

V.A.Romaka^{1,2}, P.Rogl³, Yu.V.Stadnyk⁴, L.P.Romaka⁴,
D. Kaczorowski⁵, V.Ya. Krayovskyy², R.O.Korzh², A.M.Horyn⁴

¹ Ya. Pidstryhach Institute for Applied Problems of Mechanics and Mathematics 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 Universität Wien, 42, Währinger Str., A-1090, Wien, A-1090, Österreich;

⁴ Ivan Franko National University of Lviv, 6, Kyryla and Mefodiya Str., 79005, Lviv, Ukraine;

⁵ W.Trzebiatowski Institute of Low Temperature and Structural Research Polish Academy of Sciences, 2, Okolna St., Wroclaw, 50-950 Poland

FIATURES OF THE ELECTRON STRUCTURE AND CONDUCTION MECHANISMS IN THE $Zr_{1-x}Ce_xNiSn$ THERMOELECTRIC MATERIAL

The crystal and electronic structures, the temperature and concentration dependencies of the magnetic susceptibility, resistivity, and the Seebeck coefficient of the $Zr_{1-x}Ce_xNiSn$ thermoelectric material in the ranges: $T = 80 - 400$ K, $x = 0.01 - 0.10$ were studied. Increasing values of the thermoelectric power factor $Z^(x)$ were for the first time observed in n -ZrNiSn doped with Ce atoms in Ce^{4+} valence state. This leads to the generation of donor defects in the crystal and makes $Zr_{1-x}Ce_xNiSn$ solid solution a promising thermoelectric material.*

Key words: electronic structure, resistivity, Seebeck coefficient.

Introduction

Attempts to obtain thermoelectric materials with high efficiency of thermal into electric energy conversion [1] by doping of n -ZrNiSn semiconductor with the atoms of rare-earth metals (R) were unsuccessful [2-4]. In [5] it is shown that with substitution of Zr by R atoms structural defects of acceptor nature are formed in crystal, causing a drift of the Fermi level ε_F from conduction band and leading to increase in the values of resistivity and decrease in the Seebeck coefficient.

The point is that at formation of solid solutions with participation of R atoms, their valence electrons go into formation of chemical bonds or pass to conduction band, and electrons of partially filled $4f$ - shell due to their small size (~ 0.04 nm) remain localized on the ion core. A typical valence value of rare-earth metal is $3+$ (R^{3+}). It means that R atom is left by 3 valence electrons, their $4f$ -shell is filled only partially, and a defect generated in $Zr_{1-x}R_xNiSn$ is of acceptor nature. In all previously investigated $Zr_{1-x}R_xNiSn$ solid solutions [6] the valence of R atoms was $3+$, and for $4f$ - electrons the case of maximum localization was always realized, namely the respective electron shells behaved as atomic ones and were characterized by the same quantum numbers L , S , J as the states of the respective isolated ion.

In a series of rare-earth metals, such as Ce and Sm , Eu , Yb , the valence, alongside with $3+$, can acquire the values of $4+$ and $2+$, respectively (abnormal valence) [7]. Thus, in the case of Ce^{3+} , the $4f$ -shell comprises 1 uncoupled electron ($4f^1$) and is vacant ($4f^0$) in case of Ce^{4+} valence (Ce atom leaves 4 valence electrons). As a result, for the respective atoms different valence states are energetically close, and atoms of rare-earth elements can possess the average fractional number of $4f$ -electrons

(intermediate valence) [7]). In compounds with participation of R metals that are semiconductors, the $4f$ -level is located close to conduction band (ϵ_c).

That is, it can be expected that in the case of doping of n - $ZrNiSn$ semiconductor, for instance, with Ce atoms their $4f$ -shell can lose stability. Hence the idea to use the property of Ce to change valence at doping of n - $ZrNiSn$, which can bring about the generation in crystal of structural defects, this time of *donor* nature, and meet the condition of producing material with high efficiency of thermal into electric energy conversion [8]. In turn, research on the magnetic susceptibility of Ce compounds allows in paramagnetic area to identify the degree of occupancy of $4f$ -shell [9]. The purpose of this work is to study the conductivity mechanisms of n - $ZrNiSn$ doped with Ce which will permit to predict the behaviour of the kinetic characteristics of $Zr_{1-x}Ce_xNiSn$ and study the conditions of producing material with high efficiency of thermal into electric energy conversion.

Investigation procedures

The object to be investigated included crystalline structure, electron density distribution (DOS), the magnetic, electrokinetic and energy characteristics of $Zr_{1-x}Ce_xNiSn$. 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 [10] was employed for the calculation of structural characteristics. The chemical and phase compositions of 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) [11] with the use of Moruzzi-Janak-Williams exchange-correlation potential [12]. 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 method) of $Zr_{1-x}Ce_xNiSn$ samples in the ranges: $T = 80$ – 400 K, $N_D^{Ce} \approx 1.9 \cdot 10^{20} \text{ cm}^{-3}$ ($x = 0.01$)– $1.9 \cdot 10^{21} \text{ cm}^{-3}$ ($x = 0.10$) and the magnetic field intensity $H \leq 10$ kE.

