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Investigation of Structural, Thermodynamic and Energy State Characteristics of the $ZrNi_{1-x}Rh_xSn$ Solid Solution

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The peculiarities of crystal and electronic structures, thermodynamic and energy state characteristics of the $ZrNi_{1-x}Rh_xSn$ semiconductive solid solution were investigated. It has been shown that in the ZrNiSn compound simultaneously exist two types of structural defects of the donor nature which generate two donor bands with different ionization energy in the band gap: a) the donor band ε_D^1, formed as a result of a partial, up to ~ 1 %, occupation of 4*a* position of Zr atoms by Ni atoms (mechanism of "a priori doping") and deep donor band ε_D^2, formed as a result of partial occupation of the tetrahedral voids by Ni atoms (Vac). The substitution in 4*c* position of the Ni atoms by Rh ones in $ZrNi_{1-x}Rh_xSn$ generates structural defects of acceptor nature and creates an impurity acceptor band ε_A in the band gap, which, in addition to the existence of ε_D^1 та ε_D^2 donor bands, makes semiconductor highly doped and strongly compensated. The obtained results allow to understand the mechanisms of electrical conductivity of thermoelectric materials based on *n*-ZrNiSn and the ways of conscious optimization of their characteristics for obtaining the maximum efficiency of conversion of thermal energy into electric.

Keywords: electrical conductivity, thermopower coefficient, Fermi level, electronic structure.

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Introduction

Investigation of electrokinetic and magnetic characteristics of thermoelectric material based on the $ZrNi_{1-x}Rh_xSn$ semiconductive solid solution revealed an interesting feature in the behavior of Fermi level ε_F depending on the concentration of Rh atoms and temperature [1]. These results allowed the authors to suggest that either donors of unknown origin with an ionization energy ε_D^2 higher than the acceptors ε_A are generated simultaneously with these acceptors ε_A and / or they are formed yet in ZrNiSn in a manner different from the mechanism of "a priori doping" [2]. As known, according to the mechanism of "a priori doping" [2], the structure of ZrNiSn (MgAgAs-type, space group $F\bar{4}3m$ [3]) is disordered as a result of partial, up to ~ 1 % ($z = 0.01$), occupation of 4*a* position of Zr atoms ($4d^25s^2$) by Ni ($3d^84s^2$) atoms, which generates the structural defects of donor nature and corresponding donor band ε_D^1 (Ni has more ***d***-electrons), and formula of compound can be written as $(Zr_{1-z}Ni_z)NiSn$. The dissolution of rare earth atoms and/or ***d***-, ***p***-elements in ZrNiSn leads to ordering of structure (Ni leaves 4***a*** position) and at impurity concentration ~ 1 % the defects of donor nature and ε_D^1 band disappear.

Thus, in Ref. [1] it was established that in $ZrNi_{1-x}Rh_xSn$ at $T = 80$ K and the lowest concentration of Rh ($x = 0.005$) the sign of thermopower coefficient $\alpha(x)$ changes from negative (for ***n***-ZrNiSn) to positive. Such change of $\alpha(x)$ sign was predicted because substitution of Ni atoms by Rh ($4d^85s^1$) in 4***c*** position generates the structural defects of acceptor nature (Rh has less ***s***-electrons). The change of $\alpha(x)$ sign also indicates that the number of ionized acceptors exceeds the number of ionized donors. It is possible when the concentration of acceptors is higher than concentration of donors at the close values of ionization energies (depths of location of energy levels relative to the edges of bands), or when ionization energy of donor is higher than acceptor, but the temperature is sufficient for ionization of acceptor and is not sufficient to throw the electron into the conductivity band. The positive $\alpha(x)$ values of $ZrNi_{1-x}Rh_xSn$ indicate that the holes are the major current carriers and the Fermi level ε_F is located near the valence band. The behavior of Fermi level ε_F at $T = 80$ K is a reaction of *n*-type semiconductor on its doping by acceptors which makes it heavily doped and highly compensated (HDCS) [4]. The similar behavior of Fermi level ε_F and thermopower coefficient $\alpha(x)$ of $ZrNi_{1-x}Rh_xSn$ was observed also for higher Rh concentration, in particular $x = 0.01$ and $x = 0.03$.

However, in the $ZrNi_{1-x}Rh_xSn$ samples at $x = 0.005$, $x = 0.01$ and $x = 0.03$ with increase of temperature higher than $T_{inv.} \geq 254$ K, $T_{inv.} \geq 295$ K and $T_{inv.} \geq 362$ K, respectively, the $\alpha(x)$ sign unexpectedly became negative, indicating that electrons again, as in *n*-ZrNiSn, are major current carriers. Thus, at these concentrations of $ZrNi_{1-x}Rh_xSn$ with increase of temperature Fermi level ε_F drifts from the valence band (low temperatures) to the conduction band (high temperatures), crossing the middle of the band gap ε_g (complete compensation) at $T_{inv.} \approx 254$ K, $T_{inv.} \approx 295$ K and $T_{inv.} \approx 362$ K, respectively. And this happens despite the fact the concentration of acceptors is much higher than the concentration of donors ε_D^1 in the model of disordered structure of ZrNiSn compound [2].

Such behavior of the Fermi level ε_F of $ZrNi_{1-x}Rh_xSn$ clearly indicates that in the crystal simultaneously with acceptors ε_A the structural defects of donor nature ε_D^2 are generated by yet unknown mechanism with ionization energy higher than of acceptors, and the change of temperature affects the electronic structure of the semiconductor. However, investigations performed in [1] appeared to be insufficient for understanding the mechanism of appearance of donors ε_D^2 in $ZrNi_{1-x}Rh_xSn$, which is important for optimizing the characteristics of thermoelectric material by appropriate doping. Therefore, during analysis of kinetic properties of ZrNiSn compound and solid solutions based on it, it is necessary, along with mechanism of “a priori doping” [2], to investigate other mechanisms of appearance of defects which change the electronic structure of the semiconductor. Present work is devoted to solving this problem.

