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Investigation of Electronic Structure of $Zr_{1-x}V_xNiSn$ Semiconductive Solid Solution

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The peculiarities of electronic and crystal structures of $Zr_{1-x}V_xNiSn$ ($x = 0 - 0.10$) semiconductive solid solution were investigated. To predict Fermi level ε_F behavior, band gap ε_g and electrokinetic characteristics of $Zr_{1-x}V_xNiSn$, the distribution of density of electronic states (DOS) was calculated. The mechanism of simultaneous generation of structural defects of donor and acceptor nature was determined based on the results of calculations of electronic structure and measurement of electrical properties of $Zr_{1-x}V_xNiSn$ semiconductive solid solution. It was established that in the band gap of $Zr_{1-x}V_xNiSn$ the energy states of the impurity donor e_D^2 and acceptor e_A^1 levels (donor-acceptor pairs) appear, which determine the mechanisms of conduction of semiconductor.

Keywords: resistivity, thermopower coefficient, Fermi level.

Work arrived to the editor 22.04.2019; accepted for printing 15.06.2019.

Introduction

The present work completes the study of conduction mechanisms of $Zr_{1-x}V_xNiSn$ semiconductive solid solution, begun in [1]. Experimental investigations of structural, electrokinetic and energy state characteristics showed the contradictory nature of introduction of V atoms in the matrix of n -ZrNiSn semiconductor. Thus, the value of unit cell parameter $a(x)$ for $Zr_{1-x}V_xNiSn$ was enlarged unexpectedly with increasing of V concentration. Since the atomic radius of V atom ($r_V = 0.134$ nm) was smaller than Zr ($r_{Zr} = 0.160$ nm), the decreasing of $a(x)$ value is logical.

On the other hand, the substitution of Zr ($4d^25s^2$) atoms in the $4a$ crystallographic position by V ($3d^34s^2$) atoms should generate structural defects of donor nature, and the Fermi level ε_F at certain concentrations of donor had to cross the percolation level of conduction band. In this case, the conductivity of $Zr_{1-x}V_xNiSn$ semiconductor should have changed from activation to metallic [2]. However, the presence of high temperature activation parts on the $\ln\rho(1/T)$ dependence for $Zr_{1-x}V_xNiSn$ even at the "giant" concentration of donor impurity ($N_D^V \approx 1.9 \cdot 10^{21}$ cm⁻³ for $x = 0.10$) and the negative values of thermoelectric coefficient $\alpha(x, T)$ indicate that the Fermi level ε_F is in the band gap near the bottom of conduction band ε_C [1]. In a n -type semiconductor doped

by donors this can be possible, provided that in $Zr_{1-x}V_xNiSn$, except donors, the structural defects of acceptor nature, which compensate donors (catch free electrons, reducing their concentration) appear simultaneously by unknown mechanism. Such process is able to slow down the motion of Fermi level ε_F to the conduction band ε_C .

It also appeared that the motion rate of Fermi level ε_F to the conduction band ε_C is not the same at different concentration ranges of V impurity. At the lowest concentration of impurity in $Zr_{1-x}V_xNiSn$, $x = 0.01$, the Fermi level ε_F with the rate $\Delta\varepsilon_F/\Delta x \approx 77.8$ meV/%V rapidly approached to the percolation level of conduction band ε_C at the distance of 19.8 meV, while in n -ZrNiSn it was at the distance of 97.6 meV. However, at higher concentrations of V atoms, the rapid decrease of motion rate of Fermi level ε_F in the direction to conduction band occurred. Thus, at the concentration range $x = 0.01 - 0.03$, the motion rate of Fermi level ε_F is $\Delta\varepsilon_F/\Delta x \approx 2.2$ meV/%V, and in the $x = 0.03 - 0.10$ range it is even smaller and equal to $\Delta\varepsilon_F/\Delta x \approx 0.7$ meV/%V. Since the concentration of impurity V atoms, which should generate the donors, is introduced into the n -ZrNiSn matrix linearly, then the Fermi level ε_F would have to move in the same way to the percolation level of conduction band ε_C of $Zr_{1-x}V_xNiSn$. It can be assumed that the generation of structural defects of acceptor

nature by unknown mechanism simultaneously with donors in $Zr_{1-x}V_xNiSn$ causes the “inhibition” of Fermi level ε_F to conduction band. The experimental results presented in [1] showed that in $Zr_{1-x}V_xNiSn$, in addition to donors, acceptors are generated.

