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## Modeling of Structural and Energetic Parameters of $p$ -Er<sub>1-x</sub>Sc<sub>x</sub>NiSb Semiconductor

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The energy expediency of the existence of Er<sub>1-x</sub>Sc<sub>x</sub>NiSb substitutional solid solution up to the concentration  $x \approx 0.10$  was established by modeling the variation of free energy  $\Delta G(x)$  values (Helmholtz potential). At higher Sc concentrations,  $x > 0.10$ , there is stratification (spinoidal decomposition of phase). It is shown that in the structure of  $p$ -ErNiSb semiconductor there are vacancies in positions  $4a$  and  $4c$  of Er and Ni atoms, respectively, generating structural defects of acceptor nature. The number of vacancies in position  $4a$  is twice less than in position  $4c$ . This ratio also remains for  $p$ -Er<sub>1-x</sub>Sc<sub>x</sub>NiSb. Doping of  $p$ -ErNiSb semiconductor by Sc atoms by substitution of Er atoms is also accompanied by the occupation of vacancies in position  $4a$ . In this case, Ni atoms occupy vacancies in position  $4c$ , which can be accompanied by the process of ordering the  $p$ -Er<sub>1-x</sub>Sc<sub>x</sub>NiSb structure. Occupation of vacancies by Sc and Ni atoms leads to an increase of the concentration of free electrons, an enlarge of the compensation degree of semiconductor, which changes the position of the Fermi level  $\varepsilon_F$  and the mechanisms of electrical conductivity.

**Keywords:** semiconductor, electrical conductivity, thermopower coefficient, Fermi level.

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### Introduction

Important components of modern research are both experimental results obtained using a variety of highly efficient equipment and theoretical studies that describe, explain experimental data, and, in most cases, serve as a basis for the predictive search for new materials and optimization of their functional characteristics.

Semi-Heusler phases RNiSb (R is a rare earth metal) and solid solutions based on them with a structure of the MgAgAs type proved to be promising in the direction of searching for new thermoelectric materials. The study of  $p$ -RNiSb semiconductors (R – Sc, Y, Gd, Er, Lu) established a defectivity in their crystal structure [1-5], and in Refs. [3, 6] on the example of  $p$ -LuNiSb a variant of occupancy of the crystallographic positions in the unit cell was proposed: Ni( $4c$ ) = 92.65 % Ni + 1.35 % Lu + 6 % Vac; Lu( $4a$ ) = 100 % Lu; Sb( $4b$ ) = 100 % Sb. Exactly

the defectivity in the crystal structure of RNiSb compounds causes the generation of structural defects of acceptor nature in positions  $4a$  (vacancies) and  $4c$  (Lu atom contains fewer outer  $d$ -electrons than Ni atom) and the appearance of two acceptor bands  $\varepsilon_A^{Vac}$  and  $\varepsilon_A^{Lu}$  in the band gap of the semiconductor.

Experimental studies of thermoelectric semiconducting solid solution  $p$ -Er<sub>1-x</sub>Sc<sub>x</sub>NiSb,  $x = 0 - 0.10$ , (MgAgAs structure type, space group  $F4\bar{3}m$  [7]), obtained by doping the semi-Heusler phase  $p$ -ErNiSb by neutral impurity Sc introduced by substitution of the rare earth metal atoms Er in  $4a$  position, revealed the appearance of donors of unknown origin [8]. The following mechanism for possible donor generation has also been proposed. Taking into account the defective model of the crystal structure of the semiconductor, the authors [8] suggested that doping  $p$ -ErNiSb by impurity Sc atoms by substitution of Er atoms in  $4a$  position is

accompanied by the occupation of existing vacancies in  $4a$  position by Sc atoms, which will reduce and eliminate structural defects of acceptor nature. At the same time, the structural defects of donor nature are generated in the  $4a$  position. The ratio of the concentrations of acceptors and donors generated in  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$  will determine the position of the Fermi level  $\varepsilon_F$  and the mechanisms of electrical conductivity.

The qualitative analysis of the obtained experimental results of  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$ ,  $x = 0 - 0.10$ , proposed by the authors [8], does not contain quantitative indicators that would allow predicting the characteristics of the semiconductor, which is a necessary condition for obtaining efficient thermoelectric materials.

A study of a related semiconducting solid solution  $p\text{-Tm}_{1-x}\text{Sc}_x\text{NiSb}$  (MgAgAs structure type) in the concentration range  $x = 0 - 1.0$  showed that the substitution of Tm atoms by Sc does not change the type of conductivity and holes remain the main carriers of electricity [9]. Below we return to the results of this work. In turn, the authors of Ref. [10] found that the ScNiSb compound, which is on the opposite side of the  $\text{Tm}_{1-x}\text{Sc}_x\text{NiSb}$  solid solution,  $x = 1.0$ , is also a  $p$ -type semiconductor, and the thermopower coefficient value  $\alpha(T,x)$  is maximal at temperature  $T \approx 450$  K ( $\alpha = 240 \mu\text{V/K}$ ). According to the authors [10], only vacancies in the position  $4c$  of Ni atoms, which generate the defects of acceptor nature, are responsible for the hole type of conductivity for  $p\text{-ScNiSb}$ .

