V.A. Romaka[1,2], L.P. Romaka[3], Yu.V. Stadnyk[3],
V.Ya. Krayovskyy[2], V.V. Romaka[2], A.M. Horyn[3]

[1]Ya. Pidstryhach Institute for Applied Problems of Mechanics and Mathematics, the National Academy of Sciences of Ukraine, 3-b, Naukova Str., Lviv, 79060, Ukraine;
[2]National University "Lvivska Polytechnika", 12, S. Bandera Str., Lviv, 79013, Ukraine;
[3]Ivan Franko National University of Lviv, 6, Kyryla and Mefodiya Str., Lviv, 79005, Ukraine

RESEARCH ON ELECTRICAL CONDUCTIVITY MECHANISMS OF THERMOELECTRIC MATERIAL BASED ON *n-ZrNiSn* DOPED WITH *Ga*

The crystalline and electronic structures, the temperature and concentration dependences of resistivity, the Seebeck coefficient and magnetic susceptibility of $ZrNiSn_{1-x}Ga_x$ thermoelectric material were investigated in the ranges: T = 80 – 400 K, x = 0.01 – 0.15. The electrical conductivity mechanisms of $ZrNiSn_{1-x}Ga_x$, were established which determine the simultaneously generated structural defects of both donor and acceptor nature (donor-acceptor pairs) in 4b crystallographic position of Sn atoms. The simultaneous generation of donor-acceptor pairs assures electrical neutrality and structural stability of thermoelectric material, as well as stability and reproducibility of its characteristics.

Key words: electronic structure, resistivity, Seebeck coefficient.

Introduction

Thermoelectric materials obtained by heavy doping of *n-TiNiSn, n-ZrNiSn* and *n-HfNiSn* intermetallic semiconductors with acceptor and/or donor impurities, demonstrate high values of thermoelectric figure of merit, possess high efficiency of thermal into electric energy conversion and are among the most studied today. Specifically, in $Ti_{1-x-y}Zr_xHf_yNiSn$ ($0 \le x \le 1$; $0 \le y \le 1$) [1] та $Ti_{0.5}Zr_{0.25}Hf_{0.25}Ti_{0.5}NiSn_{0.998}Sb_{0.002}$ materials [2] the value of *ZT* at temperature $T = 800$ K is ~ 1.4, which corresponds to the best performance of materials based on tellurides, clathrates, skutterudites, etc.

However, widespread introduction of these materials is prevented by incompletely studied transformation processes of crystalline and electronic structures at performance optimization by doping of the basic semiconductor which is accompanied with unpredicted generation of structural defects changing the electronic structure of material and its properties. Thus, donors of unknown origin appear on doping of *n-ZrNiSn* with acceptor impurities *M* = *Cr*, *Mn*, *Fe*, *Co* introduced into the structure by substitution of *Ni* atoms [3 – 5]. Generation in $ZrNi_{1-x}M_xSn$ of only structural acceptor defects looked logical, since the number of 3*d*-electrons in *Ni* exceeds that in *Cr*, *Mn*, *Fe* and *Co*. However, electrokinetic and galvanomagnetic investigations revealed the emergence of a large number of donors whose concentration grows with increasing the number of acceptors. In $TiNiSn_{1-x}Ga_x$ thermoelectric material obtained by doping of *n-TiNiSn* with *Ga* ($4s^24p^1$) atoms by substitution of *Sn* ($5s^25p^2$) there was also discovered a *simultaneous* generation of both acceptor defects (*Ga* possesses a smaller number of *p*-electrons than *Sn*) and donor defects of unknown origin whose concentration grows with increasing *Ga* content [6].

As is known, thermoelectric materials based on intermetallic semiconductors are synthesized by melting the batch of the source components with subsequent cooling of the melt, and this,

according to H. Mott [7], is one of the ways of obtaining amorphous solids and generates essential structural defects. Moreover, performance optimization by controlled doping of a semiconductor additionally generates defects of donor, acceptor or neutral nature, and in the energy gap there appear the respective energy states which determine its properties. Hence, according to fabrication technique, such thermoelectric material is a heavily doped and strongly compensated semiconductor (HDSC) [8]. Unpredicted emergence in materials of donor and/or acceptor defects both during synthesis and in the process of performance optimization causes an uncontrolled change in compensation ratio (the ratio between donors and acceptors), complicating technology for obtaining materials with specified characteristics.

B. Shklovsky and A. Efros showed that in the presence in semiconductor of a large number of unlike charged defects whose arrangement is of fluctuation nature, its electron structure is radically changed leading to fluctuation of potential relief and modulation of continuous energy bands [9, 10]. At low temperatures, a heavily doped crystalline semiconductor is a disordered system that reminds amorphous systems. Moreover, the authors of [10] proposed a scheme of a completely compensated semiconductor as a model of amorphous semiconductor (Fig. 1). The electron is regarded not in a periodic crystal field, but in a chaotic field of defects, and the potential energy of such a field cannot be considered small.

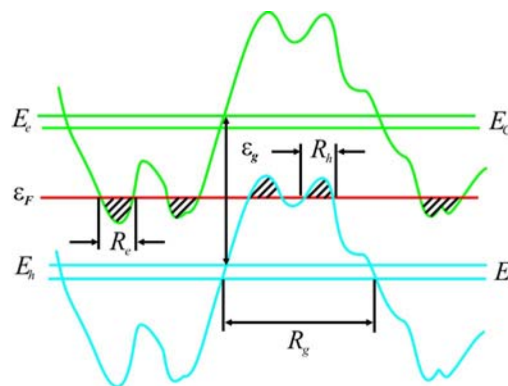


Fig. 1. Energy scheme of a completely compensated semiconductor [10]. The upper and lower lines – unperturbed states of conduction band bottom E_C and valence band peak E_V, the middle line – the Fermi level ε_F, E_e and E_h – percolation levels of conduction band and valence band. Wavy lines – the edge of bands modulated with electrostatic potential of charged defects. Occupied areas (drops) are shaded. R_e, R_h and R_g are the size of electron, hole drops and fluctuation.

Using approaches [9, 10] for the description of disordered systems, such as thermoelectric materials based on intermetallic semiconductors, an attempt was made to study the mechanisms of generation of donors in $ZrNiSn_{1-x}Ga_x$ thermoelectric material obtained by doping of *n-ZrNiSn* with *Ga* atoms by substitution of *Sn*, which makes semiconductor material HDSC. The results obtained will allow control of performance optimization of thermoelectric materials through adequate doping [11].

Investigation procedures

The object to be investigated included crystalline structure, electronic density distribution (DOS), electrokinetic, energy and magnetic characteristics of $ZrNiSn_{1-x}Ga_x$. The samples were synthesized in the laboratory of Institute for Physical Chemistry, Vienna University. The X-ray structural analysis (powder method) was used to obtain the data arrays (diffractometer Guinier-Huber image plate system, $CuK\alpha_1$), and Fullprof program [12] was employed for the calculation of

structural characteristics. The chemical and phase compositions of the samples were controlled by microprobe analyzer (EPMA, energy-dispersive X-ray analyzer). The electronic structure calculations were performed by the Korringa-Kohn-Rostoker (KKR) method in coherent potential approximation (CPA) and local density approximation (LDA) [13] with the use of Moruzzi-Janak-Williams exchange-correlation potential [14]. The accuracy of calculating the position of the Fermi level ε_F is ± 8 meV. The temperature and concentration dependences of the electrical resistivity (ρ) and the Seebeck coefficient (α) were measured with respect to copper and magnetic susceptibility (χ) (Faraday's method) of $ZrNiSn_{1-x}Ga_x$ samples in the ranges: $T = 80 – 400$ K, $N_A^{Ga} \approx 1.9\cdot10^{20}$ cm^{-3} ($x = 0.01$) – $2.9\cdot10^{21}$ cm^{-3} ($x = 0.15$) and magnetic field strength $H \leq 10$ кE.