It should be noted that structural investigations did not reveal such defects, since their concentration is beyond the accuracy of X-ray methods. The purpose of this work is to determine such a mechanism, which will allow predicting characteristics of $Zr_{1-x}V_xNiSn$ thermoelectric material.

I. Experimental

The electronic structure of $Zr_{1-x}V_xNiSn$ solid solution was calculated by Korringa–Kohn–Rostoker (KKR) method in the coherent potential (CPA) and local density (LDA) approximations [3]. Thermodynamic calculations were carried out in the harmonic oscillation approximation (LMTO) within the theory of functional density DFT. The values of lattice parameter in the k -space of $10 \times 10 \times 10$ k -points and the type of parameterization of Moruzzi–Janak–Williams exchange–correlation potential [4] were used in the calculations. The width of energy window was 22 eV, and the accuracy of Fermi level calculation was $\varepsilon_F \pm 8$ meV.

II. Modeling of the electron energy state, electrokinetic and structural characteristics of $Zr_{1-x}V_xNiSn$

Proceeding from the fact that the above results of $Zr_{1-x}V_xNiSn$ studies did not give an answer to the mechanisms of generation of structural defects of different nature, we will solve the inverse task. It’s known that in order to calculate the electron energy in the first Brillouin zone, it is necessary to know the distribution of atoms (or their absence - vacancies) in the sites of unit cell. On the other hand, the smallest structural disturbances change the local symmetry and the distribution of density of electronic states in a semiconductor. In this case, the adequacy of results of calculating the distribution of density of electronic states (DOS) and the results of experimental studies of electron energy state characteristics of the semiconductor material assumes that the model of its crystal structure is adequate to the spatial distribution of atoms in the real material. Therefore, the results of calculation of electronic structure in comparison with the results, for example, electrokinetic or energy state characteristics, give an opportunity to obtain information about the real structure of crystal, which is not available to X-ray methods of research [2].

With the experimental results of drift rate of Fermi level ε_F as activation energy $\varepsilon_1^p(x)$ for $Zr_{1-x}V_xNiSn$ [1], we searched for the compensation degree (relation of structural defects of acceptor and donor nature), which would give the motion rate of Fermi level ε_F as close as possible to rate from $\varepsilon_1^p(x)$. The electronic structure of $Zr_{1-x}V_xNiSn$ for various variants such as distribution of

atoms in the unit cell, as well as the degree of occupancy of crystallographic positions of all atoms by their own or other atoms was calculated. Based on new results of atomic distribution in the crystal structure of $Zr_{1-x}V_xNiSn$, the calculation of density of electronic states distribution and, in particular, the density of states at the Fermi level $g(\varepsilon_F)$, as well as, for example, the thermoelectric coefficient at different temperatures, which are consistent with the experimental results, was refined.

a). DOS calculation of $Zr_{1-x}V_xNiSn$ for ordered structure version.

To predict the Fermi level ε_F behavior, band gap ε_g and electrokinetic characteristics for $Zr_{1-x}V_xNiSn$, the distribution of density of electronic states (DOS) was calculated. Let us perform an analysis of the results of DOS calculation for an ordered variant of the structure of $Zr_{1-x}V_xNiSn$ semiconductive solid solution (Fig. 1), in which there is a substitution in the crystallographic position $4a$ of Zr atoms by V ones. As already mentioned, the substitution of atoms Zr by V generates the structural defects of donor nature in the crystal (V has more d -electrons than Zr), and the impurity donor level (band) e_D^2 is formed in the band gap near the conduction band ε_C . As known, in the n -ZrNiSn the Fermi level ε_F is located in the donor band ε_D^1 , formed as a result of partial, up to $\sim 1\%$, occupation of $4a$ crystallographic position of Zr atoms by Ni ones (the mechanism of “a priori doping” [5]). In this case, the structure of ZrNiSn compound is disordered.

