Synthesis, Structural, Electrical Transport and Energetic Characteristics of ZrNi$_{1-x}$V$_x$Sn Solid Solution

The samples of ZrNi$_{1-x}$V$_x$Sn solid solution ($x = 0 – 0.10$) based on the ZrNiSn half-Heusler phase (MgAgAs structure type) were synthesized by direct arc-melting with homogenous annealing at 1073 K. The electrokinetic and energy state characteristics of the ZrNi$_{1-x}$V$_x$Sn semiconducting solid solution were investigated in the temperature range $T = 80 - 400$ K. An analysis of behavior of the electrokinetic and energetic characteristics, in particular, the motion rate of the Fermi level, $\Delta \varepsilon / \Delta x$ for ZrNi$_{1-x}$V$_x$Sn, allows to assume about the simultaneous generation of the structural defects of donor and acceptor nature in the crystal. The additional researches are required to establish the mechanisms of donor generation.

Keywords: electrical conductivity, thermopower coefficient, Fermi level.

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Introduction

One of the methods for optimization of the thermoelectric characteristics of materials is the doping of intermetallic semiconducting compounds with a structure type MgAgAs (half-Heusler phases) by different types of impurities in all three crystallographic positions of the initial structure. Among the semiconducting phases proposed for obtaining of thermoelectric materials, the materials based on the ZrNiSn half-Heusler phase are studied intensively [1-5].

Investigations of the crystal and electronic structures, electrokinetic, energetic and magnetic characteristics of the Zr$_{1-x}$V$_x$NiSn semiconducting solid solution obtained by introducing of V (3$d^4$4$s^2$) atoms into the structure of the Zr$_2$NiSn half-Heusler phase by substitution of Zr (4$d^5$5$s^2$) in 4$a$ position allowed to establish that the V impurity atoms also simultaneously substitute Ni atoms (3$d^4$4$s^2$) in 4$c$ position [6,7]. As a result, the structural defects of donor (V has higher number of d-electrons than Zr) and acceptor (Ni has more 3$d$-electrons than V) nature are generated simultaneously in the semiconducting Zr$_{1-x}$V$_x$NiSn material. In this case, the energy levels of the impurity donor $\varepsilon_D$ and acceptor $\varepsilon_A$ bands (donor-acceptor pairs), which determine the electrical conductivity of the semiconductor, appear in the band gap of Zr$_{1-x}$V$_x$NiSn.

These conclusions are based, on the one hand, on the results of experimental studies of the temperature and concentration dependences of the electrical resistivity $\rho(T, x)$ and thermopower coefficient $\alpha(T, x)$ of Zr$_{1-x}$V$_x$NiSn, and on the other hand, on the results of modeling of the electronic structure and choosing such its variant, when the results of calculation of the Fermi level $\varepsilon_F$ behavior, the electrical resistivity $\rho(T, x)$ and the thermopower coefficient $\alpha(T, x)$ within standart diviations are in agreement with the obtained experimental dependencies.

The most convincing argument in favor of simultaneous generation of donor-acceptor pairs in the Zr$_{1-x}$V$_x$NiSn crystal was the results of the Fermi level $\varepsilon_F$ behavior. It turned out that the motion rate of the Fermi level $\varepsilon_F$ to the conduction band $\varepsilon_C$ is not the same at different V concentrations. In the concentration range $x = 0$-0.01, the Fermi level $\varepsilon_F$ moved to the percolation level of the conduction band $\varepsilon_C$ with a rate $\Delta \varepsilon / \Delta x = 77.8$ meV/V and approached it at the distance 19.8 meV. However, at higher V concentrations, a rapid decrease of the motion rate was observed, in particular, in the concentration range $x = 0.01$–0.03, it was $\Delta \varepsilon / \Delta x = 2.2$ meV/V, and in the range $x = 0.03$–0.10 it decreased up to $\Delta \varepsilon / \Delta x = 0.7$ meV/V. Since the concentration of the V atoms, which could generate the donors, is introduced in the ZrNiSn compound according
to the linear law, the Fermi level \( \varepsilon_F \) would have to move in the same way to the level of the conduction band \( \varepsilon_c \) of Zr\(_{1-x}\)V\(_x\)NiSn. An analysis of the obtained results in Refs.\([6,7]\) showed that the only reason of the “inhibition” of the Fermi level \( \varepsilon_F \) is simultaneous generation of the donors and structural defects of acceptor nature in the Zr\(_{1-x}\)V\(_x\)NiSn solid solution by the mechanism described above.