Structural research on $Zr_{1-x}Ce_xNiSn$

The microprobe analysis of the concentration of atoms on the surface of $Zr_{1-x}Ce_xNiSn$ samples has shown their conformity to the initial charge compositions, and the X-ray phase and structural analyses have revealed no traces of other phases. As was expected, replacement of smaller-size Zr atoms ($r_{Zr} = 0.1602$ nm) by larger-size Ce atoms ($r_{Ce} = 0.172$ nm) leads to increase in the values of unit cell period $a(x)$ of $Zr_{1-x}Ce_xNiSn$ (Fig. 1).

Refinement of $Zr_{1-x}Ce_xNiSn$ crystalline structure by powder method with a simultaneous refinement of the isotropic parameters of atomic substitution and occupancy of $(4a)$ crystallographic position of Zr has shown that the lowest value of coefficient of mismatch between a model of crystalline structure and an array of Bragg reflections was obtained for a model where the occupancy of position of $Zr(Ce)$ atoms for $x \geq 0.01$ is 100%. In other words, like in the previous cases of $Zr_{1-x}R_xNiSn$ [6], ordering of crystalline structure makes it resistant to temperature and time changes, which creates prerequisites for preparation of material with stable characteristics. Recall that n - $ZrNiSn$ structure is disordered by virtue of partial, up to $\sim 1\%$ ($y \approx 0.01$), occupancy by Ni ($3d^8 4s^2$) atoms of $4a$

position of Zr ($4d^25s^2$) atoms, which creates donor structural defects and accounts for the nature of electron conductivity type, and the compound formula is $(Zr_{1-y}Ni_y)NiSn$ [6].

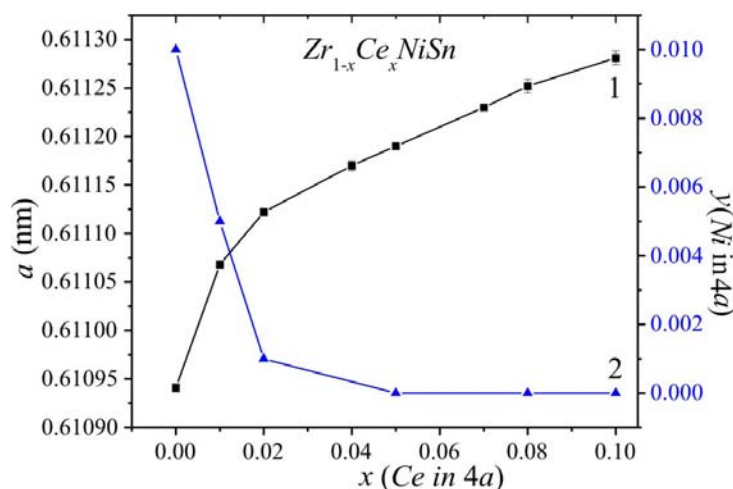


Fig. 1. Change in the values of unit cell period $a(x)$ (1) and concentration of Ni atoms in 4a position of Zr atoms (2) in $Zr_{1-x}Ce_xNiSn$

On the other hand, ordering of $Zr_{1-x}Ce_xNiSn$ crystalline structure for $x > 0.01$ testifies that in the area of $x = 0-0.02$ Ni atoms leave the position of Zr atoms (4a) (Fig. 1): there is “healing” of donor structural defects which is accompanied by a reduced concentration of donors. Simultaneously, in the same 4a crystallographic position with substitution of Ce for Zr atoms, either acceptor structural defects can be generated, when the valence state of Ce^{3+} , or donor defects, when the valence state of Ce^{4+} .

Therefore, doping of $n-ZrNiSn$ with the atoms of rare-earth metal Ce by substitution of Zr is accompanied by a simultaneous reduction of donor defects (Ni atoms in 4a position of Zr atoms) and generation in the same position of donor or acceptor defects depending on the valence state of Ce. This raises the question as to what is the valence of Ce in $Zr_{1-x}Ce_xNiSn$ and whether it will be influenced by a change in concentration. After all, these are key parameters for the calculation of the electron structure of solid solution. Therefore, determination of the valence state of Ce in $Zr_{1-x}R_xNiSn$ is a prerequisite for understanding the conduction mechanisms of semiconductor.

Research on the magnetic state of Ce in $Zr_{1-x}Ce_xNiSn$

Doping of $n-ZrNiSn$ weak diamagnetic ($\chi = -0.07 \cdot 10^{-6} \text{ cm}^3/\text{g}$) [6] with the lowest in our experiment concentration of Ce ($x = 0.01$) causes the origination of paramagnetic state, and low values of magnetic susceptibility ($\chi = 0.23 \cdot 10^{-6} \text{ cm}^3/\text{g}$), independence of magnetic field intensity and temperature are indicative of Pauli paramagnetism (Fig. 2).

