PHYSICS AND CHEMISTRY OF SOLIDSTATE
V. 19, № 1 (2018) P. 21-28
DOI: 10.15330/pcss.19.1.21-28

ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 19, № 1 (2018) С. 21-28

PACS: 537.311.322

ISSN 1729-4428

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

Study of Electrokinetic and Magnetic Properties of $ZrNi_{1-x}Rh_xSn$ Semiconductive Solid Solution

[1]Ivan Franko National University of Lviv, 6, Kyryla and Mefodiya Str., Lviv, 79005, Ukraine, e-mail: lyubov.romaka@gmail.com
[2]Ya. Pidstryhach Institute for Applied Problems of Mechanics and Mathematics National Academy of Sciences of Ukraine, 3-b, Naukova Str., Lviv, 79060, Ukraine;
[3]National University "Lvivska Politechnika", 12, S. Bandera Str., Lviv, 79013, Ukraine

The features of electrokinetic, energy state and magnetic characteristics of $ZrNi_{1-x}Rh_xSn$ semiconductive solid solution were investigated in the range: T = 80 - 400 K, x = 0 - 0.10. It was shown that substitution of Ni atoms ($3d^84s^2$) by Rh atoms ($4d^85s^1$) in the structure of ZrNiSn compound generated the structural defects with acceptor nature, and holes became the main charge carriers in the $ZrNi_{1-x}Rh_xSn$ at low temperature. Based on analysis of the motion rate of the Fermi level $\Delta\varepsilon_F/\Delta x$ in $ZrNi_{1-x}Rh_xSn$ to the valence band and change of sign of thermopower coefficient from positive to negative it was suggested that the structural defects with acceptor and donor natures were generated simultaneously (donor-acceptor pairs), and deep donor band ε_D^2 was formed.

Keywords: electric conductivity, thermopower coefficient, Fermi level.

Article acted received 30.12.2017; accepted for publication 05.03.2018.

Introduction

The present work continues the program of investigations of the electric conductivity mechanisms in the *n*-ZrNiSn, *n*-HfNiSn and *n*-TiNiSn intermetallic semiconductors for different methods of doping and types of impurities [1]. The importance of such studies is due to the fact that thermoelectric materials based on the above-mentioned compounds have high efficiency of conversion of thermal energy into electric and stable characteristics in the wide temperature range (T = 1.7-1000 K), and optimization of their characteristics is performed by appropriate doping [2].

Previous researches [3] established the reason of electron type of conductivity for *n*-ZrNiSn. It turned out that crystal structure of ZrNiSn compound is disordered due to partial up to about 1% ($y\approx0.01$) occupation of ($4a$) position of Zr ($4d^25s^2$) atoms by Ni ($3d^84s^2$) atoms, which generates structural defects of donor nature in the crystal (Ni has a higher number of *d*-electrons than Zr), and the donor band ε_D^1 appears in the band gap. In this case, the formula of compound can be written as $(Zr_{1-y}Ni_y)NiSn$.

Investigation of $ZrNi_{1-x}M_xSn$ semiconductive substitution solid solutions, where M = Cr, Mn, Fe, Co, revealed the appearance of electrons of unknown origin, which was shown up by a change of the sign of the thermopower coefficient from positive to negative at low concentrations of impurity atoms [1] and indicated the appearance of free electrons of unknown origin. Taking into account that the number of 3*d*-electrons of Ni is greater than of Cr, Mn, Fe and Co, the generation of only structural defects with acceptor nature was expected. Obviously, the appearance of electrons in $ZrNi_{1-x}M_xSn$ is connected with the presence of additional, unknown mechanism of donor generation as a result of structural changes not identified by X-ray methods.

The investigation of *p*-$HfNi_{1-x}Rh_xSn$ solid solution [4] showed that with increase of temperature at certain concentrations of acceptors appears the state when almost all generated defects of the acceptor nature become ionized (catch free electrons), and semiconductor becomes highly doped and compensated HDCS [1,5]. And this despite the fact that the number of acceptors introduced into *n*-ZrNiSn in order exceeded the number of defects with donor nature.

In this context, the question arises what is the origin of the structural defects of donor nature in the $ZrNi_{1-x}M_xSn$ and $HfNi_{1-x}Rh_xSn$ solid solutions obtained by substitution of Ni atoms when only structural defects with acceptor nature had to be generated in the crystal (Rh ($4d^85s^1$) contains less *s*-electrons, than Ni)? The proposed paper, which is the first part of studies, contains

the results of experimental measurements of temperature and concentration dependencies of electrokinetic, electron energy state and magnetic characteristics for $ZrNi_{1-x}Rh_xSn$. The answer to this question can only be obtained after studying the features of the crystal and electronic structures of $ZrNi_{1-x}Rh_xSn$, to which the next work will be devoted.

I. Experimental details

The electrokinetic, energy state and magnetic characteristics of $ZrNi_{1-x}Rh_xSn$ solid solution were studied. The samples were synthesized by a direct twofold arc melting of the constituent elements in an inert atmosphere, followed by homogenizing annealing for 720 h at 1073 K. The chemical and phase compositions of the alloys were examined by X-ray phase analysis (diffractometer DRON-4.0, Fe$K\alpha$-radiation) and scanning electron microscopy (electron scanning microscope REMMA 102-02). The temperature and concentration dependences of the specific electric resistivity (ρ), thermopower coefficient (α) with pure copper as a reference material and magnetic susceptibility (χ) (Faraday method) of $ZrNi_{1-x}Rh_xSn$ samples were measured in the temperature range $T = 80 – 400$ K and at concentrations $N_A^{Rh} \approx 3.8 \cdot 10^{19}$ cm^{-3} ($x = 0.005$) $–1.9 \cdot 10^{21}$ cm^{-3} ($x = 0.10$).