In this context, it is logical to get an answer to the question concerning the behavior of the V atoms in the structure of the ZrNiSn half-Heusler phase when they are included in the structure by substitution of Ni atoms in 4c position that would result in the generation of the structural defects of acceptor nature in ZrNi\(_{1-x}\)V\(_x\)Sn? Will it be under these conditions energetically possible to occupy the crystallographic position 4a of Zr atoms by V atoms, while generating the structural defects of the donor nature? This formulation of the problem for ZrNi\(_{1-x}\)V\(_x\)Sn semiconducting solid solution is a mirror image to the already studied case of the Zr\(_{1-x}\)V\(_x\)NiSn solid solution \([6,7]\).

I. Experimental

The samples of the ZrNi\(_{1-x}\)V\(_x\)Sn solid solution (\(x=0\)–0.10) were synthesized by an arc melting of the pure elements using a tungsten electrode under high purity argon atmosphere (Ti as a getter). For alloys equilibrium the homogenous annealing was performed for 720 h at a temperature of 1073 K, followed by quenching in cold water. The chemical and phase compositions of the samples were controlled by the method of energy dispersive X-ray spectroscopy (EDRS) using electron microscope-microanalyzer REMMA-102-02. The crystallographic parameters were calculated using X-ray powder diffraction data (diffractometer DRON-4.0, FeK\(_\alpha\)-radiation) with Fullprof Suite software package \([8]\). The calculations of the electronic structure were carried out by Corringa-Kohn-Rostoker (KKR) methods in the approximation of the coherent potential (CPA) and local density (LDA) \([9]\) using the exchange-correlation potential Moruzzi-Janak-Williams \([10,11]\). Location of the Fermi level \( \varepsilon_F \) was carried out with an accuracy of \( \pm 8 \) meV. The temperature and concentration dependences of the electrical resistivity \( \rho \), thermopower coefficient \( \alpha \) (in relation to copper) of the ZrNi\(_{1-x}\)V\(_x\)Sn solid solution samples were measured at temperatures \( T = 80-400 \) K and concentrations \( N_\alpha = 1.9 \times 10^{20} \) cm\(^{-3} \) \((0.01) \times 1.9 \times 10^{21} \) cm\(^{-3} \) \((0.10)\).

II. Investigation of crystal and electronic structures of Zr\(_{1-x}\)V\(_x\)NiSn

X-ray phase and structural analyses of the ZrNi\(_{1-x}\)V\(_x\)Sn semiconducting solid solution showed that the obtained X-ray powder patterns of the samples were indexed in the MgAgAs structure type \([12]\) and there are no reflections which belong to other phases. In turn, the study of the elemental composition of the surface of the samples has established their correlation with the initial composition.

