V.A.Romaka[1,2], P.F.Rogl[3], L.P.Romaka[4], V.Ya.Krayovskyy[2], Yu.V.Stadnyk[4], D.Kaczorowski[5], A.M.Horyn[4]

[1]Ya. Pidstryhach Institute for Applied Problems of Mechanics and Mathematics, the National Academy of Sciences of Ukraine, 3-b, Naukova Str., Lviv, 79060, Ukraine;
[2]National University "Lvivska Politechnika", 12, S. Bandera Str., Lviv, 79013, Ukraine;
[3]Universität Wien, 42, Währinger Str., Wien, A-1090, Österreich;
[4]Ivan Franko National University of Lviv, 6, Kyryla and Mefodiya Str., Lviv, 79005, Ukraine;
[5]W. Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences, 2, Okolna Str., Wroclaw, 50 – 422, Poland

RESEARCH ON THE FEATURES OF CONDUCTION MECHANISMS IN $Hf_{1-x}Tm_xNiSn$ THERMOELECTRIC MATERIAL

The crystal and electronic structures, the temperature and concentration dependencies of resistivity and the Seebeck coefficient of $Hf_{1-x}Tm_xNiSn$ thermoelectric material were studied in the range $T = 80 \div 400$ K, $x = 0.01 \div 0.30$. The mechanisms for the simultaneous generation in a crystal of the acceptor and donor structural defects which change the compensation ratio of semiconductor material and determine conduction mechanisms in $Hf_{1-x}Tm_xNiSn$ were established.
***Keywords**: electronic structure, resistivity, the Seebeck coefficient.*

Introduction

This paper presents the results of research on $Hf_{1-x}Tm_xNiSn$ thermoelectric material obtained by heavy doping of *n - HfNiSn* semiconductor with the atoms of rare-earth *Tm* metal introduced by *Hf* substitution. Doping was performed for optimization of thermoelectric material parameters in order to obtain maximum values of thermoelectric figure of merit Z ($Z = \alpha^2 \cdot \sigma/\kappa$, where α is the Seebeck coefficient, σ is electric conductivity, κ is thermal conductivity) [1]. This motivated a research on the effect of *Tm* doping impurity on the change in structural, energy and kinetic characteristics of $Hf_{1-x}Tm_xNiSn$ thermoelectric material that allowed revealing the features of its conduction mechanisms.

The interest in thermoelectric materials based on intermetallic semiconductors, in particular, *n - HfNiSn*, *n - ZrNiSn* and *n - TiNiSn*, is aroused by the high values of electric conductivity and the Seebeck coefficient [2, 3], as well as by reproducibility of characteristics up to $T \approx 1300$ K [4], assuring high efficiency of thermal into electric energy conversion in a wide temperature range. All the above mentioned makes intermetallic semiconductors one of the most extensively studied and promising thermoelectric materials [5 – 8].

Investigation procedures

The object to be investigated included crystalline structure, electronic density distribution (DOS), the electrokinetic and energy characteristics of $Hf_{1-x}Tm_xNiSn$. 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, $CuK\alpha_1$), and Fullprof program [9] was employed for the calculation of structural characteristics. The chemical and phase compositions of the 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) [10] with the use of Moruzzi-Janak-Williams exchange-correlation potential [11]. 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 in the temperature range $T = 80 \div 400$ K, in the samples of $Hf_{1-x}Tm_xNiSn$, $x = 0.01 \div 0.10$ ($N_A^{Tm} \approx 1.9 \cdot 10^{20}$ см$^{-3} \div 1.9 \cdot 10^{21}$ см$^{-3}$).