II. Investigation of electrokinetic and energy state characteristics of $ZrNi_{1-x}Rh_xSn$

X-ray phase and structural analyzes have shown that the powder patterns of the $ZrNi_{1-x}Rh_xSn$ samples are indexed with cubic MgAgAs structure type [6] and do not contain traces of other phases. According to the

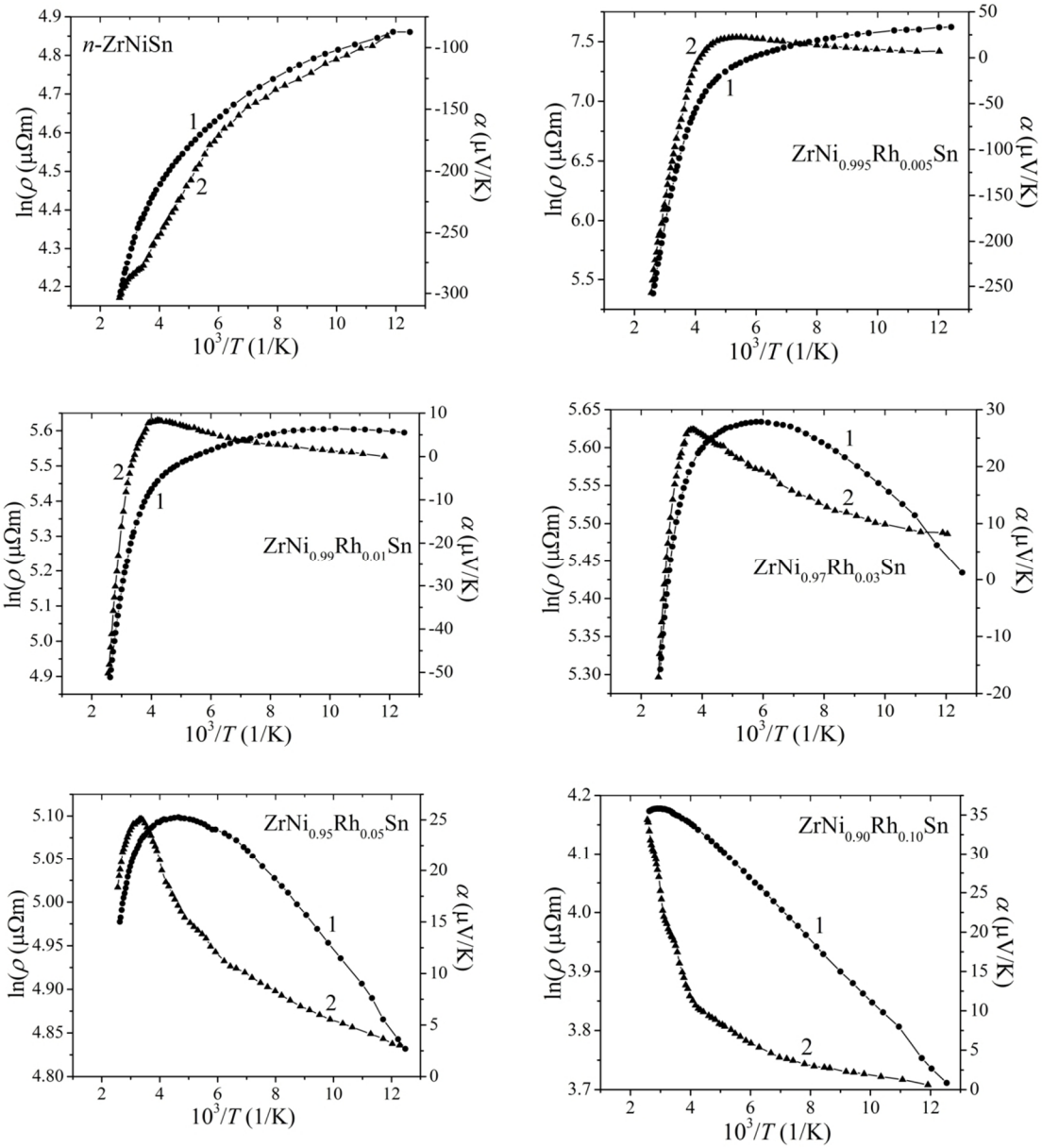


Fig. 1. Temperature dependences of electric resistivity lnρ(1/T) (1) and thermopower coefficient α(1/T) (2) for $ZrNi_{1-x}Rh_xSn$.

microprobe analysis of the atoms concentration on the surface, the compositions of the samples corresponded to the initial compositions of the alloys, confirming the substitution of Ni atoms by Rh.

