows predicting its characteristics, in particular, the Seebeck coefficient, the electric resistivity, etc. To calculate the Seebeck coefficient α, use was made of ratio [9] as a working formula [9]:

$$\alpha = \frac{2\pi^2}{3}\frac{k^2 T}{e}\left(\frac{d}{d\varepsilon}\ln g(\varepsilon_F)\right) ,$$

where $g(\varepsilon_F)$ is density of states at Fermi level. As an example, Fig. 3 shows a change in the values of the Seebeck coefficient $\alpha(x)$ of *Hf₁₋ₓYₓNiSn* at different temperatures. It is seen that at different

concentrations of *Y* one can get in thermoelectric material high positive and negative values of the Seebeck coefficient and conductivity, which is one of the reasons for obtaining high thermoelectric figure of merit values.
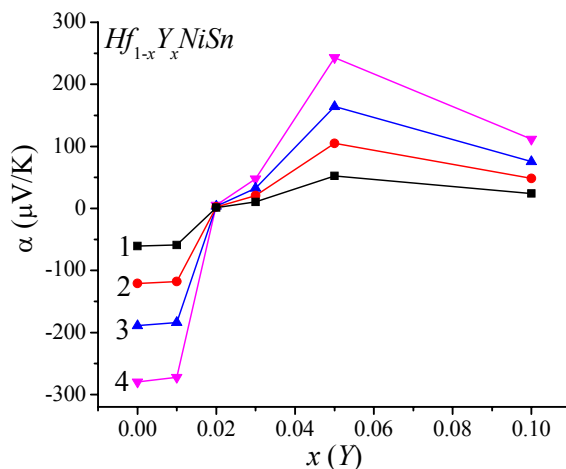

Fig. 3.Calculation of the change in the Seebeck coefficient of Hf₁₋ₓYₓNiSn
at temperatures: 1 – 80; 2 – 160; 3 – 250; 4 – 380 K.

Thus, the results of calculation of the electron density of states of $Hf_{1-x}Y_xNiSn$ based on the results of structural research prove the predicted acceptor nature of structural defects. The results of experimental investigations given below will show correspondence of calculated results to real processes in thermoelectric material.

Research on the electrokinetic and energy characteristics of $Hf_{1-x}Y_xNiSn$

The temperature dependences of resistivity $\ln\rho(1/T)$ and the Seebeck coefficient $\alpha(1/T)$ for $Hf_{1-x}Y_xNiSn$, $x = 0 \div 0.30$, are typical for semiconductors (Fig. 4) and vary in conformity with the results of calculation of density of states distribution. We can see that in $Hf_{1-x}Y_xNiSn$, $x = 0 \div 0.10$ samples, on the $\ln\rho(1/T)$ dependences there are high-temperature activation areas, which points to arrangement of Fermi level ε_F in the energy gap, from where charge carriers are activated from continuous energy band. Thus, the negative values of the Seebeck coefficient at $x = 0$ are understandable and related to "a priori doping" of base *n-HfNiSn* semiconductor with donors (position of *Hf* atoms up to ~1% is occupied with *Ni* atoms) [8].

In turn, the negative values of the Seebeck coefficient for the case of $x = 0.01$ (Fig. 4, 5*b*) testify that concentration of generated defects of acceptor nature with substitution of *Hf* atoms by *Y* atoms is lower than concentration of defects of donor nature due to disordered structure of *HfNiSn* compound, hence, the Fermi level ε_F is arranged on the impurity donor band and closer to conduction band.

For cases of $Hf_{1-x}Y_xNiSn$, $x = 0.02 \div 0.10$, the positive values of the Seebeck coefficient indicate that concentration of defects of acceptor nature has exceeded that of donor nature, and Fermi level ε_F is now fixed on the impurity acceptor band generated in a crystal as a result of substitution of *Hf* atoms by *Y*. High-temperature activation area on $\ln\rho(1/T)$ dependences reflects thermal ejection of holes from acceptor to valence band, which is accompanied by increase in the number of free holes. Instead, the metallic variation of $\ln\rho(1/T)$ dependence and positive coefficient values for $Hf_{1-x}Y_xNiSn$, $x = 0.30$, testify that Fermi level ε_F has crossed the valence band ceiling, as was predicted by calculations of electron structure of $Hf_{1-x}Y_xNiSn$, namely, dielectric-metal transition has occurred [9]. In so doing, it

must be understood that *Hf$_{1-x}$Y$_x$NiSn*, $x = 0.30$ sample will continue to be a semiconductor, and the mechanism of activation conduction in the investigated temperature range is absent due to the entrance of Fermi level ε_F into valence band.