Research on the crystalline and electronic structures of $Hf_{1-x}Tm_xNiSn$

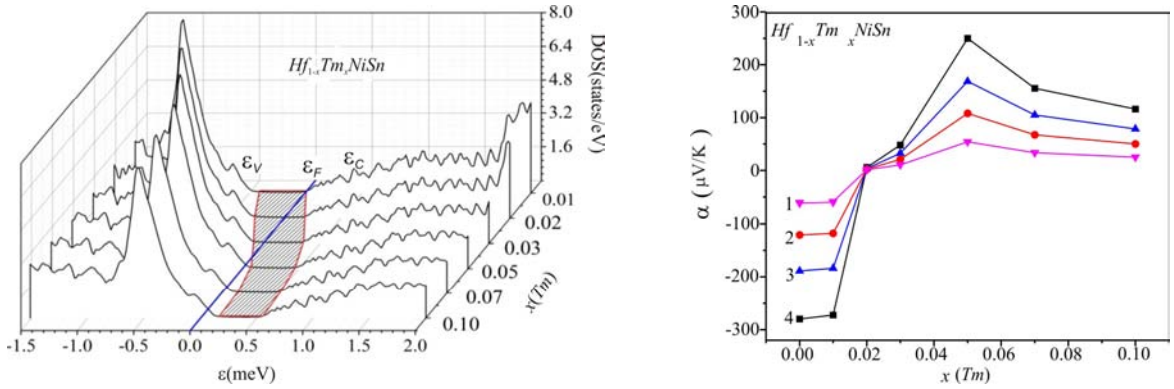
A microprobe analysis of the concentration of atoms on the surface of $Hf_{1-x}Tm_xNiSn$, $x = 0 \div 0.10$, samples has shown their conformity to the initial charge compositions, and X-ray phase and structural analyses have revealed no traces of other phases in the samples. Refinement of $Hf_{1-x}Tm_xNiSn$ crystalline structure by the powder method has confirmed the result of [8] as regards crystal structure disorder of *n - HfNiSn*, the key point of which lies in a partial, up to ~1%, occupancy by *Ni* atoms of the crystallographic position 4*a* of *Hf* atoms, and the semiconductor formula can be written as $(Hf_{1-y}Ni_y)NiSn$, $y \le 0.01$. If it is remembered that *Ni* ($3d^8 4s^2$) atom possesses a larger number of *d*-electrons than *Hf* ($5d^2 6s^2$) atom, a structural defect of the donor nature is created in a crystal ("a priori" doping with donors [3]), and electrons are the majority carriers.

On the other hand, crystalline structure refinement of $Hf_{1-x}Tm_xNiSn$, $x = 0.01 \div 0.10$, samples has shown that introduction of *Tm* atoms puts into order crystalline structure ("heals" structural defects), and *Ni* atoms leave the position of *Hf* (4*a*) atoms. Ordering of $Hf_{1-x}Tm_xNiSn$ structure makes it resistant, and the kinetic characteristics become reproducible during thermocycling. Besides, ordering contributes to the redistribution of the electronic density of states. If in *n - HfNiSn* there exist structural defects of the donor nature as a result of displacement of up to ~1% of *Hf* atoms by *Ni* atoms [8], then ordering of $Hf_{1-x}Tm_xNiSn$ structure is accompanied 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 *Tm* ($4f^{13}5d^0 6s^2$) atom has two 5*d* – electrons less than *Hf* atom, structural defects of the acceptor nature are generated in the crystal.

Thus, in $Hf_{1-x}Tm_xNiSn$, $x = 0 \div 0.01$, 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 (*Tm* atoms occupy the position of *Hf* atoms). In this case, doping of n - *HfNiSn* semiconductor with the lowest concentrations of acceptor impurity ($0 < x \le 0.02$) will increase the compensation ratio (the ratio between donors and acceptors) [3, 12]. 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 must change and the compensation ratio will decrease. [2, 3].

The electronic structure of $Hf_{1-x}Tm_xNiSn$, $x = 0 \div 0.01$, was calculated for simulation of electric conductivity mechanisms, the Fermi level behaviour, the energy gap of semiconductor. As long as doping of *n - HfNiSn* with *Tm* atoms puts into order crystalline structure, calculation of the electronic density of states was done for the case of ordered structure version (Fig. 1*a*).

On introducing into *n-HfNiSn* of minimum attainable in experiment concentrations of *Tm* impurity, the Fermi level ε_F starts drifting from the conduction band ε_C, spaced ~ 81.3 meV from it [8], to the midgap ε_g (dashed line in Fig. 1*a*) at $x \approx 0.02$ and then to the valence band, to cross it at $x \approx 0.04$.



a) *b)*

Fig. 1. Calculation of the electronic density of states DOS (a) and a change in the values of the Seebeck coefficient (b) of $Hf_{1-x}Tm_xNiSn$ at the temperatures: 1 – 80; 2 – 160; 3 – 250; 4 – 380 K

The drift of ε_F from the conduction band edge ε_C to the valence band ε_V also means a change in the ratio of $Hf_{1-x}Tm_xNiSn$ majority carriers. Thus, for the concentrations of $Hf_{1-x}Tm_xNiSn$, $x < 0.02$, when the Fermi level ε_F is between the conduction band ε_C and the midgap ε_g, electrons are the majority carriers. Conversely, at $x > 0.02$ and right up to crossing by the Fermi level of the valence band, holes are the majority carriers. Besides, crossing of the valence band by the Fermi level ε_F will also cause a change from the activation to metal conduction mechanism (the dielectric-metal transition which is referred to as the Anderson transition [12]).