A priori, in case of substitution of Ni atoms \((r_N=0.124 \) nm) in the 4c crystallographic position by V \((r_V=0.134 \) nm) in ZrNi\(_{1-x}\)V\(_x\)Sn an increase of the lattice parameter values \( a(x) \) would be expected, since the atomic radius of V is larger, than Ni. Obtained experimental results demonstrate exactly such general tendency to increase of the \( a(x) \) values for ZrNi\(_{1-x}\)V\(_x\)Sn (Fig. 1). However, the character of the \( a(x) \) dependence for ZrNi\(_{1-x}\)V\(_x\)Sn depending on the V atom concentration is different. Thus, the variation rate of lattice parameter \( a(x) \) for ZrNi\(_{1-x}\)V\(_x\)Sn (the angle of slope of the \( a(x) \) dependence) in the concentration ranges \( x = 0.01 \pm 0.03 \) and \( x = 0.07 \pm 0.10 \) is close, but much less than in the range \( x = 0.03 \pm 0.07 \). This behavior of the lattice parameter \( a(x) \) for ZrNi\(_{1-x}\)V\(_x\)Sn gives reason to suppose that the V impurity atoms introduced into the matrix of the ZrNiSn half-Heusler phase could also partially occupy other crystallographic positions, in particular, 4a position of Zr atoms \([6,7]\). Taking into account the smaller atomic radius of V atom comparing with Zr \((r_Z = 0.160 \) nm), the partial occupation of the crystallographic position 4a of Zr atoms by V atoms could reduce the integral index of the variation rate of the lattice parameter value \( a(x) \) for ZrNi\(_{1-x}\)V\(_x\)Sn. This assumption can be confirmed (or denied) by the results of electrokinetic characteristics of the semiconducting solid solution.

The crystal structure refinements of ZrNi\(_{1-x}\)V\(_x\)Sn by the powder method did not allow to determine unambiguously the degree of its ordering. It’s worth to remind that previous studies \([6,7]\) showed that the structure of the Zr\(_{1-x}\)V\(_x\)NiSn solid solution is disordered also due to the simultaneous partial substitution of Ni atoms. Similar behavior would be expected in the case of the introduction of V atoms into the structure of the ZrNiSn compound by substitution of the Ni atoms. In the case of substitution of Ni \( (3d^84s^2) \) atoms in the crystallographic positions 4c by V \( (3d^44s^2) \) atoms in a semiconducting ZrNi\(_{1-x}\)V\(_x\)Sn solid solution the structural defects of acceptor nature would be generated, since the number of 3d-electrons of V is lower than Ni. This leads to the appearance of energy levels of the impurity acceptor band \( E_A \) in the band gap of ZrNi\(_{1-x}\)V\(_x\)Sn, and at higher V atoms concentration the electrical conductivity
of semiconductor will be determined by free holes, and it should be accompanied by positive values of the thermopower coefficient $\alpha(T, x)$ in the experiment.

Instead, in the case of partial occupation of the crystallographic position $4a$ of Zr atoms $(4d^5S^2)$ by V atoms the structural defects of the donor nature will also be generated in the crystal, since V has more $d$-electrons. It will result in the appearance of energy levels of the impurity donor band $\varepsilon_D^0$ and will cause realization of mixed conductivity in ZrNi$_{1-x}$V$_x$Sn with the participation of donor-acceptor pairs [13]. During this the sign of the thermopower coefficient $\alpha(T, x)$ of ZrNi$_{1-x}$V$_x$Sn and the type of main carriers of current will be determined by the ratio of the concentrations of structural defects of the acceptor and donor nature, generated in the semiconductor.

A third variant of the behavior of V impurity atoms in the ZrNi$_{1-x}$V$_x$Sn structure is also possible. It consists in the possible partial occupation of tetrahedral voids of the structure, which make up $\sim 24\%$ of the total unoccupied atomic volume of the unit cell, by V atoms [14]. Herewith, the structural defects of the donor nature are generated in the crystal, and the obtained ZrNi$_{1-x}$V$_x$Sn samples will be heavily doped and highly compensated semiconductors (HDHCS) [15], as shown in Refs. [6,7].

It can be stated that the structural studies of ZrNi$_{1-x}$V$_x$Sn in principle did not allow to establish a certain number of atoms or their statistical mixture in a particular crystallographic position. This information is beyond the accuracy of the X-ray diffraction method. We can only evaluate the occupancy of the crystallographic position of a compound by a certain type of atoms on a qualitative level. At the same time, the combination of the results of structural studies with the electrophysical properties allows to narrow down the variation of the occupation of a particular crystallographic position by a certain type of atoms or their statistical mixture. Performed on this base the calculation of the electronic structure of the solid solution and its comparison with the results of physical properties investigation allows us to choose the result of calculations obtained for a particular Wigner-Seitz cell, which is essentially reverse to a real crystal. Thus, the results of the electronic structure calculation in combination with the results of the physical properties of the crystal provide information on the crystal structure which is unavailable by using X-ray methods.