The temperature and concentration dependences of electric resistivity ρ and thermopower coefficient α for $ZrNi_{1-x}Rh_xSn$ are shown in Figs. 1, 2. The $\ln\rho(1/T)$ and $\alpha(1/T)$ dependences for $ZrNi_{1-x}Rh_xSn$ samples (Fig. 1) are typical for heavily doped and highly compensated semiconductors [5] and the present activation regions indicate several mechanisms of charge transport. Such mechanisms are the activation of current carriers from the Fermi level ε_F to continuous energy band (high temperatures) (except for $x = 0.10$) and hopping conductivity (except for $x \geq 0.03$) within the energy states close to ε_F (low temperature). The dependences of $\ln\rho(1/T)$ for $ZrNi_{1-x}Rh_xSn$ can be described by known relation [5]:

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

where the first term ε_1^{ρ} describes the activation of the current carriers from the Fermi level ε_F to the percolation levels of continuous energy band at high temperatures, and the second term ε_3^{ρ} is the energy of hopping conduction at low temperature.

The temperature dependencies of thermopower coefficient $\alpha(1/T)$ for $ZrNi_{1-x}Rh_xSn$ are described by relation [7]:

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

where γ is a parameter which depends on the scattering mechanisms. The values of the activation energy ε_1^{α}, which are proportional to the amplitudes of large-scale fluctuations of continuous energy bands, have been calculated from the high-temperature part of $\alpha(1/T)$ dependencies. The values of the activation energy ε_3^{α}, which are proportional to the amplitudes of modulation of the small-scale fluctuations in HDCS [1, 5], have been calculated from the low temperature part of $\alpha(1/T)$ dependencies.

From the high temperature part of $\ln\rho(1/T)$ dependence for non-doped semiconductor *n*-ZrNiSn (Fig. 1) the value of activation energy of electrons from donor band ε_D^1 to the percolation level of conduction band was calculated: $\varepsilon_1^{\rho} = 97.6$ meV. The fact that exactly the activation of electrons to the conduction band takes place was confirmed by negative values of thermopower coefficient of *n*-ZrNiSn at all temperatures. Since the Fermi level ε_F is fixed at the donor band ε_D^1, the calculated value of activation energy of electrons ε_1^{ρ} reflects the depth of drifting of Fermi level ε_F relative to the edge of the conduction band. Such result coincides with the previously obtained [1, 3].

The presence of low-temperature activation on the $\ln\rho(1/T)$ dependence for *n*-ZrNiSn indicates the existence of hopping conduction over the energy states of donor band ε_D^1 with activation energy $\varepsilon_3^{\rho} = 11.9$ meV. In turn, the values of the activation energies $\varepsilon_1^{\alpha} = 83.8$ meV and $\varepsilon_3^{\alpha} = 11.5$ meV were calculated from the high and low temperature parts of $\alpha(1/T)$ dependence, respectively. Since the value of activation energy ε_1^{α} represents the modulation amplitude of continuous energy bands [1, 5], the closeness of the ε_1^{α} and ε_1^{ρ} values is a feature of high compensation of semiconductor.

The introduction of Rh impurity atoms into the structure of ZrNiSn compound is accompanied by drastic change of behavior of $\ln\rho(1/T)$ and $\alpha(1/T)$ dependencies and values of electric resistivity and thermopower coefficient (Figs. 1, 2). The introduction of the smallest concentration of Rh atoms ($x = 0.005$) leads to the rapid increase of electrical resistivity values, for example, at 80 K from $\rho(x = 0) = 129.1$ μΩ·m to $\rho(x = 0.005) = 2042.6$ μΩ·m. At the same time the termopower coefficient $\alpha(x)$ for $ZrNi_{1-x}Rh_xSn$ changes its sign from positive to negative: $\alpha(x = 0) = -88.6$ μV/K and $\alpha(x = 0.005) = 7.0$ μV/K. Such change of the sign for $\alpha(x)$ was predictable since it is assumed that the structural defects of acceptor nature are generated in crystallographic position 4*c* of Ni(Rh) atoms. On the other hand, the change of the sign of thermopower coefficient $\alpha(x)$ for $ZrNi_{1-x}Rh_xSn$ at 80 K indicates that at such temperatures the number of ionized acceptors is higher than the number of ionized donors, the holes become the main current carriers, and the Fermi level is located closer to the valence band. In this case the compensation degree (ratio of donors and acceptors) of HDCS [1,5] should be significantly increased.

From the high temperature part of $\ln\rho(1/T)$ dependence for $ZrNi_{1-x}Rh_xSn$, $x = 0.005$, the value of activation energy of electrons was calculated: $\varepsilon_1^{\rho}(x = 0.005) = 127.2$ meV (Fig. 4). The obtained result indicates that the Fermi level ε_F at concentration $x = 0.005$ deepened into the band gap of semiconductor and is located closer to the valence band than to the conduction band. Such drift of the Fermi level ε_F from conduction band is typical reaction on doping of semiconductor with electron type of conductivity by acceptor impurity.

The values of activation energy calculated from the high temperature part of $\alpha(1/T)$ dependence (Fig. 4) $\varepsilon_1^{\alpha}(x = 0.005) = 219.8$ meV indicate the increase of compensation degree of $ZrNi_{1-x}Rh_xSn$, $x = 0.005$. While for *n*-ZrNiSn the modulation amplitude of continuous energy bands, which represents the ratio of ionized donors and acceptors, is $\varepsilon_1^{\alpha} = 83.8$ meV, for $ZrNi_{1-x}Rh_xSn$, x=0.005, this ratio increases in ~2.6 times, which caused the location of the Fermi level ε_F deep in the band gap.