In this case, the magnetic susceptibility of $Zr_{1-x}Ce_xNiSn$ is defined by free electrons, and its values are proportional to the electron density of states at the Fermi level $g(\epsilon_F)$ (for Pauli paramagnetic $\chi \sim g(\epsilon_F)$). Taking into account that in the concentration $x = 0-0.08$ the dependence $\chi(x)$ in $Zr_{1-x}Ce_xNiSn$ increases, one can state that structural defects of donor nature are generated in the crystal. The absence of a magnetic moment in $Zr_{1-x}Ce_xNiSn$ samples (Pauli paramagnetism) results from the absence of uncoupled electron on $4f$ - shell (it is vacant ($4f^0$)), therefore the valence state of Ce^{4+} . Incomprehensible is the reduction of $\chi(x)$ values of $Zr_{1-x}Ce_xNiSn$ at $x > 0.08$, pointing to the reduction of $g(\epsilon_F)$. One of the reasons for such $\chi(x)$ behaviour can be

generation in the crystal of *acceptors* by the mechanism unknown so far, but this calls for a detailed investigation.

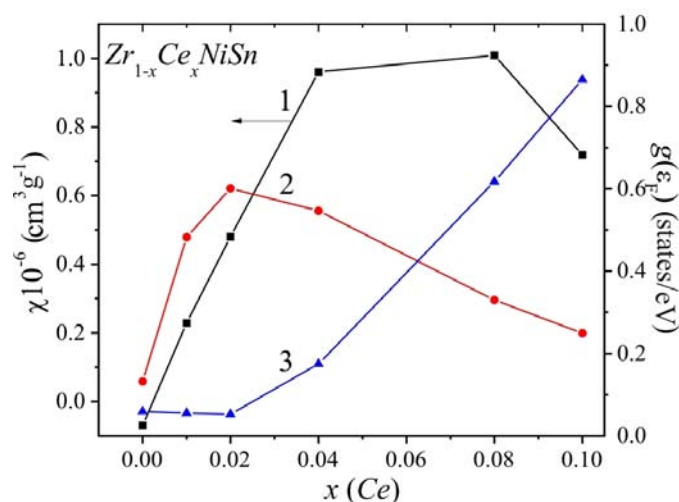


Fig. 2. Change in the values of magnetic susceptibility χ at $T=276$ K (1) and the electron density of states at the Fermi level $g(\epsilon_F)$ in $Zr_{1-x}Ce_xNiSn$ for the valence of Ce^{4+} (2) and Ce^{3+} (3)

Thus, research on the magnetic susceptibility of $Zr_{1-x}Ce_xNiSn$ has shown that *Ce* atoms do not possess local magnetic moment in the area of concentrations $x = 0 - 0.08$, and the generated structural defects are of donor nature.

Research on the electron structure of $Zr_{1-x}Ce_xNiSn$

To predict the behaviour of the Fermi level ϵ_F , the energy gap ϵ_g and the kinetic characteristics of *n-ZrNiSn* doped with *Ce*, the electron density of states (DOS) was calculated for the case of ordered structure and valence states of Ce^{3+} and Ce^{4+} (Fig. 3).

As was expected, in the case of Ce^{3+} the acceptor-nature structural defects are generated in the crystal, and so, with increasing impurity concentration, the Fermi level ϵ_F moves from the edge of the conduction band ϵ_C to the valence band of ϵ_V $Zr_{1-x}Ce_xNiSn$ and will cross it at $x \approx 0.05$. Instead, in the case of Ce^{4+} the conduction band ϵ_C is reconstructed, the energy gap is reduced, and the Fermi level ϵ_F is fixed close to the conduction band by virtue of the donor nature of defects generated in the crystal.

In this context, it is interesting to compare the results of change in the magnetic susceptibility values of $Zr_{1-x}Ce_xNiSn$ Pauli paramagnetic and the electron density of states at the Fermi level $g(\epsilon_F)$ of $Zr_{1-x}Ce_xNiSn$ for the valence states of Ce^{3+} and Ce^{4+} (Fig. 2). Calculations show that in the case of Ce^{3+} , when acceptors are generated in a crystal, the density of states $g(\epsilon_F)$ slightly decreases in the area $x = 0 - 0.02$, passing through the minimum at $x \approx 0.02$ related to crossing the midgap by the Fermi level ϵ_F . At $x > 0.02$, the semiconductor is recompensated, the holes become the main charge carriers, and the Fermi level approaches the valence band and will cross it at $x \approx 0.06$, which is accompanied by increasing values of density of states at the Fermi level $g(\epsilon_F)$. That is, a change in the density of states at the Fermi level $g(\epsilon_F)$ of $Zr_{1-x}Ce_xNiSn$ for the case of Ce^{3+} is not matched with the behaviour of magnetic susceptibility $\chi(x)$ which within the concentration $x = 0.06$ passes through the maximum and slightly decreases thereafter.