Research on structural features of $ZrNiSn_{1-x}Ga_x$

A microprobe analysis of the concentration of atoms on the surface of $ZrNiSn_{1-x}Ga_x$ samples has established their conformity to the initial batch compositions, and X-ray phase and structural analyses have shown that X-ray diffraction patterns of samples up to composition $x = 0 – 0.15$ are indexed in structural type *MgAgAs* (spatial group [15]) and have no traces of other phases.

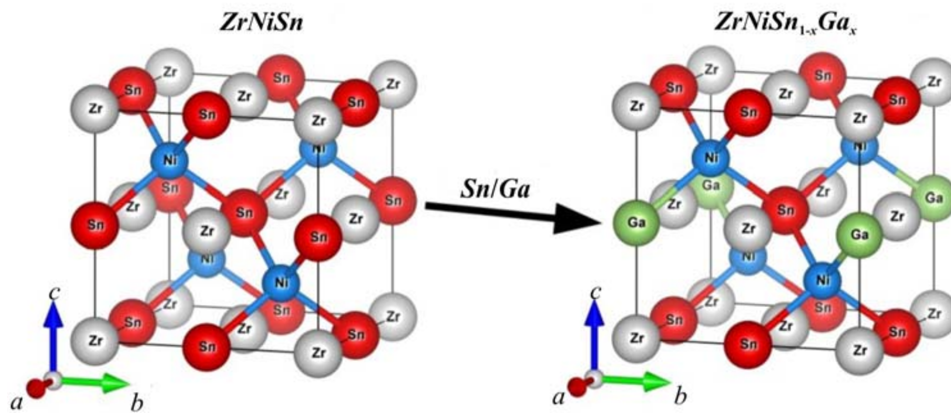


Fig. 2. Unit cell model of ZrNiSn compound (structural type MgAgAs, spatial group).

Thermodynamic calculations in the approximation of harmonic vibrations of atoms in the framework of density functional theory (DFT) have shown that a change in the values of free energy $\Delta G(x)$ (Helmholtz potential) passes through the minimum in the range of concentration $x \approx 0.4$ at the temperature of homogenizing annealing of samples $T = 1073$ K (Fig. 3*a*), pointing to solubility limit of *Ga* atoms in the structure of *ZrNiSn* compound. Thus, the compositions of studied samples $ZrNiSn_{1-x}Ga_x$, $x = 0 – 0.15$, are within the solubility limits, which is also evidenced by the absence of foreign phases in them.

In [16] it is shown that crystalline structure of *ZrNiSn* is disordered (local amorphization) due to partial, up to ~ 1 % ($z \approx 0.01$), occupancy by *Ni* ($3d^84s^2$) atoms of 4*a* position of *Zr* ($4d^25s^2$) atoms, which generates in a semiconductor structural defects of donor nature ("a priori doping"), as long as *Ni* has more *d*-electrons, and donor states ε_D^1 appear in the energy gap. The compound formula takes on the form $(Zr_{1-z}Ni_z)NiSn$. Structural investigations also showed that introduction of *Ga* atoms puts into order crystalline structure ("heals" structural defects): *Ni* atoms leave 4*a* position of *Zr* atoms, and the value $z \to 0$.

Taking into account smaller atomic radius of *Ga* ($r_{Ga} = 0.141$ nm) as compared to *Sn* ($r_{Sn} = 0.162$ nm), it would be logical to expect a reduction in the values of unit cell period $a(x)$ $ZrNiSn_{1-x}Ga_x$. However, as is seen in Fig. 3*b*, a change in $a(x)$ values is not monotonous, reflecting the processes of structural transformations caused by impurity atoms of *Ga*. Consider in detail these

changes, as they also cause alterations in the electronic structure and affect the properties of thermoelectric material. Attention will be called to the character of change in $a(x)$ values in the area $0 \leq x \leq 0.03$ (Fig. 3*b*).

As shown by structural investigations, in the process of introducing *Ga* atoms into *ZrNiSn* structure, in the concentration area $0 \leq x \leq 0.01$ its ordering takes place by displacement of small *Ni* atoms ($r_{Ni} = 0.124$ nm) from 4*a* position by larger *Zr* atoms ($r_{Zr} = 0.160$ nm) (Fig. 3*b*). Alongside with displacement of *Ni* atoms, there is a process of substitution in 4*b* position of large *Sn* atoms by smaller *Ga* atoms. Taking into account that the difference in atomic radii of *Zr* and *Ni* is $(r_{Zr} - r_{Ni}) = 0.036$ nm, and *Sn* and *Ga* $(r_{Sn} - r_{Ga}) = 0.021$ nm, a change in $a(x)$ values at concentration site $0 \leq x \leq 0.01$ will determine the process of displacement of *Ni* from 4*a* position by large *Zr* atoms that will cause the growth of dependence $a(x)$ (Fig. 3*b*). After *Ni* atoms are displaced from *Zr* position (structure ordering), a change in $a(x)$ values will determine occupancy by *Ga* atoms of *Sn* (4*b*) position, and they will decrease in concentration area $0.02 \leq x \leq 0.15$. Note that ordering of the structure of $ZrNiSn_{1-x}Ga_x$ thermoelectric material makes stable its operational characteristics during heating-cooling cycles.

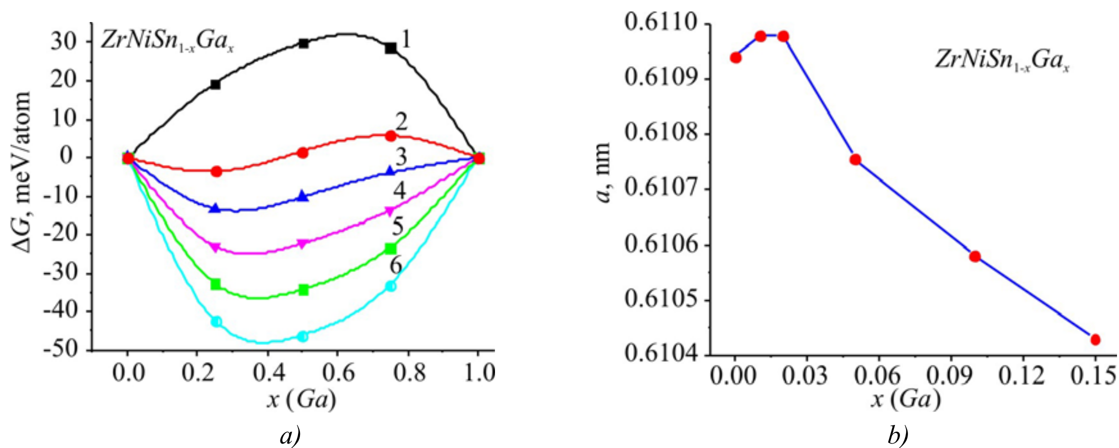


Fig. 3. Change in the values of thermodynamic potential ΔG(x) at different temperatures (a):
1 – T = 0 K; 2 – T = 473 K; 3 – T = 673 K; 4 – T = 873 K; 5 – T= 1073 K;
5 – T = 1273 K and unit cell period a(x) (b) for $ZrNiSn_{1-x}Ga_x$.

Changes in crystalline structure of $ZrNiSn_{1-x}Ga_x$ in the process will necessarily lead to a respective transformation of electronic structure. In particular, if in *n-ZrNiSn* in the energy gap there are donor states ε_D^1 formed due to displacement of ~ 1 % of *Zr* atoms by *Ni* atoms [16], then structure ordering (displacement of *Ni* from *Zr* position (4*a*)) can lead to reduction in the number of structural defects of donor nature, and donor states ε_D^1 must disappear.

