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Features of Structural, Electrokinetic, and Energy State Characteristics of $ZrNiSn_{1-x}Ga_x$ Solid Solution

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Features of structural, electrokinetic, and energy state characteristics of $ZrNiSn_{1-x}Ga_x$ semiconductive solid solution were investigated in the temperature ranges T = 80 - 400 K and x = 0 - 0.15. Disorder of crystal structure for *n*-ZrNiSn compound as a result of occupation of Zr ($4d^25s^2$) atoms in 4*a* sites by Ni ($3d^84s^2$) ones up to ~ 1 % was confirmed. It generated donor levels band ε_{D1} in the band gap. It was shown that introduction of Ga ($4s^24p^1$) atoms by means of substitution of Sn ($5s^25p^2$) ones ordered crystal structure. In this case acceptor defects were generated in 4*b* sites and it created extended acceptor impurity band ε_A. It was suggested that with generation of acceptor structural defects the vacancies in the Sn (4*b*) atomic sites simultaneously generated donor defects and formed deep donor band ε_{D2} (donor-acceptor pair took place).

Keywords: crystal and electronic structures, conductivity, thermopower coefficient.

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Introduction

In studying of thermoelectric materials formed by heavy doping of *n*-ZrNiSn, *n*-HfNiSn and *n*-TiNiSn intermetallic semiconductors by acceptor impurity, the appearance of electrons with unknown origin mechanism was observed. A number of research results of previously obtained solid solutions based on ZrNiSn compound hasn't an adequate explanation because the emergence of donors during the substitution of Ni atoms by M = Cr, Mn, Fe, Co, etc. [1] was incomprehensible. The generation of structural defects with only acceptor nature in $ZrNi_{1-x}M_xSn$ was more logical because the Ni atoms have the number of 3*d*-electrons more than Cr, Mn, Fe and Co. However, electrokinetic studies revealed the emergence of a significant number of donors of unknown origin, and their concentration increased with increasing number of acceptors. Structural studies have found no such defects because their concentration is outside the X-ray methods accuracy [2].

Recent studies of solid solutions based on HfNiSn and TiNiSn discovered a previously unknown mechanism for generating structural defects with donor nature, which involves the appearance of vacancies in the positions of Sn (4*b*) atoms [3-6]. For example, in the case of doping *n*-TiNiSn by Ga ($4s^24p^1$) atoms by means of substitution of Sn ($5s^25p^2$) atoms it was found that in the same 4*b* crystallographic position as acceptor defects (Ga has a smaller number of *p*-electrons than Sn) so donor defects as a vacancies in the position of Sn atoms were simultaneously generated. It's noted that donor's concentration increases with increasing Ga content [6], and the semiconductor is heavy doped and compensated (HDCS) [1,7].

This unexpected result is logical, because the stability of the structure and the electrical neutrality principle of $TiNiSn_{1-x}Ga_x$ crystal provided the appearance of a significant number of acceptors ($N_A^{Ga} \approx 3 \cdot 10^{21}$ см$^{-3}$) ensures generation of structural defects with donor nature, effective charge of which is opposite. In this case, the formula looks like a solid solution $TiNiSn_{1-x-y}Ga_x$, where y is the concentration of vacancies in 4*b* positions of Sn atoms.

Today the question is open whether this mechanism works in the case of doping *n*-ZrNiSn? Therefore, provided the work can be regarded as the first

experimental phase of the study on the availability of donor mechanism for generating a vacancy in the Sn (4*b*) atomic site upon the doping of *n*-ZrNiSn with Ga atoms which substituted Sn atoms. The calculation and analysis of the electronic structure for $ZrNiSn_{1-x}Ga_x$ will be the subject of further work which will establish conduction mechanisms at various concentrations and temperatures.

I. Experimental details

The $ZrNiSn_{1-x}Ga_x$ samples were prepared by a direct twofold arc melting of the constituent elements under high purity Ti-gettered argon atmosphere on a water-cooled copper crucible. Then the pieces of the as-cast buttons were annealed for one month at 1073 K in evacuated silica tubes and then water quenched. The lattice parameters were calculated using the powder diffraction patterns (diffractometer Guinier-Huber image plate system, Cu$K\alpha_1$ radiation) [2], the crystallographic parameters (atomic coordinates, isotropic displacement parameters, the site occupancies) were determined using WinPLOTR program package [8]. To increase the precision of the structural study the calculations were performed taking into account radiation of α- and β-lines. The chemical and phase compositions of the obtained samples with accuracy ~ 1 at.% were examined by Scanning Electron Microscopy (SEM) using Carl Zeiss DSM 962 scanning microscope. For $ZrNiSn_{1-x}Ga_x$ samples, $x = 0 - 0.15$ ($N_A^{Ga} \approx 0 - 3\cdot10^{21}$ cm^{-3}), the temperature dependencies of electrical resistivity (ρ) and differential thermopower (α) (pure copper as a reference material) were measured in the 80 – 400 K temperature range.