Instead, the pattern of change in the values of density of states at the Fermi level $g(\epsilon_F)$ of $Zr_{1-x}Ce_xNiSn$ for the case of Ce^{4+} , when donors are generated in a crystal, is close to dependence $\chi(x)$ (Fig. 2), which proves the earlier conclusion on the valence state of Ce^{4+} . We call attention to the fact of splitting the conduction band ϵ_C in the case of Ce^{4+} which becomes apparent at $x \approx 0.05$ (Fig. 3b) as two extremes

pointing to the reduction of the electron density of states at the Fermi level. One may state that decay of dependence $\chi(x)$ at $x > 0.08$ reflects the fact of reconstruction of the electronic structure of $Zr_{1-x}Ce_xNiSn$ and is not related to generation of acceptor structural defects.

The results of the kinetic investigations of $Zr_{1-x}Ce_xNiSn$ will further permit to determine the valence state of Ce , as well as the nature of generated defects and their effect on the compensation degree of a semiconductor.

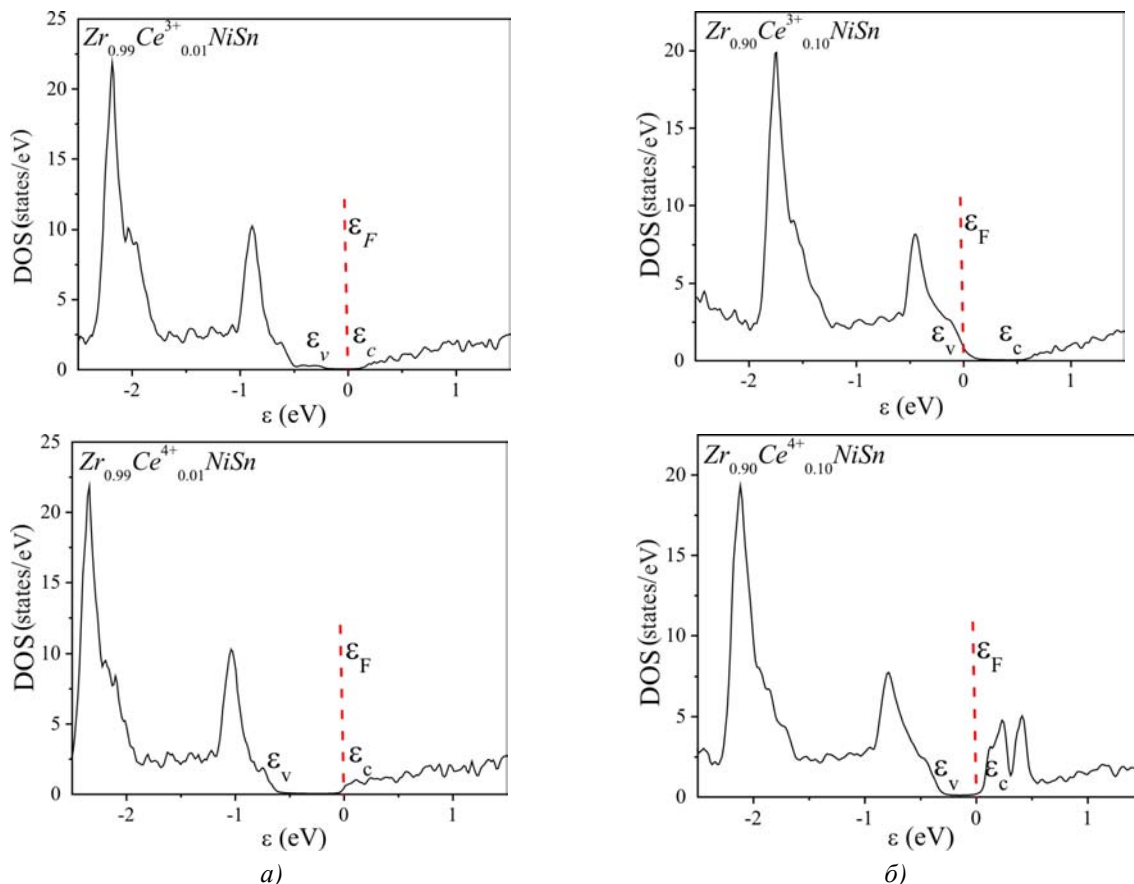


Fig. 3. Calculation of the electron density of states DOS of $Zr_{1-x}Ce_xNiSn$ for Ce^{3+} (a) and Ce^{4+} (b)

Research on the electrokinetic and energy characteristics of $Zr_{1-x}Ce_xNiSn$

The temperature and concentration dependences of the electric resistivity ρ and the Seebeck coefficient α for $Zr_{1-x}Ce_xNiSn$ samples are given in Figs. 4 and 5. The temperature dependences $\ln \rho(1/T)$ and $\alpha(1/T)$ are typical of doped semiconductors with high- and low-temperature activation areas [13] used to calculate the energy parameters of semiconductor. Thus, the activation areas of dependences $\ln \rho(1/T)$ were used to calculate the values of activation energies from the Fermi level ε_F to percolation level of the conduction band ε_1^p and electron jumps ε_3^p in the states with energies close to the Fermi level, and the activation areas of dependences $\alpha(1/T)$ were used to calculate the values of activation energies ε_1^α and ε_3^α which yield, respectively, the values of modulation amplitude of continuous energy bands and small-scale fluctuation of doped and compensated semiconductors [6,13].