For modeling of the electrical conductivity mechanisms in the ZrNi$_{1-x}$V$_x$Sn solid solution, the Fermi level behavior $\epsilon_F$, the density of electron states at the Fermi level $g(\epsilon_F)$, the width of band gap $\epsilon_g$, etc., the density of electronic states (DOS) was calculated (Fig. 2a). The first iteration in the electronic structure calculations of ZrNi$_{1-x}$V$_x$Sn was the calculation of the distribution of the density of electronic states (DOS) for the case of an ordered crystal structure assuming that V atoms occupy only the $4c$ crystallographic position of Ni atoms (Fig. 2a). The results of the DOS calculation for the case of an ordered ZrNi$_{1-x}$V$_x$Sn crystal structure are predictable and imply a smooth drift of the Fermi level $\epsilon_F$ from the edge of conduction band $\epsilon_C$ through the band gap $\epsilon_g$ to the valence band $\epsilon_V$, which will be crossed at $x=0.04$, as it’s illustrated in Fig. 2a.

The result of the Fermi level $\epsilon_F$ drift from the conduction band $\epsilon_C$ to the valence band $\epsilon_V$ shows the dynamics of the electron and hole concentration change in ZrNi$_{1-x}$V$_x$Sn. Thus, at concentrations $x<0.02$ of ZrNi$_{1-x}$V$_x$Sn, when the Fermi level $\epsilon_F$ is located between the bottom of the conduction band $\epsilon_C$ and the middle of the band gap $\epsilon_g$, electrons are the main carriers of electric current. In this case, the doping of the $n$-ZrNi$_{1-x}$V$_x$Sn semiconductor of the electron conduction type by the lowest concentration of acceptors will be accompanied by an increase of the compensation degree [14,15], and in the experiment it should be manifested by an increase in the amplitude values of the large-scale fluctuation of the continuous energy band $\epsilon_{C}^{F}$. At the same time, at concentrations $x>0.02$ and up to crossing of the top of the valence band $\epsilon_V$ by the Fermi level $\epsilon_F$, holes are the main carriers of electric current. Now the doping of the $p$-type semiconductor with acceptor impurities should lead to a decrease of the compensation degree and energy values $\epsilon_{C}^{F}$. At the Fermi level $\epsilon_F$ crossing the edge of the valence band, the transition of electrical conductivity of ZrNi$_{1-x}$V$_x$Sn from activation to metallic, which is the Anderson transition [15], will take place.
All described above can also be seen in dependence of the density of electronic states at the Fermi level $g(\varepsilon_F)$ for ZrNi$_{1-x}$V$_x$Sn (Fig. 2b). The decrease of the density of electron states values at the Fermi level $g(\varepsilon_F)$ in the concentration range $0 \leq x \leq 0.02$ is associated with a decrease in the concentration of free electrons due to their "freezing" on the impurity states of the generated acceptor band $\varepsilon^b_F$. At the same time, the smallest value of the density of electron states at the Fermi level $g(\varepsilon_F)$ takes place provided that the maximum distance of the Fermi level $\varepsilon_F$ from the continuous energy bands is achieved when the Fermi level is passing through the middle of the band gap $\varepsilon_F$ ($x \approx 0.02$). After passing the middle of the band gap by the Fermi level $\varepsilon_F$ and its approaching to the valence band $\varepsilon_V$, activation of the states in the valence band is facilitated, which result in the increase of their concentration and the values of the density of electron states at the Fermi level $g(\varepsilon_F)$ of ZrNi$_{1-x}$V$_x$Sn.