We consider that at low temperatures and lowest Rh concentration ($x = 0.005$), the activation energy of electron is insufficient to throw it into conduction band (to ionize donors) due to the deep location of donor band ε_D^1 relative to the edge of the conduction band. Therefore, the concentration of free holes dominates the electron concentration, and the holes are the main current carriers. At higher temperatures when the ionization of donors becomes possible (activation of electrons into the conduction band) the concentration of free electrons increases and starts to prevail over the holes concentration. Under these conditions the sign of thermopower coefficient for $ZrNi_{1-x}Rh_xSn$, $x = 0.005$ changes from positive to negative, and now the Fermi level ε_F is located near the middle of the band gap, but

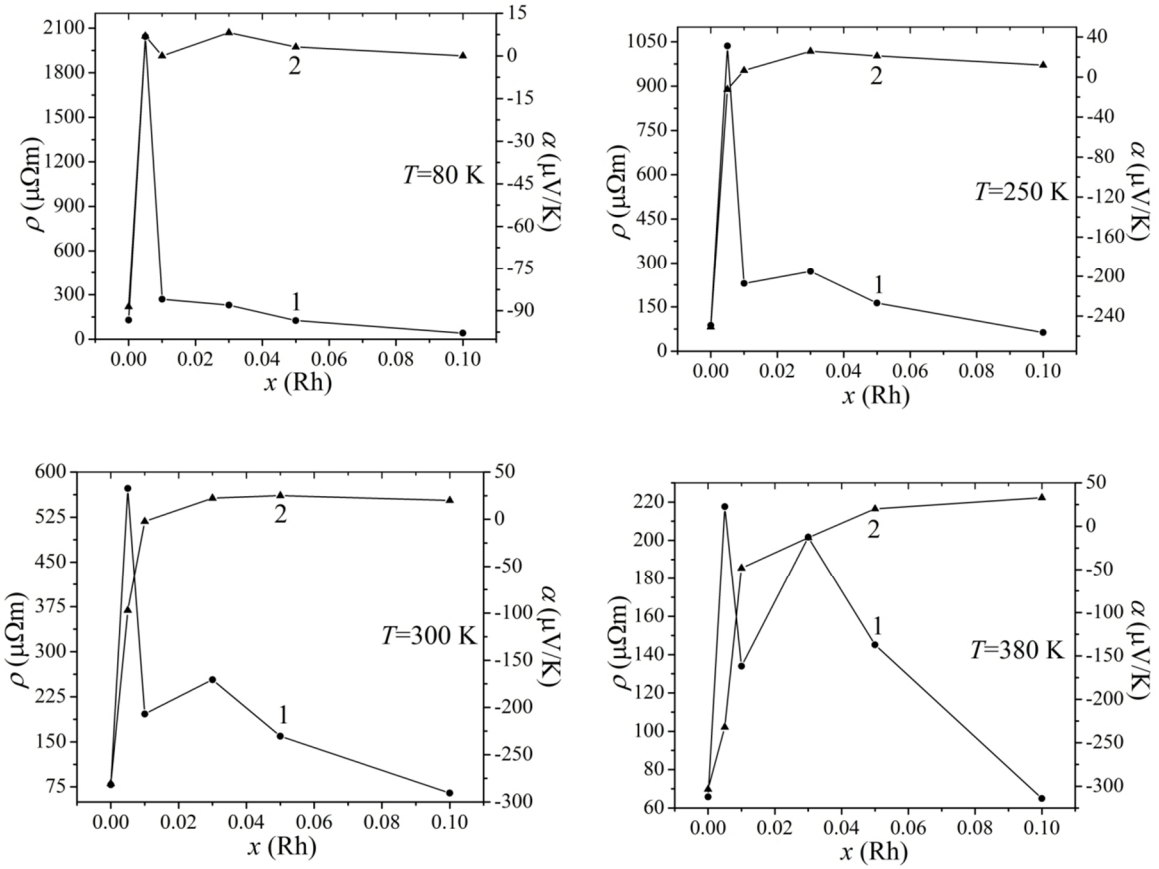


Fig. 2. Variation of electric resistivity values $\rho(x)$ (1) and thermopower coefficient $\alpha(x)$ (2) for $ZrNi_{1-x}Rh_xSn$ at different temperatures.

closer to the conduction band, which is indicated by negative values of thermopower coefficient. As known, at the equal concentrations of free electrons and holes (ionized donors and acceptors), the Fermi level ε_F would be located in the middle of the band gap of HDCS [5]. We can assume that at the lowest impurity concentration in $ZrNi_{1-x}Rh_xSn$, $x = 0.005$, the number of generated acceptors is not sufficient to catch all free electrons, and depth of location of the donor band ε_D^1 is significantly higher than acceptor band ε_A.

Whether holes concentration in $ZrNi_{1-x}Rh_xSn$ is related exceptionally with generation of acceptors in 4*c* position of Ni atoms during substitution of Ni by Rh and increases linearly with increase of Rh concentration, electron concentration would have to decrease by the same law at "freezing" onto the generated acceptor states. Ideally, the number of generated acceptors will equal to the number of eliminated electrons when they are captured by the acceptors (ionization of acceptors). As seen from Fig. 3., at $T_{inv.} \geq 254$ K the sign of thermopower coefficient of $ZrNi_{1-x}Rh_xSn$, x=0.005, changes from positive to negative indicating that electrons again become the main current carriers (as in *n*-ZrNiSn). This result is consistent with mentioned above conclusion that the number of generated acceptors is insufficient to capture all electrons, and the depth of location of donor band ε_D^1 is greater than acceptor band ε_A.

