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Synthesis, Structural, Electrical Transport and Energetic Characteristics of $ZrNi_{1-x}V_xSn$ Solid Solution

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The samples of $ZrNi_{1-x}V_xSn$ 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 $ZrNi_{1-x}V_xSn$ 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, $\Delta\varepsilon_F/\Delta x$ for $ZrNi_{1-x}V_xSn$, 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 $Zr_{1-x}V_xNiSn$ semiconducting solid solution obtained by introducing of V ($3d^34s^2$) atoms into the structure of the $ZrNiSn$ half-Heusler phase by substitution of Zr ($4d^25s^2$) in $4a$ position allowed to establish that the V impurity atoms also simultaneously substitute Ni atoms ($3d^84s^2$) in $4c$ 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 $3d$ -electrons than V) nature are generated simultaneously in the semiconducting $Zr_{1-x}V_xNiSn$ material. In this case, the energy levels of the impurity donor ε_D^2 and acceptor ε_A^1 bands (donor-acceptor pairs), which determine the electrical conductivity of the semiconductor, appear in

the band gap of $Zr_{1-x}V_xNiSn$.

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 $Zr_{1-x}V_xNiSn$, 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 ε_F behavior, the electrical resistivity $\rho(T,x)$ and the thermopower coefficient $\alpha(T,x)$ within standart deviations are in agreement with the obtained experimental dependencies.

The most convincing argument in favor of simultaneous generation of donor-acceptor pairs in the $Zr_{1-x}V_xNiSn$ crystal was the results of the Fermi level ε_F behavior. It turned out that the motion rate of the Fermi level ε_F to the conduction band ε_C is not the same at different V concentrations. In the concentration range $x = 0-0.01$, the Fermi level ε_F moved to the percolation level of the conduction band ε_C with a rate $\Delta\varepsilon_F/\Delta x \approx 77.8$ 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 $\Delta\varepsilon_F/\Delta x \approx 2.2$ meV/%V, and in the range $x=0.03-0.10$ it decreased up to $\Delta\varepsilon_F/\Delta x \approx 0.7$ 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 ε_F would have to move in the same way to the level of the conduction band ε_C of $Zr_{1-x}V_xNiSn$. An analysis of the obtained results in Refs.[6,7] showed that the only reason of the "inhibition" of the Fermi level ε_F is simultaneous generation of the donors and structural defects of acceptor nature in the $Zr_{1-x}V_xNiSn$ 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 $ZrNi_{1-x}V_xSn$? 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 $ZrNi_{1-x}V_xSn$ semiconducting solid solution is a mirror image to the already studied case of the $Zr_{1-x}V_xNiSn$ solid solution [6,7].

I. Experimental

The samples of the $ZrNi_{1-x}V_xSn$ 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 ε_F was carried out with an accuracy of ± 8 meV. The temperature and concentration dependences of the electrical resistivity (ρ), thermopower coefficient (α) (in relation to copper) of the $ZrNi_{1-x}V_xSn$ solid solution samples were measured at temperatures $T = 80-400$ K and concentrations $N_A^V \approx 1.9 \cdot 10^{20} \text{ cm}^{-3}$ ($x=0.01$) $\div 1.9 \cdot 10^{21} \text{ cm}^{-3}$ ($x=0.10$).

II. Investigation of crystal and electronic structures of $Zr_{1-x}V_xNiSn$

X-ray phase and structural analyses of the $ZrNi_{1-x}V_xSn$ 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.

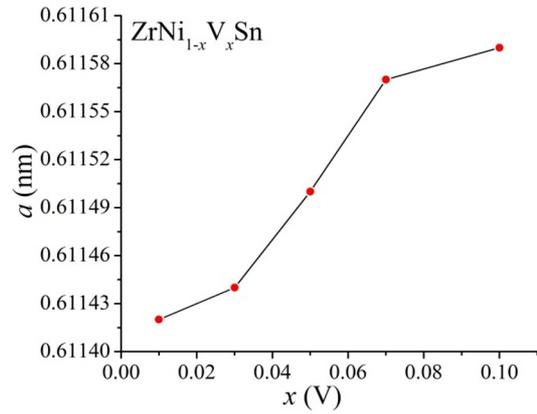


Fig. 1. Variation of the lattice parameter $a(x)$ of $ZrNi_{1-x}V_xSn$.