At concentrations of the acceptor impurity which correspond to the ZrNi$_{1-x}$V$_x$Sn compositions, $x \approx 0.04$, the acceptor band $\varepsilon^b_F$ merges with the levels of the valence band, forming a "tail of density states". However, this result can only be considered hypothetical, since the structural studies of ZrNi$_{1-x}$V$_x$Sn have shown a rather complicated mechanism of the inclusion of V atoms in the structure of the ZrNiSn compound. Moreover, after performed structural studies of the ZrNi$_{1-x}$V$_x$Sn solid solution we do not have complete information about its crystal structure.

Does this mean that we are not entitled to obtain an adequate electronic structure of ZrNi$_{1-x}$V$_x$Sn? After all, there is a problem in which way to construct a Wigner- Seitz cell and what statistical mixture of atoms is placed in its crystallographic sites to calculate DOS? The first step to solving this problem is the study of the electrokinetic properties of ZrNi$_{1-x}$V$_x$Sn which will allow to obtain the energetic characteristics of the semiconductor and to use them for modeling of an adequate electronic structure.

III. Investigations of electrokinetic and energetic characteristics of ZrNi$_{1-x}$V$_x$Sn

The temperature and concentration dependencies of electric resistivity $\rho$ and thermopower coefficient $\alpha$ of ZrNi$_{1-x}$V$_x$Sn are presented in Figs. 3, 4. The dependencies $\ln(\rho(T))$ and $\alpha(T)$ of ZrNi$_{1-x}$V$_x$Sn (Fig. 3) are typical for heavily doped and highly compensated semiconductors [15] and activation parts at high and low temperatures indicated several electrical conductivity mechanisms.

For studied samples (except sample with V content $x=0.10$) at high temperatures activation of the current carriers from the Fermi level $\varepsilon_F$ to the continuous energy bands takes place. At low temperatures hopping conductivity on the energy states closed to the Fermi level $\varepsilon_F$ is realized. Variation of electric resistivity values $\rho(T)$ of ZrNi$_{1-x}$V$_x$Sn is described by the next relation [15]:

$$\rho^{-1}(T) = \rho^{-1}_1 \exp\left(\frac{-\varepsilon^b_F}{k_B T}\right) + \rho^{-1}_2 \exp\left(\frac{-\varepsilon^a_F}{k_B T}\right)$$  \hspace{1cm} (1)

where the first high-temperature term describes an activation of the current carriers $\varepsilon^b_F$ from the Fermi level $\varepsilon_F$ to the percolation levels of the continuous energy bands; second low-temperature term describes the hopping conductivity $\varepsilon^a_F$. From the high- and low-temperature parts of the $\ln(\rho(T))$ dependencies, the energy activation values $\varepsilon^b_F$ and $\varepsilon^a_F$, respectively, were calculated (Fig. 5a). In turn, the temperature dependencies of the thermopower coefficient $\alpha(T)$ of ZrNi$_{1-x}$V$_x$Sn are described by relation [16]:

$$\alpha = \frac{k_B}{e} \left( \frac{\varepsilon^b_F}{k_B T} - \gamma + 1 \right)$$  \hspace{1cm} (2)

where $\gamma$ is a parameter which depends on the scattering mechanism. From high-temperature parts of $\alpha(T)$ dependencies, the activation energy values $\varepsilon^b_F$ which are proportional to the amplitude of the large-scale fluctuation of the continuous energy bands were calculated. From the low-temperature parts of $\alpha(T)$ dependencies energy activation values $\varepsilon^a_F$ which are proportional to the amplitude of small-scale fluctuation HDHCs (Fig. 5a) [14, 15] were obtained.

The inclusion of V impurity atoms into the structure of the ZrNiSn half-Heusler phase by the substitution of Ni atoms changes the behavior of $\ln(\rho(T))$ and $\alpha(T)$ temperature dependencies and values of the electric resistivity $\rho(x,T)$ and thermopower coefficient $\alpha(x,T)$ (Figs. 3,4). First of all, which immediately indicates disagreement between energy characteristics modeling of ZrNi$_{1-x}$V$_x$Sn provided the crystal structure ordering upon substitution of the Ni atoms by V ones are negative values of the thermopower coefficient $\alpha(x,T)$ at all concentrations and temperatures (Figs.3,4b). It means that at high temperatures the activation parts of $\ln(\rho(T))$ and $\alpha(T)$ dependencies represent thermal throwing of electrons from impurity donor level to the conduction band. Question concerning the nature of this level appears.