It could seem that behavior of $\ln\rho(1/T)$ and $\alpha(1/T)$ dependences upon the doping of semiconductor with electron type of conductivity by the lowest concentration of the acceptor impurity Rh ($x = 0.005$) is related only to reduction of the number of free electrons due to their "freezing" onto generated acceptor levels at substitution of Ni atoms by Rh. In the case of $ZrNi_{1-x}Rh_xSn$, the decrease of electrons number at the lowest Rh concentrations is caused by additional mechanism based on structural changes within the ordering of structure of

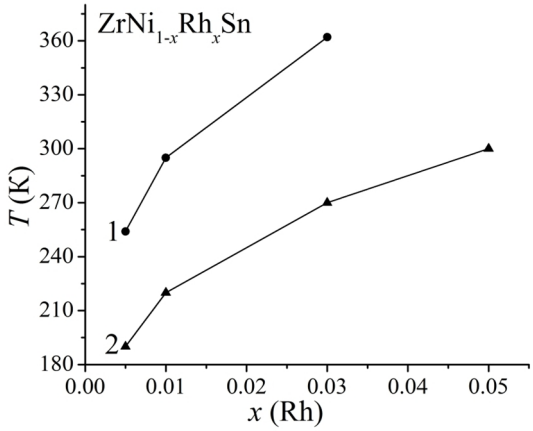
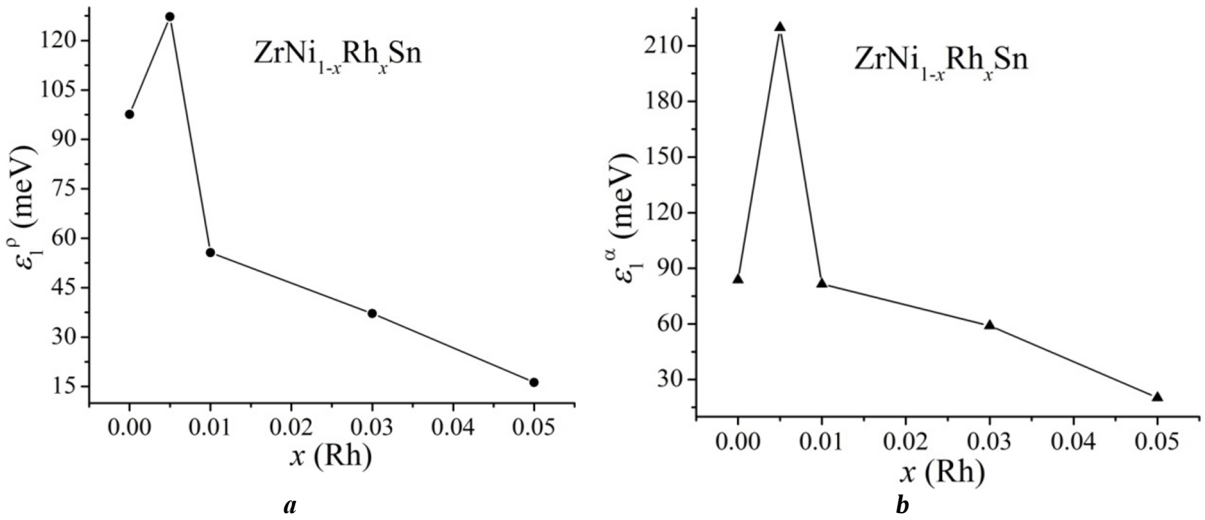


Fig. 3. Variation of inversion temperature $T_{inv.}$ of sigh of thermopower coefficient α from positive to negative (*1*) and extremum $T_{max.}$ on $\alpha(1/T)$ dependences (*2*) for $ZrNi_{1-x}Rh_xSn$.



a ***b***

Fig. 4. Variation of the energy activation values $\varepsilon_1^{\rho}(x)$ (*a*) and $\varepsilon_1^{\alpha}(x)$ (*b*) of $ZrNi_{1-x}Rh_xSn$.

semiconductor.

It was mentioned above that the structure of ZrNiSn is disordered due to partial occupation of Zr (4*a*) position by Ni atoms, which generates the defects of donor nature [3]. Investigation of the structure of $ZrNi_{1-x}M_xSn$ solid solutions [1] showed that at concentration $x \approx 0.01$ all Ni atoms are displaced from 4*a* position; structure becomes ordered, and the defects are healed. Previous structural studies of $ZrNi_{1-x}Rh_xSn$ indicated effectiveness of this mechanism of defects healing in Zr (4*a*) position, that will result in reduction of number of free electrons (our next work will be devoted to the analysis of crystal and electronic structures of $ZrNi_{1-x}Rh_xSn$).

Thus, in case of $ZrNi_{1-x}Rh_xSn$ within the concentration range $x = 0.005$ - 0.10, the assumption that the number of free electrons is reduced on the number of generated acceptors should be corrected because the rate of decrease of number of free electrons is higher in comparison with the growth rate of free hole concentration on such reasons:

- "freezing" of the electrons to generated acceptor levels (band), when Ni atoms are substituted by Rh;

- reduction of the number of donors due to ordering of structure, as a result of elimination of Ni atoms from the position of Zr atoms in the 4*a* site ("healing" of the defects with donor nature).