Calculation of $Hf_{1-x}Tm_xNiSn$ electronic structure allows predicting the kinetic characteristics of thermoelectric material, in particular, the behaviour of the Seebeck coefficient $\alpha(x,T)$ at different temperatures (Fig. 1*b*). Below is given the working formula used for the calculation of $\alpha(x,T)$ [12]:

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

where $g(\varepsilon_F)$ is density of states at the Fermi level. From Fig. 1*b* it is seen that at different concentrations of *Tm* one can obtain in thermoelectric material high values of the Seebeck coefficient of both signs, as well as of the electric conductivity, assuring high values of thermoelectric figure of merit [1].

Thus, the results of calculation of the electronic density of states of $Hf_{1-x}Tm_xNiSn$, based on structural research data, prove only the acceptor nature of structural defects generated in a crystal. The results of research on the kinetic characteristics of $Hf_{1-x}Tm_xNiSn$ will show the degree of conformity of such calculations to real processes occurring in material.

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

The temperature dependences of resistivity $\ln\rho(1/T)$ and the Seebeck coefficient $\alpha(1/T)$ for $Hf_{1-x}Tm_xNiSn$, $x = 0 \div 0.10$, presented in Fig. 2, are typical for heavily doped and compensated semiconductors with several activation areas, which is indicative of several conduction mechanisms [12]. From the high-temperature activation areas of $\ln\rho(1/T)$ dependences the activation energy from the Fermi level ε_F to the bands of continuous energies ε_1^{ρ} was calculated, and from the same

$\alpha(1/T)$ dependences – the activation energies ε_1^{α} yielding the value of modulation amplitude of continuous energy bands for heavily doped compensated semiconductors [3, 12].