A priori, in case of substitution of Ni atoms ($r_{Ni}=0.124$ nm) in the 4c crystallographic position by V ($r_V=0.134$ nm) in $ZrNi_{1-x}V_xSn$ 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 $ZrNi_{1-x}V_xSn$ (Fig. 1). However, the character of the $a(x)$ dependence for $ZrNi_{1-x}V_xSn$ depending on the V atom concentration is different. Thus, the variation rate of lattice parameter $a(x)$ for $ZrNi_{1-x}V_xSn$ (the angle of slope of the $a(x)$ dependence) in the concentration ranges $x = 0.01 \div 0.03$ and $x = 0.07 \div 0.10$ is close, but much less than in the range $x = 0.03 \div 0.07$. This behavior of the lattice parameter $a(x)$ for $ZrNi_{1-x}V_xSn$ 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 ($r_{Zr} = 0.160$ 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 $ZrNi_{1-x}V_xSn$. This assumption can be confirmed (or denied) by the results of electrokinetic characteristics of the semiconducting solid solution.

The crystal structure refinements of $ZrNi_{1-x}V_xSn$ 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 $Zr_{1-x}V_xNiSn$ 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 ($3d^34s^2$) atoms in a semiconducting $ZrNi_{1-x}V_xSn$ 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 ε_A^1 in the band gap of $ZrNi_{1-x}V_xSn$, and at higher V atoms concentration the electrical conductivity

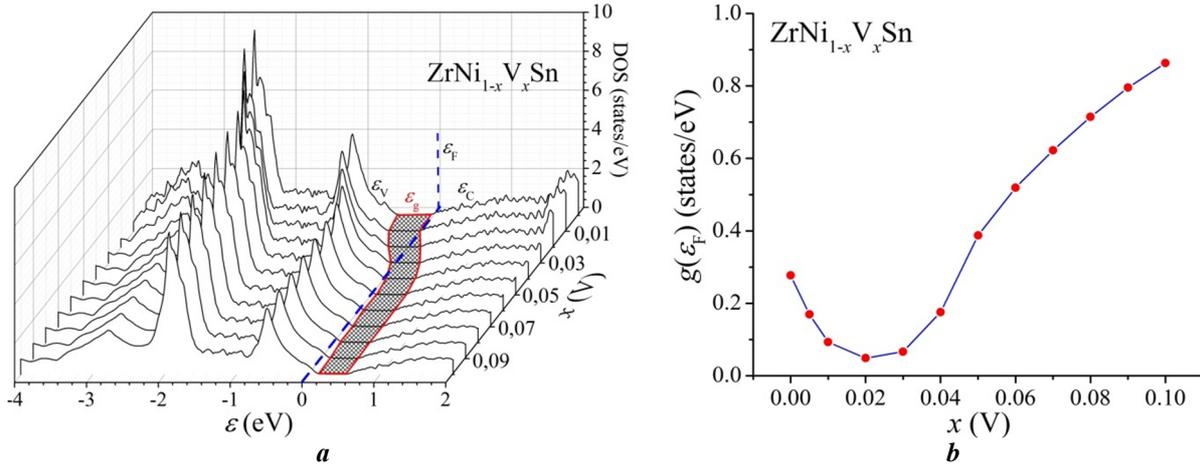


Fig. 2. Variations of the distribution of electron density states DOS (a) and the density of states at the Fermi level $g(\epsilon_F)$ (b) in the $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ solid solution (case of Ni atom substitution by V atoms).

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 ($4d^25s^2$) 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 ϵ_D^2 and will cause realization of mixed conductivity in $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ with the participation of donor-acceptor pairs [13]. During this the sign of the thermopower coefficient $\alpha(T,x)$ of $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ 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 $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ 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 $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ 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 $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ 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 $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ solid solution, the Fermi level behavior ϵ_F , the density of electron states at the Fermi level $g(\epsilon_F)$, the width of band gap ϵ_g , etc., the density of electronic states (DOS) was calculated (Fig. 2a). The first iteration in the electronic structure calculations of $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ 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 $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ crystal structure are predictable and imply a smooth drift of the Fermi level ϵ_F from the edge of conduction band ϵ_C through the band gap ϵ_g to the valence band ϵ_V , which will be crossed at $x \approx 0.04$, as it's illustrated in Fig. 2a.