On the other hand, since *Ga* atom possesses one *p*-electron less than *Sn*, substitution of *Sn* atom by *Ga* generates in 4*b* position a defect of acceptor nature, which will cause the emergence in the energy gap of impurity acceptor states ε_A. The presence of a large number of acceptors and donors will affect the band structure of $ZrNiSn_{1-x}Ga_x$ which is bound to appear in the investigation of electrokinetic and energy characteristics.

Research on the electronic structure of $ZrNiSn_{1-x}Ga_x$

To predict the behaviour of the Fermi level ε_F, the energy gap ε_g and the kinetic characteristics of $ZrNiSn_{1-x}Ga_x$, the electronic density of states (DOS) was calculated (Fig. 4). Taking into account that according to the results of structural investigations the crystalline structure of $ZrNiSn_{1-x}Ga_x$, $x \geq 0.01$ is ordered, calculation of DOS was performed for the case of ordered structure version. As is

evident from Fig. 4, on introducing into *n-ZrNiSn* the lowest attainable in the experiment concentrations of *Ga* acceptor impurity, the Fermi level ε_F (dashed line) starts drifting from the bottom of the conduction band ε_C, spaced ~ 97.6 meV from it [3], toward the midgap ε_g and then to valence band ε_V, to cross it at certain concentrations of *Ga*.

Crossing of the midgap ($x \approx 0.025$) by the Fermi level ε_F and further motion toward the valence band will cause a change in semiconductor conduction type, and holes will become majority carriers. Note that apart from drift of the Fermi level ε_F due to a change in semiconductor compensation degree, there is also a reduction in the energy gap values.

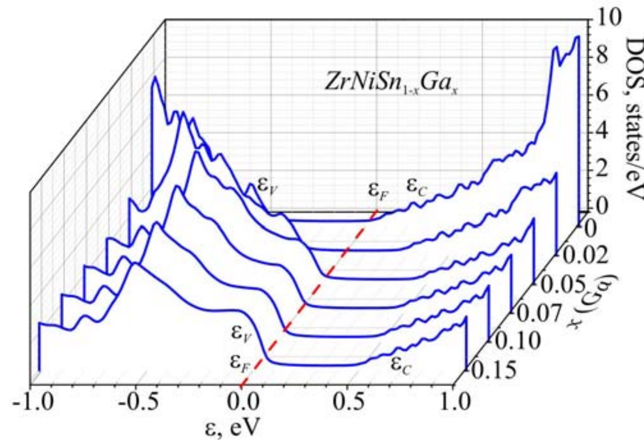


Fig. 4. Calculation of the electronic density of states for $ZrNiSn_{1-x}Ga_x$.

Thus, the results of calculation of the electronic density of states for $ZrNiSn_{1-x}Ga_x$, based on structural research data, prove the predicted acceptor nature of structural defects. The results of experimental research given below will show the conformity of calculated results to real processes occurring in thermoelectric material.

Research on the electrokinetic, energy and magnetic characteristics of $ZrNiSn_{1-x}Ga_x$

The temperature and concentration dependences of the electric resistivity ρ and the Seebeck coefficient α of $ZrNiSn_{1-x}Ga_x$ are presented in Fig. 5, 6. The dependences $\ln\rho(1/T)$ and $\alpha(1/T)$ $ZrNiSn_{1-x}Ga_x$ (Fig. 5) are typical for HDSC semiconductors, and the available activation areas point to several mechanisms of charge carrier transport [3, 7, 8]. The dependences $\ln\rho(1/T)$ are approximated using the known relationship [8]:

$$\rho^{-1}(T) = \rho_1^{-1} \exp\left(-\frac{\varepsilon_1^{\rho}}{k_B T}\right) + \rho_3^{-1}\left(-\frac{\varepsilon_3^{\rho}}{k_B T}\right), \quad (1)$$

where the first, high-temperature, summand describes activation of current carriers ε_1^{ρ} from the Fermi level ε_F to percolation level of continuous energy bands, and the second, low-temperature summand, – hopping conductivity ε_3^{ρ}. In turn, the temperature dependences of the Seebeck coefficient $\alpha(1/T)$ of $ZrNiSn_{1-x}Ga_x$ can be approximated using the following relationship [7]:

$$\alpha = \frac{k_B}{e}\left(\frac{\varepsilon_i^{\alpha}}{k_B T} - \gamma + 1\right), \quad (2)$$

where γ is parameter that depends on the nature of scattering. From the high-temperature area of the dependence $\alpha(1/T)$ the values of activation energy ε_1^{α} were calculated which, as shown in [3], are proportional to the amplitude of large-scale fluctuation of continuous energy bands (Fig. 1), and from the low-temperature area – the value of activation energy ε_3^{α} proportional to modulation amplitude of small-scale fluctuation of HDSC semiconductors [8 – 10].

The presence on the dependences lnρ(1/*T*) for all compositions of $ZrNiSn_{1-x}Ga_x$ of high-temperature activation areas testifies that the Fermi level ε_F is located in the forbidden zone from where thermal activation of current carriers occurs at percolation level. However, the obtained result contradicts the results of calculation of DOS for $ZrNiSn_{1-x}Ga_x$ (Fig. 4) which predicted crossing of the valence band at *Ga* concentration $x \approx 0.04$ by the Fermi level ε_F and by dielectric-metal transition which is the Anderson transition [7].