Introduction to n - $ZrNiSn$ of the lowest concentration of Ce atoms does not lead to a change in conduction type of $Zr_{1-x}Ce_xNiSn$, as it was in the previous cases of semiconductor doping with atoms of rare-earth metals [6], and the Seebeck coefficient values remain negative for all values of

temperature and Ce concentration (Fig. 4b, 5b). Thus, at 80 K, the Seebeck coefficient values vary from $\alpha(x=0) = -14 \mu V \cdot K^{-1}$ to $\alpha(x=0.01) = -106.5 \mu V \cdot K^{-1}$ and $\alpha(x=0.10) = -8 \mu V \cdot K^{-1}$. Such a behaviour of $\alpha(x)$ allows stating that structural defects formed in the crystal are of donor nature, which is possible only with the valence of Ce^{4+} .

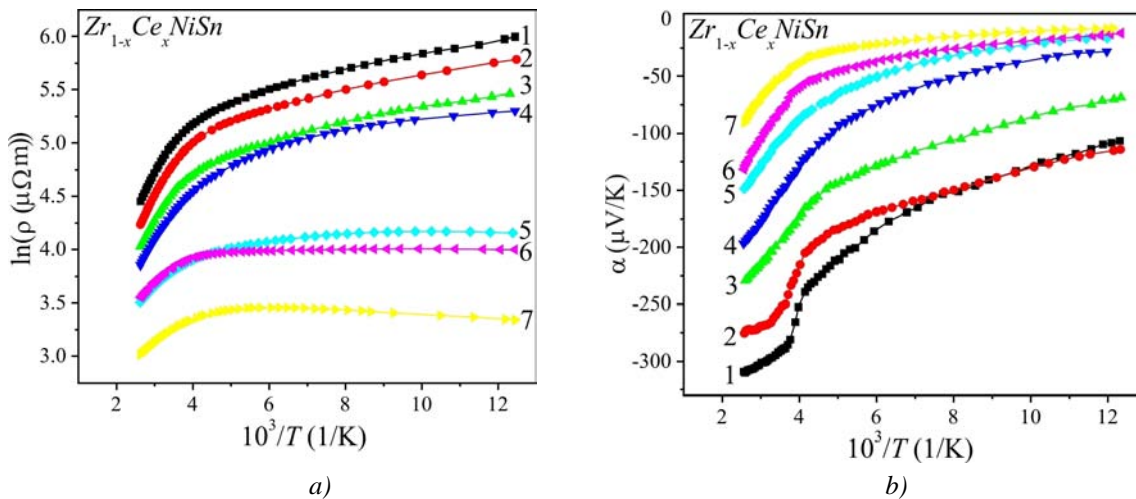


Fig. 4. Temperature dependences of resistivity (a) and the Seebeck coefficient (b) of $Zr_{1-x}Ce_xNiSn$:
 1 – $x = 0.01$; 2 – $x = 0.02$; 3 – $x = 0.04$; 4 – $x = 0.05$; 5 – $x = 0.07$; 6 – $x = 0.08$; 7 – $x = 0.10$

The fact that Ce atoms introduced into n - $ZrNiSn$ generate donors is also shown by dependences of change in the values of resistivity $\rho(x)$ (Fig. 5a). Thus, introduction of the lowest in the experiment concentration of Ce is attended by the drastic reduction of $\rho(x)$ values, for instance, at 80 K, from $\rho(x=0) = 4751.1 \mu\Omega \cdot m$ to $\rho(x=0.01) = 402.48 \mu\Omega \cdot m$ and $\rho(x=0.10) = 28.20 \mu\Omega \cdot m$, which is only possible under condition of semiconductor doping with donors. In this case, the valence of Ce^{4+} .