The result of the Fermi level ϵ_F drift from the conduction band ϵ_C to the valence band ϵ_V shows the dynamics of the electron and hole concentration change in $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$. Thus, at concentrations $x < 0.02$ of $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$, when the Fermi level ϵ_F is located between the bottom of the conduction band ϵ_C and the middle of the band gap ϵ_g , electrons are the main carriers of the electric current. In this case, the doping of the n - ZrNiSn 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 ϵ_1^α . At the same time, at concentrations $x > 0.02$ and up to crossing of the top of the valence band ϵ_V by the Fermi level ϵ_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 ϵ_1^α . At the Fermi level ϵ_F crossing the edge of the valence band, the transition of electrical conductivity of $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ 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 $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ (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 ε_A^1 . 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 ε_F from the continuous energy bands is achieved when the Fermi level is passing through of the middle of the band gap ε_F ($x \approx 0.02$). After passing the middle of the band gap by the Fermi level ε_F and its approaching to the valence band ε_V , activation of the holes 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 $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$.

At concentrations of the acceptor impurity which correspond to the $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ compositions, $x \geq 0.04$, the acceptor band ε_A^1 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 $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ 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 $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ 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 $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$? 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 $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ 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 $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$

The temperature and concentration dependencies of electric resistivity ρ and thermopower coefficient α of $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ are presented in Figs. 3, 4. The dependencies $\ln\rho(1/T)$ and $\alpha(1/T)$ of $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ (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 ε_F to the continuous energy bands takes place. At low temperatures hopping conductivity on the energy states closed to the Fermi level ε_F is realized. Variation of electric resistivity values $\rho(T,x)$ of $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ is described by the next relation [15]:

$$r^{-1}(T) = r_1^{-1} \exp\left(-\frac{e_1^r}{k_B T}\right) + r_3^{-1} \exp\left(-\frac{e_3^r}{k_B T}\right) \quad (1)$$

where the first high-temperature term describes an activation of the current carriers ε_1^p from the Fermi level ε_F to the percolation levels of the continuous energy bands; second low-temperature term describes the hopping conductivity ε_3^p . From the high- and low-temperature parts of the $\ln\rho(1/T)$ dependencies, the energy activation values ε_1^p and ε_3^p , respectively, were calculated (Fig. 5a). In turn, the temperature dependencies of the thermopower coefficient $\alpha(T,x)$ of $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ are described by relation [16]:

$$a = \frac{k_B}{e} \left(\frac{e_i^a}{k_B T} - g + 1 \right) \quad (2)$$

where γ is a parameter which depends on the scattering mechanism. From high-temperature parts of $\alpha(1/T)$ dependencies, the activation energy values ε_1^a which are proportional to the amplitude of the large-scale fluctuation of the continuous energy bands were calculated. From the low-temperature parts of $\alpha(1/T)$ dependencies energy activation values ε_3^a 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 $\ln\rho(1/T)$ and $\alpha(1/T)$ 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 $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ 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 $\ln\rho(1/T)$ and $\alpha(1/T)$ 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 $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ 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 ε_A^1 . Nevertheless, there is no agreement between obtained results of electric resistivity $\rho(T,x)$ and thermopower coefficient $\alpha(T,x)$ values and modeling of the energetic characteristics of $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ (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 $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ crystal.