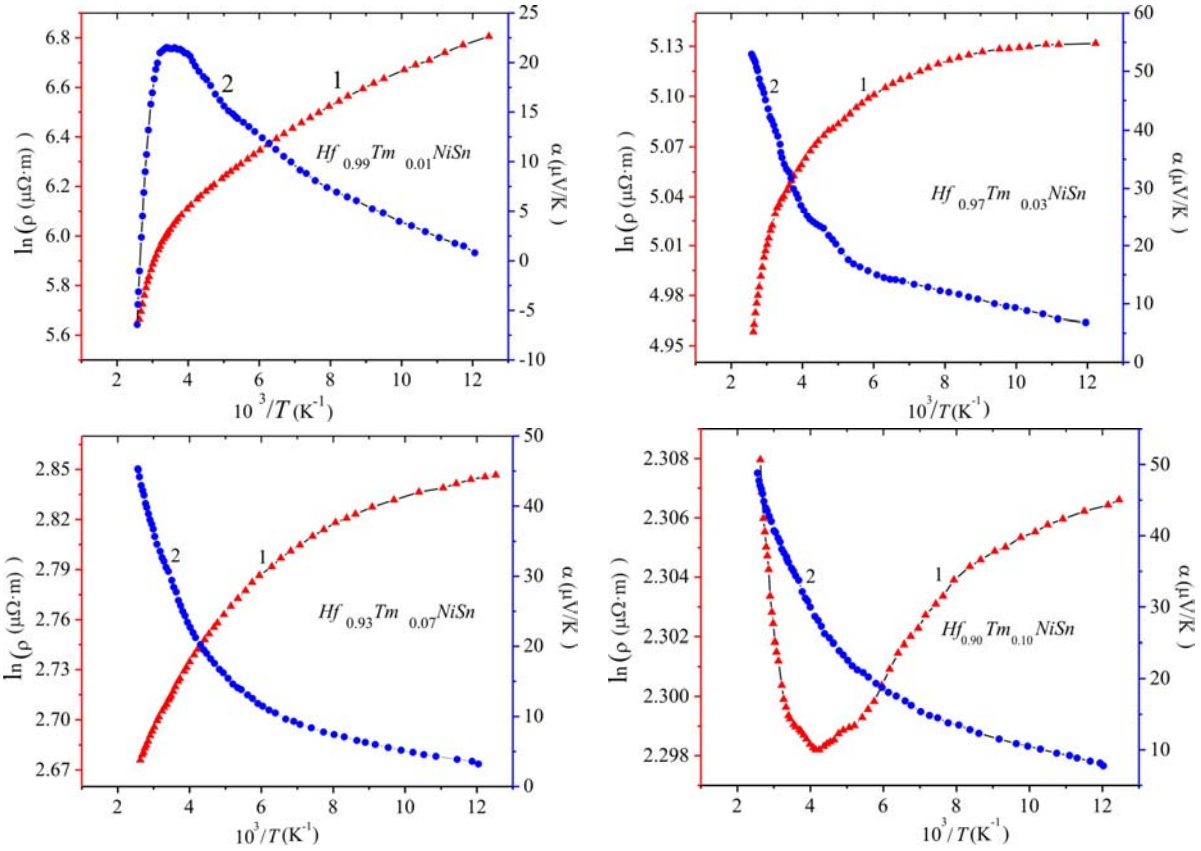
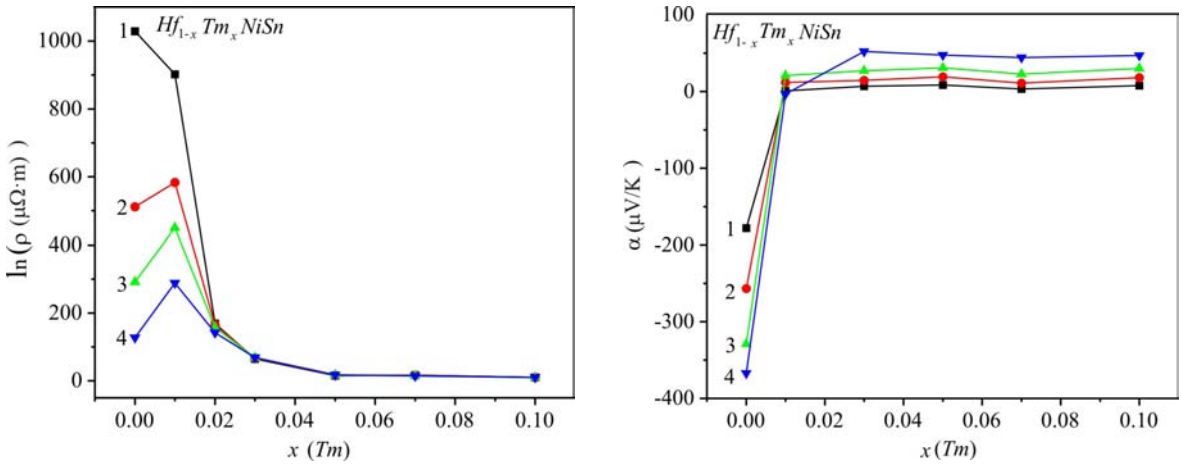


Fig. 2. Temperature dependences of the electric resistivity and the Seebeck coefficient of $Hf_{1-x}Tm_xNiSn$

The presence on the dependences $\ln\rho(1/T)$ for $Hf_{1-x}Tm_xNiSn$, $x = 0 \div 0.07$, of high-temperature activation areas points to the arrangement of the Fermi level ε_F in the energy gap. The result obtained contradicts to the results of calculations of DOS (Fig. 1*a*) which predicted crossing by the Fermi level ε_F of the valence band at concentration *Tm* $x \approx 0.04$ and the dielectric-metal conduction transition [12].For $Hf_{1-x}Tm_xNiSn$, $x = 0.10$ the activation area on $\ln\rho(1/T)$ is present only at low temperatures, pointing to hopping conduction mechanism in the impurity acceptor band.