Therefore, the conclusion that in $ZrNi_{1-x}Rh_xSn$, $x = 0.005$, the number of generated acceptors is insufficient to catch all electrons, has the right to exist, since the concentration of structural defects of donor nature in *n*-ZrNiSn is $y \approx 0.01$ ($(Zr_{1-y}Ni_y)NiSn$) [3] and is twice as large as the number of generated acceptors ($x = 0.005$).

In this context, it is interesting to consider the behavior of electrokinetic and energy state characteristics of $ZrNi_{1-x}Rh_xSn$, $x \geq 0.01$, when the number of introduced acceptors corresponds to or exceeds the number of available donors in *n*-ZrNiSn. Thus, with an increase of Rh impurity concentration ($x > 0.005$) at 80 K the values of electric resistivity for $ZrNi_{1-x}Rh_xSn$ rapidly decrease from $\rho(x = 0.01) = 269.0$ μΩ·m to $\rho(x = 0.05) = 125.4$ μΩ·m and $\rho(x = 0.10) = 40.9$ μΩ·m. We can state that at low concentrations of Rh acceptor impurity, the maximum of $\rho(x)$ dependence for $ZrNi_{1-x}Rh_xSn$ around the concentration $x \approx 0.005$ (Fig. 2) is caused by exhaustion of donors, the values of electric resistivity are maximal and semiconductor is highly compensated. In turn, the positive values of thermopower coefficient for $ZrNi_{1-x}Rh_xSn$, $x = 0.005$ - 0.10, at 80 K indicate that the concentration of ionized acceptors is higher, than donors concentration, and the Fermi level would have to drift in the direction to the valence band, that is accompanied by an increase of the number of free holes and their contribution to the conductivity of semiconductor (Fig. 2).

The rapid decrease of the values of activation energy $\varepsilon_1^{\rho}(x)$ from $\varepsilon_1^{\rho}(x = 0.005) = 127.2$ meV to $\varepsilon_1^{\rho}(x = 0.01) = 55.7$ meV and $\varepsilon_1^{\rho}(x = 0.05) = 16.3$ meV and positive values of thermopower coefficient $\alpha(1/T)$ (Fig. 1) clearly indicate that the Fermi level ε_F moves exactly to the valence band (Fig. 4). Such behavior of the Fermi level ε_F can be caused only by appearance of acceptors in $ZrNi_{1-x}Rh_xSn$ crystal, which catch free electrons, decreasing their concentration, which increases the compensation degree of semiconductor (ratio of acceptors and donors).

However, the question arises, why the motion rate of the Fermi level ε_F for $ZrNi_{1-x}Rh_xSn$ in the direction of the valence band is different within the concentration ranges $x = 0.005$ - 0.01 and $x = 0.01$–0.10. After all, Rh impurity concentration in $ZrNi_{1-x}Rh_xSn$, $x = 0$ - 0.10, increases linearly, then the number of generated structural defects of acceptor nature should increase in the same way. In this case, the Fermi level ε_F after the overcompensation of semiconductor should move to the valence band with the same rate. However, at the concentration ranges $x = 0.005$ - 0.01 and $x = 0.01$ - 0.10 the slope of $\varepsilon_1^{\rho}(x)$ dependence is different.

From the linear type of the behavior of $\varepsilon_1^{\rho}(x)$ in the concentration range $x = 0.005$ - 0.01, it can be stated that the Fermi level ε_F is closing to the valence band with the rate $\Delta\varepsilon_F/\Delta x \approx 143$ meV/%Rh, and in the concentration range $x = 0.01$–0.10 this rate is almost 18 times smaller and equals $\Delta\varepsilon_F/\Delta x \approx 8$ meV/%Rh. Since the position of the Fermi level ε_F is defined by the ratio of ionized donors and acceptors, then significantly lower motion rate of ε_F to the edge of the valence band at Rh concentration range $x = 0.01$ - 0.10 indicates that

simultaneously with acceptors the donors of unknown origin are generated that "inhibit" this motion. Positive values of thermopower coefficient show that the number of generated acceptors still prevails the number of generated donors of unknown origin.

This conclusion is in agreement with the change of values of activation energy $\varepsilon_1^{\alpha}(x)$ for $ZrNi_{1-x}Rh_xSn$, $x \geq 0.005$, (Fig. 4), which reflects the compensation degree of semiconductor. Simultaneous generation of the defects of donor and acceptor natures in the crystal is accompanied by a change in the compensation degree, as well as by the change in the amplitude of the modulation of continuous energy bands of HDCS [1, 5] by the law which reflects the ratio of ionized acceptors and donors. The decrease of compensation degree of $ZrNi_{1-x}Rh_xSn$, $x \geq 0.005$ is indicated by decrease of the values of activation energy from $\varepsilon_1^{\rho}(x = 0.005) = 127.2$ meV to $\varepsilon_1^{\alpha}(x = 0.01) = 81.5$ meV and $\varepsilon_1^{\alpha}(x = 0.05) = 20.2$ meV, which can be observed only if the semiconductor of *p*-type conductivity is doped with an acceptor impurity.