At first sight, the behaviour of $\rho(x)$ dependence in the area of $x = 0 \div 0.10$ (Fig. 5*a*) is somewhat contradictory. Thus, introduction into *HfNiSn* compound of the lowest in experiment concentration of *Y* atoms is attended with a drastic decrease in the electric resistivity values, for instance, at 160 K, from the values of $\rho(x = 0) = 487.2$ μΩ·m to $\rho(x = 0.01) = 121.1$ μΩ·m.
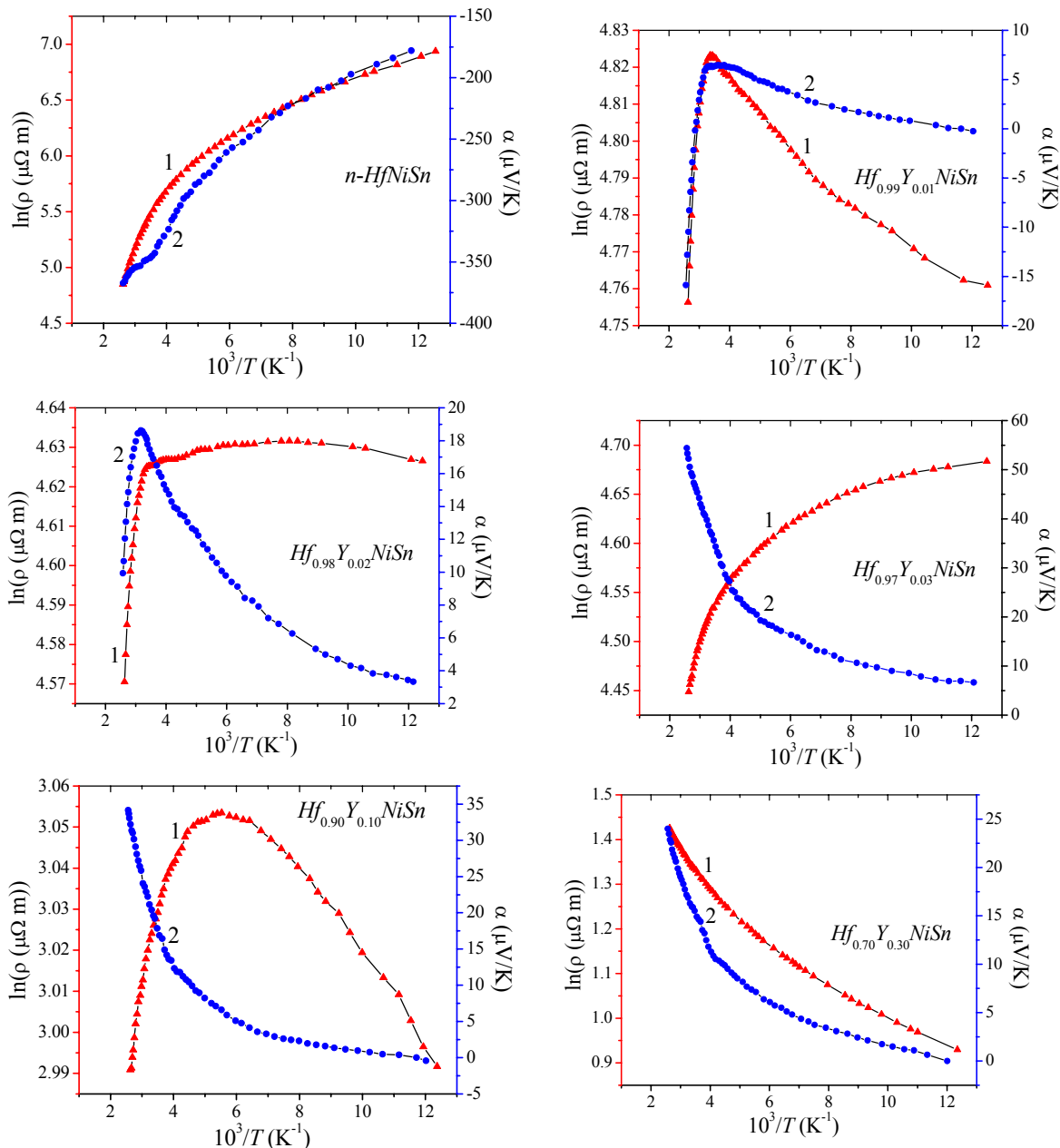