As seen from Fig. 1, at the lowest concentration of V donor impurity the Fermi level ε_F of $Zr_{1-x}V_xNiSn$ started to drift to the conduction band ε_C and was located in the impurity donor band e_D^1 [1]. At the concentration of V impurity, $x \geq 0.01$, the Fermi level ε_F will cross the percolation level of conduction band ε_C , and the insulator–metal conductivity transition (Anderson transition [6]) will occur. It is quite clear that the electrons are still the main carriers of electricity for $Zr_{1-x}V_xNiSn$, and in the experiment we get negative values of the thermoelectric coefficient $\alpha(x)$.

For this model of the $Zr_{1-x}V_xNiSn$ structure at small

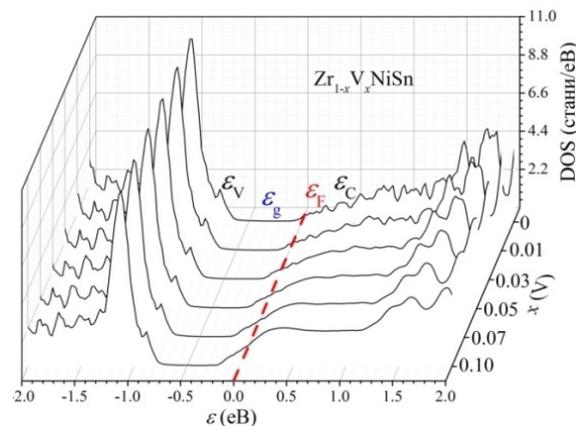


Fig. 1. Calculation of the electron density of states DOS for ordered structure of $Zr_{1-x}V_xNiSn$.

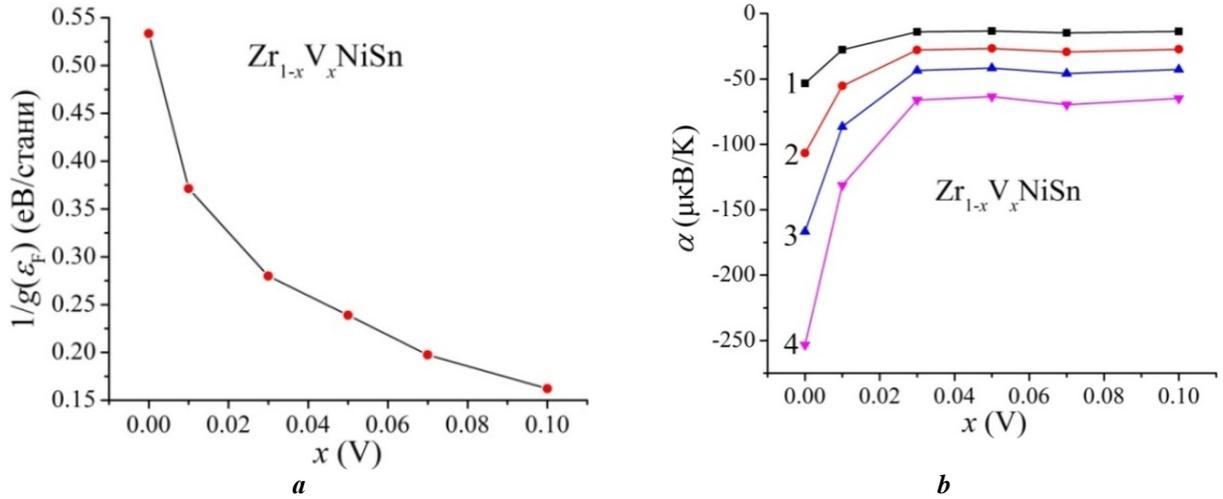


Fig. 2. Calculation of the variation values of $1/g(\varepsilon_F)$ (a) and thermopower coefficient $\alpha(x, T)$ (b) for $Zr_{1-x}V_xNiSn$ at temperatures: 1 - 80 K; 2 - 160 K; 3 - 250 K; 4 - 380 K.