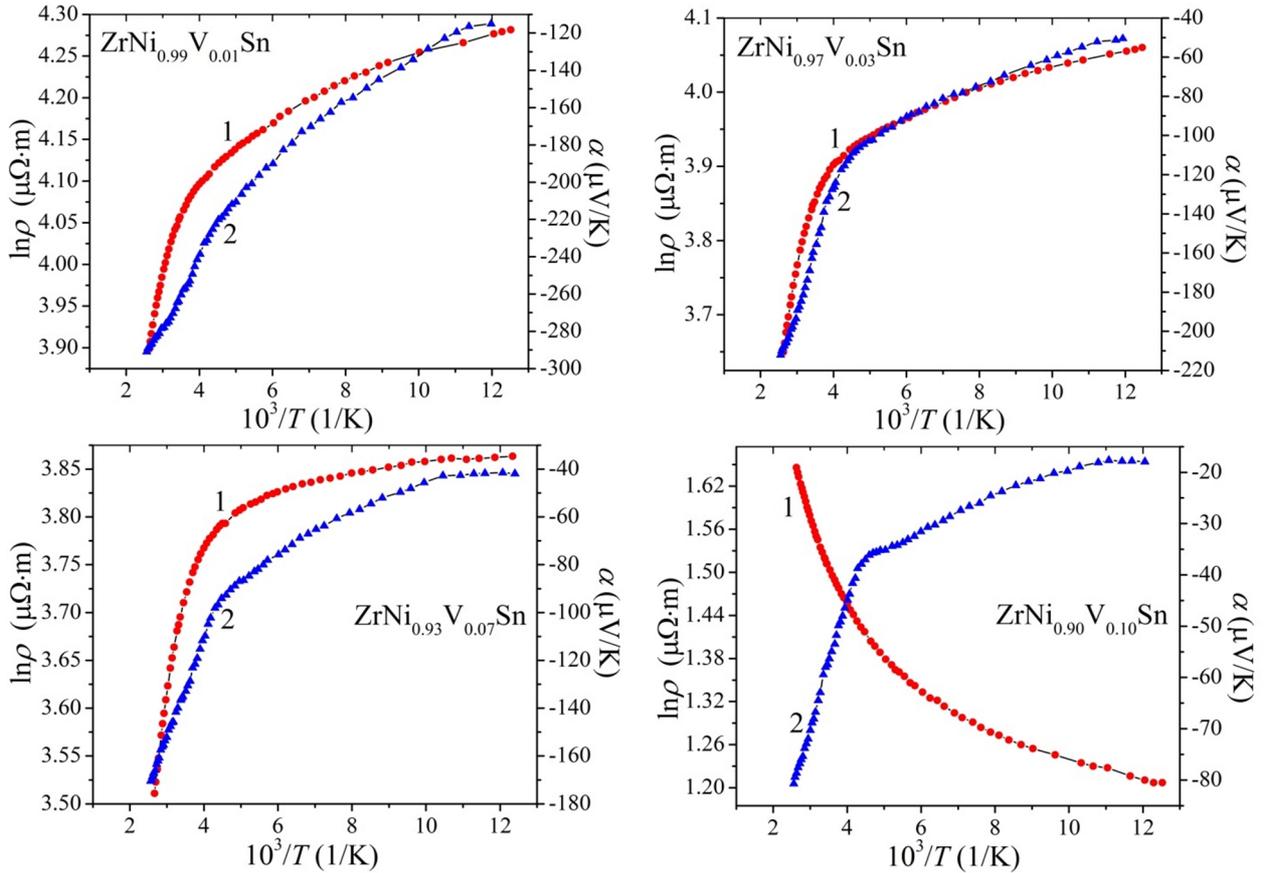


Fig. 3. Temperature dependencies of electric resistivity $\ln\rho(1/T)$ (1) and thermopower coefficient $\alpha(1/T)$ (2) of $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$.

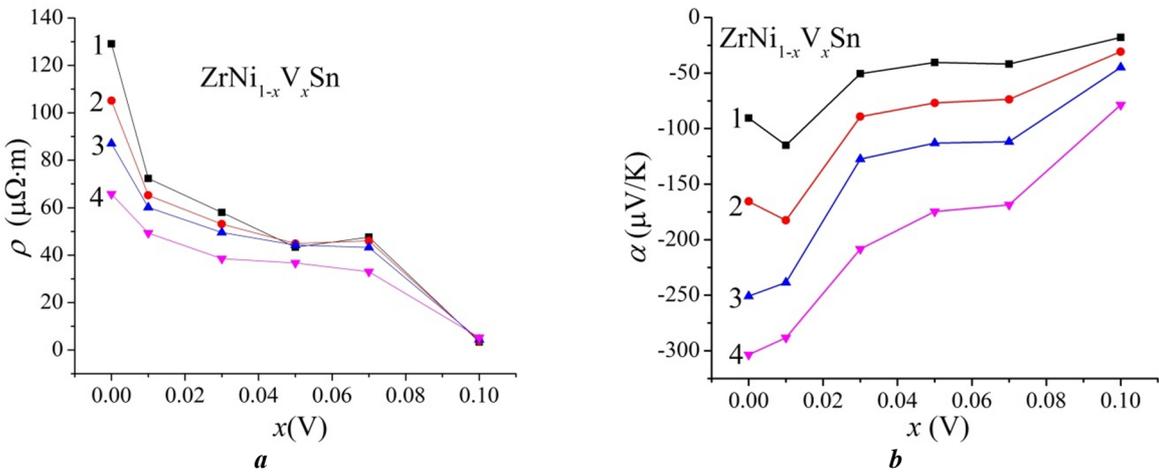


Fig. 4. Variation of electric resistivity $\rho(x)$ (a) and thermopower coefficient $\alpha(x)$ (b) values of $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ at different temperatures: 1 – $T=80$ K; 2 – $T=160$ K; 3 – $T=250$ K; 4 – $T=380$ K.