The negative values of the Seebeck coefficient of *n - HfNiSn* 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]. Whereas in the sample of $Hf_{1-x}Tm_xNiSn$, $x = 0.01$, the concentration of *Tm* acceptor impurity corresponds to concentration of donors available in *n - HfNiSn* ("a priori doping" [3]) and the state close to full compensation is realized, when the Fermi level must be located near the midgap ε_g. Thus, the positive values of the Seebeck coefficient at low temperatures (Fig. 2, 3) indicate that concentration of generated acceptors with substitution of *Hf* atoms by *Tm* atoms exceeds the number of defects caused by disordered structure of *HfNiSn*, hence the Fermi level ε_F is fixed by impurity acceptor band (close to the valence band). However, at $T = 380$ K the sign of the Seebeck coefficient of $Hf_{1-x}Tm_xNiSn$, $x = 0.01$ (Fig. 3*b*) remains negative: $\alpha(x = 0.01) = -3.13$ μVK^{-1}. Obviously, the number of ionized donors and acceptors changes with temperature [13]. An extreme point on $\alpha(1/T)$ dependence for the sample of $Hf_{1-x}Tm_xNiSn$, $x = 0.01$, at $T \approx 270$ K reflects

crossing by the Fermi level of the midgap and a drift back to conduction band. It turns out that in $Hf_{1-x}Tm_xNiSn$, x = 0.01, the concentration of donors exceeds that of acceptors, though they have to be equal. It can be assumed that donors are also generated in a crystal by the mechanism which is yet unknown.



a) *b)*

Fig. 3. Change in the values of electric resistivity ρ(x) (a) and the Seebeck coefficient α(x) (b) of $Hf_{1-x}Tm_xNiSn$ at the temperatures: 1 – 80; 2 – 160; 3 – 250; 4 – 380 K

From the character of change in the values of resistivity ρ(*x*) $Hf_{1-x}Tm_xNiSn$, $x = 0 \div 0.01$, at different temperatures (Fig. 3*a*) one can see the above described structural feature of semiconductor which accounts for a simultaneous reduction of free electrons by two mechanisms: (1) – decreasing the number of donors, when *Ni* atoms leave position 4*a* of *Hf* atoms("healing" of donor-nature defects) and (2) – freezing out of free electrons to acceptor band generated at occupation by *Tm* atoms of the position of *Hf* atoms. Thus, introduction of the lowest concentration of *Tm* (x = 0.01) at the temperature of 80 K is accompanied by a reduction in the electric resistivity values from $\rho(x=0)=1029.1$ μΩ·m до $\rho(x=0.01)=902.32$ μΩ·m and $\rho(x=0.03)=169.31$ μΩ·m. With a lower concentration of introduced acceptors or a larger concentration of free electrons we would have observed growth of ρ(*x*) values due to a reduction in the number of free electrons in *n* - type semiconductor at doping with acceptors. We however immediately get a *p* - type semiconductor. On the other hand, a maximum on dependence ρ(*x*) of $Hf_{1-x}Tm_xNiSn$, $x \geq 0.01$, at temperatures $T \geq 160$ K (Fig. 3*a*) shows that the Fermi level ε_F drifts to the midgap ε_g, which is accompanied by a reduction in the number of free electrons by the hitherto unknown mechanism that changes the semiconductor compensation ratio.

For the cases of $Hf_{1-x}Tm_xNiSn$, $x = 0.02 \div 0.10$, the positive values of the Seebeck coefficient at low temperatures indicate that the concentration of acceptor defects generated in a crystal is greater than that of donor defects, and the Fermi level ε_F is fixed on the impurity acceptor band. The proof of the fact that the Fermi level ε_F drifts in the direction of $Hf_{1-x}Tm_xNiSn$ valence band is the behaviour of the Seebeck coefficient α(*x*) (Fig. 3*b*). Thus, the Seebeck coefficient at 80 K changes from the values of $\alpha(x=0)=-178.1$ μVK^{-1} to $\alpha(x=0.01)=0.82$ μVK^{-1} and $\alpha(x=0.03)=6.82$ μVK^{-1}, which testifies to a change in the type of majority carriers from electrons, at x = 0, to holes, at $x \geq 0.01$.

Now, the high-temperature activation area on dependences $\ln\rho(1/T)$ of $Hf_{1-x}Tm_xNiSn$, $x = 0.02 \div 0.10$ (Fig. 2) is a manifestation of thermal flow of holes from the Fermi level which is fixed by acceptor band to the valence band, increasing the number of free holes. Instead, the

metallic dependence $\ln\rho(1/T)$ at high temperatures and the positive values of the Seebeck coefficient for $Hf_{1-x}Tm_xNiSn$, $x = 0.10$, testify that the Fermi level ε_F has crossed the valence band ceiling, i.e. the dielectric–metal conduction transition has taken place [12]. In so doing, at $T < 250$ K, the hopping conduction mechanism shows that the Fermi level ε_F leaves the valence band for the energy gap. This is possible only on condition of donors appearing in a semiconductor by the hitherto unknown mechanism which compensate the introduced acceptors and force the Fermi level ε_F to leave the valence band.