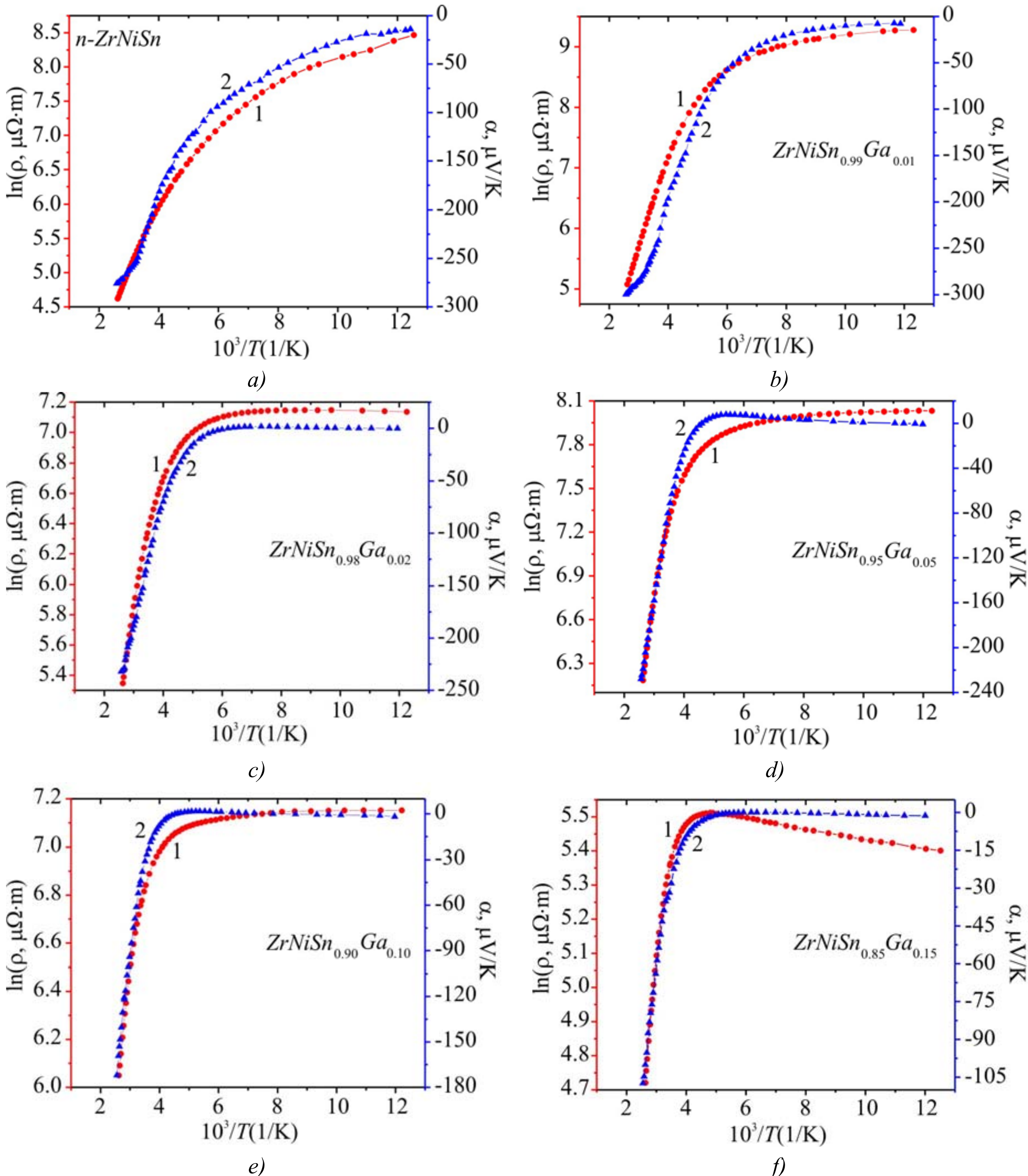


Fig. 5. Temperature dependences of resistivity lnρ(1/T) (1) and the Seebeck coefficient α(1/T) (2) of $ZrNiSn_{1-x}Ga_x$.

Assuming that in $ZrNiSn_{1-x}Ga_x$, as expected, only acceptor defects are generated, then at *Ga* concentration, for instance, $x = 0.15$ ($N_A^{Ga} \approx 3\cdot10^{21}$ cm^{-3}), the Fermi level ε_F must have long crossed the valence band. However, at high temperatures no conduction metallization takes place, which is

possible only on condition of simultaneous generation, along with acceptors, of donors of unknown origin which compensate acceptors, which will force the Fermi level ε_F to remain in the forbidden energy band, reflecting compensation ratio of $ZrNiSn_{1-x}Ga_x$.

It was predicted that substitution of *Ga* atoms for *Sn* atoms will be accompanied by generation in position 4*b* of acceptor structural defects and the emergence of impurity acceptor states ε_A. At the concentration of *Ga* atoms, when the Fermi level ε_F will cross the midgap and start approaching the percolation level of valence band, free holes will be the majority carriers. Such assumptions are logical, since at *Ga* concentration $x > 0.01$ the number of generated acceptors ε_A already exceeds the number of donors with the energy ε_D^1 in *n-ZrNiSn* (the number of *Ni* atoms in position of *Zr* (4*a*)).

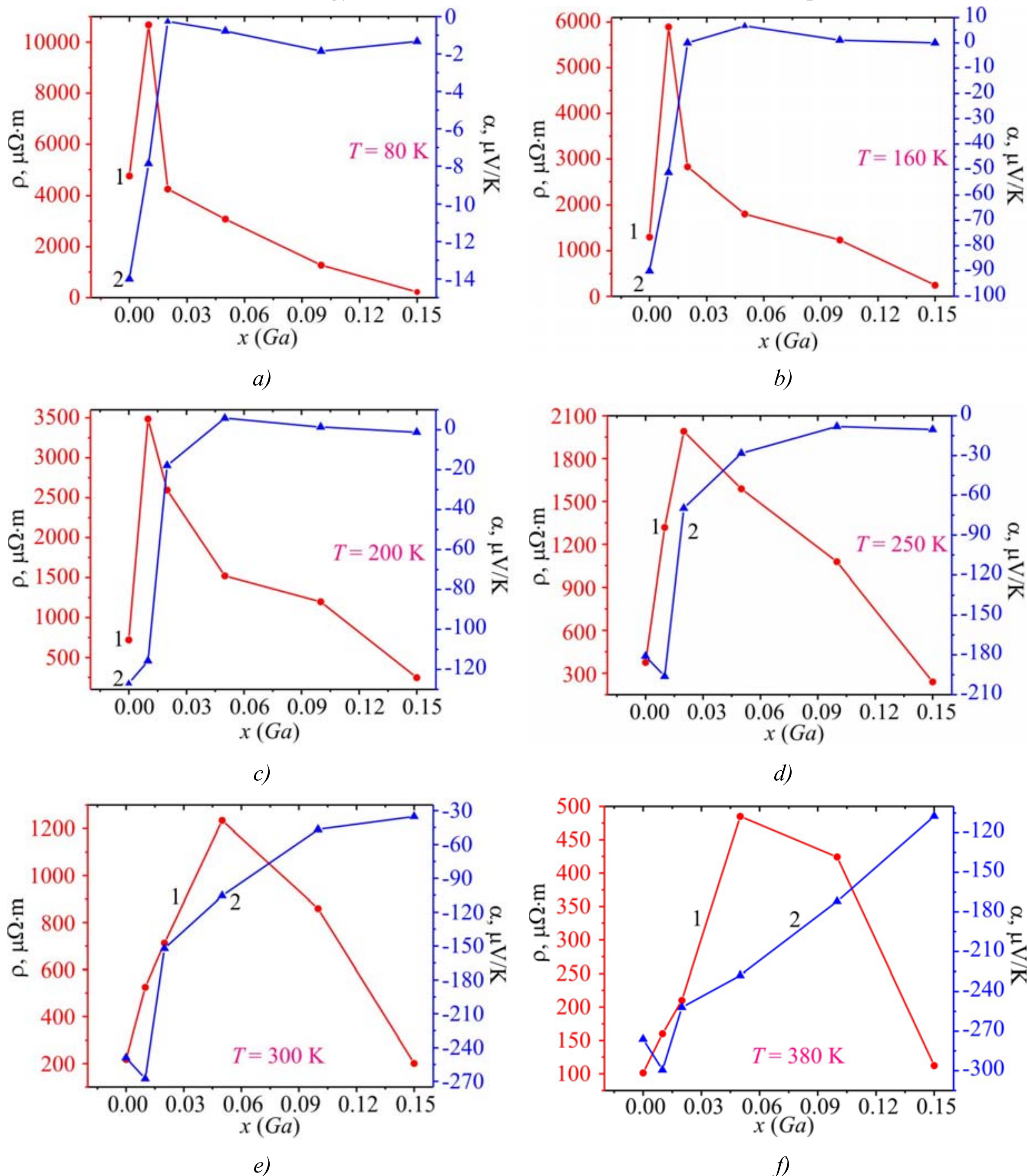


Fig. 6. Change in the values of resistivity ρ(x) and the Seebeck coefficient α(x) of $ZrNiSn_{1-x}Ga_x$ at different temperatures.

On the other hand, if we assume that *ZrNiSn* has no donor structural effects and the semiconductor is intrinsic (donor states ε_D^1 are absent), then with introduction of *Ga* atoms the values of electric resistivity $\rho(x)$ will decrease at all temperatures and concentrations due to the appearance and increase in the number of free holes in the valence band at ionization of acceptors ε_A. It is clear that the sign of the Seebeck coefficient in this case will be positive.