It is known that ZrNiSn structure is disordered due to the partial occupation of Zr ($4a$) position by Ni atoms which generates the structural defects of the donor nature and the impurity donor band ε_D^1 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 $4a$ position of Zr atoms and the defects of the donor nature disappear (“healed” [14,15]). It can be assumed that in $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ in the

concentration range $x=0-0.01$ the decrease of the electron concentration caused by disappearance of an impurity donor band ε_D^1 due to displacement of Ni atoms from $4a$ position of Zr atoms and structure ordering take place. In other words, the ordering of the $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ 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 $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ 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

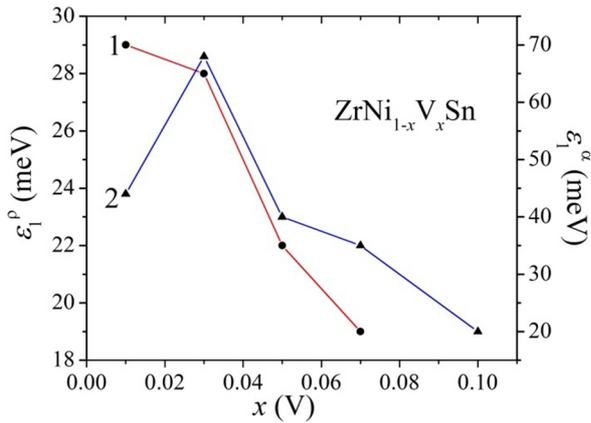


Fig. 5. Variation of the activation energy values $\varepsilon_1^p(x)$ (1) and $\varepsilon_1^a(x)$ (2) of $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$.

electric resistivity $\rho(x,T)$ and thermopower coefficient $\alpha(x,T)$ values for $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ indicates an increase of the electron concentration. Such behavior of $\rho(x,T)$ and $\alpha(x,T)$ confirmed that the number of generated structural defects of the donor nature in $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ crystal exceeds acceptor concentration.

Conclusion concerning the generation of the structural defects of the acceptor nature in $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ is based on analysis of the compensation degree change of semiconductor. Presence of the high-temperature activation part on $\alpha(1/T)$ dependence for $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ (Fig. 3) allows to calculate activation energy values ε_1^a which are proportional to an amplitude of the large-scale fluctuation of the continuous energy bands of HDHCS. 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 ε_F is located at the middle of the band gap and $\varepsilon_1^a = 1/2\varepsilon_g$ [14, 15].

As shown in Fig. 5 (curve 2), maximum of $\varepsilon_1^a(x)$ dependence for $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ at V concentration $x \approx 0,03$ takes place. Taking into account that ZrNiSn compound is semiconductor with electron type of conductivity, a change of compensation degree and maximum on the $\varepsilon_1^a(x)$ dependence can only occur due to acceptor appearance, that partially compensate present donors in the crystal. Thus, appearance of the acceptor in $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ 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 $\alpha(T,x)$ 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 $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ is demonstrated by behavior of activation energy of electrons $\varepsilon_1^p(x)$ from the Fermi level ε_F to the mobility edge of the conduction band (Fig. 5, curve 1). Decreasing of activation energy values ε_1^p provided negative values of the thermopower coefficient $\alpha(T,x)$ indicates the motion of the Fermi level ε_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 ε_F moving to the conduction band (slope of $\varepsilon_1^p(x)$ behavior) in the concentration range $x=0.01-0.03$ is $\Delta\varepsilon_F/\Delta x \approx 0.5$ meB/%V, in the range $x=0.03-0.05$ it equals $\Delta\varepsilon_F/\Delta x \approx 3$ meB/%V. Appearance of the acceptors in the crystal causes “braking” of motion of the Fermi level ε_F to the conduction band.

Thus, the obtained experimental results of the structural, electrokinetic and energetic studies of the $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ 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 $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ 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 of 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 $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ 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 $\text{ZrNi}_{1-x}\text{V}_x\text{Sn}$ semiconducting solid solution in our next work.

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Синтез, структурні, електротранспортні та енергетичні характеристики твердого розчину $ZrNi_{1-x}V_xSn$

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Зразки твердого розчину $ZrNi_{1-x}V_xSn$ ($x = 0 - 0,10$) на основі напів-Гейслерової фази $ZrNiSn$ (структурний тип $MgAgAs$) синтезовано методом електродугового плавлення з гомогенізувальним відпалюванням за температури 1073 К. Електрокінетичні та енергетичні характеристики напівпровідникового твердого розчину $ZrNi_{1-x}V_xSn$ досліджено в інтервалі температур $T = 80 - 400$ К. На основі аналізу поведінки кінетичних та енергетичних характеристик, зокрема, швидкості руху рівня Фермі $\Delta\varepsilon_F/\Delta x$ $ZrNi_{1-x}V_xSn$, 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.