In this context it is interesting to trace the character of change in the energy characteristics of $Hf_{1-x}Tm_xNiSn$ obtained from the experimental investigations. From Fig. 4 it is seen that in $Hf_{1-x}Tm_xNiSn$ with increasing concentration of acceptors there is a reduction in the values of activation energy $\varepsilon_1^{\rho}(x)$. It is important to explain that the value of energy $\varepsilon_1^{\rho}(x)$ for the undoped semiconductor *n-HfNiSn* represents the energy gap between the position of the Fermi level ε_F and the conduction band edge. At the same time, the values of activation energy $\varepsilon_1^{\rho}(x)$ for the lowest and all subsequent concentrations of *Tm* atoms represent the energy gap between ε_F and the valence band edge. The fact that the value of activation energy $\varepsilon_1^{\rho}(x=0)$ falls on dependence $\varepsilon_1^{\rho}(x)$ is quite accidental.

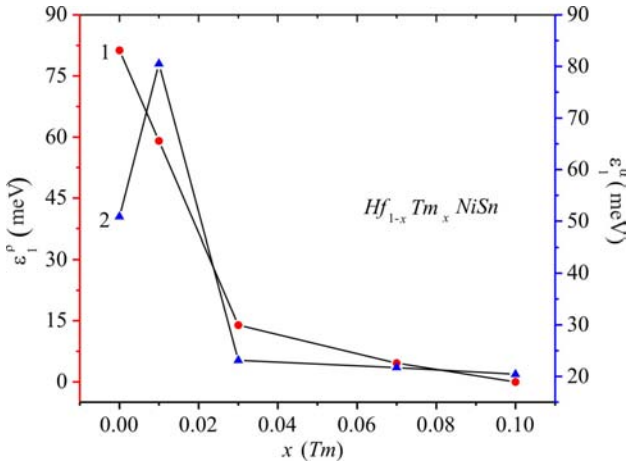


Fig. 4. Change in the values of activation energy $\varepsilon_1^{\rho}(x)$ (1) and $\varepsilon_1^{\alpha}(x)$ (2) of $Hf_{1-x}Tm_xNiSn$

An assumption of the simultaneous generation in $Hf_{1-x}Tm_xNiSn$, in addition to acceptors, of unknown structural defects of the donor nature is substantiated when analyzing the drift rate of the Fermi level. If we compare the drift rate of the Fermi level ε_F to the valence band, obtained both from the calculations of DOS (Fig. 1*a*), when only acceptor structural defects are generated in a crystal, and from the experimental investigations (Fig. 4), in the experiment it is less by a factor of ~ 2.5. What might "impede" this drift?

As long as the position of the Fermi level ε_F determines the ratio between donors and acceptors (compensation ratio), an obvious conclusion offers itself again that in $Hf_{1-x}Tm_xNiSn$ not only acceptor structural defects are generated, but also donors of unknown mechanism which "impede" the drift of the Fermi level ε_F towards the valence band.

Moreover, from the behaviour of $\varepsilon_1^{\rho}(x)$ (Fig. 4) it is obvious that in the area of *Tm* impurity concentration $x = 0 \div 0.03$ the drift rate of the Fermi level ε_F to the valence band edge is $\Delta\varepsilon_F / \Delta x = 22.6$ meV/% *Tm*, and in the area of $x = 0.03 \div 0.10$ – $\Delta\varepsilon_F / \Delta x = 2.3$ meV/% *Tm*.

At first sight, the result obtained seems to be illogical. As long as the concentration of *Tm* acceptor impurity is increased according to linear law, structural defects of the acceptor nature would have to be generated in a crystal in similar fashion. In such a case, why the Fermi level does not drift to the valence band edge according to the same law? What is it that again "impedes" this motion, reducing the drift rate of the Fermi level ε_F? This can occur only on condition when in $Hf_{1-x}Tm_xNiSn$, in addition to acceptors, there are donors generated by unknown mechanism, their generation rate increasing with *Tm* concentration growth.