Fig. 4. Temperature dependences of the electrical resistivity and the Seebeck coefficient of Hf$_{1-x}$Y$_x$NiSn.

The point is that the concentration of acceptors generated in *Hf$_{1-x}$Y$_x$NiSn* on introducing the lowest concentration of *Y* ($x = 0.01$) is too high, and we jump over the concentration gap whereby

Fermi level ε_F would move from conduction band edge to the midgap, which would be accompanied by growth of electric resistivity values due to reduction of density of states at Fermi level $g(\varepsilon_F)$ in the n-type semiconductor doped with acceptors. Thus, with the lowest concentration of acceptor impurity Y ($x = 0.01$) the values of the Seebeck coefficient become positive. For instance, the values of the Seebeck coefficient at 160 K vary from $\alpha(x = 0) = -252.5$ μVK^{-1} to $\alpha(x = 0.01) = 3.4$ μVK^{-1}, which points to increase in the concentration of holes as Fermi level ε_F approaches valence band. That is, in $Hf_{1-x}Y_xNiSn$, $x = 0.01$, the concentration of acceptors is sufficient to change the type of semiconductor conductivity.
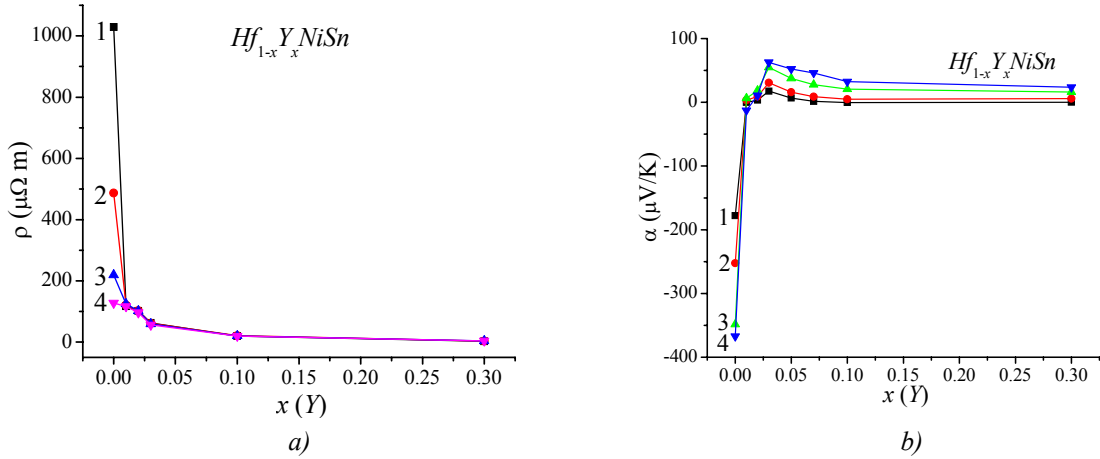

Fig. 5. Change in the values of electric resistivity $\rho(x)$ (a) and the Seebeck coefficient $\alpha(x)$
(b) of Hf$_{1-x}$Y$_x$NiSn at temperatures: 1 – 80 K; 2 – 160 K; 3 – 250 K; 4 – 380 K.