II. Crystal structure refinements of $ZrNiSn_{1-x}Ga_x$

The X-ray analysis showed that the $ZrNiSn_{1-x}Ga_x$ samples are single phases, the powder patterns of the $ZrNiSn_{1-x}Ga_x$ samples were indexed with cubic MgAgAs-type [9]. According to microprobe analysis the compositions of the synthesized samples correspond to the initial compositions of the alloys, confirming the substitution of Sn atoms by Ga.

The crystal structure refinements of $ZrNiSn_{1-x}Ga_x$ by powder method including the refinements of isotropic displacement parameters and occupancy of crystallographic site Zr (4*a*) confirmed the result [3] concerning disordering of ZrNiSn structure (1 % ($z \approx 0.01$) Ni ($3d^8 4s^2$) occupies 4*a* site of Zr($4d^2 5s^2$)). This leads to generate the structural defects of donor nature caused by higher number of *d*-electrons of Ni, and the donor impurity band appears in the band gap. Thus, the chemical formula should be written as $(Zr_{1-z}Ni_z)NiSn$.

On the other hand the crystal structure study of $ZrNiSn_{1-x}Ga_x$ indicated, that the smallest value of final reliability factor ($R_{Br.} \approx 2.9$ %) for structure refinements was observed for structure model where the occupancy of 4*a* position by Zr atoms is 100% for $x \geq 0.01$. Thus, introduction of Ga atoms in the structure of ZrNiSn compound leads to ordering of the crystal structure

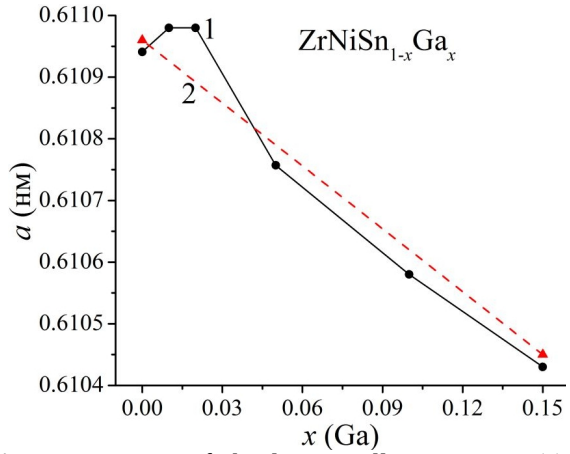


Fig. 1. Variation of the lattice cell parameter $a(x)$ $ZrNiSn_{1-x}Ga_x$: 1 – experimental data; 2 – calculation.

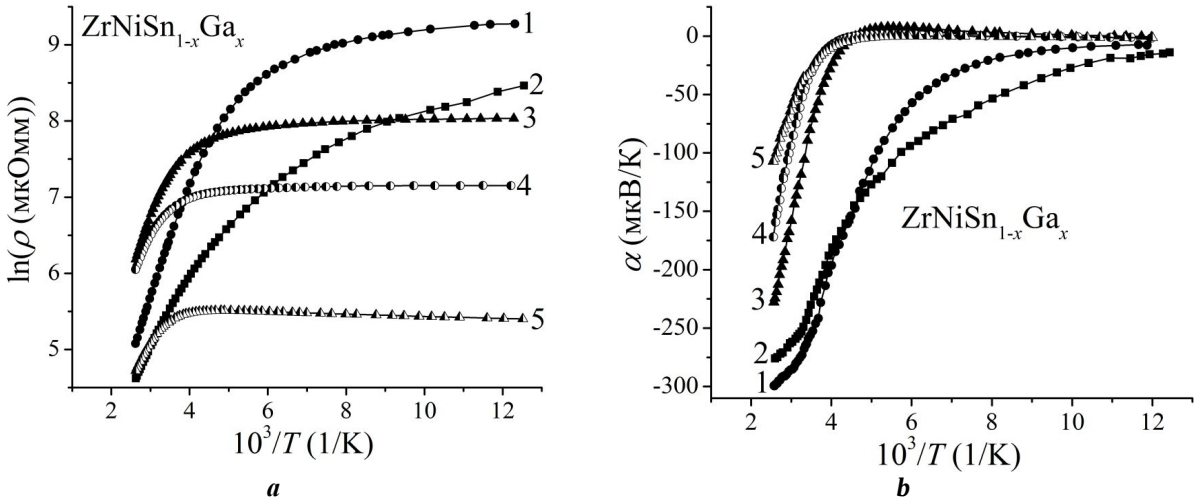
("healing" of structural defects): the Ni atoms disappear in position Zr (4*a*). The similar result was obtained for $TiNiSn_{1-x}Ga_x$ [6].

Taking to account that the atomic radius of Ga (r_{Ga} = 0.141 nm) is lower than Sn (r_{Sn} = 0.162 nm), it was expected reducing of the unit cell parameter $a(x)$ for $ZrNiSn_{1-x}Ga_x$ with increasing of Ga content. However, variation of the $a(x)$ values was not monotonic, that reflected the complex processes in the crystal. It's worth to consider the behavior of $a(x)$ values in the $0 \leq x \leq 0$ region. (Fig. 1).