The fact that *Ga* atoms introduced into *n-ZrNiSn* generate structural defects of acceptor nature is demonstrated by the dependences of change in the values of resistivity $\rho(x, T)$ and the Seebeck coefficient $\alpha(x, T)$ over the entire concentration and temperature ranges (Fig. 6). To begin with, we will analyze the dependences $\rho(x)$ anda $\alpha(x)$ at temperature 80 K. Thus, introduction of the lowest in experiment *Ga* concentration drastically increases the value of resistivity $\rho(x)$ at $T = 80$ K from the values $\rho(x = 0) = 4751.1$ μΩ·m to $\rho(x = 0.01) = 10677.7$ μΩ·m. It can be assumed that a sample with concentration $x = 0.01$ is strongly compensated, as long as the number of generated acceptors is close to the number of donors in *n-ZrNiSn* [16]. Drastic growth of the dependence $\rho(x)$ in the area $x = 0 – 0.01$ is determined by two processes:

– decreasing the number of donor states ε_D^1 at ordering of $ZrNiSn_{1-x}Ga_x$ structure, when *Zr* atoms displace *Ni* atoms from 4*a* position, "healing" structural defects of donor nature;

– "freezing out" of free electrons toward energy gap to impurity acceptor states ε_A formed at substitution of *Sn* by *Ga*.

However, at concentration of $x > 0.01$ and $T = 80$ K, the values of resistivity $\rho(x)$ of $ZrNiSn_{1-x}Ga_x$ just as drastically decrease 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, pointing to increase in the number of free current carriers. The maximum on the dependence $\rho(x)$ on introducing to *n*-type semiconductor of *Ga* acceptor impurity shows balancing of competing processes which determine conductivity mechanisms. Let us study the type and origin of current carriers which account for a decline in the dependence $\rho(x)$ (Fig. 6).

As is seen from Fig. 5 and 6, at temperature 80 K the sign of the Seebeck coefficient of $ZrNiSn_{1-x}Ga_x$ remains negative for all concentrations, and electrons are majority carriers. And this is despite the fact that concentration of generated structural defects of acceptor nature in a sample, for instance, $ZrNiSn_{1-x}Ga_x$, $x = 0.10$, exceeds by an order of magnitude the concentration of donors in *n-ZrNiSn*. This is possible only on condition of such depth of occurrence of acceptor states, that temperature 80 K is insufficient for the ionization of acceptors (overcoming by the hole of the energy barrier between the percolation level of valence band and the acceptor level ε_A).

With a rise in temperature ($T > 80$ K), the dependence $\rho(x)$ of $ZrNiSn_{1-x}Ga_x$ is transformed, showing changes in semiconductor electron structure. On the dependence $\rho(x)$ at temperature $T = 160$ K in the concentration range of $x \approx 0.06$ at first there appears a step which gradually grows into an extremum ($T = 300$ K) which with a rise in temperature $T = 380$ K is displaced into the region of higher concentrations $x \approx 0.08$. In so doing, the maximum on the dependence $\rho(x)$ in the range of $x \approx 0.01$ disappears.

Thus, at low concentrations of *Ga* acceptor impurity, the maximum on the dependence $\rho(x)$ of $ZrNiSn_{1-x}Ga_x$ at a concentration of $x \approx 0.01$ (Fig. 6) is related to the existence in the energy gap of donor states ε_D^1 (*Ni* atoms in 4*a* position of *Zr* atoms). At the concentration of acceptors which corresponds to the concentration of generated donors ($x \approx 0.01$) there is a depletion of donors, the values of electric resistivity are maximum, and semiconductor is strongly compensated. As long as the values of the Seebeck coefficient at temperature 80 K remain negative for all concentrations, this temperature is insufficient for complete ionization of acceptors.

Note that in $ZrNiSn_{1-x}Ga_x$, $x = 0.01$, the concentration of donors with the energy ε_D^1 in fact will be much lower than the number of generated acceptors with the energy ε_A, since at the lowest concentrations of *Ga* the structure is put into order, reducing the number of donors with the energy ε_D^1.

At the concentrations $x \geq 0.02$, when the number of generated acceptors exceeds the number of donors in *n-ZrNiSn*, with a rise in temperature from $T = 80$ K to $T = T_1^{inv}$ the sign of the Seebeck coefficient changes from negative to positive (Fig. 7). That is, for the samples of $ZrNiSn_{1-x}Ga_x$, $x \approx 0.02$ and $x \approx 0.05$, the temperature ~ 93 K is sufficient for the ionization of acceptors ε_A.

However, with a further rise in temperature, in the samples of $ZrNiSn_{1-x}Ga_x$, $x \approx 0.02$ and $x \approx 0.05$, 0, 10, at temperatures $T \approx 156$ K and $T \approx 216$ K, respectively, the sign of the Seebeck coefficient is unexpectedly changed from positive to negative at T_2^{inv} (Fig. 7), and electrons again become majority carriers. And this is despite the fact that concentration of generated acceptors in $ZrNiSn_{1-x}Ga_x$, $x > 0.01$, exceeds the number of donors with the energy ε_D^1 in *n-ZrNiSn* (the number of *Ni* in *Zr* position (4*a*)). Such a behaviour of the Seebeck coefficient in $ZrNiSn_{1-x}Ga_x$ at $T = T_2^{inv.}$ is possible under condition that in semiconductor, alongside with impurity acceptor states ε_A, donor states ε_D^2 are generated with their energy levels deeper than ε_D^1, and ionization of ε_D^2 donors and overcoming of a barrier to the percolation level of conduction band requires larger energies. It seems that in a semiconductor there are s*imultaneously* generated donor-acceptors pairs whose energy levels are arranged in the forbidden energy band.

The same conclusion is arrived at by analyzing the behaviour of $\rho(x)$ of $ZrNiSn_{1-x}Ga_x$ at different temperatures. As long as the extremum on the dependence $\rho(x)$ of $ZrNiSn_{1-x}Ga_x$ is a result of balancing of competing processes in semiconductor electronic structure, with a rise in temperature the disappearance of maximum $\rho(x)$ at low concentrations of *Ga* ($x \approx 0.01$) and the emergence of a new extremum $\rho(x)$ in the range of concentrations $x \approx 0.06$ unambiguously points to the existence of donor states ε_D^2 whose depth of occurrence is larger than ε_D^1. Indeed, at concentrations $x \geq 0.02$ and temperatures whose values are insufficient for ionization of donor ε_D^2, the concentration of acceptors in $ZrNiSn_{1-x}Ga_x$ exceeds the concentration of donors, and the sign of the Seebeck coefficient is predictably positive. However, with a rise in temperature at $T \geq T^{inv.}$ there begins ionization of donors ε_D^2, drastically increases the number of free electrons which become majority carriers, which is indicated by the negative values of the Seebeck coefficient (Fig. 7).

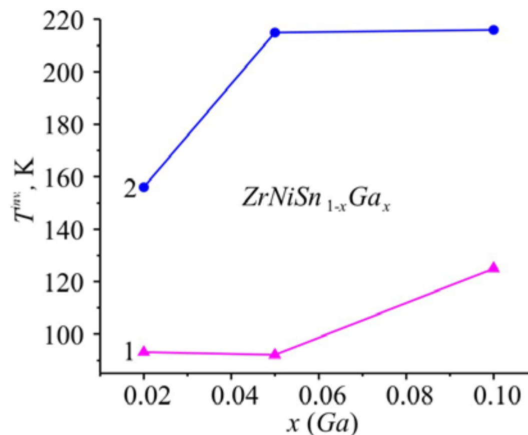


Fig. 7. Change in the values of inversion temperature $T^{inv.}$: 1 – $T_1^{inv.}$ (change of sign from negative to positive); 2 – $T_2^{inv.}$ (change of sign from positive to negative) $ZrNiSn_{1-x}Ga_x$.

