Study of the Structural, Electrokinetic and Magnetic Characteristics of the Er$_{1-x}$Zr$_x$NiSb Semiconductor

Peculiarities of the structural, electrokinetic, energetic, and magnetic characteristics of Er$_{1-x}$Zr$_x$NiSb semiconductive solid solution, $x = 0 - 0.10$, were studied. It was suggested that when Zr (4$d^55$s$^2$) atoms were introduced into the structure of the ErNiSb half-Heusler phase by substitution of Er (5$d^8$5$s^2$) atoms in 4$a$ position, Zr atoms can also simultaneously occupy the 4$c$ position of Ni (3$d^8$4$s^2$) atoms. As a result, in Er$_{1-x}$Zr$_x$NiSb semiconductor, the structural defects of donor nature in position 4$a$ and ones of acceptor nature in position 4$c$ were generated simultaneously. In this case, in the band gap of Er$_{1-x}$Zr$_x$NiSb, the energy states of impurity donor $\varepsilon_B^\mathrm{D}$ and acceptor $\varepsilon_A^\mathrm{A}$ bands (donor-acceptor pairs) appear and determine the electrical conductivity mechanism of the semiconductor.

Keywords: electrical conductivity, thermopower coefficient, Fermi level.

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Introduction

RNiSb compounds and corresponding solid solutions (R – rare earth metal) are promising, but not enough studied class of thermosensitive materials with MgAgAs structure type. Study of the phase equilibria in the R–Ni–Sb ternary systems results in the existence of the equiatomic compounds [1]. However, for cases of light rare earth metals (La, Ce, Pr, Nd, Sm), the compounds crystallize in two structure types - AlB$_2$ and ZrBeSi [2, 3]. Instead, the RNiSb compounds with heavy rare earth crystallize in MgAgAs structure type. In turn, the antimonide GdNiSb exists in two structural modifications – high-temperature with hexagonal structure (AlB$_2$-type) and low-temperature one with MgAgAs-type. We will remind that Gd is in the middle of the lanthanide series and its 4$f$-shell contains 7 electrons out of 14.

RNiSb compounds, which have a structure of the MgAgAs type, are semiconductors and promising thermosensitive materials [4, 5]. This is the main motivator of our attention to this series of compounds.

The combination of high thermoelectric characteristics and magnetic properties of half-Heusler phases based on rare earth and transition metals is a good starting point for a new class of thermoelectric materials.

In Refs. [6, 7] it was shown that the thermoelectric properties of half-Heusler phases in many cases strongly depend on heat treatment, which affects the defectivity of the crystal material. In this context, the study of phase equilibria in the corresponding system is an important step in understanding the influence of the preparation method, heat treatment, and charge and size factors on the existence of compounds and solid solutions based on them. Such studies will allow the synthesis of multicomponent thermosensitive materials with stable and reproducible characteristics up to the temperature of homogenizing annealing by doping the half-Heusler phases.

The study of the features of structural peculiarity, energetic and electrokinetic characteristics of the $p$-GdNiSb and $p$-LuNiSb semiconductors in the temperature range 4.2 - 400 K allowed to propose (offer) the model of the crystal structure for the LuNiSb compound [8]. Calculations of the density distribution of
A priori we reasoned as follows. If in the ErNiSb compound the Er atoms ($r_E = 0.178$ nm) in position 4c is substituted by Zr atoms ($r_{Zr} = 0.160$ nm), it was expected that the lattice parameter values $a(x)$ would decrease, because the atomic radius Er is larger than Zr. However, the $a(x)$ values of Er$_{1-x}$Zr$_x$NiSb at concentrations $x = 0 - 0.02$ increase rapidly (Fig. 1). At higher concentrations, in the range $x = 0.02 - 0.03$, the $a(x)$ values decrease rapidly, and then similarly enlarge at $x = 0.03 - 0.05$. And only at $x>0.05$ lattice parameter values $a(x)$ of the Er$_{1-x}$Zr$_x$NiSb thermosensitive material decrease.

Initially, we associated the nonmonotonic variation of the lattice parameter values $a(x)$ of Er$_{1-x}$Zr$_x$NiSb with uncontrolled processes during sample preparation. After all, the accuracy of the X-ray diffraction method lies outside the concentrations of impurities in the semiconductor and does not allow them to be identified. However, the results of previous studies of the structural characteristics of Er$_{1-x}$Zr$_x$NiSb, in particular, changes in the lattice parameter values $a(x)$ for both series of

Fig. 1. Variation of the lattice parameter values $a(x)$ of Er$_{1-x}$Zr$_x$NiSb. Insert: variation of $a(x)$ for the samples prepared earlier.
samples showed their similarity (Fig. 1). This suggests that the peculiarities detected in the \( a(x) \) dependences of \( \text{Er}_1 \text{ZrNiSb} \) are a manifestation of changes in the structure during the introduction of Zr atoms and cannot be related to the quality of sample preparation by arc-melting the charge in an electric arc furnace followed by homogenizing annealing.