As was noted above, the ZrNiSn structure is disordered by partial occupation of Zr positions by Ni atoms [5]. During the introduction of Ga atoms into the ZrNiSn structure in the $0 \leq x \leq 0.01$ concentration ranges its ordering takes place by means of the displacement of small Ni atoms (r_{Ni} = 0.124 nm) from 4*a* position by larger Zr atoms (r_{Zr} = 0.160 nm). Also the displacement of Ni atoms in 4(*a*) site was accompanied by substitution of big Sn atoms by smaller Ga in position 4*b*. Taking to consideration that the difference of atomic radii of Zr and Ni ($r_{Zr} - r_{Ni}$) = 0.036 nm, and Sn and Ga ($r_{Sn} - r_{Ga}$) = 0.021 nm, the variation in $a(x)$ values in the $0 \leq x \leq 0.01$ concentration range was caused by process of Ni displacement by larger Zr atoms in 4*a* position. It led to some growing in $a(x)$ dependence (Fig. 1).

After displacement of Ni atoms from Zr position (ordering of structure) the $a(x)$ dependence was determined by Ga atoms occupying Sn (4*b*) positions. It corresponded to a decrease of $a(x)$ values at the $0.02 \leq x \leq 0.15$ concentration range.

Variation $a(x)$ also was calculated for $ZrNiSn_{1-x}Ga_x$ (ordered structure variant) with suggestion that the ZrNiSn compound is ordered (Fig. 1, curve 2). The calculated value of the lattice parameter $a(x)$ for ZrNiSn is larger than experimental value because in the real compound, as mentioned above, ~ 1% Zr atoms displaced by smaller Ni atoms. Comparison of the calculated and experimental values of the lattice parameter $a(x)$ for $ZrNiSn_{1-x}Ga_x$ (Fig. 1) showed that the more complex changes appeared in the crystal structure. In particular, the fact that calculated values of unit cell parameter $a(x)$ for $ZrNiSn_{1-x}Ga_x$ at $x = 0.15$ were higher than obtained experimentally was unclear and required



a ***b***

Fig. 2. Temperature dependencies of electrical resistivity lnρ(1/T) (***a***) and differential thermopower α(1/T) (***b***) for $ZrNiSn_{1-x}Ga_x$ at different compositions: 1 – x = 0.01; 2 – x = 0; 3 – x = 0.05; 4 – x = 0.10; 5 – x = 0.15.

additional study (Fig. 1).

The $ZrNiSn_{1-x}Ga_x$ crystal_structure ordering in addition to structural changes was accompanied by a restructuring of the electronic structure in the semiconductor. For example, if the *n*-ZrNiSn in the band gap has donor band $\varepsilon_D{}^1$ as a result of the substitution of up to ~ 1% Zr atoms by Ni atoms [3], then the ordering of the $ZrNiSn_{1-x}Ga_x$ structure (displacement of Ni atoms from a Zr (4*a*) site) results in decreasing of donor number and elimination of donor band $\varepsilon_D{}^1$.

At the same time, since the Ga ($4s^24p^1$) atom has one *p*-electron less than Sn ($5s^25p^2$), then the substitution of Sn atom by Ga generated acceptor defect in the 4*b* site that led to an appearance in the band gap impurity acceptor level, which in a significant number of impurities formed extended impurity acceptor band ε_A. The presence of a large number of donors and acceptors affect the $ZrNiSn_{1-x}Ga_x$ band structure [1, 3], that will be observed in the study of the electrokinetic and energy state characteristics.

III. Investigations of electrokinetic and energy state characteristics of $ZrNiSn_{1-x}Ga_x$

The temperature and concentration dependences of electrical resistivity ρ and thermopower coefficient α for $ZrNiSn_{1-x}Ga_x$ are shown in Fig. 2-4. The lnρ(1/T) and α(1/T) dependences for $ZrNiSn_{1-x}Ga_x$ samples (Fig. 2) are typical for heavily doped and highly compensated semiconductors, and existing activation regions indicate several mechanisms of charge transport [1, 3]. These mechanisms are activation of current carriers from the Fermi level ε_F to continuous energy band levels (high temperature) and hopping conduction (except for x = 0.15) within the energy states close to ε_F (low temperature). From the activation regions of the lnρ(1/T) dependences plots the activation energies from the Fermi level ε_F to the percolation levels of the conduction band (valence band) $\varepsilon_1{}^\rho$ and hopping conduction energy $\varepsilon_3{}^\rho$ were calculated. From the activation regions of α(1/T) dependences plots the values of activation energy $\varepsilon_1{}^\alpha$ and $\varepsilon_3{}^\alpha$ were obtained; they give the values of the modulation amplitude of continuous energy bands, and small-scale HDCS fluctuations, respectively [1, 7].