On the other hand, the larger number of acceptors is generated in $ZrNiSn_{1-x}Ga_x$, the larger energies (higher temperatures) are needed for the number of ionized donors ε_D^2 to exceed the number of ionized acceptors ε_A. We can *assume* that in $ZrNiSn_{1-x}Ga_x$ to assure structural *stability* and electroneutrality *principle,* in 4*b* position structural defects of both acceptor and donor nature are *simultaneously* generated whose concentration grows with increasing *Ga* content. In this case the formula of semiconductor thermoelectric material is of the form $(Zr_{1-z}Ni_z)Ni\ Sn_{1-x-y}Ga_x$, where *y* is concentration of vacancies in 4*b* position of *Sn* atoms.

Analysis of behaviour of the energy characteristics of $ZrNiSn_{1-x}Ga_x$, in particular, a change in the values of activation energy $\varepsilon_1^\rho(x)$ and modulation amplitude of continuous energy bands ε_1^α also shows that acceptors and donors are simultaneously generated in semiconductor (Fig. 8). Thus, in *n-ZrNiSn* the value of energy $\varepsilon_1^\rho(x = 0) = 97.6$ meV shows the energy gap between the position of the Fermi level ε_F and percolation level of conduction band. Doping of *n*-type semiconductor with *Ga* acceptor impurity increases compensation ratio, and the Fermi level ε_F goes deeply into forbidden band at the distance of $\varepsilon_1^\rho(x = 0.01) = 138.8$ meV and $\varepsilon_1^\rho(x = 0.02) = 153.2$ meV. Taking into account that at high temperatures the sign of the Seebeck coefficient remains negative, we can conclude that the values of activation energies $\varepsilon_1^\rho(x = 0.01)$ and $\varepsilon_1^\rho(x = 0.02)$ represent the energy barrier to percolation level of conduction band. Recall that the value of activation energy $\varepsilon_1^\rho(x)$ is calculated exactly from the high-temperature activation area of the dependence $\ln\rho(1/T)$ (Fig. 5).

The negative values of the Seebeck coefficient and decrease in the values of $\varepsilon_1^\rho(x)$ at 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 testify that the Fermi level ε_F has been reversed and is again moving toward conduction band. It means that in $ZrNiSn_{1-x}Ga_x$ there appear electrons of unknown origin, and this on doping of *n*-type semiconductor with acceptor impurity is possible only on condition of a simultaneous generation of donors ε_D^2 whose concentration is not lower than that of acceptors.

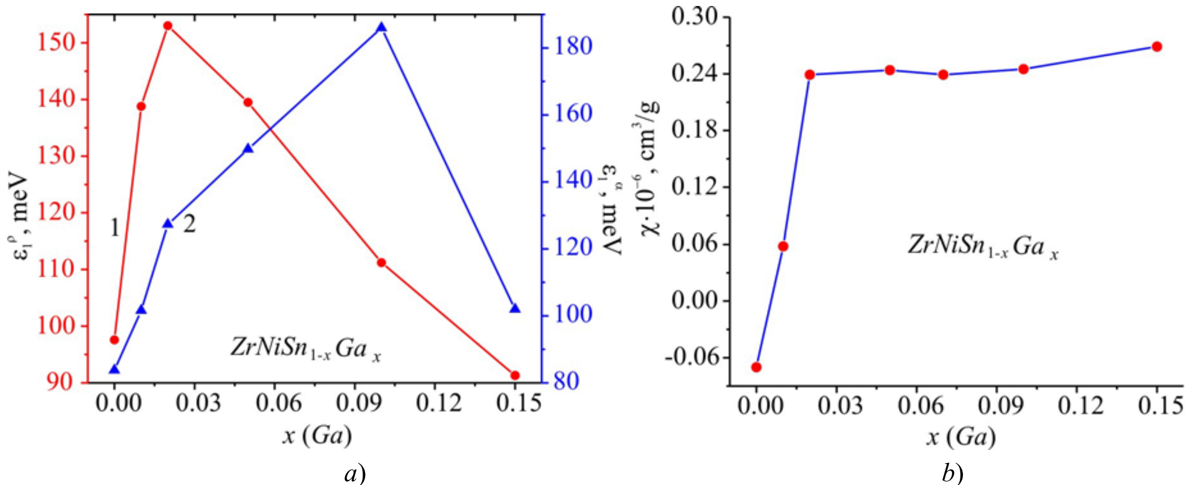


Fig. 8. Change in the values of activation energies $\varepsilon_1^\rho(x)$ (1) and $\varepsilon_1^\alpha(x)$ (2) (a) and magnetic susceptibility $\chi(x)$ (b) of $ZrNiSn_{1-x}Ga_x$.

On the other hand, simultaneous generation in $ZrNiSn_{1-x}Ga_x$ of donors and acceptors changes compensation ratio and the value of modulation energy of continuous energy bands of HDSC semiconductor [3, 8]. Fig. 8 shows a change in the values of activation energy $\varepsilon_1^\alpha(x)$ which is proportional to modulation amplitude of continuous energy bands of $ZrNiSn_{1-x}Ga_x$. We can see that in the case of *n-ZrNiSn* the modulation amplitude is $\varepsilon_1^\alpha(x = 0) = 83.8$ meV. Introduction into

n-type semiconductor of the lowest concentration of *Ga* acceptor impurity ($x = 0.01$) drastically increases compensation ratio, which is indicated by increase in the values of modulation amplitude to $\varepsilon_1^{\alpha}(x = 0.01) = 101.6$ meV.

Further increase in the concentration of acceptors in a semiconductor where electrons are majority carriers due to simultaneous generation of donors increases compensation ratio and modulation amplitude of continuous energy 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. A decline in the dependence $\varepsilon_1^{\alpha}(x)$ at concentrations of $ZrNiSn_{1-x}Ga_x$, $x > 0.10$ shows that the number of ionized donors increases faster than that of acceptors, so compensation ratio is reduced. At large concentrations of generated donor-acceptor pairs $ZrNiSn_{1-x}Ga_x$, $x = 0.15$, when wave functions of localized states ε_D^2 overlap, there is metallization of conductivity (absence of low-temperature activation area on the dependence $\ln\rho(1/T)$ (Fig. 5).

Of interest are the results of studies on magnetic susceptibility χ of $ZrNiSn_{1-x}Ga_x$ (Fig. 8*b*) which confirm the conclusion made on the simultaneous generation of acceptor and donor defects. Investigations showed that the samples of $ZrNiSn_{1-x}Ga_x$, $x>0.01$, are Pauli paramagnetics wherein magnetic susceptibility χ is determined exceptionally by electronic gas and is proportional to density of states at the Fermi level $g(\varepsilon_F)$. As is seen from Fig. 8*b*, the dependence $\chi(x)$ at $x > 0.03$ drastically changes the slope, achieves plateau and scarcely changes up to $x = 0.15$. That is, increase in the concentration of acceptor impurity and possible increase in the concentration of free holes scarcely changes the values $g(\varepsilon_F)$. Such a behaviour of $\chi(x)$ ($\chi \sim g(\varepsilon_F)$) is possible only on condition of appearance in $ZrNiSn_{1-x}Ga_x$ of opposite-sign current carriers of the concentration close to holes as a result of generation of donor-acceptor pairs which will account for density of states permanence at the Fermi level $g(\varepsilon_F)$. Note that *n-ZrNiSn* semiconductor is not Pauli paramagnetic, but a weak diamagnetic, which is evidenced by the negative values of magnetic susceptibility: $\chi(x = 0) = -0.07$ cm^3/g. Therefore, we cannot attribute growth of the dependence $\chi(x)$ in the concentration area $x = 0 - 0.01$ to increase in the values $g(\varepsilon_F)$.