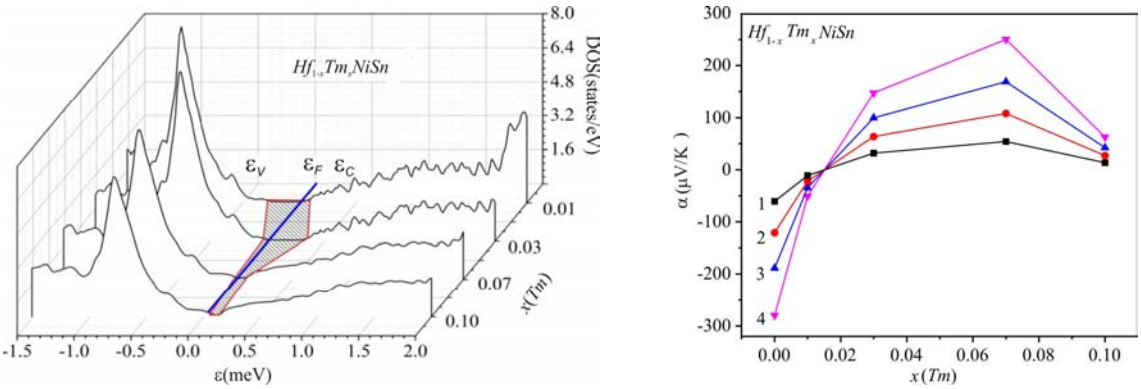
The simultaneous generation in a crystal of the donor and acceptor structural defects with different rate is accompanied by a change in the compensation ratio, as well a change in the modulation amplitude of continuous energy bands of heavily doped compensated semiconductors [3, 12] according to the law reflecting the ratio between ionized acceptors and donors. Fig. 4 shows a change in the values of activation energy $\varepsilon_1^{\alpha}(x)$, proportional to the modulation amplitude of continuous energy bands of $Hf_{1-x}Tm_xNiSn$. It can be seen that in the case of *n* - *HfNiSn* the modulation amplitude is $\varepsilon_1^{\alpha}(x=0)=50.9$ meV. Introduction into *n*-type semiconductor of the least in the experiment concentration of *Tm* impurity corresponding to composition $x = 0.01$, is accompanied by a drastic increase in the compensation ratio, as indicated by the modulation amplitude $\varepsilon_1^{\alpha}(x=0.01)=80.5$ meV. Moreover, at concentration $x = 0.01$ the type of semiconductor conduction is changed, i.e. holes become the majority carriers.

Doping of now semiconductor *p* - $Hf_{1-x}Tm_xNiSn$, $x = 0.01$ with *Tm* acceptor impurity reduces the compensation degree, that is, the difference in the number of ionized acceptors and donors will increase, which is manifested in the reduction of modulation amplitude values $\varepsilon_1^{\alpha}(x=0.03)=23.1$ meV, and on the dependence $\varepsilon_1^{\alpha}(x)$ there will appear a maximum. 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 will be reduced as well (Fig. 4). Taking into account that in experiment the concentration of acceptors is linearly increased in a semiconductor where holes are majority carriers, it would be logical to expect the same reduction in the modulation amplitude values of $Hf_{1-x}Tm_xNiSn$ continuous energy bands. However, a change in the values of dependence $\varepsilon_1^{\alpha}(x)$ (Fig. 4) for the cases of $x > 0.01$ reminds a change in the values of $\varepsilon_1^{\rho}(x)$, which can testify to the simultaneous generation in a crystal of acceptors and donors by unknown mechanism.

Thus, the results of kinetic investigations of $Hf_{1-x}Tm_xNiSn$ enable us to speak of a complicated mechanism for the simultaneous generation in a crystal of the acceptor and donor structural defects on introducing the atoms of rare-earth *Tm* metal into the structure of *HfNiSn* compound by substitution of *Hf* atoms. Note that no such defects have been revealed by structural investigations, as long as their concentration is beyond the accuracy of X-ray investigation methods.