The presence of high-temperature activation parts in the lnρ(1/T) dependences for all $ZrNiSn_{1-x}Ga_x$ samples shows that the Fermi level ε_F is located in the band gap, from which the thermal activation of carriers to the percolation levels takes place. Assuming that introduction of Ga impurity atoms into ZrNiSn crystal generates, as expected, only structural defects with acceptor nature, then at the Ga concentration, for example, x = 0.15 ($N_A{}^{Ga} \approx 3\cdot10^{21}$ cm^{-3}), the Fermi level ε_F would cross the percolation level in valence band and insulator-metal transition of conductivity would occur (Anderson transition) [1,7]. However, the shapes of dependencies lnρ(1/T) for $ZrNiSn_{1-x}Ga_x$ at high temperatures show that the conductivity metallization is absent.

This behavior of the semiconductor at appropriate impurity concentration is possible only if along with the generation of the acceptors occurs the simultaneous generation of the donors of unknown origin, which compensate acceptors, forcing the Fermi level ε_F to stay within the energy band gap and reflect the compensation degree of $ZrNiSn_{1-x}Ga_x$.

The fact that the atoms of Ga, introduced into *n*-ZrNiSn, generate structural defects with acceptor nature, can be seen from the dependences of changes in the values of resistivity $\rho(x,T)$ and thermoelectric coefficient $\alpha(x,T)$ in all concentration and temperature ranges (Figs. 3 and 4). First, we analyze the dependences $\rho(x)$ and $\alpha(x)$ at 80 K.

For example, the introduction of the smallest Ga concentration in the experiment rapidly increases the value of the resistivity $\rho(x)$ at T = 80 K from $\rho(x = 0)$ = 4751.1 μΩ·m to $\rho(x = 0.01)$ = 10677.7 μΩ·m. We can assume that the sample with the concentration x = 0.01 is highly compensated, since the number of generated acceptors is close to the number of donors in *n*-ZrNiSn [1]. The rapid growth of $\rho(x)$ dependence at the x = 0 - 0.01 results from two processes:

- Reducing the number of donors in the band $\varepsilon_D{}^1$ due

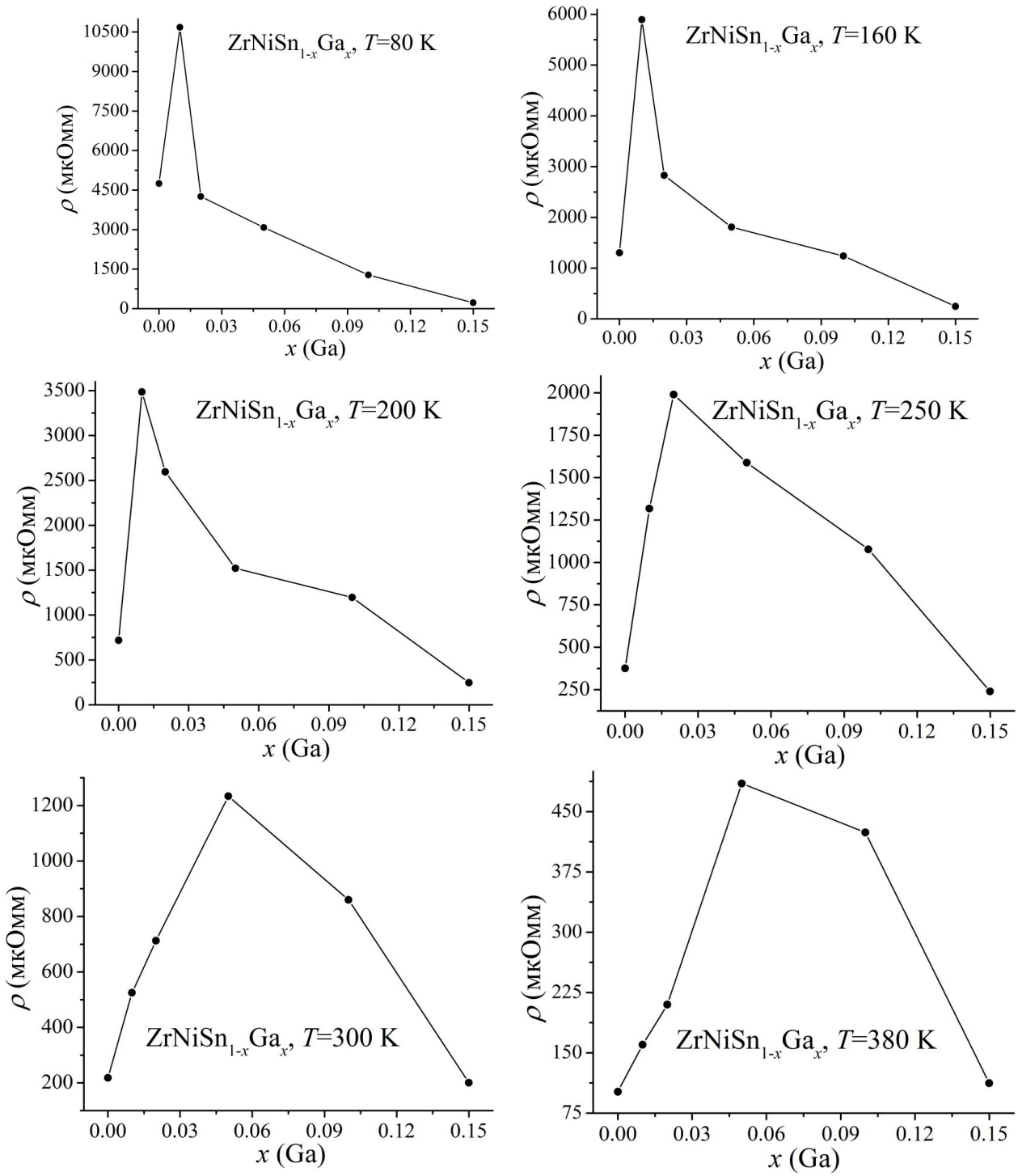


Fig. 3. Variation of electrical resistivity $\rho(x)$ for $ZrNiSn_{1-x}Ga_x$ at different temperatures.

to ordering of $ZrNiSn_{1-x}Ga_x$ structure when Zr atoms replace Ni atoms in the 4*a* site, "healing" the structural defects of donor nature;

- "Freezing off" the free electrons at formed acceptor band ε_A when Sn is replaced by Ga.

However, at the concentration $x > 0.01$ and T=80 K the values of the resistivity $\rho(x)$ for $ZrNiSn_{1-x}Ga_x$ decrease drastically in the same manner from $\rho(x=0.02)$ = 4255.89 μΩ·m to $\rho(x = 0.05)$ = 3079.7 μΩ·m and $\rho(x = 0.10)$ = 1275.7 μΩ·m, indicating the growth of the number of free charge carriers. We will determine their type and origin.

The maxima on the $\rho(x)$ dependence at introducing into the *n*-ZrNiSn semiconductor with the electron-type conductivity the Ga acceptor impurity reflects the equilibration of the competing processes which determine the mechanisms of conductivity. For example, at doping of *n*-ZrNiSn with the acceptor impurity Y the dependence $\rho(x)$ within the concentration range $x = 0 – 0.02$ also increased drastically, passed through its maxima at $x \approx 0.02$ and decreased at $x > 0.02$, accompanied by the change of the conductivity type for $Zr_{1-x}Y_xNiSn$, $x \geq 0.02$, from electron-type to hole-type [1]. It is caused by the passing by the Fermi level of the middle of the

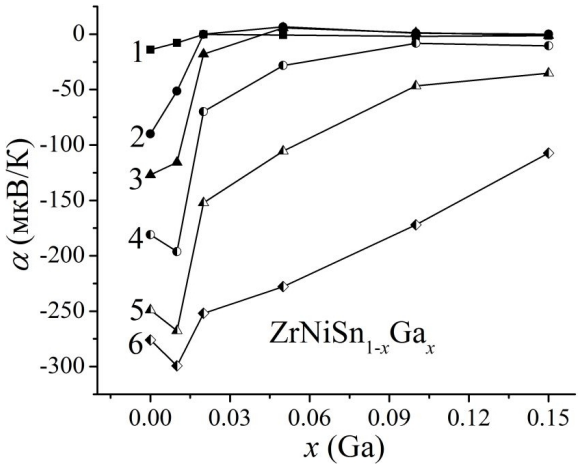


Fig. 4. Variation of thermopower $\alpha(x)$ for $ZrNiSn_{1-x}Ga_x$ at different temperatures: 1 – 80 K; 2 – 160 K; 3 – 200 K; 4 – 250 K; 5 – 300 K; 6 – 380 K.

band gap and its drift to the valence band, which increases the number of free holes and, as a result, the sign of the thermopower coefficient becomes positive, and the dependence $\rho(x)$ decreases drastically.

On the other hand, assuming that in ZrNiSn structural defects of donor nature are absent, and the semiconductor is intrinsic (donor levels band ε_D^1 is absent), then at introducing of the Ga atoms the values of the resistivity $\rho(x)$ also decreased within all temperature and concentration ranges due to appearance and increasing of the free holes number in the valence band upon ionization of acceptors in the impurity acceptor band ε_A. It is clear that the sign of the thermoelectric coefficient in this case will also be positive.

It was predicted that as in the case of $Zr_{1-x}Y_xNiSn$ [1], replacing Sn atoms by Ga atoms would be accompanied by the generation of structural defects with acceptor nature in 4*b* crystallographic position and appearance of impurity acceptor band ε_A close to the valence band. At the concentration of Ga atoms, when the Fermi level ε_F crosses the mid gap and begin to drift to percolation levels of the valence band, the free holes become main charge carriers. Such an assumption is logical, because at concentration of Ga, $x > 0.01$, the number of generated acceptors ε_A already exceeds the number of donors with the energy ε_D^1 for *n*-ZrNiSn (i.e. number of Ni atoms in Zr (4*a*) position).