concentration of V atoms, when the Fermi level ε_F approaches to the percolation level of conduction band ε_C at the $k_B T$ distance, the rapid increase of density of states at the Fermi level $g(\varepsilon_F)$ occurs due to the growth of free hole concentration at donor ionization of e_D^2 (Fig. 2, a). The further change in $g(\varepsilon_F)$ values occurred much more slowly when the Fermi level ε_F entered into the conduction band ε_C . The dependence, inverse to the density of states at Fermi level $g(\varepsilon_F)$, the value of which is proportional to the resistivity of the semiconductor material, is shown in Fig. 2, a. Variation of calculated thermopower coefficient is given in Fig. 2, b.

The analyzed ordered model of the $Zr_{1-x}V_xNiSn$ semiconductive solid solution is not consistent with the results of experimental studies [1], where the activation of electrons in the conduction band took place on the $\ln\rho(1/T)$ dependences at high temperatures for all concentrations of V impurity. This also is an indication that the Fermi level ε_F for unknown reason did not cross the percolation level of conduction band and remains in the band gap of $Zr_{1-x}V_xNiSn$. Obviously, the variant of ordered model of structure for $Zr_{1-x}V_xNiSn$ semiconductive solid solution does not correspond to the spatial distribution of atoms in a real crystal.

b). DOS calculation of $Zr_{1-x}V_xNiSn$ for disordered structure version.

From the point of view of physics of semiconductors, it is clear that the reason for “inhibition” of motion of Fermi level ε_F in its movement to conduction band ε_C is the simultaneous generation of structural defects donor and acceptor types in $Zr_{1-x}V_xNiSn$. The question is, in what way are the acceptors generated?

The distribution of density of electronic states for disordered variant of $Zr_{1-x}V_xNiSn$ structure is shown in Fig. 3. As seen from Fig. 3, in the $Zr_{1-x}V_xNiSn$ due to the substitution of Zr atoms by V ones and appearance of structural defects of donor type in the band gap the extended donor band e_D^2 was generated, value of which increases with increase of concentration of V atoms, and

it occupies a significant part of the band gap ε_g .

On the other hand, taking into account that the Ni ($3d^84s^2$) atom has more 3d electrons than V ($3d^34s^2$) one, and the atomic radius of Ni ($r_{Ni} = 0.124$ nm) is slightly smaller than atomic radius of V, we assumed that during introduction of V atoms into $ZrNiSn$ half-Heusler phase they can simultaneously occupy 4a positions of Zr atoms and 4c positions of Ni atoms in various ratios. In case of partial occupation of Ni atoms in 4c position by V atoms, the values of unit cell parameter $a(x)$ for $Zr_{1-x}V_xNiSn$ would have increase (as in experiment [1]), and in the band gap the impurity acceptor band e_A^1 is formed, in which the corresponding number of free electrons was “frozen”. At the same time, the Fermi level ε_F slowly drifts to conduction band ε_C , being in the band gap between the energy levels of donor band e_D^2 and percolation level of conduction band ε_C .

Such position of the Fermi level ε_F ensures, on the one hand, the activation of electrons into the conduction band (the presence of activation parts in the $\ln\rho(1/T)$ dependences of $Zr_{1-x}V_xNiSn$), and on the other hand, the

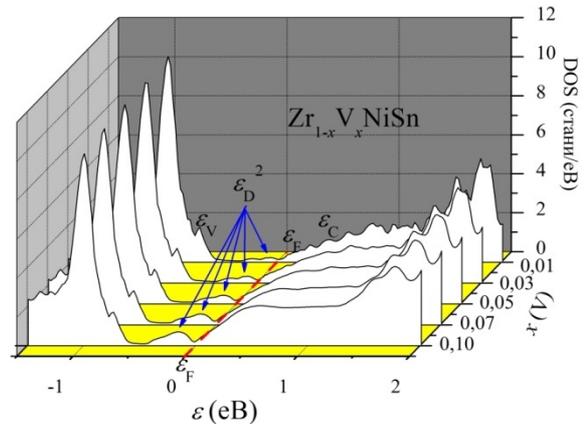


Fig. 3. Calculation of the electron density of states DOS for disordered $Zr_{1-x}V_xNiSn$ structure.