I. Experimental details

The samples were synthesized by arc melting of the constituent elements in an electric arc furnace under inert atmosphere, followed by homogenizing annealing at 1073 K for 720 hours. The crystallographic data were obtained by means of X-ray diffraction analysis (powder method, Guinier-Huber image plate system diffractometer, Cu$K\alpha_1$ radiation), and the structural characteristics were calculated using the Fullprof program [5]. The chemical and phase compositions of the samples were examined by microprobe analyzer (EPMA, energy-dispersive *X*-ray analyzer). The calculations of electronic structure of $ZrNi_{1-x}Rh_xSn$ were carried out using Korringa–Kohn–Rostoker (KKR) methods in the approximation of the coherent potential (CPA) and local density (LDA) [6]. Thermodynamic calculations were performed in the harmonic oscillation approximation (LMTO) within the theory of functional density DFT. The experimental values of the lattice parameter in the k-space of 10×10×10 *k*-points and type of parameterization of exchange-cross-correlation potential Moruzzi-Janak-Williams [7] were used. The width of energy window was equal to 22 eV, and deviation of calculation of the Fermi level position ε_F was equal to ± 8 meV.

II. Peculiarity of crystal structure of $ZrNi_{1-x}Rh_xSn$

The microprobe analysis of atom concentration on surface of $ZrNi_{1-x}Rh_xSn$ samples showed their accordance to initial compositions of the ingots, and X-ray phase and structural analyses showed that powder patterns of the samples are indexed in MgAgAs-type [3] and do not contain traces of other phases. Substitution of Ni atoms ($r_{Ni} = 0.124$ nm) by bigger Rh ($r_{Rh} = 0{,}136$ nm) expectedly results in increase of lattice parameter $a(x)$. Modeling of variation of $a(x)$ values of $ZrNi_{1-x}Rh_xSn$ also showed increasing of $a(x)$ values in case of occupation of 4*c* crystallographic position of Ni atoms by Rh atoms (Fig. 1, curve 2). However, in the experiment there is a maximum on $a(x)$ dependence (Fig. 1, curve 1), which is characteristic feature of solid solution based on ZrNiSn and one of the arguments of disordered structure model [2]. Let’s examine it more detailed.

The crystal structure refinements of $ZrNi_{1-x}Rh_xSn$ showed that at Rh content $x \geq 0.01$ the structure is ordered, i.e. the occupancy of Zr position is 100 %, and the defects of donor nature are “healed” by elimination of small Ni atoms from 4*a* position by bigger Zr atoms ($r_{Zr} = 0.160$ nm). Simultaneously, the substitution of Ni atoms in 4*c* position by bigger Rh atoms occurs. Since the difference between the atomic radii of Zr and Ni ($r_{Zr}-r_{Ni}$) = 0.036 nm is greater than that for Rh and Ni ($r_{Rh}-r_{Ni}$) = 0.011 nm, the amplitude of variation of $a(x)$ values in the ranges $0 \leq x \leq 0.01$ and $0.01 < x \leq 0.10$is different. In first case, these variations are bigger due to the displacement of Ni atoms from 4*a* position by Zr atoms (growth of $a(x)$ dependence). After displacement of Ni atoms from 4*a* position of Zr atoms (ordering of structure), the increase of $a(x)$ values in the $0.01 \leq x \leq 0.10$ range (Fig. 1) occurs as a result of occupation of the position of Ni (4*c*) by the Rh atoms.

Within such a mechanism of realization of $ZrNi_{1-x}Rh_xSn$ substitution solid solution, structural changes lead to changes in the electronic structure,

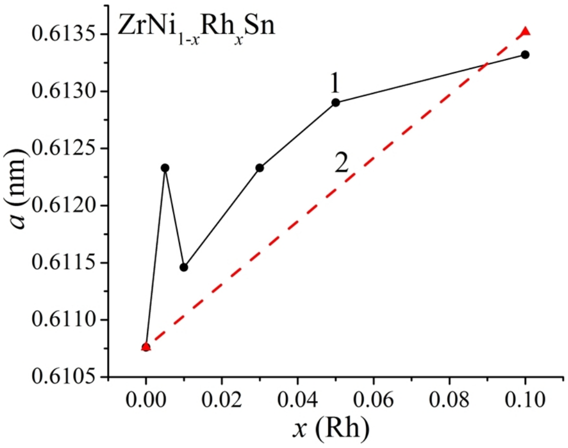
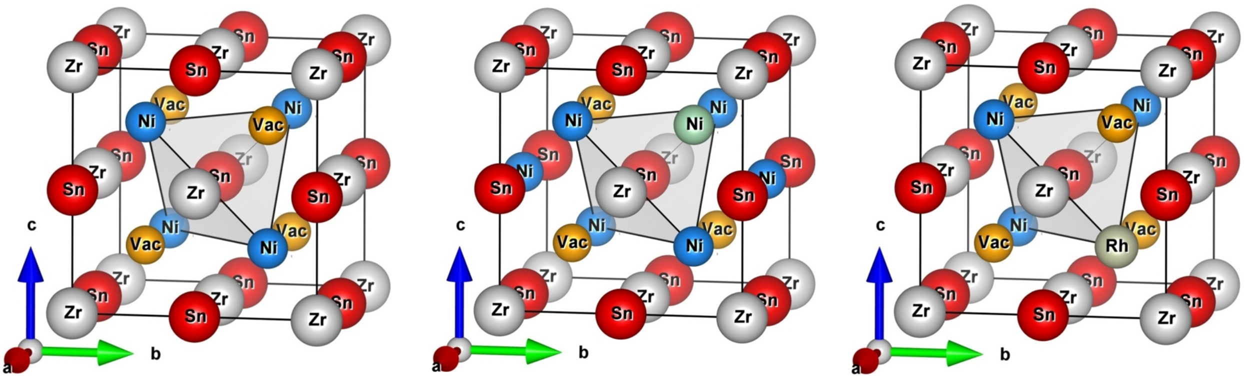