However, as seen in Figs. 2 and 4, at 80 K sign of the thermoelectric coefficient for $ZrNiSn_{1-x}Ga_x$ remains negative for all concentrations, and electrons are the main carriers. And despite the fact that the concentration of generated structural defects with acceptor nature in a sample, for example, $ZrNiSn_{1-x}Ga_x$, $x = 0.10$, is in one order higher than the concentration of donors in *n*-ZrNiSn. It is possible only provided that the depth of the acceptor band is such that 80 K is not sufficient for hole to overcome the energy barrier between the percolation level in the valence band and acceptor level ε_A.

With increasing temperature ($T > 80$ K) the $\rho(x)$ dependence for $ZrNiSn_{1-x}Ga_x$ transformed, reflecting changes in the electronic structure of the semiconductor. For example, in the dependence $\rho(x)$ at $T = 160$ K and concentration in the vicinity of $x \approx 0.06$ a step first appears, which gradually develops into extreme ($T = 300$ K). At higher temperature, $T = 380$ K, it is shifted in the region of higher concentrations $x \approx 0.08$. At the same time the maximum in the dependence $\rho(x)$ at concentration about $x \approx 0.01$ disappears.

It can be stated that at low concentrations of Ga acceptor impurity the maximum in the dependence $\rho(x)$ for $ZrNiSn_{1-x}Ga_x$ at concentration about $x \approx 0.01$ (Fig. 3) is due to the existence of the donor level ε_D^1 in the band gap, generated by structural defects with donor nature (Ni atoms in 4*a* positions of Zr atoms). At acceptor concentration, which corresponds to the concentration of generated donors ($x \approx 0.01$) the depletion of donor occurs, the electrical resistivity gains maximum values and semiconductor is highly compensated. Since the values of thermopower coefficient at 80 K are negative for all concentrations, then the temperature is insufficient to complete ionization of acceptors (thermal transport of hole to percolation level in the valence band). In this context it should be noted that in the semiconductor $ZrNiSn_{1-x}Ga_x$, x=0.01, concentration of donors with energy ε_D^1 will be much smaller than the number of generated acceptors with energy ε_A. At the least concentration of Ga impurity atoms it is caused by the process of structure ordering that rapidly reduces the concentration of donors with energy ε_D^1.

At concentrations $x \geq 0.02$, when the number of generated acceptors exceeds number of donors in *n*-ZrNiSn, with the temperature increasing from $T = 80$ K to $T = T_1^{inv}$ sign of the thermopower coefficient changes from negative to positive (Fig. 5). Namely for samples $ZrNiSn_{1-x}Ga_x$, $x \approx 0.02$ and $x \approx 0.05$, the temperature $T \sim 93$ K is sufficient for hole to overcome the energy barrier between the percolation level in the valence band and acceptor levels band ε_A. Conduction mechanism in this temperature range corresponds to that in $Zr_{1-x}Y_xNiSn$ [1].

With further increasing of temperature in the samples $ZrNiSn_{1-x}Ga_x$, $x \approx 0.02$ and $x \approx 0.05$, 0,10, at temperatures $T \approx 156$ K and $T \approx 216$ K, respectively, sign of the thermopower coefficient abruptly changes from positive to negative at $T_2^{inv.}$ (Fig. 5), and electrons again become the main charge carriers. And despite the fact that the concentration of generated acceptors in $ZrNiSn_{1-x}Ga_x$, $x > 0.01$ is higher than the number of donors with energy ε_D^1 in the *n*-ZrNiSn (number of Ni atoms in Zr(4*a*) position). That behavior of thermopower coefficient for $ZrNiSn_{1-x}Ga_x$ at $T = T_2^{inv.}$ is possible provided that in the semiconductor, along with the acceptor impurity band ε_A the donors with ε_D^2 are generated, energy levels of which form a donor band ε_D^2, deeper than ε_D^1. It is noted that for the ionization of donors with ε_D^2 and overcoming barriers to the percolation level of the conduction band needed higher energy. It seems that in the semiconductor donor-acceptor pairs are generated simultaneously, energy levels of which are in the band gap of semiconductor.

The analysis of the $\rho(x)$ behavior for $ZrNiSn_{1-x}Ga_x$ at different temperatures leads to the same conclusion. As an extremum on $\rho(x)$ dependence of $ZrNiSn_{1-x}Ga_x$ represents equilibration of the competing processes in the electronic structure of the semiconductor, so the

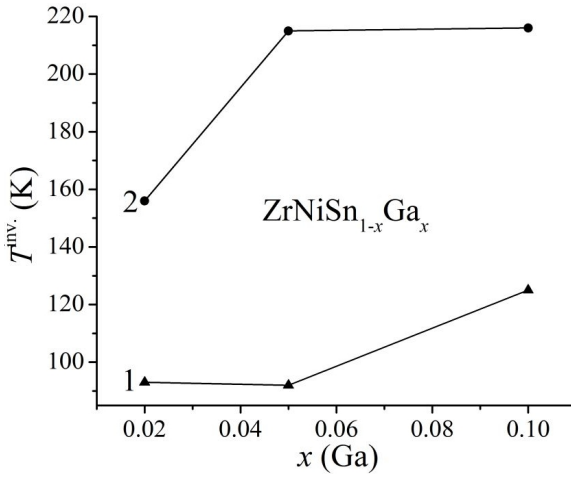


Fig. 5. Variation of inversion temperature $T_{inv.}$ of thermopower coefficient for $ZrNiSn_{1-x}Ga_x$: 1 – $T_1^{inv.}$ (sign inversion from negative to positive); 2 – $T_2^{inv.}$ (sign inversion from positive to negative).