We predicted that in the case of substitution of Ni atoms by V ones in ZrNi$_{1-x}$V$_x$Sn crystal, the structural defects of the acceptor nature should be generated, that is accompanied by a change in the sign of the thermopower coefficient $\alpha(x,T)$ from negative to positive and an increase of the electric resistivity $\rho(x,T)$ values due to the decrease of free electron concentration caused by their "freezing" on the energy states of the acceptor impurity band $\varepsilon^b_F$. Nevertheless, there is no agreement between obtained results of electric resistivity $\rho(x,T)$ and thermopower coefficient $\alpha(T)$ values and modeling of the energetic characteristics of ZrNi$_{1-x}$V$_x$Sn (Fig. 2). Furthermore, decreasing of the electric resistivity $\rho(x,T)$ values (Fig. 4a) is possible due to increasing of the free electron concentration (thermopower coefficient $\alpha(x,T)$ is negative (Fig. 4b)) at their thermal activation from impurity donor level (band). We come again to the question concerning the nature of this level (band) and mechanism of the generation of the structural defect of donor nature in the ZrNi$_{1-x}$V$_x$Sn crystal.
It is known that ZrNiSn structure is disordered due to the partial occupation of Zr (4\(a\)) position by Ni atoms which generates the structural defects of the donor nature and the impurity donor band \(\varepsilon_{D1}\) is generated in the band gap ("apriori" doping by donors) [14,15]. On the other hand, experimental studies showed that the formation of the solid solutions based on ZrNiSn compound in different ways was usually accompanied by the structure ordering at impurity atom concentration \(x \approx 0.01\). In this case, all Ni atoms leave 4\(a\) position of Zr atoms and the defects of the donor nature disappear ("healed" [14,15]). It can be assumed that in ZrNi\(_{1-x}\)V\(_x\)Sn in the concentration range \(x = 0-0.01\) the decrease of the electron concentration caused by disappearance of an impurity donor band \(\varepsilon_{D1}\) due to displacement of Ni atoms from 4\(a\) position of Zr atoms and structure ordering take place. In other words, the ordering of the ZrNi\(_{1-x}\)V\(_x\)Sn structure is similar to the doping of the semiconductor by acceptors which capture free electrons reducing their concentration.

If the substitution of Ni atoms by V in ZrNi\(_{1-x}\)V\(_x\)Sn would take place, then the acceptor effect of reducing the concentration of free electrons would have to be even more pronounced. However, the results of change in the
Fig. 5. Variation of the activation energy values $\varepsilon_1^p(x)$ (1) and $\varepsilon_1^p(x)$ (2) of ZrNi$_{1-x}$V$_x$Sn.

Conclusion concerning the generation of the structural defects of the acceptor nature in ZrNi$_{1-x}$V$_x$Sn is based on analysis of the compensation degree change of semiconductor. Presence of the high-temperature activation part on $a(1/T)$ dependence for ZrNi$_{1-x}$V$_x$Sn (Fig. 3) allows to calculate activation energy values $\varepsilon_1^p$ which are proportional to an amplitude of the large-scale fluctuation of the continuous energy bands of DHHCs. In turn, the fluctuation amplitude of continuous energy bands determines the compensation degree and is maximal provided full compensation of the semiconductor, when concentration of ionized acceptors and donors is the same. In this case the Fermi level $\varepsilon_F$ is located at the middle of the band gap and $\varepsilon_1^p=1/2\varepsilon_F$ [14, 15].