Fig. 1. Variation of lattice parameter $a(x)$ $ZrNi_{1-x}Rh_xSn$: 1 – experiment, 2 – calculation.



a *b* *c*

Fig. 2. Models of crystal structures ZrNiSn (***a***), ZrNi[Ni_y]Sn (***b***) and $ZrNi_{1-x}Rh_xSn$ (***c***).

redistributing the density of electronic states through the following processes:

- elimination of structural defects of donor nature due to replacing of ~ 1 % (*z*) Ni atoms from (4*a*) position of Zr;
- generation of structural defects of acceptor nature due to substitution of Ni atoms (4*c*) by Rh.

Presented changes in the crystal and electronic structures of $ZrNi_{1-x}Rh_xSn$ suggest simultaneous increase of concentration of structural defects of acceptor nature and decrease of defects of donor nature, which at Rh concentration $x \geq 0.01$ should disappear and holes should be major current carriers at all temperatures. However, experimental investigations of kinetic characteristics of $ZrNi_{1-x}Rh_xSn$ samples, $x = 0.01$ and $x = 0.03$ [1] have revealed the presence of significant number of donors of unknown origin. Thus, the described above changes of crystal structure of $ZrNi_{1-x}Rh_xSn$ solid solution cannot be considered complete and exhaustive.

The feature of crystal structure of ZrNiSn compound which redistributes the density of electronic states was studied in Ref. [8]. Thus, the analysis of phase diagram of Zr-Ni-Sn system showed the coexistence of ZrNiSn and $ZrNi_2Sn$ ($MnCu_2Al$ structure type, space group $Fm\bar{3}m$ [3]) compounds. The crystal structures of both compounds are related and characterized by cubic symmetry: $ZrNi_2Sn$-Heusler phase, and ZrNiSn - half-Heusler phase. Principal difference between them consists in centrosymmetric structure of Heusler phase and non-centrosymmetric of half-Heusler phase. Absence of the center of the symmetry in half-Heusler phase generates strong tetrahedral bonds which provides semiconductive properties of this compound. The peculiarity of crystal structure of ZrNiSn, like other semiconductors with cubic structures [3] consists in presence of the tetrahedral voids which make up ~ 24 % of total unit cell volume (Fig. 2).

Under the term “relationship” the scientists understand the following. If we assume hypothetically that the atoms of the smallest size (Ni) can be located in tetrahedral voids of ZrNiSn and consider void as vacancy (Vac) in crystallographic position 4*d*, then occupation of 4*d* position by Ni atom (filling of vacancy) will lead to change of crystal symmetry and realization at certain Ni concentration of $ZrNi_2Sn$ compound. It is worth to note that difference in symmetry of ZrNiSn and $ZrNi_2Sn$ compounds results in absence of the continuous solid solution between them [2, 3].

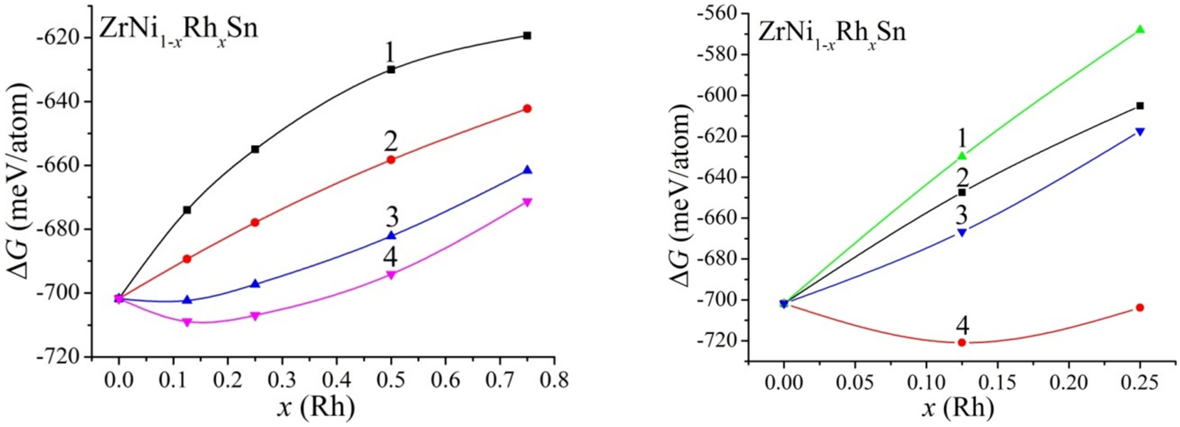
Authors [8] educed an effect of accumulation of Ni atoms in these voids in ZrNiSn, including and additional Ni_{1+y} atoms (further [Ni_y]) without change of structure symmetry up to concentrations $y \leq 0.30$, which generate the structural defects of donor nature and formula of the compound transforms into ZrNi[Ni_y]Sn (Fig. 2*b*). It also appeared that the width of the band gad ε_g of ZrNi[Ni_y]Sn depends on the concentration of Ni atoms [Ni_y] in such voids. The conclusion was made that in semiconductors with cubic symmetry, covalent bonding and tetrahedral voids the last play role of vacancies for own atoms as well as for impurity atoms, generating the structure defects which determine their properties. Study of thermodynamic processes in Zr-Ni-Sn system [9] confirmed the results of Ref. [8] concerning of accumulation of [Ni_y] atoms in tetrahedral voids of ZrNiSn compound.