disappearance of the maximum on ρ(x) with increasing temperature at low concentration of Ga impurity ($x \approx 0.01$) and appearance of new extremum on $\rho(x)$ at the concentrations $x \approx 0.06$ indicate an existence of donor band ε_D^2, the depth of which more than ε_D^1. Indeed, at the concentrations $x \geq 0.02$ and the temperatures, values of which are insufficient for ionisation of donor ε_D^2, the concentration of acceptors in $ZrNiSn_{1-x}Ga_x$ prevails the concentration of donors, and the sign of thermopover coefficient is positive. With increasing temperature $T \geq T_{inv}$ ionising of donors begins, the number of free electrons which become the main carriers of current grows headily. It's indicated by the negative values of thermopower coefficient (Fig. 4).

On the other hand, as the higher number of the acceptors are generated in the $ZrNiSn_{1-x}Ga_x$ semiconductor, so higher energies (temperatures) are needed to prevail the number of ionized donors ε_D^2 over the number of the ionized acceptors ε_A. It means that the defects with donor nature appear in the crystal simultaneously with the structural defects with acceptor nature in position 4*b* at the substitution of Sn atoms by Ga.

Based on obtained results, similar to the case of $TiNiSn_{1-x}Ga_x$ [6], now we can only assume that in $ZrNiSn_{1-x}Ga_x$ to ensure stability of the structure and electrical neutrality principle both the structural acceptor defects and defects with donor nature as the vacancies in position 4*b* are simultaneously generated (an effective charges of which are opposite) and the concentration of which increases with increasing of Ga content. In this case the formula of the semiconductive solid solution can be expressed as $ZrNiSn_{1-x-y}Ga_x$, where y – concentration of vacancies in 4*b* position of Sn atoms.

The noted above suggestion about appearance of the vacancies in (4*b*) position of Sn atoms explains the fact that at x=0.10 the calculated values of the lattice parameter $a(x)$ are higher than values obtained from the experiment (Fig. 1). Since only the substitution of the Sn atoms by Ga was taken into account at calculations and appearance of vacancies is not taken into account, then the presence of the last would result in the certain "compression of the structure" and decreasing of $a(x)$ values in the real crystal.

Analysis of the behaviour of the energy state characteristics of $ZrNiSn_{1-x}Ga_x$, in particular, changes of the values of activation energy $\varepsilon_1^{\rho}(x)$ from the Fermi level ε_F to the percolation level of conduction band and the modulation amplitude of continuous energy band ε_1^{α} in HDCS [1, 7] also shows that the acceptors and donors are simultaneously generated in the semiconductor. For example, in *n*-ZrNiSn the value of energy $\varepsilon_1^{\rho}(x = 0) = 97.6$ meV represents a energy gap between position of the Fermi level ε_F and percolation level of conduction band. Doping of the semiconductor with *n*-type conductivity by least concentrations of Ga acceptor impurity increases the compensation degree, and the Fermi level ε_F go deep into the band gap in the intervals $\varepsilon_1^{\rho}(x = 0.01) = 138.8$ meV and $\varepsilon_1^{\rho}(x = 0.02) = 153.2$ meV. Taking into account that at high temperatures the sign of the thermopower coefficient remains negative, it is possible to state, that the values of activation energies $\varepsilon_1^{\rho}(x = 0.01)$ and $\varepsilon_1^{\rho}(x = 0.02)$ represent an energy barrier to the percolation level of the conduction band. It is warth to remind that the value of activation energy $\varepsilon_1^{\rho}(x)$ is calculated from high temperature activation region of $\ln\rho(1/T)$ dependence (Fig. 2).

The negative values of the thermopower coefficient and decreasing of $\varepsilon_1^{\rho}(x)$ values at the concentrations x>0.02 from $\varepsilon_1^{\rho}(x = 0.05) = 139.5$ meV to $\varepsilon_1^{\rho}(x = 0.10) = 111.2$ meV and $\varepsilon_1^{\rho}(x = 0.15) = 91.3$ meV show that the Fermi level reverse and moves again in the direction to conduction band. It means that in the $ZrNiSn_{1-x}Ga_x$ crystal appear the electrons of unknown origin. During the doping of *n*-type semiconductor by acceptor impurity it is possible only provided the simultaneous generation of donors ε_D^2, the concentration of which is not less than acceptors.