Thus, the results of structural, electrokinetic, energy and magnetic investigations of $ZrNiSn_{1-x}Ga_x$ allow speaking about a complicated mechanism of simultaneous generation in a crystal of acceptor and donor structural defects and making assumptions regarding their nature. However, they cannot definitely prove the existence of this or other mechanism of generation of donor-acceptor pairs. The following mechanism will be proposed below.

Refinement of crystalline and electronic structures of $ZrNiSn_{1-x}Ga_x$

Based on the fact that the above results of research on $ZrNiSn_{1-x}Ga_x$ did not provide any answer concerning the mechanisms for generation of structural defects of various nature, let us solve the inverse problem. It is known that for the calculation of electron energy in the first Brillouin zone one should know spatial arrangement of atoms (or their absence – vacancies) in the sites of the unit cell. On the other hand, the slightest structural changes modify local symmetry and the electronic density of states. In this case the adequacy of the results of calculation of the electronic density of states distribution and the results of experimental research on the energy characteristics of semiconductor material specifies that the model of its crystalline structure is adequate to spatial arrangement of atoms in a real material. Exactly for this reason the results of electronic structure calculation as compared to the results, for instance, of electrokinetic or energy characteristics, yield information on the real structure of crystal which is beyond reach of X-ray methods.

Having the experimental results of the Fermi level drift velocity as activation energy $\varepsilon_1^{\rho}(x)$

$ZrNiSn_{1-x}Ga_x$ (Fig. 8*a*, curve 1), the compensation ratio (the ratio between donors and acceptors) was sought for, which will set the velocity of the Fermi level ε_F maximum close to $\varepsilon_1^\rho(x)$ (Fig. 9).

Calculations of the electronic density distribution DOS were performed almost for all variants of atoms arrangement in the unit cell sites, and the degree of occupancy of all positions by intrinsic and /or foreign atoms, as well as the presence of vacancies in them. It turned out that the most acceptable is the variant of atoms arrangement in the ordered but deformed structure, wherein the following changes took place:

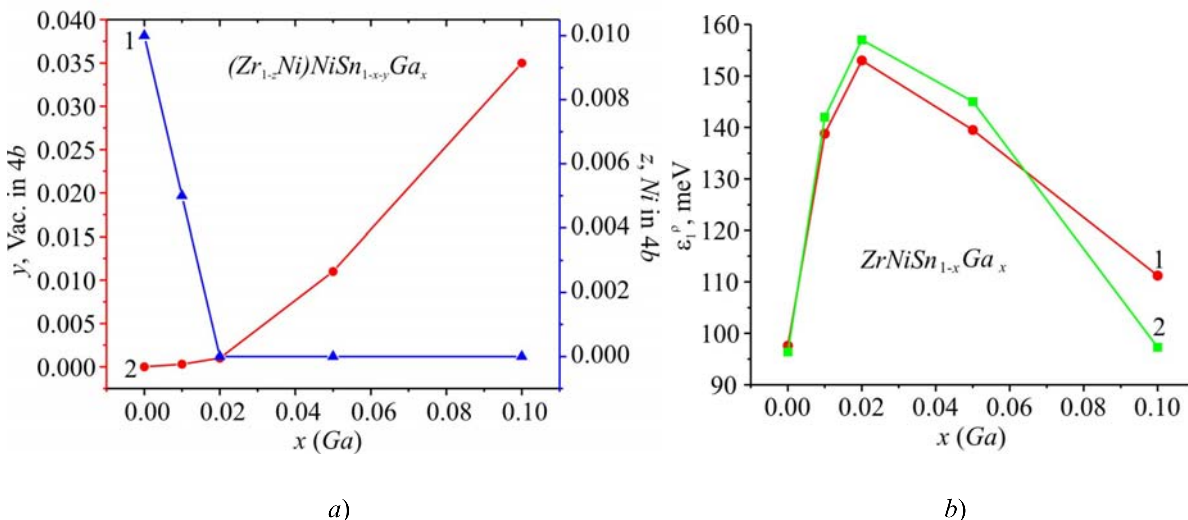
a) crystalline structure of *n-ZrNiSn* is disordered (local amorphization) due to partial occupancy, up to ~ 1 % ($z \approx 0.01$), by *Ni* atoms of position 4*a* of *Zr* atoms, which generates in a semiconductor structural defects of donor nature (semiconductor formula $(Zr_{1-z}Ni_z)NiSn$);

b) introduction of *Ga* atoms puts structure into order and reduces the number of donor defects: *Ni* atoms leave position 4*a* of *Zr* atoms ($z \to 0$), and semiconductor formula acquires the form $(Zr_{1-z}Ni_z)Ni\ Sn_{1-x}Ga_x$;

c) occupancy by *Ga* impurity atoms of crystallographic position 4*b* of *Sn* atoms generates structural defects of acceptor nature;

d) generation and increase of the number of vacancies (y) in position 4*b* of *Sn* atoms (end formula is transformed into $(Zr_{1-z}Ni_z)Ni\ Sn_{1-x-y}Ga_x$).

Item *d*), being the result of formal mathematical calculations, has a profound physical meaning, as long as *simultaneous* generation of donor-acceptor pairs assures electroneutrality *principle* in position *4b* and *stability* of thermoelectric material structure.



a) *b*)

Fig. 9. Dynamics of change in the concentration of Ni atoms (z) in position 4a of Zr atoms (1) and vacancies (y) in position 4b of Sn atoms (2) (a) and experimentally obtained (1) and calculated (2) dependence of activation energy ε_1^ρ (b) for $ZrNiSn_{1-x}Ga_x$.

Fig. 9*a* shows the results of calculation of the dynamics of change in all structural defects at heavy doping of *n-ZrNiSn* with *Ga* acceptor impurity, which provides within the error of calculations the proximity of calculated velocity of the Fermi level ε_F (Fig. 9*b*, curve 2) to that obtained from the high-temperature areas of dependences $\ln\rho(1/T)$ (Fig. 9*b*, curve 1).

Based on the obtained results of spatial arrangement of atoms in $ZrNiSn_{1-x}Ga_x$, the electronic density of states distribution DOS was calculated, which adequately shows the compensation ratio of semiconductor material (Fig. 10). In particular, we can see the distinctions in the energy gap and the

position of the Fermi level ε_F for the ordered version of *ZrNiSn* structure and in the presence of "local amorphization" in *n-ZrNiSn* semiconductor.