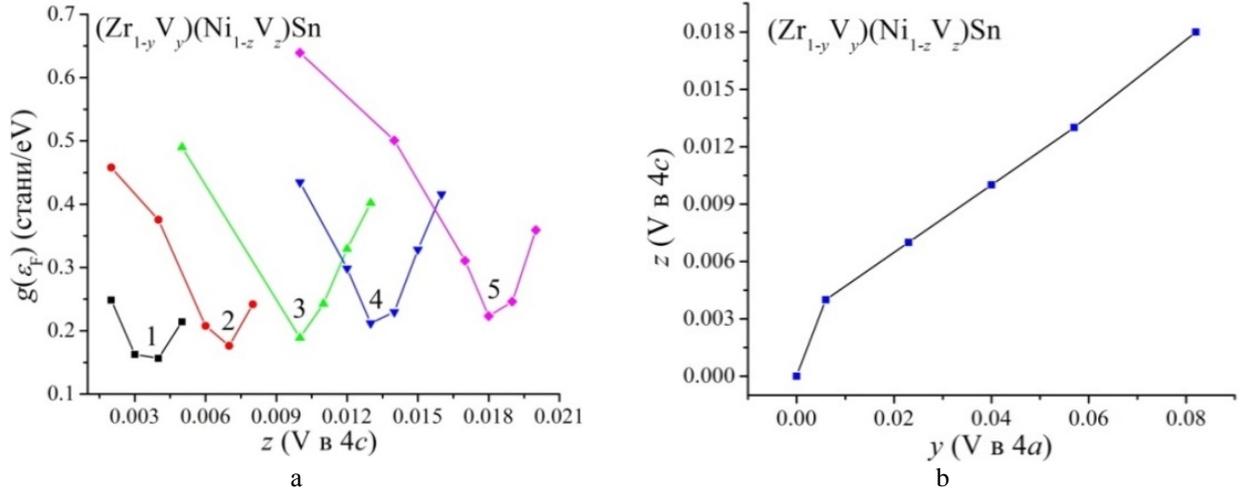


Fig. 4. Calculation of the variation in the density of states at the Fermi level $g(\epsilon_F)$: 1 – $x = 0.01$; 2 – $x = 0.03$; 3 – $x = 0.05$; 4 – $x = 0.07$; 5 – $x = 0.10$ (a) and the number of donors (y) and acceptors (z) in minimum of $g(\epsilon_F)$ dependence (b) for $(Zr_{1-y}V_y)(Ni_{1-z}V_z)Sn$.