Thus, the behavior of the lattice parameter \( a(x) \) of \( \text{Er}_1 \text{ZrNiSb} \) suggests that impurity Zr atoms introduced into half-Heusler \( \text{ErNiSb} \) phase may also partially occupy other crystallographic positions, in particular, 4c position of Ni atoms, or cause the appearance of other structural defects, for example, vacancies or atoms in the structural voids [6-8].

Considering, that the atomic radius of Ni (\( r_{\text{Ni}} = 0.124 \text{ nm} \)) is the smallest in \( \text{Er}_1 \text{ZrNiSb} \) (\( r_{\text{Sb}} = 0.159 \text{ nm} \)), the increase of the cell parameter \( a(x) \) of the thermosensitive material \( \text{Er}_1 \text{ZrNiSb} \) can be caused only by the simultaneous partial occupation of 4c position of Ni atoms by impurity Zr atoms. By analogy, the increase of \( a(x) \) values at \( x = 0.03 - 0.05 \) can also be explained by the displacement of Ni atoms from position 4c by Zr atoms. On the other hand, the substitution of Ni (3d\(^8\)) atoms by Zr (4d\(^2\)5s\(^2\)) atoms generates the structural defects of the acceptor nature in the crystal, because the Zr atom contains fewer d-electrons. In this case, the samples \( \text{Er}_1 \text{ZrNiSb}, x = 0 - 0.02 \), will be semiconductors of the p-type conduction with positive values of the thermopower coefficient \( \alpha(x,T) \).

The decrease of lattice parameter values \( a(x) \) in the concentration range \( x = 0.02 - 0.03 \) can be caused by the occupation of 4a position of Er atoms (4d\(^2\)6s\(^2\)) by impurity Zr atoms, which generates the structural defects of donor nature. In the experiment, the thermopower coefficient values \( \alpha(x,T) \) should be negative. The logic of reasoning is similar for samples of thermosensitive material \( \text{Er}_1 \text{ZrNiSb}, x > 0.05 \), when lattice parameter \( a(x) \) also decreases.

We are aware that the given above considerations concerning the elemental substitutions in the
Er$_{1-x}$Zr$_x$NiSb structure are far from complex structural changes in the real crystal. Considering also the defective structure of the isostructural LuNiSb compound [8], in which vacancies (6 %) and Lu atoms (1.35 %) are available in the $4c$ position of Ni atoms, we can assume the complex character of changes in different crystallographic sites of Er$_{1-x}$Zr$_x$NiSb solid solution.

The results of the study of the electrokinetic, energetic, and magnetic characteristics of Er$_{1-x}$Zr$_x$NiSb samples, $x = 0 - 0.15$, combined with modeling of these characteristics allow to reduce in the future the variability of models of their crystal and electronic structures and establish a crystal structure as close as possible to the real state of the material.

### III. Study of the electrokinetic, energetic and magnetic characteristics of Er$_{1-x}$Zr$_x$NiSb

Temperature and concentration dependencies of electrical resistivity $\rho$ and thermopower coefficient $\alpha$ of the Er$_{1-x}$Zr$_x$NiSb samples, $x = 0 - 0.10$, are shown in Figs. 2 and 3, respectively. The dependencies $\ln(\rho(1/T))$ and $\alpha(1/T)$ for Er$_{1-x}$Zr$_x$NiSb, $x = 0 - 0.03$, are typical for compensated semiconductors with activation regions and a change in the sign of thermopower coefficient $\alpha(T,x)$, which indicates the presence of several types of activation mechanisms of electrical conduction involving electrons and holes.

For samples Er$_{1-x}$Zr$_x$NiSb, $0 \leq x \leq 0.03$, in which the dependencies $\ln(\rho(1/T))$ have high-temperature activation parts, the Fermi level $\varepsilon_F$ is located in the band gap. From the high-temperature activation parts of the $\ln(\rho(1/T))$ dependencies, the activation energy values $\varepsilon^p_1$ from the Fermi level $\varepsilon_F$ to the continuous energy bands are calculated, and from the $\alpha(1/T)$ dependencies the activation energy values $\varepsilon^\alpha_1$, which give the values of the modulation amplitude of continuous energy bands of heavily doped and highly compensated semiconductor, are obtained [10].

