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Investigation of Electronic Structure of Zr₁₋ₓVₓNiSn
Semiconductive Solid Solution

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The peculiarities of electronic and crystal structures of Zr₁₋ₓVₓNiSn (x = 0 - 0.10) semiconductive solid solution were investigated. To predict Fermi level εₓ behavior, band gap εₓ and electrokinetic characteristics of Zr₁₋ₓVₓNiSn, 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 Zr₁₋ₓVₓNiSn semiconductive solid solution. It was established that in the band gap of Zr₁₋ₓVₓNiSn the energy states of the impurity donor εₓ² and acceptor εₓ¹ levels (donor-acceptor pairs) appear, which determine the mechanisms of conduction of semiconductor.

Keywords: resistivity, thermopower coefficient, Fermi level.

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Introduction
The present work completes the study of conduction mechanisms of Zr₁₋ₓVₓNiSn 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 Zr₁₋ₓVₓNiSn was enlarged unexpectedly with increasing of V concentration. Since the atomic radius of V atom (rₓ = 0.134 nm) was smaller than Zr (rₓ = 0.160 nm), the decreasing of a(x) value is logical.

On the other hand, the substitution of Zr (4d⁰5s²) atoms in the 4a crystallographic position by V (3d⁰4s²) atoms should generate structural defects of donor nature, and the Fermi level εₓ at certain concentrations of donor had to cross the percolation level of conduction band. In this case, the conductivity of Zr₁₋ₓVₓNiSn semiconductor should have changed from activation to metallic [2]. However, the presence of high temperature activation parts on the ln(ρ/1/T) dependence for Zr₁₋ₓVₓNiSn even at the 2800 ppm concentration of donor impurity (Nₓ ≈ 1.9·10¹¹ cm⁻³ for x = 0.10) and the negative values of thermoelectric coefficient α(x, T) indicate that the Fermi level εₓ is in the band gap near the bottom of conduction band εₓC [1]. In a n-type semiconductor doped by donors this can be possible, provided that in Zr₁₋ₓVₓNiSn, 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 εₓ to the conduction band εₓC.

It also appeared that the motion rate of Fermi level εₓ in the direction to conduction band εₓC is not the same at different concentration ranges of V impurity. At the lowest concentration of impurity in Zr₁₋ₓVₓNiSn, x = 0.01, the Fermi level εₓ with the rate Δεₓ/Δx ≈ 77.8 meV/%V rapidly approached to the percolation level of conduction band εₓC 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 εₓ in the direction to conduction band occurred. Thus, at the concentration range x = 0.01 - 0.03, the motion rate of Fermi level εₓ is Δεₓ/Δx = 2.2 meV/%V, and in the x = 0.03 - 0.10 range it is even smaller and equal to Δεₓ/Δx = 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 εₓ would have to move in the same way to the percolation level of conduction band εₓC of Zr₁₋ₓVₓNiSn. It can be assumed that the generation of structural defects of acceptor
nature by unknown mechanism simultaneously with donors in Zr$_{1-x}$V$_x$NiSn causes the “inhibition” of Fermi level $\varepsilon_F$ to conduction band. The experimental results presented in [1] showed that in Zr$_{1-x}$V$_x$NiSn, 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$_x$NiSn thermoelectric material.

I. Experimental

The electronic structure of Zr$_{1-x}$V$_x$NiSn 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$^3$ 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$_x$NiSn

Proceeding from the fact that the above results of Zr$_{1-x}$V$_x$NiSn 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 $\varepsilon_F$ as activation energy $\varepsilon_0^0(x)$ for Zr$_{1-x}$V$_x$NiSn [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 $\varepsilon_F$ as close as possible to rate from $\varepsilon_0^0(x)$. The electronic structure of Zr$_{1-x}$V$_x$NiSn 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$_x$NiSn, 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$_x$NiSn for ordered structure version.

To predict the Fermi level $\varepsilon_F$ behavior, band gap $\varepsilon_g$ and electrokinetic characteristics for Zr$_{1-x}$V$_x$NiSn, 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$_x$NiSn 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) $\varepsilon_D^2$ is formed in the band gap near the conduction band $\varepsilon_C$. As known, in the n-ZrNiSn the Fermi level $\varepsilon_F$ is located in the donor band $\varepsilon_D$, formed as a result of partial, up to ~ 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 $\varepsilon_F$ of Zr$_{1-x}$V$_x$NiSn started to drift to the conduction band $\varepsilon_C$ and was located in the impurity donor band $\varepsilon_D^0$ [1]. At the concentration of V impurity, $x \geq 0.01$, the Fermi level $\varepsilon_F$ will cross the percolation level of conduction band $\varepsilon_C$, 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$_x$NiSn, and in the experiment we get negative values of the thermoelectric coefficient $\alpha(x)$.