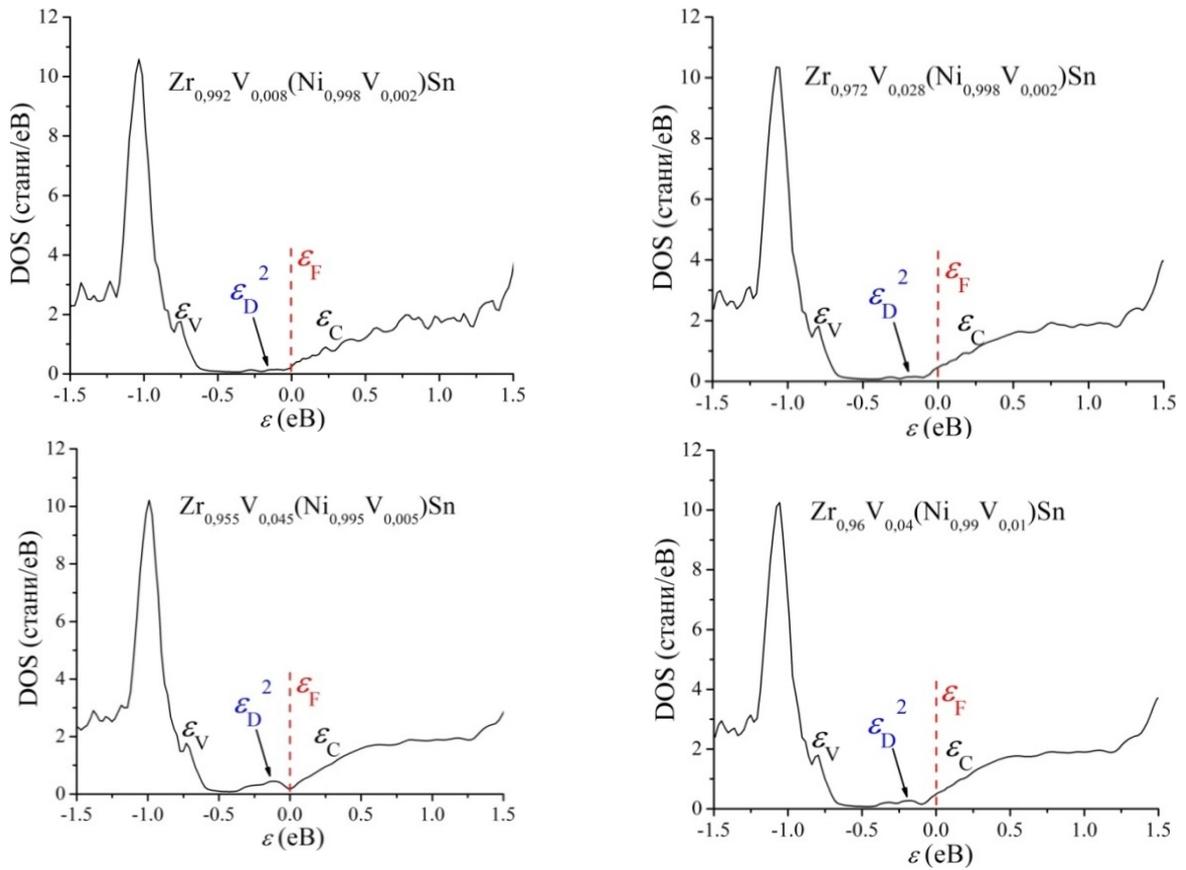


Fig. 5. DOS calculation for $(Zr_{1-y}V_y)(Ni_{1-z}V_z)Sn$ disordered structure at concentrations of V atoms in 4c position of Ni atoms, where the minimum density of states at the Fermi level $g(\epsilon_F)$ appears.

value of thermoelectric coefficient $\alpha(x,T)$ remains negative, corresponding to the results of measurements [1]. In addition, the process of variation of the compensation degree for $Zr_{1-x}V_xNiSn$ semiconductive solid solution could slow motion of the Fermi level ϵ_F to the conduction band ϵ_C .

In DOS calculations (Fig. 4), we conventionally divided the total concentration of V(x) atoms between

two positions: 4a of Zr (y) atoms and 4c of Ni (z) atoms. The V (x) atoms in 4a positions of Zr (y) atoms and 4c positions of Ni (z) atoms in sum are equal to the total concentration of vanadium impurity $x = y + z$ in the studied samples $Zr_{1-x}V_xNiSn$, where $x = 0.01$, $x = 0.03$, $x = 0.05$, $x = 0.07$ and $x = 0.10$. In this case, the solid solution formula transforms into $(Zr_{1-y}V_y)(Ni_{1-z}V_z)Sn$. Thus, by increasing the content of V atoms in 4c position

of Ni atoms, simultaneously, at the same amount, we reduce V concentration in 4a position of Zr atoms and vice versa. From the point of view of semiconductor physics, this means that the increase of concentration of acceptors in Zr_{1-x}V_xNiSn simultaneously reduces the concentration of generated donors by the same amount. Thus, the ratio of structural defects of acceptor and donor nature (compensation degree) provides the location of the Fermi level ε_F in the band gap.