At the same time, simultaneous generation of donors and acceptors in $ZrNiSn_{1-x}Ga_x$ changes the compensation degree and modulation amplitude value of continuous energies band in HDCS [1,7]. The variation of the values of activation energy $\varepsilon_1^{\alpha}(x)$, which is proportional to modulation amplitude of continuous energy band in $ZrNiSn_{1-x}Ga_x$, is shown in Fig. 6. It's seen that in the case of *n*-ZrNiSn the value of modulation amplitude is $\varepsilon_1^{\alpha}(x = 0) = 83.8$ meV. The introduction of Ga ($x = 0.01$) acceptor impurity with the smallest concentration into the semiconductor with electronic type conductivity is accompanied by increasing of the compensation degree, confirmed by increasing of modulation amplitude up to $\varepsilon_1^{\alpha}(x = 0.01) = 101.6$ meV. The further increasing of acceptors concentration in the semiconductor, when the electrons play the principal role in conduction due to the simultaneous generation of donors, increases the compensation degree and modulation amplitude of continuous energies bands from $\varepsilon_1^{\alpha}(x = 0.02) = 127.3$ meV to $\varepsilon_1^{\alpha}(x$=0.05) =149.8 meV and $\varepsilon_1^{\alpha}(x = 0.10) = 186$ meV. However, slump of the dependence $\varepsilon_1^{\alpha}(x)$ at the concentrations of $ZrNiSn_{1-x}Ga_x$, x>0.10, shows that the number of the ionized donors increases quicker than the acceptors, and the compensation degree decreases.

At high concentrations of generated donor-acceptor pairs in $ZrNiSn_{1-x}Ga_x$, $x = 0.15$, when the wave functions

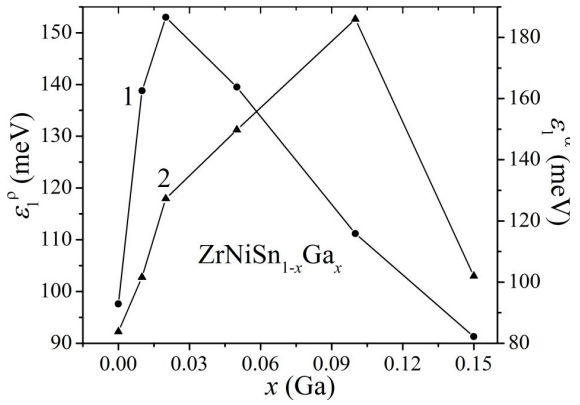


Fig. 6. Variation of activation energy $\varepsilon_1^{\rho}(x)$ (1) and $\varepsilon_1^{\alpha}(x)$ (2) for $ZrNiSn_{1-x}Ga_x$.

of the localized states of donor band ε_D^2 are recovered, the metallization of conductivity within this band take place, confirmed by absence of the low temperature activation region on $\ln\rho(1/T)$ dependence (Fig. 2).

Conclusions

Thus, as a result of comprehensive study of structural, kinetic and energy state characteristics of $ZrNiSn_{1-x}Ga_x$ semiconductor solid solution it was shown that introduction of Ga atoms ($4s^24p^1$) by substituting for Sn ($5s^25p^2$) orders the crystal structure of $ZrNiSn_{1-x}Ga_x$ generating the structural defects of acceptor nature, which form the acceptor impurity band ε_A. It was suggested that simultaneously with acceptors structural defects with donor nature were generated as vacancies in position 4*b* of Sn atoms (donor-acceptor pair), which formed extended donor band ε_D^2 in the band gap.

For a final conclusion concerning to the mechanism of generation of structural defects with donor nature upon heavy doping *of n*-ZrNiSn by Ga acceptor impurity it is necessary to perform the electronic structure calculations of $ZrNiSn_{1-x}Ga_x$ for the different crystal structure models and to find such variant of atomic positions arrangement when the calculated behavior of Fermi level ε_F will coincide with experimental. The obtained results will give an answer for correctness of suggestion concerning to appearance of vacancies in position 4*b* of Sn atoms for $ZrNiSn_{1-x}Ga_x$ and extended deep donor band ε_D^2.

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Особливості структурних, кінетичних та енергетичних характеристик твердого розчину $ZrNiSn_{1-x}Ga_x$

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Досліджено особливості структурних, кінетичних та енергетичних характеристик напівпровідникового твердого розчину $ZrNiSn_{1-x}Ga_x$ у діапазоні: T = 80 - 400 K, x = 0 – 0,15. Підтверджено невпорядкованість кристалічної структури *n*-ZrNiSn як результат зайняття атомами Ni ($3d^8 4s^2$) до ~ 1 % позиції 4*a* атомів Zr ($4d^2 5s^2$), що генерує у забороненій зоні донорну зону ε_D^1. Показано, що уведення атомів Ga ($4s^2 4p^1$) шляхом заміщення Sn ($5s^2 5p^2$) упорядковує кристалічну структуру, генеруючи у позиції 4*b* структурні дефекти акцепторної природи, які породжують протяжну домішкову акцепторну зону ε_A. Висунуто припущення про одночасне з акцепторами генерування структурних дефектів донорної природи (донорно-акцепторна пара) у вигляді вакансій у позиції атомів Sn (4*b*), які породжують глибоку донорну зону ε_D^2.

Ключові слова: кристалічна і електронна структури, електропровідність, коефіцієнт термо-ерс.