In the case of the ErNiSb compound, the sign of the thermopower coefficient $\alpha(T,x)$ is positive and indicates the hole type of conduction, and the Fermi level is located near the valence band at a distance $\varepsilon^\alpha_1 = 45.2$ meV from the percolation level (Fig. 4). A similar location of the Fermi level $\varepsilon_F$ was observed for RNiSb compounds (R = Gd, Lu) [8]. In turn, the modulation amplitude of continuous energy bands in the ErNiSb semiconductor is $\varepsilon^\alpha_1 = 34.3$ meV.

Assuming that in the ErNiSb compound, as in the case of LuNiSb, the crystallographic site 4$c$ of Ni atoms is partially, up to ~ 1 %, occupied by Er atoms and characterized by vacancies (~ 6 %), then the structural defects of acceptor nature are generated in the crystal. This will lead to the appearance of several acceptor levels with different depth of occurrence in the band gap of the semiconductor, and the Fermi level $\varepsilon_F$ is located near the percolation level of the valence band. In the experiment, the thermopower coefficient $\alpha(T,x)$ will have positive values. The suggested model of the atom arrangement in ErNiSb is in agreement with the results of the electrokinetic studies (Figs. 2, 3).

We planned that the substitution of Er atoms by Zr

![Fig. 3. Variation of the electrical resistivity values $\rho(x,T)$ (a) and thermopower coefficient $\alpha(x,T)$ (b) of Er$_{1-x}$Zr$_x$NiSb at different temperatures: 1 – $T = 80$ K, 2 – $T = 250$ K, 3 – $T = 300$ K, 4 – $T = 380$ K.](image1.png)

![Fig. 4. Variation of the activation energy values $\varepsilon^\alpha_1(x)$ of Er$_{1-x}$Zr$_x$NiSb.](image2.png)
ones in 4a position would generate donors in the crystal. In this case, the electrical resistivity values \( \rho(x,T) \) should increase due to the reduction of the concentration of free holes during ionization of acceptors, and thermopower coefficient \( \alpha(T,x) \) should change the sign from positive to negative. However, the introduction of the lowest in the experiment concentration of Zr atoms \((x=0.005)\) into the structure of the ErNiSb compound did not change the sign of the thermopower coefficient \( \alpha(T,x) \) and led to a decrease in the resistivity values \( \rho(x,T) \) (Fig. 3). The depth of occurrence of the Fermi level \( \varepsilon_F \) relative to the percolation level of the valence band decreased to \( \varepsilon_F^p = 39.8 \text{ meV} \) (Fig. 4).

The obtained result is unexpected, because for a \( p \)-type semiconductor this is possible only if the concentration of acceptor impurities increases, accompanied by an increase in the concentration of free holes, a drift of the Fermi level \( \varepsilon_F \) to the valence band, and a decrease of the electrical resistivity values \( \rho(x,T) \) of Er\(_{1-x}\)Zr\(_x\)NiSb at \( x = 0.005 \). Moreover, it turns out that the impurity Zr atoms do not generate donors and do not occupy crystallographic site 4a of Er atoms.

This experimental result shows that in the crystal structure of the Er\(_{1-x}\)Zr\(_x\)NiSb semiconductor, \( x = 0.005 \), the changes take place, which generate the structural defects of acceptor nature and additional impurity acceptor level in the band gap. This is also indicated by the decrease of the modulation amplitude of the continuous energy bands of Er\(_{1-x}\)Zr\(_x\)NiSb at \( x = 0.005 \) to value \( \varepsilon_x^p = 17.5 \text{ meV} \) (Fig. 5, curve 1). This is possible in the case of occupation of the crystallographic position 4c of Ni atoms \((3d^84s^2)\) by impurity Zr atoms, which generates the structural defects of acceptor nature in the crystal (Zr atom has fewer d-electrons than Ni).

The sign of thermopower coefficient \( \alpha(T,x) \) of Er\(_{1-x}\)Zr\(_x\)NiSb semiconductor, \( x = 0.01 \), becomes negative at all temperatures, and electrons are the main current carriers. At concentration \( x = 0.01 \), the Fermi level \( \varepsilon_F \) is located near the conduction band at a distance 6.7 meV from its percolation level. At higher concentrations of impurity Zr atoms \((0.01 < x)\) the sign of the thermopower coefficient remains negative at all temperatures, the activation parts of \( \ln(\rho(1/T)) \) dependencies disappear, and the electrical resistivity values increase with temperature.