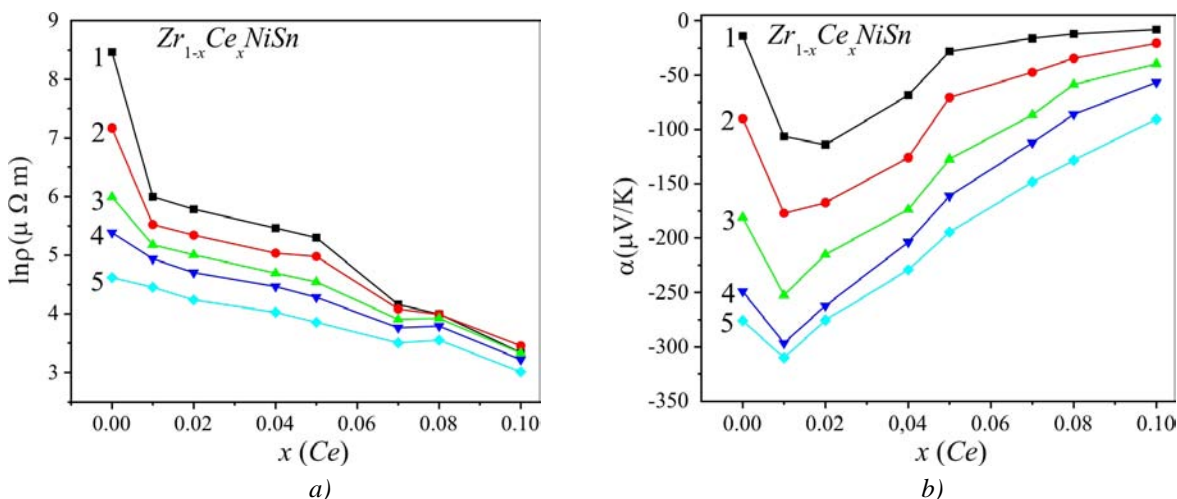


Fig. 5. Change in the values of electric resistivity $\rho(x)$ (a) and the Seebeck coefficient $\alpha(x)$ (b) of $Zr_{1-x}Ce_xNiSn$ at temperatures: 1 – 80 K; 2 – 160 K; 3 – 250 K; 4 – 300 K; 5 – 380 K

Therefore, the two experimental results, namely the change in the values of electric resistivity $\rho(x)$ and the Seebeck coefficient $\alpha(x)$ of $Zr_{1-x}Ce_xNiSn$, point to the presence of a mechanism of generation of donor structural defects, testifying to Ce^{4+} . And it means that the degree of compensation of $Zr_{1-x}Ce_xNiSn$ semiconductor (the ratio between ionized donors and acceptors) should be only

reduced, since we add donors to n-type semiconductor $n-ZrNiSn$ by generation of structural donor defects. The obtained result is in full conformity with the experimental research on magnetic state of Ce in $Zr_{1-x}Ce_xNiSn$, as well as with the results of calculation of semiconductor electron structure.

A change in the values of activation energy $\varepsilon_1^p(x)$ $Zr_{1-x}Ce_xNiSn$ (activation energy from the Fermi level ε_F to the edge of the conduction band) does not give grounds for stating the presence of acceptors in the crystal. Thus, in $n-ZrNiSn$ the value of energy $\varepsilon_1^p(x)$ reflects the position of the Fermi level ε_F to the edge of the conduction band, whereas doping of semiconductor with the lowest in the experiment concentration of Ce ($x = 0.01$) results in the reduction of $\varepsilon_1^p(x)$ values (Fig. 6a). That is, the Fermi level ε_F drifts in the direction of the conduction band, which is only possible at generation of donors in the crystal under condition of Ce^{4+} .

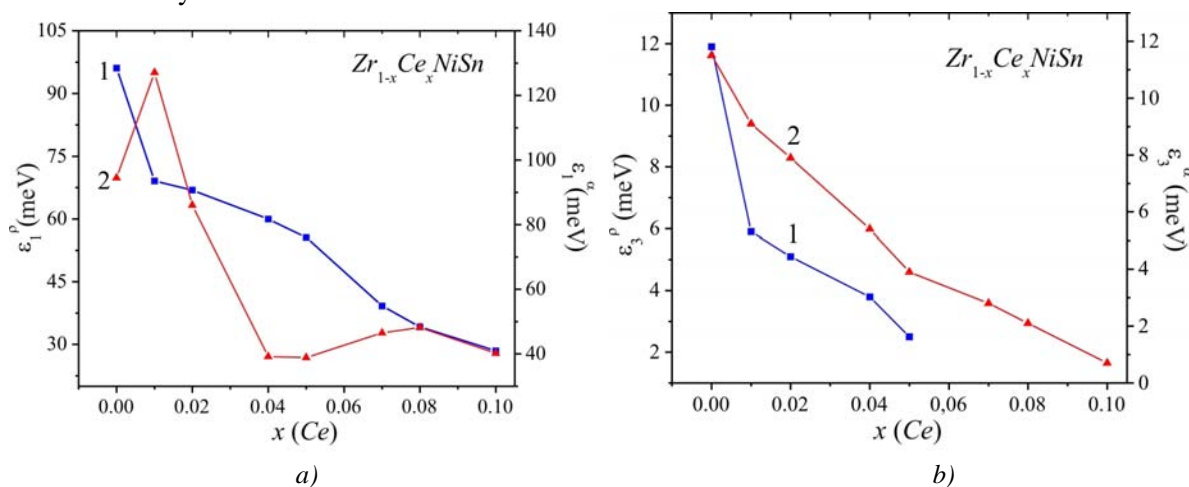


Fig. 6. Change in the values of activation energies $\varepsilon_1^p(x)$ (1) and $\varepsilon_1^α(x)$ (2) (a) and $\varepsilon_3^p(x)$ (1) and $\varepsilon_3^α(x)$ (2) (b) of $Zr_{1-x}Ce_xNiSn$