For the identification of defects that determine conduction mechanism of $Hf_{1-x}Tm_xNiSn$ thermoelectric material, the following method proposed in [3] was employed. The electronic structure of $Hf_{1-x}Tm_xNiSn$ was calculated for different variants of atoms arrangement in the unit cell sites and for a different degree of occupancy of crystallographic positions of all atoms by proper or foreign atoms. In so doing, the drift rate of the Fermi level ε_F was "tied" to the numerical values of activation energy ε_1^{ρ} from the Fermi level ε_F to the valence band edge of $Hf_{1-x}Tm_xNiSn$, and the compensation ratio was sought for to assure the experimentally established drift rate of the Fermi level (Fig. 4, curve 1). It turned out that the most acceptable version of atoms arrangement provides

for the emergence of vacancies in position (4*b*) of *Sn* atoms, whose concentration grows with increase in the number of *Tm* atoms. Based on the new results of the spatial arrangement of atoms in $Hf_{1-x}Tm_xNiSn$ crystalline structure, more refined calculations were made of the electronic density of states distribution and, specifically, the density of states at the Fermi level $g(\varepsilon_F)$, as well as the Seebeck coefficient at different temperatures (Fig. 5) that are in complete agreement with the results of experimental investigations.



a) *b)*

Fig. 5. Refined calculation of the electronic density of states DOS (a) and a change in the values of the Seebeck coefficient (b) of $Hf_{1-x}Tm_xNiSn$ at the temperatures: 1 – 80; 2 – 160; 3 – 250; 4 – 380 K

Conclusions

Thus, as a result of integrated research on the structural, energy and kinetic characteristics of *n* - *HfNiSn* intermetallic semiconductor heavily doped with the atoms of rare-earth *Tm* metal, the mechanisms for the simultaneous generation in a crystal of structural defects of the acceptor and donor nature have been revealed that change the compensation ratio of thermoelectric material and determine the electric conduction mechanisms.

The work was performed in the framework of grants of the National Academy of Sciences and Ministry of Education and Science of Ukraine, № 0113U007687 and № 0114U005464.

References

1. L.I.Anatychuk, *Thermoelements and Thermoelectric Devices* (Kyiv: Naukova Dumka, 1979), 768 p.
2. V.A.Romaka, P.Rogl, V.V.Romaka, D.Kaczorowski, Yu.V.Stadnyk, R.O.Korzh, V.Ya.Krajovskii, and T.M.Kovbasyuk, Features of the Band Structure and Conduction Mechanisms of *n* - HfNiSn Semiconductor Heavily Lu-Doped, *Semiconductors* **49**(3), 290 – 297 (2014).
3. V.V.Romaka, L.P.Romaka, V.Ya.Krajovskii., and Yu.V.Stadnyk, *Rare-Earth and Transient Metal Stannides* (Lviv:Lvivska Polytechnika, 2015), 224 p.
4. V.A.Romaka, V.V.Romaka, and Yu.V.Stadnyk, *Intermetallic Semiconductors: Properties and Application* (Lviv:Lvivska Polytechnika, 2011), 488 p.
5. T.M.Tritt, M.A.Sabramanian, Thermoelectric Materials, Phenomena, and Applications: A Bird's Eye View, *MRS Bulletin* **31**(3), 188 – 198 (2006).
6. G.S.Nolas, J.Poon, and M.Kanatzidis, Recent Developments in Bulk Thermoelectric Materials, MRS Bulletin **31**(3), 199 – 205 (2006).
7. S.R.Culp, S.J.Poon, N.Hickman, T.M.Tritt, and J.Blumm, Effect of Substitutions on the

Thermoelectric Figure of Merit of Half-Heusler Phases at 800^0 C, *Appl. Phys. Letters* **88**(16), 042106 – 1 – 3 (2006).

8. V.V.Romaka, P.Rogl, L.Romaka, Yu.Stadnyk, A.Grytsiv, O.Lakh, and V.Krayovsky, Peculiarites of Structural disorder in Zr- and Hf- Containing Heusler and Half-Heusler Stannides, *Intermetallics* 35, 45 – 52 (2013).
9. T.Roisnel, J.Rodriguez-Carvajal, WinPLOTR: a Windows Tool for Powder Diffraction Patterns Analysis, *Mater. Sci. Forum, Proc. EPDIC7* 378-381, 118 – 123 (2001).
10. M.Schruter, H.Ebert, H.Akai, P.Entel, E.Hoffmann, and G.G.Reddy, First-Principles Investigations of Atomic Disorder Effects on Magnetic and Structural Instabilities in Transition-Metal Alloys, *Phys. Rev. B* **52**, 188 – 209 (1995).
11. V.L.Moruzzi, J.F.Janak, and A.R.Williams, *Calculated Electronic Properties of Metals* (NY: Pergamon Press, 1978), 348 p.
12. B.I.Shklovsky, *Electron Properties of Doped Semiconductors* (Moscow: Nauka, 1979), 416 p.

Submitted 27.12.2015.