Thus, in $ZrNi_{1-x}Rh_xSn$ solid solution, besides the abovementioned two mechanisms of modification of structural defects, in particular, elimination of donors ε_D^1 due to displacement of ~ 1 % ($z = 0.01$) Ni atoms from Zr position (4*a*) and generation of acceptors ε_A due to substitution of Ni atoms (4*c*) by Rh, it is necessary to take into account mechanism of ε_D^2 donors generation due to occupation of vacancies by atoms. They can be both small Ni atoms and Rh atoms. We can assume that in $ZrNi_{1-x}Rh_xSn$ the part of Ni and Rh atoms occupy both the Ni (4*c*) position and vacancies in different ratios, generating structural defects of acceptor and donor nature, respectively.

In this context it is worth to note that it is difficult to determine the accumulation of Ni and/or Rh in tetrahedral voids and thereof generation of structural defects of donor nature using X-ray methods for crystal structure investigation. For practical solving of this problem it is necessary to use more precise methods, in particular, to study the thermodynamic and energy state characteristics of $ZrNi_{1-x}Rh_xSn$ in terms of their accordance with experimental measurements [1].

III. Investigation of thermodynamic characteristics of $ZrNi_{1-x}Rh_xSn$

While performing thermodynamic calculations, we were guided by the following considerations. Realization



a ***b***

Fig. 3. Variation of thermodynamic potential $\Delta G(x)$ of $\mathrm{ZrNi}_{1-x}\mathrm{Rh}_x\mathrm{Sn}$: ***a***-substitution of Ni/Rh atoms in 4c position at different temperatures: **1** – $T = 0$ K, **2** – $T = 473$ K, **3** – $T = 873$ K, **4** – $T = 1273$ K; ***b*** - Ni/Rh in 4*c* and Rh atoms in 4*d* at $T = 0$ K; **2** – Ni/Rh in 4*c* and Ni atoms in 4*d* at $T = 0$ K; **3** – Ni/Rh in 4*c* and Rh atoms in 4*d* at $T = 1273$ K; **4** – Ni/Rh in 4*c* and Ni atoms in 4*d* at $T = 1273$ K.

of semiconductive substitution solid solution $\mathrm{ZrNi}_{1-x}\mathrm{Rh}_x\mathrm{Sn}$ ("ideal" model) involves substitution of Ni atoms by Rh in crystallographic position 4*c*, generating the structural defects of acceptor nature. Herewith no atoms are situated in tetrahedral voids (Vac). In this model decrease of values of formation enthalpy is observed, which indicates an absence of solubility at $T = 0$ K (Fig. 3*a*). However, with increase of temperature the contribution of configuration entropy, in the equation of which total number of atoms in the unit cell remains constant, becomes more significant and minimum appears on the dependence curve $\Delta G(x)$, which shifts towards higher concentrations of Rh. Thus, in the given model the entropy constituent of thermodynamic potential is decisive for the formation of semiconductive solid solution $\mathrm{ZrNi}_{1-x}\mathrm{Rh}_x\mathrm{Sn}$.

As the peculiarity of the crystal structure of ZrNiSn is the presence of tetrahedral voids (Vac) (Fig. 2), the variant of atom distribution, which provides the substitution of Ni atoms by Rh in 4*c* position, is possible. In this case Ni atoms ($[\mathrm{Ni}_y]$) partially occupy tetrahedral voids, and formula of the compound transforms into $\mathrm{Zr(Ni}_{1-x}\mathrm{Rh}_x)[\mathrm{Ni}_y]\mathrm{Sn}$. In this model, taking into account the results of Refs. [8,9], cases where Ni atoms, on the one hand, are displaced from 4*c* position by Rh atoms, generating the structural defects of acceptor nature ε_A, and on the other hand, occupy vacancies partially, generating the structural defects of donor nature $\varepsilon_\mathrm{D}{}^2$, are considered.

Substitution of Ni atoms by Rh in 4*c* position in the presence of Ni atoms in tetrahedral voids increases the formation enthalpy of alloys. However, maximum of configuration entropy shifts towards lower Rh concentration caused due to the increase of atoms number in the unit cell. It results in strong decrease of thermodynamic potential at 1273 K compared to ordered solid solution. Consequently, the presence of Ni atoms in tetrahedral voids (Vac) makes the process of substitution of Ni by Rh energy-efficient at high temperatures (minimum at $\Delta G(x)$ dependence, Fig. 3*b*, curve 4).

Another variant of atom distribution due to doping of ZrNiSn compound by Rh is model $\mathrm{ZrNi[Rh}_x]\mathrm{Sn}$, in which Ni atoms completely fill the crystallographic site 4*c* and partially occupy the position 4*d* (tetrahedral voids), and Rh atoms displace Ni atoms from these voids (Vac), generating the structural defects of donor nature. According to performed calculations (Fig. 3*b*, curves 2,3) the substitution of Ni atoms by Rh in vacancies is thermodynamically inefficient even at high temperatures.