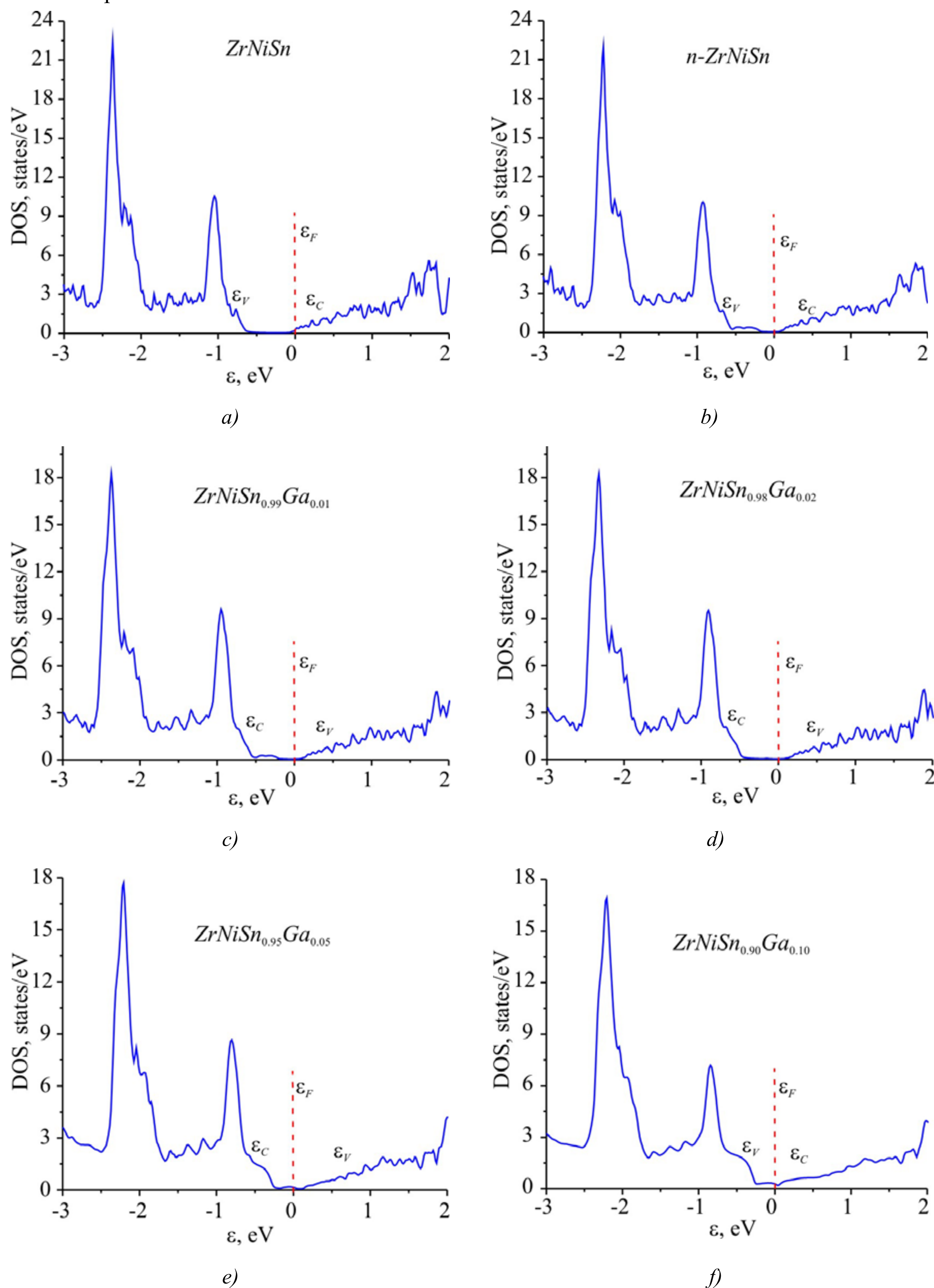


Fig. 10. Calculation of the electronic density of states DOS for different concentrations of $ZrNiSn_{1-x}Gax$.

From Fig. 10 it is also seen that the Fermi level ε_F of $ZrNiSn_{1-x}Ga_x$ for all concentrations of *Ga*

acceptor impurity changes its location with respect to percolation level of conduction band, which corresponds to negative values of the Seebeck coefficient (Fig. 5*b*) and is consistent with the results of electrokinetic characteristics of material.

Conclusions

Thus, as a result of integrated research on the crystalline and electronic structures, the kinetic and magnetic characteristics of $ZrNiSn_{1-x}Ga_x$ thermoelectric materials, the mechanisms for simultaneous generation of the acceptor and donor structural defects (donor-acceptor pairs) have been identified that change the compensation ratio and determine the electric conductivity mechanisms of material. The investigated $ZrNiSn_{1-x}Ga_x$ semiconductor is a promising thermoelectric material, and crystalline structure orderliness is key to stability and reproducibility of characteristics.

The work was performed in the framework of grants of Ministry of Education and Science of Ukraine, № 0115U003257 and № 0114U005464.

References

1. M. Gurth, G. Rogl, V.V. Romaka, E. Bauer, and P. Rogl, Thermoelectric High ZT Half-Heusler Alloys $Ti_{1-x-y}Zr_xHf_yNiSn$ ($0 \le x \le 1$; $0 \le y \le 1$), *Acta Materialia* 104, 210 – 222 (2016).
2. M. Schwall, B. Balke, Phase Separation as a Key to a Thermoelectric High Efficiency, *Phys. Chem. Chem. Phys* **15**(6), 1868 – 1872 (2013).
3. V.A. Romaka, V.V. Romaka, and Yu.V. Stadnyk, *Intermetallic Semiconductors: Properties and Application* (Lviv:Lvivska Polytechnika, 2011), 488 p.
4. V.A. Romaka, M.G. Shelyapina, Yu.K. Gorelenko, D. Fruchart, Yu.V. Stadnyk, L.P. Romaka, and V.F. Chekurin, Special Features of Conductivity Mechanisms in Heavily Doped *n-ZrNiSn* Intermetallic Semiconductors, *Semiconductors* **40**(6), 655 – 661(2006).
5. V.A. Romaka, Yu.V. Stadnyk, D. Fruchart, L.P. Romaka, A.M. Goryn, Yu.K Gorelenko, T.I. Dominuk Features of Structural, Electron-Transport, and Magnetic Properties of Heavily Doped *n-ZrNiSn* emiconductor: *Fe* Acceptor Impurity, *Semiconductors* **43**(3), 278 – 284 (2009).
6. V.A. Romaka, P. Rogl, L.P. Romaka, Yu.V. Stadnyk, V.Ya. Krayovskyy, D. Kaczorowski, and A.M. Horyn, Features of Structural, Energy and Kinetic Characteristics of $TiNiSn_{1-x}Ga_x$ Thermoelectric Material, *J.Thermoelectricity* 3, 24 – 33 (2016).
7. B.I. Shklovsky, *Electron Properties of Doped Semiconductors* (Moscow: Nauka, 1979), 416 p.
8. L.I. Anatychuk, *Thermoelements and Thermoelectric Devices* (Kyiv: Naukova Dumka, 1979), 768 p.
9. H. Mott, T.Davis, *Electronic Processes in Non-Crystalline Substances* (Moscow: Mir, 1982), 368p.
10. B.I. Shklovsky, A.L. Efros, Transition from Metallic to Activation Conduction in Compensated Semiconductors, *JETP* **61**(2), 816 – 825 (1971).
11. B.I. Shklovsky, A.L. Efros, Fully Compensated Crystalline Semiconductor as a Model of Amorphous Semiconductor, *JETP* **62**(3), 1156 – 1165 (1972).
12. T. Roisnel, J.Rodriguez-Carvajal, WinPLOTR: a Windows Tool for Powder Diffraction Patterns Analysis, *Mater. Sci. Forum, Proc. EPDIC7* 378-381, 118 – 123 (2001).

13. M. Schruter, H. Ebert, H. Akai, P. Entel, E. Hoffmann, and G.G. Reddy, First-Principles Investigations of Atomic Disorder Effects on Magnetic and Structural Instabilities in Transition-Metal Alloys, *Phys. Rev. B* **52**, 188 – 209 (1995).
14. V.L. Moruzzi, J.F. Janak, and A.R. Williams, *Calculated Electronic Properties of Metals* (NY: Pergamon Press, 1978), 348 p.
15. V.V. Romaka, L.P. Romaka, V.Ya. Krayovsky, and Yu.V. Stadnyk, *Stannides of Rare-Earth and Transition Metals* (Lviv: Lvivska Polytechnika Publ., 2015), 224 p.
16. V. Romaka, P. Rogl, L. Romaka, Yu. Stadnyk, A. Grytsiv, O. Lakh, and V. Krayovsky, Peculiarites of Structural Disorder in *Zr*- and *Hf*- Containing Heusler and Half-heusler Stannides, *Intermetallics* 35, 45 – 52 (2013).

Submitted 02.09.2016