The variation in the density of states at the Fermi level $g(\varepsilon_F)$ for the investigated samples (Zr_{1-y}V_y)(Ni_{1-z}V_z)Sn, as function of the concentration of V atoms in the 4c crystallographic position of Ni(z) atoms, is shown in Fig. 4, a. For example, for the sample of Zr_{1-x}V_xNiSn at $x = 0.01$, the density of states at the Fermi level $g(\varepsilon_F)$ passes through the minimum at V concentration in 4c position of Ni atoms $z \approx 0.004$ (Fig. 4a, curve 1), and for the sample at $x = 0.10$, the Fermi dependence $g(\varepsilon_F)$ passes through the minimum at V concentration in 4c position $z \approx 0.018$ (Fig. 4a, curve 5).

On the other hand, if the Fermi level ε_F is in the donor impurity band e_D^2 , the simultaneous generation of donors and acceptors in various ratios would change the compensation degree that changes the Fermi level position ε_F , as well as the value of density of states at the Fermi level $g(\varepsilon_F)$. The $g(\varepsilon_F)$ values will be the smallest provided the structural defects of acceptor type generated in the crystal (V in 4c position) change the compensation degree in such a way that the Fermi level ε_F is located in the band gap between the percolation level of conduction band and the energy levels of the donor band e_D^2 (see Fig. 4). It's clear that the higher total concentration of V atoms in Zr_{1-x}V_xNiSn, the minimum of dependence on the density of states at the Fermi level $g(\varepsilon_F)$ will appear at the higher concentration of acceptors. The results of modeling of the distribution of density of electronic states for disordered structure of (Zr_{1-y}V_y)(Ni_{1-z}V_z)Sn at

the concentrations of V atoms in 4c position of Ni atoms, when the minimum of density of states at the Fermi level $g(\varepsilon_F)$ appears, are given in Fig. 5.

Conclusions

Thus, the obtained results of DOS calculation show that during introduction of V atoms into the structure of ZrNiSn half-Heusler phase, the V atoms simultaneously substitute Zr atoms in 4a position and occupy 4c position of Ni atoms. As a result, in the Zr_{1-x}V_xNiSn semiconductive material the structural defects of donor type (V has a greater number of *d*-electrons than Zr) and of acceptor type (there is more 3*d*-electrons in Ni than in V) are generated simultaneously. In this case, the energy states of the impurity donor e_D^2 and acceptor e_A^1 bands (donor-acceptor pairs), which determine the mechanism of conduction of the semiconductor, appear in the band gap of Zr_{1-x}V_xNiSn. The results of calculations explain the peculiarities of changes in the values of parameter of unit cell $a(x)$, resistivity $\rho(T, x)$, thermoelectric coefficient $\alpha(T, x)$ and Fermi level ε_F in the Zr_{1-x}V_xNiSn semiconductive solid solution [1] to model the characteristics of thermoelectric material in wide concentration and temperature ranges.

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Дослідження електронної структури напівпровідникового твердого розчину $Zr_{1-x}V_xNiSn$

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Досліджено особливості електронної та кристалічної структур напівпровідникового твердого розчину $Zr_{1-x}V_xNiSn$ ($x = 0 - 0,10$). Для прогнозування поведінки рівня Фермі ϵ_F , ширини забороненої зони ϵ_g та кінетичних характеристик $Zr_{1-x}V_xNiSn$ розраховано розподіл густини електронних станів (DOS). За результатами розрахунків електронної структури та вимірювання електротранспортних властивостей напівпровідникового твердого розчину $Zr_{1-x}V_xNiSn$ визначено механізм одночасного генерування структурних дефектів донорної та акцепторної природи. Встановлено, що у забороненій зоні $Zr_{1-x}V_xNiSn$ з'являються енергетичні стани домішкових донорної e_D^2 та акцепторної e_A^1 зон (донорно-акцепторні пари), які визначають механізми електропровідності напівпровідника.