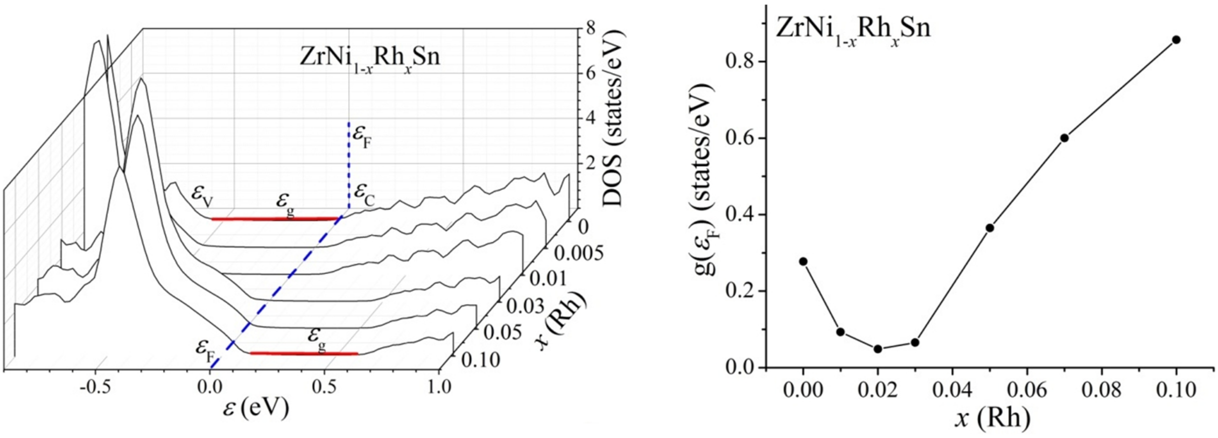
Thus, the results of thermodynamic calculations unequivocally indicate that for the formation of $\mathrm{ZrNi}_{1-x}\mathrm{Rh}_x\mathrm{Sn}$ solid solution energy expedient is occupation of crystallographic position 4*c* by Rh atoms by substitution of Ni atoms (substitution solid solution), which generate the structural defects of acceptor nature, and simultaneously generate donors by accumulation of part of Ni atoms in tetrahedral voids (Vac) of structure (insertion solid solution).

IV. Investigation of electronic structure of $\mathrm{ZrNi}_{1-x}\mathrm{Rh}_x\mathrm{Sn}$

To predict the behavior of the Fermi level ε_F, band gap ε_g and kinetic characteristics of $\mathrm{ZrNi}_{1-x}\mathrm{Rh}_x\mathrm{Sn}$ the calculation of the density of electronic states (DOS) was performed. Calculations were performed for several variants of atom distribution model in $\mathrm{ZrNi}_{1-x}\mathrm{Rh}_x\mathrm{Sn}$ solid solution (Fig. 4).

a) "Ideal" model (Fig. 4a) of semiconductive $\mathrm{ZrNi}_{1-x}\mathrm{Rh}_x\mathrm{Sn}$ solid solution with ordered structure and substitution of Ni atoms by Rh in crystallographic position 4*c*, which generate the structural defects of acceptor nature and no atoms are located in tetrahedral voids (Vac).

As seen from Fig. 4*a*, at the smallest Rh concentrations Fermi level ε_F of $\mathrm{ZrNi}_{1-x}\mathrm{Rh}_x\mathrm{Sn}$ drifts from the conduction band ε_C, at the distance of ~ 97.6 meV from which it was in *n*-ZrNiSn [1], to the middle of the band gap ε_g and further to valence band ε_V, which it will cross at $x \approx 0.05$, i.e. the insulator-metal transition of conductivity will occur (Anderson transition) [10]. At the Fermi level ε_F crossing the middle of the band gap ($x \approx 0.02$) and further moving to the valence band ε_V the



A ***b***

Fig. 4. Calculated distribution of density of electronic states DOS (***a***) and density of electronic states at Fermi level $g(\varepsilon_F)$ (***b***) for "ideal" model of ZrNi$_{1-x}$Rh$_x$Sn: tetrahedral voids (Vac) are empty.

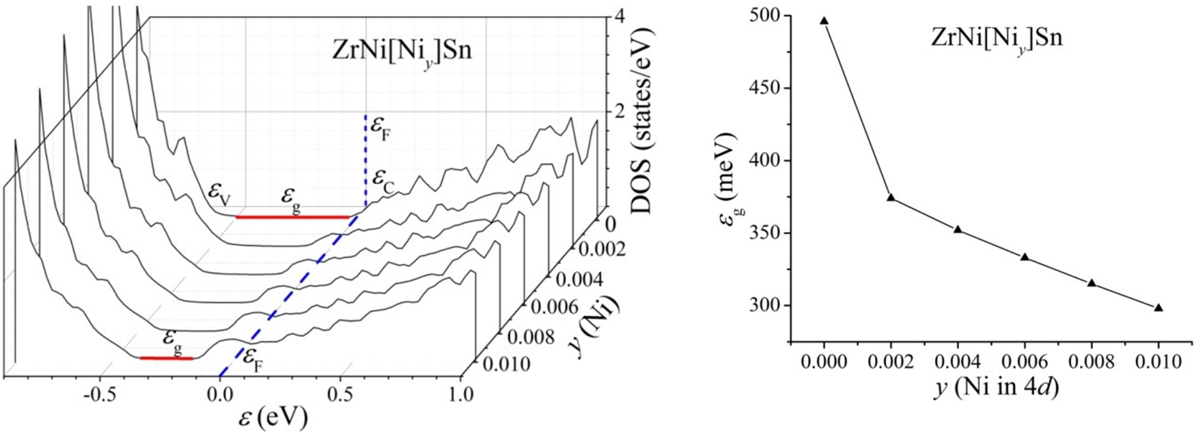
type of conductivity will change, and the holes will become the main charge carriers. Besides the drift of Fermi level ε_F, caused by the change of compensation degree of semiconductor, the width of the band gap ε_g of ZrNi$_{1-x}$Rh$_x$Sn decreases.