In this case, what is the reason for the origination of maximum at $x = 0.01$ on the dependence $\varepsilon_1^α(x)$ the values of which are proportional to modulation amplitude of continuous energy bands $\varepsilon_1^α(x)$ (Fig. 6a), which reflects a change in semiconductor compensation degree? At first sight, it looks like a manifestation of the mechanism for generation of acceptors by so far unknown mechanism which compensates donors, as long as maximum $\varepsilon_1^α(x)$ at $x = 0.01$ reflects a decrease in the number of donors in $Zr_{1-x}Ce_xNiSn$. And this despite the fact that there is constant increase in the number of donors generated in the crystal as a result of occupation by Ce^{4+} of Zr atoms position.

To explain this effect, it is necessary to involve the results of structural investigations which showed that in $(Zr_{1-y}Ni_y)NiSn$ undoped semiconductor the position of Zr atoms (4a) up to $\sim 1\%$ ($y = 0.01$) is occupied by Ni atoms that are the source of donors. In the concentration area of impurity atoms $x = 0-0.02$ there is a reduction and full liquidation of donor structural defects (by decreasing the number of donors) when Ni atoms leave crystallographic positions 4a of Zr atoms due to structure ordering (Fig. 1). As long as Ce impurity atoms generate donors in crystal, in the area $x = 0-0.02$ per each x number of donors introduced into crystal (Ce atoms) the available number of donors is reduced by y value (Ni atoms leave 4a position). In other words, maximum on the dependence $\varepsilon_1^α(x)$ $Zr_{1-x}Ce_xNiSn$ at $x = 0.01$ reflects the fact of reducing the rate of generation of donors, which in semiconductor usually takes place only under the emergence of acceptors, which results in the increase of compensation degree [13].

And only at higher Ce concentrations ($x > 0.02$), when Ni atoms will leave $4a$ position ($y = 0$), the increase in the concentration of impurity atoms will correspond to the number of generated donors, which in the n -type $Zr_{1-x}Ce_xNiSn$ semiconductor will only reduce the compensation degree, as testified by the behaviour $\varepsilon_1^\alpha(x)$ (Fig. 5a). Minor extreme $\varepsilon_1^\alpha(x)$ at $x = 0.08$ is not related to the appearance of acceptors in the crystal, which might increase the semiconductor degree of compensation, but reflects the fact of reconstruction of the conduction band ε_C , as discussed above.

The reduced values of activation energy of hopping conduction $\varepsilon_3^p(x)$ (Fig. 5b) point to the reduction of electron localization radius, which in n -type semiconductor is possible with increasing number of donors [13]. The reduction of modulation amplitude values of low-scale fluctuation from $\varepsilon_3^\alpha(x=0,01)=9,1$ meV to $\varepsilon_3^\alpha(x=0,05)=3,9$ meV and $\varepsilon_3^\alpha(x=0,10)=0,7$ meV is also possible only under condition of generation of donors, which reduces the semiconductor compensation degree [13].

Thus, the results of kinetic investigations of $Zr_{1-x}Ce_xNiSn$ allow speaking of the mechanism of generation of donors, which is possible under condition of the Ce^{4+} .

Thermoelectric power factor of $Zr_{1-x}Ce_xNiSn$

Fig. 7 represents a change in thermoelectric power factor $Z^*(x)$ of $Zr_{1-x}Ce_xNiSn$, from which it is evident that over the entire concentration range of Ce impurity atoms the values of $Z^*(x)$ are higher than in n - $ZrNiSn$ undoped semiconductor. The result obtained is anticipated, as long as n -type semiconductor is doped with impurity atoms which generate donor structural defects in the crystal [8]. For the first time, the efficiency of thermal into electric energy conversion was improved [1] on doping of n - $ZrNiSn$ with the atoms of rare-earth metal, since the property of Ce to change its valence state from $3+$ to $4+$ was utilized [7, 9].

In all fairness it should be noted that the values of $Z^*(x)$ of $Zr_{1-x}Ce_xNiSn$ rank below the record ones [14], but exactly this stimulates further research on the mechanisms and nature of structural defects generated in n - $ZrNiSn$ semiconductor under heavy doping [13] and their influence on the mechanisms of electric conductivity.