As shown in Fig. 5 (curve 2), maximum of $\varepsilon_1^p(x)$ dependence for ZrNi$_{1-x}$V$_x$Sn at V concentration $x=0.03$ takes place. Taking into account that ZrNiSn compound is semiconductor with electron type of conductivity, a change of compensation degree and maximum on the $\varepsilon_1^p(x)$ dependence can only occur due to acceptor appearance, that partially compensate present donors in the crystal. Thus, appearance of the acceptor in ZrNi$_{1-x}$V$_x$Sn indicated that Ni atoms in 4c position are substituted by V atoms. On the other hand, the total number of the structural defects of the donor nature prevails the number of acceptor because thermopower coefficient values $a(T,x)$ are still negative. We cannot state definitely that the structural defects of the donor nature formed due to partial occupation of 4a position of Zr atoms by V atoms or possible occupation of the tetrahedral voids in the structure [12] by V atoms are the source of the donors. This question requires additional study.

Appearance of the acceptor in ZrNi$_{1-x}$V$_x$Sn is demonstrated by behavior of activation energy of electrons $\varepsilon_1^p(x)$ from the Fermi level $\varepsilon_F$ to the mobility edge of the conduction band (Fig. 5, curve 1). Decreasing of activation energy values $\varepsilon_1^p(x)$ provided negative values of the thermopower coefficient $a(T,x)$ indicates the motion of the Fermi level $\varepsilon_F$ toward to the percolation level of the conduction band that is possible when the donor concentration increases and prevails acceptor concentration. Nevertheless, rate of the Fermi level $\varepsilon_F$ moving to the conduction band (slope of $\varepsilon_1^p(x)$ behavior) in the concentration range $x=0.01–0.03$ is $\Delta\varepsilon/F/\Delta x=0.5$ meV/%V, in the range $x=0.03–0.05$ it equals $\Delta\varepsilon/F/\Delta x=3$ meV/%V. Appearance of the acceptors in the crystal causes “braking” of motion of the Fermi level $\varepsilon_F$ to the conduction band.

Thus, the obtained experimental results of the structural, electrokinetic and energetic studies of the ZrNi$_{1-x}$V$_x$Sn solid solution show complicated and ambiguous mechanism of V atom inclusion in the matrix of ZrNiSn half-Heusler phase. Furthermore, the formula of the solid solution ZrNi$_{1-x}$V$_x$Sn is not correct, because it does not represent the process occurring in the crystal, but it only shows the method of the sample preparation from the components for melting. Electronic structure modeling of the semiconductor is significantly complicated due to variability of V atom behavior in the ZrNiSn. As a result ambiguity concerning the nature of the donor level appears. Is it a structural defect of donor nature caused by occupation by V atoms in 4a position or Zr atoms or tetrahedral voids in the structure? Answers on these questions will be an object of our next study.

Conclusions

Based on the obtained results we can assume that in the ZrNi$_{1-x}$V$_x$Sn solid solution the structural defects of the acceptor and donor (with opposite effective charge) nature are generated simultaneously. Concentration of the donor defects increases with V content. To establish the mechanism of donor generation we will perform additional studies of the ZrNi$_{1-x}$V$_x$Sn semiconducting solid solution in our next work.

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Синтез, структурні, електротранспортні та енергетичні характеристики твердого розчину ZrNi₁₋ₓVₓSn

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Зразки твердого розчину ZrNi₁₋ₓVₓSn (x = 0 - 0.10) на основі напів-Гейслерової фази ZrNiSn (структурний тип MgAgAs) синтезовано методом електродугового плавлення з гомогенізаційним відпалюванням за температури 1073 К. Електрокінетичні та енергетичні характеристики напівпровідникового твердого розчину ZrNi₁₋ₓVₓSn досліджено в інтервалі температур T = 80 – 400 К. На основі аналізу поведінки кінетичних та енергетичних характеристик, зокрема, швидкості руху рівня Фермі Δψ/Δχ ZrNi₁₋ₓVₓSn, зроблено припущення про одночасне генерування у кристалі структурних дефектів акцепторної та донорної природи. Встановлення механізмів генерування донорів вимагає додаткових досліджень.

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