For this ZrNi$_{1-x}$Rh$_x$Sn model at small Rh concentration decrease of density of electronic states at Fermi level $g(\varepsilon_F)$ takes place, and minimum on the $g(\varepsilon_F)$ dependence (Fig. 4*b*) corresponds to crossing of the middle of the band gap ε_g by the Fermi level ε_F. At higher Rh concentration, when Fermi level approaches to the top of the valence band ε_V of semiconductor, values of density states at Fermi level $g(\varepsilon_F)$ increase. This model cannot be taken as basis, because the results of kinetic studies of ZrNi$_{1-x}$Rh$_x$Sn [1] revealed that electrons participate in electric conductivity (negative values $\alpha(x)$) at acceptor concentration $x > 0.01$, which is higher than donor concentration ε_D^1 in the model of disordered ZrNiSn structure [2].

b). Participation of electrons in electric conductivity of ZrNi$_{1-x}$Rh$_x$Sn at acceptor concentration $x > 0.01$ requires to consider in more details the mechanism of generation of structural defects of donor nature at occupation of tetrahedral voids by Ni atoms ([Ni$_y$]). Results of refined calculations of density of electronic states distribution in ZrNi[Ni$_y$]Sn are shown in Fig. 5*a*. In Ref. [8] the width of energy window used for DOS calculations was 16 eV, which is not enough for obtaining the exhaustive image of electronic structure, thus the width of energy window 22 eV was chosen for calculations.

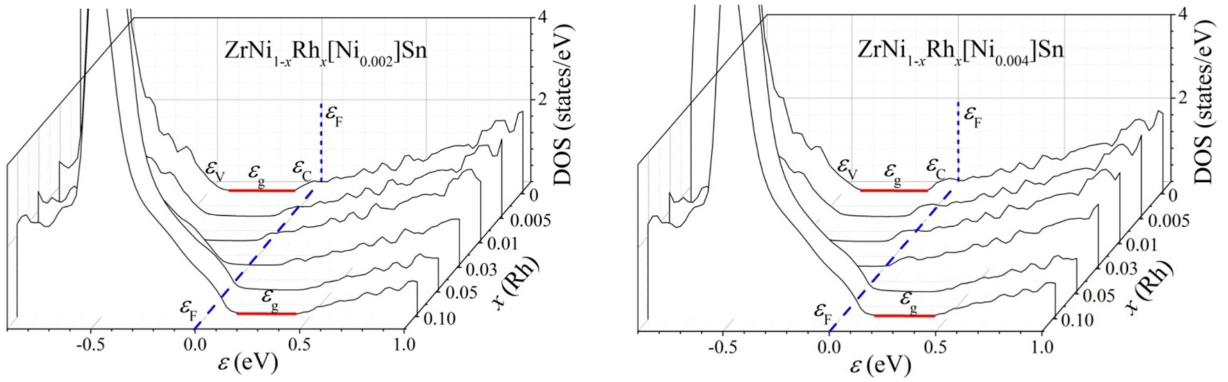
We can see that at smallest Ni atoms concentration in crystallographic position 4*d* ZrNi[Ni$_{0.002}$]Sn the Fermi level ε_F approached to conduction band ε_C and is fixed at donor band ε_D^2, formed by generated structural defects of donor nature due to occupation of tetrahedral voids by Ni atoms. At higher concentration of Ni atoms [Ni$_y$] Fermi level ε_F will cross the bottom of the conduction band ε_C and insulator-metal transition of conductivity will take place (Anderson transition [10]). Simultaneously, with change of compensation degree of ZrNi[Ni$_y$]Sn the width of band gap ε_g rapidly decreases (Fig. 5*b*). It is worth to note that the term "the width of band gap" ε_g means energy gap between the tops of continuous energy bands, but not energy gap between the mobility edges of these bands (between "tails" of the bands [4]).

Thus, occupation of tetrahedral voids ([Ni$_y$]) by Ni atoms in ZrNiSn compound is effective mechanism of generation of structural defects of donor nature ε_D^2 and has a significant influence on the value of the band gap width ε_g and compensation degree. We should note that in experimental studies the compensation degree is



A ***б***

Fig. 5. Calculated distribution of density of electronic states DOS (***a***) and width of band gap ε_g (***b***) of ZrNi[Ni$_y$]Sn.



A ***b***

Fig. 6. Calculated distribution of density of electronic states DOS of $ZrNi_{1-x}Rh_x[Ni_{0.002}]Sn$ (***a***) and $ZrNi_{1-x}Rh_x[Ni_{0.004}]Sn$ (***b***).

determined as relation of ionized acceptors and donors, and ionization processes (throwing the charge carriers into the continuous energy band) depends on temperature. In case of ***a priori*** calculations we assume that acceptors and donors are ionized, and compensation degree is determined as relation of acceptors and donors.

c) In third model the influence of substitution of Ni atoms by Rh in 4*c* position and presence of different concentrations of Ni atoms in tetrahedral voids (Vac): $ZrNi_{1-x}Rh_x[Ni_{0.002}]Sn$ (Fig. 6*a*) and $ZrNi_{1-x}Rh_x[Ni_{0.004}]Sn$ (Fig. 6*б*) on location of the Fermi level ε_F and width of band gap ε_g was investigated.