On the other hand, the sign of thermopower coefficient for $ZrNi_{1-x}Rh_xSn$ samples, $x = 0.01$ and $x = 0.03$, at $T \approx 295$ K and $T \approx 362$ K, respectively, as well as at x=0.005, changes from positive to negative at $T_{inv.}$ (Fig. 3), and electrons become again the main current carriers. And this happens despite the fact that the concentration of generated acceptors in $ZrNi_{1-x}Rh_xSn$, $x > 0.01$, is much higher than the number of donors with energy ε_D^1 in *n*-ZrNiSn (number of Ni in position Zr (4*a*)). Such behavior of thermopower coefficient for $ZrNi_{1-x}Rh_xSn$ at $T = T_{inv.}$ is possible only if in the semiconductor, additionally to the impurity acceptor band ε_A, donors are generated, energy levels of which form donor band ε_D^2 deeper than ε_D^1, and for ionization of donors ε_D^2 and overcoming the energy barrier to the conduction band the higher energies are needed. By the way, recent investigation of $ZrNiSn_{1-x}Ga_x$ solid solution [8] showed that occupation of 4*b* position of Sn ($5s^25p^2$) atoms by Ga ($4s^24p^1$) atoms results in simultaneous generation of defects with acceptor and donor nature (donor-acceptor pairs) as vacancies in 4*b* position.

The appearance of a new source of free electrons, donor band ε_D^2, is indicated by a change in the $\rho(x)$ values for $ZrNi_{1-x}Rh_xSn$ at different temperatures (Fig. 2). It can be seen that with increase of temperature ($T > 80$ K) the $\rho(x)$ dependence of $ZrNi_{1-x}Rh_xSn$ is transformed, indicating the changes of electronic structure of semiconductor. At $T = 250$ K and concentration $x \approx 0.03$ a step appears at the dependence $\rho(x)$, which gradually develops into an extremum ($T = 380$ K), the value of electric resistivity in which is close to ρ value at $x = 0.005$.

At concentration $x \geq 0.01$, when the number of generated acceptors prevails the number of donors in *n*-ZrNiSn, with increase of temperature from $T = 80$ K to $T = T_{inv.}$ the sign of thermopower coefficient changes from positive to negative (Fig. 4). Thus, for $ZrNi_{1-x}Rh_xSn$ samples at $x = 0.01$ and $x = 0.03$ the temperatures $T \approx 295$ K and $T \approx 362$ K, respectively, are sufficient for electron to overcome the energy barrier between the conduction band and donor band ε_D^2. From the above, one can conclude that the higher number of acceptors in $ZrNi_{1-x}Rh_xSn$ semiconductor is generated, the higher energies (higher temperatures) for the number of ionized donors ε_D^2 to exceed the number of ionized acceptors ε_A are needed. It means that the defects of donor nature are formed simultaneously with the defects of acceptor nature. Such simultaneous generation of donors ε_D^2, which compensate acceptors, along with the acceptors, results in location of Fermi level ε_F in the band gap even at high acceptor concentration.

And only at compositions of $ZrNi_{1-x}Rh_xSn$ solid solution $x = 0.05$ and $x = 0.10$, when the content of acceptor impurity is by an order higher than donor concentration ε_D^1 in *n*-ZrNiSn, we do not observe changes in the values of thermopower coefficient due to the limited temperature range of measurements (T = 80 - 400 K). The absence of high-temperature activation part in $\ln\rho(1/T)$ dependence of $ZrNi_{1-x}Rh_xSn$, $x = 0.10$ indicates that the Fermi level ε_F entered the valence band, the insulator-metal transition took place (Anderson transition) [7]. However, the presence of a maximum on the $\ln\rho(1/T)$ dependence and the onset of the formation of high temperature activation can indicate that at higher temperatures the Fermi level ε_F will move from valence band to band gap. It is possible only if free electrons of unknown origin along with holes participate in the conductance of the $ZrNi_{1-x}Rh_xSn$ semiconductor.

An analysis of behavior of low temperature parts of $\ln\rho(1/T)$ dependencies for $ZrNi_{1-x}Rh_xSn$ samples, $x \geq 0.01$, (Fig. 1) shows the absence of hopping conduction mechanism in the localized states of impurity acceptor band ε_A, which is possible with location of acceptor band ε_A near the top of the valence band and significant concentration of impurity when the wave functions of localized states of acceptor band overlap [1, 5].

The results of magnetic susceptibility χ investigation of $ZrNi_{1-x}Rh_xSn$ (Fig. 5) are interesting and confirm the conclusion on simultaneous generation of structural defects of acceptor and donor nature in the solid solution. Investigations have shown that $ZrNi_{1-x}Rh_xSn$ samples, $x \geq 0.01$, are Pauli paramagnets, magnetic susceptibility of which is determined exceptionally by electron gas and is proportional to density of states at Fermi level $g(\varepsilon_F)$. As seen from Fig. 5, $\chi(x)$ dependence at $x > 0.01$ rapidly changes the slope, reaches the plateau and slightly

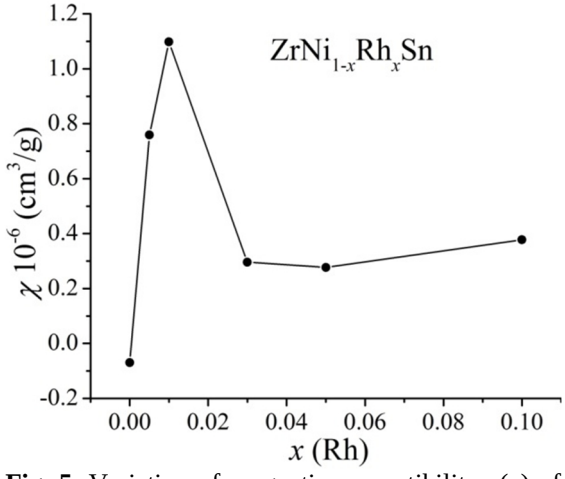


Fig. 5. Variation of magnetic susceptibility $\chi(x)$ of $ZrNi_{1-x}Rh_xSn$.