In this context it is interesting to trace the character of change in the energy characteristics of $Hf_{1-x}Y_xNiSn$ obtained from the experimental investigations (Fig. 6), which also allow for the conclusion that introduction of Y impurity atoms into the structure of $HfNiSn$ compound is accompanied by generation of structural defects of acceptor-like nature. From the activation areas of dependences $\ln\rho(1/T)$ (Fig. 4) the values of activation energies were calculated from Fermi level ε_F to percolation level of conduction band $\varepsilon_1^\rho(x)$, and from the activation areas of dependences $\alpha(1/T)$ (Fig. 4) – the values of activation energies $\varepsilon_1^\alpha(x)$ that yield the values of modulation amplitude of continuous energy bands [4].
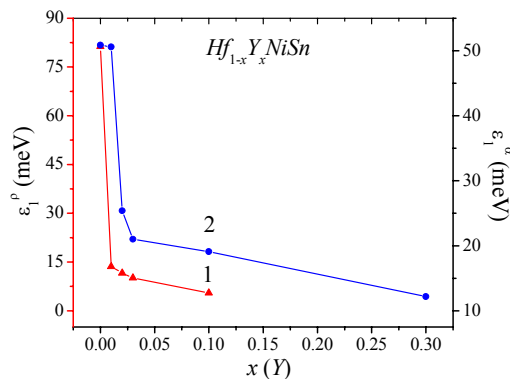

Fig. 6. Change in activation energies $\varepsilon_1^\rho(x)$ (1) and $\varepsilon_1^\alpha(x)$ (2) of Hf$_{1-x}$Y$_x$NiSn.

From Fig. 6 it is evident that doping of semiconductor results in the reduction of activation energy у $\varepsilon_1^\rho(x)$. It is important to explain that the value of energy $\varepsilon_1^\rho(x)$ for *n-HfNiSn* reflects the energy gap between the position of Fermi level ε_F and conduction band edge. At the same time, the

values of activation energy $\varepsilon_1^\rho(x)$ for the lowest and all subsequent concentrations of Y atoms reflect the energy gap between the position of ε_F and conduction band edge. From the almost linear behaviour of $\varepsilon_1^\rho(x)$ in the concentration area $x = 0.01 \div 0.10$ one can estimate the velocity of Fermi level ε_F motion to valence band edge: $\Delta\varepsilon_F/\Delta x \approx 0.9$ meV/% Y. This result is quite logical, as long as we increase the concentration of impurity Y by the linear law, which by the same law generates structural defects of acceptor nature in $Hf_{1-x}Y_xNiSn$ crystal.

A change in the values of activation energy $\varepsilon_1^\alpha(x)$ proportional to modulation amplitude of continuous energy bands in $Hf_{1-x}Y_xNiSn$ seems to be interesting. From Fig. 6 it is seen that in the case of undoped n-$HfNiSn$ semiconductor the modulation amplitude is $\varepsilon_1^\alpha(x=0) = 50.9$ meV, and introduction into n-type semiconductor of the lowest in experiment concentration of Y impurity practically does not change the semiconductor compensation ratio, as indicated by the modulation amplitude $\varepsilon_1^\alpha(x=0.01) = 50.6$ meV. This result would be discrepant, if it were not for the change in the type of majority carriers. However, as shown above, the concentration of Y $x = 0.01$ is sufficient for semiconductor overcompensation, hence the proximity of values $\varepsilon_1^\alpha(x=0) = 50.9$ meV and $\varepsilon_1^\alpha(x=0.01) = 50.6$ meV is of random character.

Adding to now p-type $Hf_{1-x}Y_xNiSn$, $x = 0.01$ semiconductor of Y acceptor impurity naturally changes compensation ratio, that is, the difference in the number of ionized acceptors and donors will increase. This effect is manifested in the reduction of modulation amplitude values to $\varepsilon_1^\alpha(x=0.02) = 25.4$ meV. It is clear that further doping of p-type semiconductor with acceptor impurity will only reduce the compensation ratio, and the values of modulation amplitude of continuous energy bands $\varepsilon_1^\alpha(x)$ will be reduced either (Fig. 6).

Conclusions

Thus, as a result of integrated research on the crystalline and electron structures, the kinetic and magnetic characteristics of Y-doped n-$HfNiSn$ intermetallic semiconductor, the mechanisms of generation of only structural defects of acceptor nature have been revealed, that change compensation ratio and determine electric conduction mechanisms. The investigated $Hf_{1-x}Y_xNiSn$ solid solution is a promising thermoelectric material, and ordered crystalline structure is a guarantee of stability and reproducibility of characteristics.

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