As seen from Fig. 6*a*, at absence of the impurity Rh atoms ($x = 0$) Fermi level ε_F is located under the bottom of conduction band in donor band ε_D^2, formed by occupation of vacancies by $[Ni_{0.002}]$ atoms. Doping of semiconductor $ZrNi_{1-x}Rh_x[Ni_{0.002}]Sn$ by the smallest concentration of impurity Rh atoms ($x = 0.005$) generates the structural defects of acceptor nature and corresponding impurity acceptor band ε_A, which does not result in significant movement of the Fermi level ε_F from the edge of conduction band ε_C. Conductivity of $ZrNi_{1-x}Rh_x[Ni_{0.002}]Sn$, $x = 0.005$, provided that donors and acceptors are ionized, will be determined by free electrons, which will result in negative sign of thermopower coefficient $\alpha(x)$. Similar behavior of Fermi level ε_F of $ZrNi_{1-x}Rh_x[Ni_{0.002}]Sn$ was observed also for higher Rh concentration $x = 0.01$.

In case of $ZrNi_{1-x}Rh_x[Ni_{0.002}]Sn$, $x = 0.03$ Fermi level ε_F is located near the middle of the band gap ε_g, and sign of thermopower coefficient $\alpha(x)$ will be sensible to the smallest changes of compensation degree (Fig. 6*a*). Fermi level ε_F will cross the middle of the band gap ε_g and will approach to the valence band ε_V only at concentration of $ZrNi_{1-x}Rh_x[Ni_{0.002}]Sn$ $x = 0.05$. An inversion of conductivity type will take place and holes will become main current carriers which will cause the change of sign of thermopower coefficient from negative to positive. At the higher Rh concentration ($x = 0.10$) Fermi level ε_F will cross the top of the valence band ε_V and the insulator-metal transition of conductivity will occur (Anderson transition) [10]. In this case $ZrNi_{1-x}Rh_x[Ni_{0.002}]Sn$, $x=0.10$ is characterized by metallic type of conductivity. Described behavior of Fermi level ε_F and thermopower coefficient $\alpha(x)$ is close to the experimental results for $ZrNi_{1-x}Rh_xSn$ [1].

The distribution of density of electronic states DOS of $ZrNi_{1-x}Rh_x[Ni_{0.004}]Sn$ solid solution with higher concentration of Ni atoms, $y=0.004$, in tetrahedral voids (Vac), is shown in Fig. 6*b*. In this case due to the significant concentration of generated structural defects of donor nature Fermi level ε_F at absence of Rh impurity $x = 0$ is located on the formed donor band ε_D^2, which unites with the bottom of conduction bands ε_C, playing the role of the mobility edge [10] or “tail” of band [4]. Doping of $ZrNi_{1-x}Rh_x[Ni_{0.004}]Sn$ by impurity Rh atoms ($x = 0.005$ - 0.03) will increase the compensation degree and cause the exit of Fermi level ε_F from the donor band ε_D^2 and its movement to the middle of the band gap ε_g. Inversion of conductivity type of $ZrNi_{1-x}Rh_x[Ni_{0.004}]Sn$ will take place at concentration $x \geq 0.05$, when main current carriers will become holes which will also result in the change of sign of thermopower coefficient.

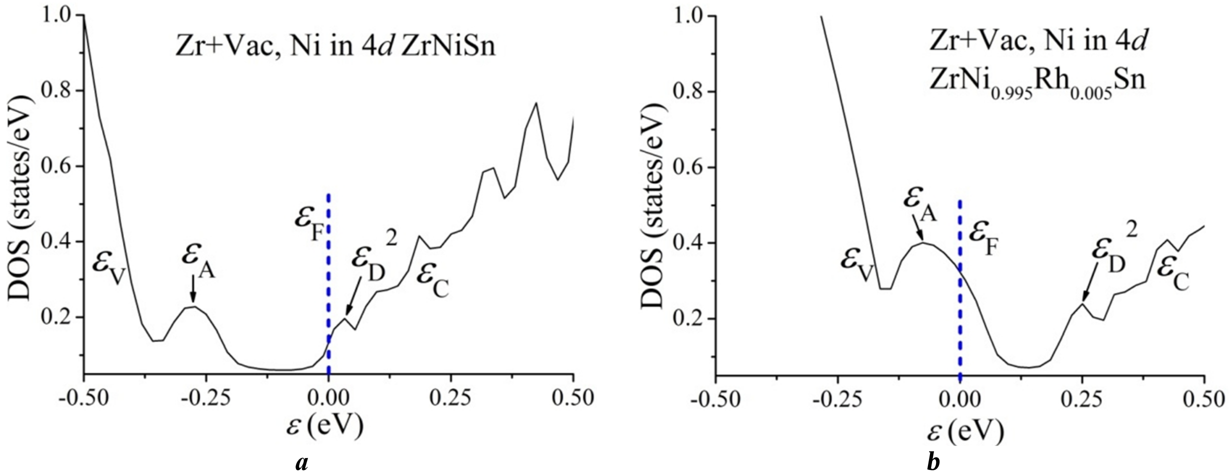
Behaviour of Fermi level ε_F in $ZrNi_{1-x}Rh_x[Ni_{0.004}]Sn$ model differs from the experimental results [1], especially at concentration of Rh atoms $x = 0.005$ - 0.01.

d) Let us look at one more model of atom distribution (or their absence) in ZrNiSn and $ZrNi_{1-x}Rh_xSn$, which demonstrates the mechanisms of generation of structural defects of acceptor and donor nature, which define the location of the Fermi level ε_F and width of the band gap ε_g of semiconductor.

Mechanism of “*a priori*” doping of ZrNiSn by donors foresees the presence of vacancies in crystallographic position 4*a* of Zr atoms, which are occupied by Ni atoms, which makes the structure disordered and generates the structural defects of donor nature ε_D^1. Note, that authors of [9] observed smaller content of Zr atoms in ZrNiSn, which may indicate the presence of vacancies in crystallographic position 4*a* of Zr atoms.

We asked ourselves a question, how the distribution of density of electronic states and position of Fermi level ε_F in ZrNiSn and $ZrNi_{1-x}Rh_xSn$ will change in case when vacancies in 4*a* position of Zr atoms are not occupied by Ni atoms, and some number of Ni atoms is placed in crystallographic position 4*d* (tetrahedral voids)?