The metallization of electrical conductivity of Er\(_{1-x}\)Zr\(_x\)NiSb, \( 0.01 < x \), is a result of the movement of Fermi level \( \varepsilon_F \) to the conduction band of the semiconductor followed by crossing the percolation level of this band. Such behavior of the Fermi level \( \varepsilon_F \) is due to an increase in the concentration of donors, the ionization of which enlarges the number of free electrons. This result can be explained by the substitution of Er atoms in 4a position by Zr atoms, which will generate donors. In this case, the decrease of compensation degree takes place, as indicated by the decrease of the modulation amplitude of the continuous energy bands from \( \varepsilon_x^p = 11.7 \text{ meV} \) at \( x = 0.01 \) to \( \varepsilon_x^p = 8.2 \text{ meV} \) at \( x = 0.05 \) (Fig. 5).

Measurements of the magnetic susceptibility \( \chi(x) \) of Er\(_{1-x}\)Zr\(_x\)NiSb at \( T = 300 \text{ K} \) (Fig. 5, curve 2) also point to the simultaneous generation of the defects of acceptor and donor nature in the crystal. The Er\(_{1-x}\)Zr\(_x\)NiSb samples are Pauli paramagnets, the magnetic susceptibility of which is determined by free electrons and is proportional to the density of electronic states at Fermi level \( g(\varepsilon_F) \). At concentrations \( x > 0 \), the dependence \( \chi(x) \) decreases rapidly and passes through the minimum at \( x = 0.01 \). Subsequently, the \( \chi(x) \) dependence grows, reaches a maximum at \( x = 0.03 \), and then decreases. Since the dependence \( \chi(x) \) is proportional to \( g(\varepsilon_F) \), the growth of \( \chi(x) \) dependence for Er\(_{1-x}\)Zr\(_x\)NiSb indicates an increase of the density of states at Fermi level \( g(\varepsilon_F) \). The decrease of \( \chi(x) \) dependence of Er\(_{1-x}\)Zr\(_x\)NiSb, at \( x > 0.03 \), indicates a decrease of the density of states at the Fermi level \( g(\varepsilon_F) \), which can be caused by the metallization of electrical conductivity of the semiconductor.

The obtained and presented experimental results of the study of Er\(_{1-x}\)Zr\(_x\)NiSb thermosensitive material are not enough for final conclusions concerning the atom distribution in the semiconductor and the construction of adequate models of electronic structure and mechanisms of electrical conductivity. This requires further research as a crystal structure, in particular, the possible existence of homogeneity range for ErNiSb compound, the study of Er\(_{1-x}\)Zr\(_x\)NiSb at higher temperatures of homogenizing annealing, as well as electrokinetic and energetic characteristics combined with modeling of these characteristics, etc.

**Conclusions**

Thus, the presented above results indicate the complex nature of including of Zr atoms into the structure of the ErNiSb compound. It was suggested that the introduction of Zr atoms \((4d^55s^2)\) into the structure of half-Heusler phase ErNiSb by substitution of Er \((5d^66s^2)\) atoms in 4a position, the Zr atoms can also simultaneously occupy the 4c position of Ni atoms \((3d^84s^2)\). As a result, in the Er\(_{1-x}\)Zr\(_x\)NiSb semiconductor, both structural defects of donor nature in 4a position (Zr has a larger number of d-electrons than Er) and acceptor defects in the 4c position of Ni atoms (Ni has more 3d electrons than Zr) are generated simultaneously. In this case, the energy states of impurity donor \( \varepsilon_\text{d1} \) and acceptor \( \varepsilon_\text{a1} \) bands (donor-acceptor pairs) appear which determine the mechanisms of electrical conduction of semiconductor.


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Дослідження структурних, кінетичних та магнітних характеристик напівпровідника Er1-xZrxBiSb

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Досліджено особливості структурних, кінетичних, енергетичних та магнітних характеристик напівпровідникового твердого розчину Er1-xZrxBiSb, х = 0 - 0.10. Зроблено припущення, що при уведення атомів Zr (4d5s2) у структуру пів-Гейслерової фази ErBiSb шляхом заміщення у позиції 4a атомів Er (5d6s2) атоми Zr також одночасно можуть займати позицію 4c атомів Ni (3d4s2). Як результат, у напівпровіднику Er1-xZrxBiSb одночасно генеруються як структурні дефекти донорної природи у позиції 4a і акцепторної у позиції 4c. При цьому у забороненій зоні Er1-xZrxBiSb з’являються енергетичні стани домішкових донорної εD 4c та акцепторної εA 4a зон (донорно-акцепторні пари), які визначають механізми електропровідності напівпровідника.

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