For this model of the Zr$_{1-x}$V$_x$NiSn structure at small

![Fig. 1. Calculation of the electron density of states DOS for ordered structure of Zr$_{1-x}$V$_x$NiSn.](image)
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concentration of V atoms, when the Fermi level \(\varepsilon_F\) approaches to the percolation level of conduction band \(\varepsilon_C\) at the \(k_BT\) 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 \(2D_e\) (Fig. 2, a).

The further change in \(g(\varepsilon_F)\) values occurred much more slowly when the Fermi level \(\varepsilon_F\) entered into the conduction band \(\varepsilon_C\). 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\(_x\)NiSn 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 \(\varepsilon_F\) for unknown reason did not cross the percolation level of conduction band and remains in the band gap of Zr\(_{1-x}\)V\(_x\)NiSn. Obviously, the variant of ordered model of structure for Zr\(_{1-x}\)V\(_x\)NiSn semiconductive solid solution does not correspond to the spatial distribution of atoms in a real crystal.

b) DOS calculation of Zr\(_{1-x}\)V\(_x\)NiSn 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 \(\varepsilon_F\) in its movement to conduction band \(\varepsilon_C\) is the simultaneous generation of structural defects donor and acceptor types in Zr\(_{1-x}\)V\(_x\)NiSn. 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\(_x\)NiSn structure is shown in Fig. 3. As seen from Fig. 3, in the Zr\(_{1-x}\)V\(_x\)NiSn 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 \(\varepsilon^+_D\) was generated, value of which increases with increase of concentration of V atoms, and it occupies a significant part of the band gap \(\varepsilon^g\).

On the other hand, taking into account that the Ni (3d\(^4\)4s\(^2\)) atom has more 3d electrons than V (3d\(^3\)4s\(^2\)) 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\(_x\)NiSn would have increase (as in experiment [1]), and in the band gap the impurity acceptor band \(\varepsilon^+_A\) is formed, in which the corresponding number of free electrons was "freezed". At the same time, the Fermi level \(\varepsilon_F\) slowly drifts to conduction band \(\varepsilon_C\), being in the band gap between the energy levels of donor band \(\varepsilon^+_D\) and percolation level of conduction band \(\varepsilon_C\).

Such position of the Fermi level \(\varepsilon_F\) 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\(_x\)NiSn), and on the other hand, the

![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\(_x\)NiSn at temperatures: 1 - 80 K; 2 - 160 K; 3 - 250 K; 4 - 380 K.](image1)

![Fig. 3. Calculation of the electron density of states DOS for disordered Zr\(_{1-x}\)V\(_x\)NiSn structure.](image2)
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$_x$NiSn semiconductive solid solution could slow motion of the Fermi level $\varepsilon_F$ to the conduction band $\varepsilon_C$.

In DOS calculations (Fig. 4), we conventionally divided the total concentration of V($x$) atoms between two positions: 4$a$ of Zr ($y$) atoms and 4$c$ of Ni ($z$) atoms. The V ($x$) atoms in 4$a$ positions of Zr ($y$) atoms and 4$c$ 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$_x$NiSn, 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 4$c$ 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$_x$NiSn 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 $\epsilon_F$ in the band gap.

The variation in the density of states at the Fermi level $g(\epsilon_F)$ for the investigated samples (Zr$_{1-x}$V$_x$)(Ni$_{1-z}$V$_z$)Sn, as function of the concentration of V atoms in the 4c crystallographic position of Ni($\bar{2}$) atoms, is shown in Fig. 4. a. For example, for the sample of Zr$_{1-x}$V$_x$NiSn at $x = 0.01$, the density of states at the Fermi level $g(\epsilon_F)$ 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 $g(\epsilon_F)$ 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 $\epsilon_F$ is in the donor impurity band $\epsilon_D^2$, the simultaneous generation of donors and acceptors in various ratios would change the compensation degree that changes the Fermi level position $\epsilon_F$, as well as the value of density of states at the Fermi level $g(\epsilon_F)$. The $g(\epsilon_F)$ 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 $\epsilon_F$ is located in the band gap between the percolation level of conduction band and the energy levels of the donor band $\epsilon_D^2$ (see Fig. 4). It’s clear that the higher total concentration of V atoms in Zr$_{1-x}$V$_x$NiSn, the minimum of dependence on the density of states at the Fermi level $g(\epsilon_F)$ 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$_{1-x}$V$_x$) (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 $g(\epsilon_F)$ 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$_x$NiSn 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 3d-electrons in Ni than in V) are generated simultaneously. In this case, the energy states of the impurity donor $\epsilon_D^2$ and acceptor $\epsilon_A^1$ bands (donor-acceptor pairs), which determine the mechanism of conduction of the semiconductor, appear in the band gap of Zr$_{1-x}$V$_x$NiSn. 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 $a(T, x)$ and Fermi level $\epsilon_F$ in the Zr$_{1-x}$V$_x$NiSn semiconductive solid solution [1] to model the characteristics of thermoelectric material in wide concentration and temperature ranges.

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_ф, 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 ε_D^2 та акцепторної ε_A^1 зон (донорно-акцепторні пари), які визначають механізми електропровідності напівпровідника.