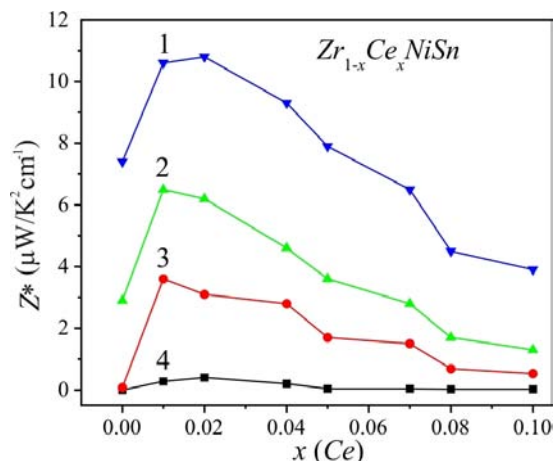


Fig. 7. Change in the values of thermoelectric power factor Z^* of $Zr_{1-x}Ce_xNiSn$:
 1 – $T = 380$ K; 2 – $T = 300$ K; 3 – $T = 250$ K; 4 – $T = 80$ K

Conclusions

For the first time, the increased values of thermoelectric power factor $Z^*(x)$ were obtained on doping of n - $ZrNiSn$ with a rare-earth metal Ce as a result of realization of Ce^{4+} valence state that

generates donor structural defects in the crystal. A complicated mechanism of change in the compensation degree of $Zr_{1-x}Ce_xNiSn$ was revealed as a result of a simultaneous reduction of the number of donor defects (Ni in $4a$ position of Zr atoms) and generation in this same position of donor defects on substitution of Zr by Ce atoms in $4+$ valence state. The investigated $Zr_{1-x}Ce_xNiSn$ solid solution is a promising thermoelectric material.

The work was performed in the framework of grants of the National Academy of Sciences and Ministry of Education of Ukraine, № 0113U007687 and № 0114U005464.

References

1. L.I. Anatychuk, *Thermoelements and Thermoelectric Devices* (Kyiv: Naukova Dumka, 1979), 768 p.
2. H. Hohl, A.P. Ramirez, C. Goldmann, G. Ernst, B. Wolfing, and E. Bucher, Efficient Dopants for $ZrNiSn$ -based Thermoelectric Materials, *J. Phys. Condens. Matter.* **11**, 1697-1709 (1999).
3. A. Slebarski, M. Orzechowski, A. Wrona, J. Szade, and A. Jezierski, Structural Properties and Electronic Structure of Some Ternary d -electron and f -electron Intermetallics, *J. Phys. Condens. Matter.* **12**, 1269-1284 (2000).
4. S. Katsuyama, R. Matsuo, and M. Ito, Thermoelectric Properties of Half-Heusler Alloys $Zr_{1-x}Y_xNiSn_{1-y}Sb_y$, *J. Alloys Compd.* **428**, 262-267 (2007).
5. Yu.V. Stadnyk, V.A. Romaka, Yu.K. Gorelenko, L.P. Romaka, D. Fruchart, and V.F. Chekurin, Metal-Insulator Transition Induced by Changes in Composition in $Zr_{1-x}Sc_xNiSn$ Solid Solution Range, *J. Alloys Compd.* **400**, 29-32 (2005).
6. V.A. Romaka, V.V. Romaka, and Yu.V. Stadnyk, *Intermetallic Semiconductors: Properties and Applications* (Lviv, Lvivska Polytechnika, 2011), 488 p.
7. D.I. Khomsky, Problem of Intermediate Valence, *Advances in Physical Sciences* **129**(3), 443-485 (1979).
8. V.A. Romaka, D. Fruchart, Yu.V. Stadnyk, J. Tobola, Yu.K. Gorelenko, M.G. Shelyapina, L.P. Romaka, and V.F. Chekurin, A Condition of Maximum Power Characteristic to Intermetallic Semiconductors of the $MgAgAs$ Structure Type, *Semiconductors* **40**(11), 1289-1395 (2006).
9. V.A. Romaka, Yu.N. Grin, Ya.P. Yarmolyuk, O.S. Zarechnyuk, and R.V. Skolozdra, Magnetic and Crystallographic Characteristics of R_2Ni_2Ga and R_2Ni_2Al Compounds, *The Physics of Metals and Metallography* **54**(4), 691-696 (1982).
10. T. Roisnel, J. Rodriguez-Carvajal, WinPLOTR: a Windows Tool for Powder Diffraction Patterns Analysis, *Mater. Sci. Forum, Proc. EPDIC7* 378-381, 118-123 (2001).
11. 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).
12. V.L. Moruzzi, J.F. Janak, and A.R. Williams, *Calculated Electronic Properties of Metals* (NY, Pergamon Press, 1978), 348 p.
13. B.I. Shklovsky, A.L. Efros, *Electronic Properties of Doped Semiconductors* (Moscow: Nauka, 1979), 416 p.
14. S.R. Culp, S.J. Poon, N. Hickman, T.M. Tritt, and J. Blumm, Effect of Substitutions on the Thermoelectric Figure of Merit of Half-Heusler Phases at $800^{\circ}C$, *Appl. Phys. Letters* **88**(16), 042106-1-3 (2006).

Submitted 02.12.2014.