The calculated DOS of ZrNiSn and $ZrNi_{1-x}Rh_xSn$ with vacancies in 4*a* position of Zr atoms and occupation of 4*d* position by Ni atoms is given in Fig. 7. In both cases vacancy concentration λ in 4*a* position is $\lambda = 0.0016$, and concentration of Ni atoms in 4*d* position



a ***b***

Fig. 7. Calculated distribution of density of electronic states DOS of ZrNiSn (***a***) and $ZrNi_{1-x}Rh_xSn$ (***b***) at the presence of vacancies in 4***a*** position of Zr atoms ($\lambda = 0.0016$) and Ni atoms in 4***d*** position ($y = 0.0018$).

is $y = 0.0018$. We can see that in case of ZrNiSn vacancies in 4*a* position generate the structural defects of acceptor nature, and in the band gap near the top of valence band ε_V (Fig. 7*a*) the strong acceptor band ε_A is formed. In the same time Ni atoms in 4*d* position generate the structural defects of donor nature, and in the band gap near the bottom of conduction band ε_C the donor band $\varepsilon_D{}^2$ is formed. As the concentration of the structural defects of donor nature ($y = 0.0018$) is higher compared to the concentration of defects of acceptor nature ($\lambda = 0.0016$), the Fermi level ε_F locates in the donor band $\varepsilon_D{}^2$.

In case of $ZrNi_{1-x}Rh_xSn$ semiconductive solid solution, $x = 0.005$, in which vacancies in 4*a* position ($\lambda = 0.0016$) also exist, and Ni atoms occupy tetrahedral voids ($y = 0.0018$), Fermi level ε_F left the donor band $\varepsilon_D{}^2$ and placed at the edge of acceptor band ε_A (Fig. 7*b*). Donor band $\varepsilon_D{}^2$ of $ZrNi_{1-x}Rh_xSn$, $x = 0.005$, is the same as in case of ZrNiSn. In the same time impurity acceptor band ε_A is more powerful, which indicates the higher acceptor concentration in $ZrNi_{1-x}Rh_xSn$, $x = 0.005$, comparing with ZrNiSn. Such transformation of acceptor band ε_A is clear because there are two mechanism of acceptor generation in $ZrNi_{1-x}Rh_xSn$:

-substitution of Ni atoms by Rh in 4*c* position;

-presence of vacancies in 4*a* position of Zr atoms.

We consider that this model is mostly methodological, demonstrating the mechanisms of influence of density of electronic states at Fermi level $g(\varepsilon_F)$, width of band gap ε_g, etc. on location of Fermi level ε_F. Possibility of the existence of high number of vacancies in multicomponent compound at presence of impurity atoms of small size is miserable in terms of physics and crystal chemistry.

Conclusions

Results of investigation of crystal and electronic structure, thermodynamic and energy state characteristics of semiconductive $ZrNi_{1-x}Rh_xSn$ solid solution showed that in the basic ZrNiSn compound simultaneously exist two types of structural defects of donor nature, which generate two donor bands with different energy of ionization in the band gap, determining the conduction mechanisms:

a) donor band $\varepsilon_D{}^1$, formed by partial occupation up to ~ 1 % ($z = 0.01$) of crystallographic position 4*a* of Zr atoms by Ni atoms (mechanism of "a priory doping" [2]);

b) deep donor band $\varepsilon_D{}^2$, formed by partial occupation of tetrahedral voids by Ni atoms (crystallographic position 4*d*).

Substitution of Ni atoms by Rh in crystallographic position 4*c* of $ZrNi_{1-x}Rh_xSn$ generates the structural defects of acceptor nature and forms an impurity acceptor band ε_A in the band gap, which together with the existence of donor bands $\varepsilon_D{}^1$ and $\varepsilon_D{}^2$ makes it heavily doped and highly compensated [4]. Obtained results allow to understand the mechanisms of electrical conduction of thermoelectric materials based on ***n***-ZrNiSn and the ways of conscious optimization of their characteristics to obtain maximum efficiency of transformation of thermal energy into electric.

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Дослідження структурних, термодинамічних та енергетичних характеристик твердого розчину $ZrNi_{1-x}Rh_xSn$

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Досліджено особливості кристалічної та електронної структур, термодинамічні та енергетичні характеристики напівпровідникового твердого розчину $ZrNi_{1-x}Rh_xSn$. Показано, що у сполуці ZrNiSn одночасно існують два види структурних дефектів донорної природи, які породжують у забороненій зоні дві донорні зони з різною енергією іонізації: а) донорна зона ε_D^1, утворена у результаті часткового, до ~ 1 %, зайняття атомами Ni позиції 4*a* атомів Zr (механізм «апріорного легування») та глибока донорна зона ε_D^2, утворена у результаті часткового зайняття атомами Ni тетраедричних пустот (Vac). Заміщення в $ZrNi_{1-x}Rh_xSn$ у позиції 4*c* атомів Ni на Rh генерує структурні дефекти акцепторної природи та породжує у забороненій зоні домішкову акцепторну зону ε_A, що поряд з існуванням у напівпровіднику донорних зон ε_D^1 та ε_D^2 робить його сильно легованим та сильно компенсованим. Отримані результати дозволяють зрозуміти механізми електропровідності термоелектричних матеріалів на основі *n*-ZrNiSn та шляхи усвідомленої оптимізації їхніх характеристик для отримання максимальної ефективності перетворення теплової енергії в електричну.

Ключові слова: електропровідність, коефіцієнт термо-ерс, рівень Фермі, електронна структура.