changes up to $x = 0.10$. Thus, an increase in the concentration of the acceptor impurity and possible increase of the free holes concentration practically does not change the $g(\varepsilon_F)$ values of $ZrNi_{1-x}Rh_xSn$ semiconductive solid solution. Such behavior of $\chi(x)$ ($\chi \sim g(\varepsilon_F)$) is possible provided that the current carriers of the opposite sign with the concentration close to the holes concentration in $ZrNi_{1-x}Rh_xSn$ appear as the result of generation of donor-acceptor pairs that will stipulate invariability of density of states at Fermi level $g(\varepsilon_F)$. It's worth to note that *n*-ZrNiSn semiconductor is not Pauli paramagnet, but a weak diamagnet, as evidenced by negative values of magnetic susceptibility: $\chi(x = 0) = -0.07$ emu/g. Therefore the growth of $\chi(x)$ dependence at concentration range $x = 0 - 0.005$ is not related to the increase of $g(\varepsilon_F)$ values.

Conclusion

Thus, based on the mentioned results, we can assume that to provide the structural stability and principle of electric neutrality in $ZrNi_{1-x}Rh_xSn$ the structural defects of acceptor and donor nature (effective charge of which is opposite) are generated simultaneously and their concentration increases with increase of the Rh content. Establishment of the mechanism of generation and the nature of the ε_D^2 donors requires additional research on $ZrNi_{1-x}Rh_xSn$ semiconductive solid solution, to which our next work will be devoted.

Romaka L. - Ph.D., Senior Scientist;
Stadnyk Yu. - Ph.D., Senior Scientist;
Romaka V. – professor; PHD, Phd;
Horyn A. - Ph.D., Senior Research;
Krayovskyy V. - Ph.D., associate professor.

[1] V.A. Romaka, V.V. Romaka, and Yu. V. Stadnyk, Intermetallic Semiconductors: Properties and Applications
[2] (Lviv, Lvivska Politekhnika, 2011) [in Ukrain.].
[3] L.I. Anatychuk, Thermoelements and Thermoelectric Devices (Kiev, Nauk. Dumka, 1979) [in Ukrain.].
[4] V.A. Romaka, D. Fruchart, V.V. Romaka, E.K. Hlil, Yu.V. Stadnyk, Yu.K. Gorelenko, L.G. Akselrud, Semiconductors 43(1), 7 (2009).
[5] V.A. Romaka, P. Rogl, Yu. Stadnyk, V.V. Romaka, E.K. Hlil, V.Ya Krayovskyy, A.M. Horyn, Semiconductors 47(9), 1145 (2013).
[6] B.I. Shklovskii and A.L. Efros, Electronic Properties of Doped Semiconductors (Springer, NY, 1984).
[7] V.V. Romaka, L.P. Romaka, V.Ya. Krayovskyy, Yu.V. Stadnyk, Stannides of rare earth and transition metals (Lviv, Lvivska Politekhnika, 2015) [in Ukrain.].
[8] N.F. Mott, E.A. Davis, Electron processes in non-crystalline materials (Clarendon Press, Oxford, 1979).
[9] L.P. Romaka, Yu.V. Stadnyk, V.V. Romaka, V.Ya. Krayovskyy, P.-F. Rogl, A.M. Horyn, Physics and Chemistry of Solid State 18(2), 187 (2017).

Л.П. Ромака[1], Ю.В. Стадник[1], В.А.Ромака[2,3], А.М. Горинь[1], В.Я. Крайовський[3]

Дослідження електрокінетичних та магнітних властивостей напівпровідникового твердого розчину $ZrNi_{1-x}Rh_xSn$

[1]Львівський національний університет ім. І.Франка, вул. Кирила і Мефодія, 6, Львів, 79005, Україна,
e-mail: lyubov.romaka@gmail.com;
[2]Інститут прикладних проблем механіки і математики ім. Я.С. Підстригача НАН України,
вул. Наукова, 3-б, Львів, 79060, Україна;
[3]Національний університет "Львівська політехніка", вул. С. Бандери, 12, Львів, 79013, Україна

Досліджено особливості кінетичних, енергетичних та магнітних характеристик напівпровідникового твердого розчину $ZrNi_{1-x}Rh_xSn$ у діапазонах: $T = 80 - 400$ K, $x = 0 – 0,10$. Показано, що уведення атомів Rh ($4d^85s^1$) у структуру сполуки ZrNiSn шляхом заміщення атомів Ni ($3d^84s^2$) генерує у кристалі структурні дефекти акцепторної природи, а основними носіями струму $ZrNi_{1-x}Rh_xSn$ за низьких температур стають дірки. На основі аналізу швидкості руху рівня Фермі $\Delta\varepsilon_F/\Delta x$ $ZrNi_{1-x}Rh_xSn$ у напрямі валентної зони та зміни знаку коефіцієнта термо-ерс з додатного на від'ємний за високих температур висунуто припущення про одночасне з акцепторами генерування структурних дефектів донорної природи (донорно-акцепторні пари), які породжують глибоку донорну зону ε_D^2.

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