In the present work, based on previously obtained experimental data [8], the results of modeling the thermodynamic, structural, energetic, and electrokinetic characteristics of the  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$  semiconductor,  $x = 0 - 0.10$ , synthesized by doping of  $p\text{-ErNiSb}$  by Sc atoms due to substitution of Er atoms ( $4a$  position), were presented. The obtained results allow to refine the spatial arrangement of atoms (or their absence) in the nodes of the unit cell, and also to identify the mechanisms of electrical conductivity to determine the conditions of synthesis of thermoelectric materials with maximum efficiency of conversion of thermal energy into electricity.

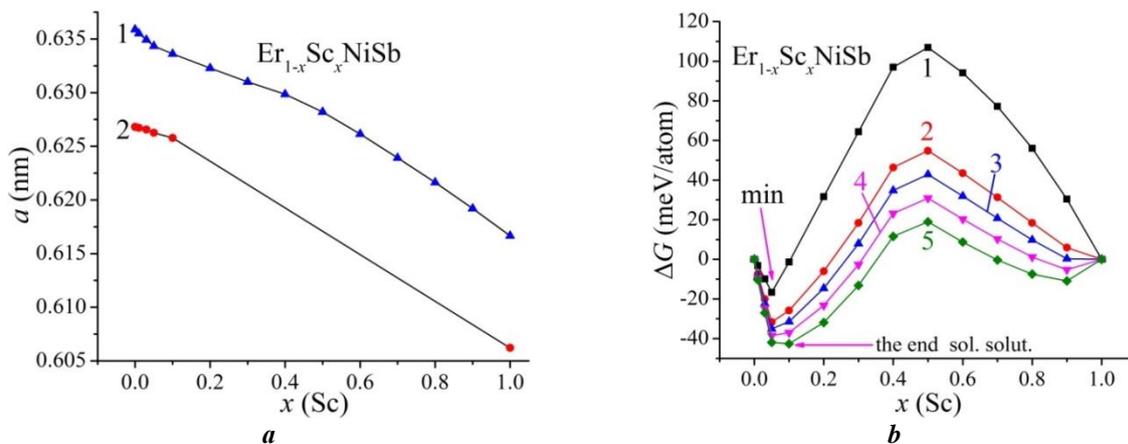
## I. Methods of investigation

Calculations of the electronic structure of the  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$  solid solution,  $x = 0 - 0.10$ , were performed by Korringa–Kohn–Rostoker (KKR) methods in the approximation of coherent potential (CPA) and local density (LDA) [11] using the exchange-correlation potential Moruzzi–Janak–Williams [12] and the linear combination of atomic orbitals (LMTO) within the theory of density functional DFT. The Brillouin zone was divided into 1000  $k$ -points, which were used for modeling of energy characteristics by calculating the density of electronic states (DOS). The width of the energy window was 22 eV and was chosen to capture all semi-core states of  $p$ -elements. Full Potential (FP) in the representation of plane waves was used in calculations by Linear Muffin-Tin Orbital (LMTO) method. The LDA approximation with MJW parameterization was also used as the exchange-correlation potential. The accuracy of calculating the position of the Fermi level  $\varepsilon_F$  is  $\pm 6$  meV. The structural characteristics of  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$  samples were calculated using the Fullprof Suite program package [13].

## II. Modeling of the structural and thermodynamic characteristics of $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$

Since both ErNiSb and ScNiSb compounds crystallize in the MgAgAs structure type [10, 14], to check the existence of a continuous substitutional solid solution  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$ , the variation of the unit cell parameter  $a(x)$  was calculated within the theory of functional density DFT in the concentration range  $x = 0 - 1.0$  (Fig. 1a, curve 1). The experimental results of the previous work [8] in the concentrations range of Sc,  $x = 0 - 0.10$ , and the lattice parameter value for  $p\text{-ScNiSb}$  according to the data [10] are also given for comparison with the calculated lattice parameter values  $a(x)$  in Fig. 1a (curve 2).

A monotonic decrease of the lattice parameter values  $a(x)$  for  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$  turned out to be expected, since the



**Fig. 1.** Calculated within the theory of the density functional DFT (1) and experimental (2) variation of the lattice parameter of  $a(x)$  (a) and Gibbs thermodynamic potential  $\Delta G(x)$  (b) for  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$  at different temperatures: 1 –  $T = 0$  K, 2 –  $T = 873$  K, 3 –  $T = 1073$  K, 4 –  $T = 1273$  K, 5 –  $T = 1473$  K.

atomic radius of Sc ( $r_{\text{Sc}} = 0.164$  nm) is smaller than that in Er ( $r_{\text{Er}} = 0.176$  nm). Therefore, the behavior of unit cell parameter values  $a(x)$  of  $\text{Er}_{1-x}\text{Sc}_x\text{NiSb}$  is one of the arguments for the existence of a substitutional solid solution where the Sc atoms occupy the crystallographic position  $4a$  of the Er atoms. Besides, the given above dependences  $a(x)$  of  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$  are almost parallel, which confirms the correctness of the simulation tools used. The question may arise, why parallel dependences  $a(x)$  of  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$ , and not coinciding?

The fact is that the simulation of the variation in the lattice parameter values  $a(x)$  of  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$  (Fig. 1a, curve 1) was carried out for an ordered variant of the structure for 100% occupation of the atoms in their crystallographic positions according to MgAgAs structure type [7]. Instead, the results of previous studies of RNiSb compounds, where R is a rare earth metal of the yttrium subgroup [1-4], and ScNiSb compound [10] showed the existence of a high number of vacancies in different crystallographic positions, which significantly deforms the structure and reduces interatomic distances in a real crystal. For this reason, the calculated and experimentally obtained  $a(x)$  dependences of  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$  samples do not coincide and are smaller in absolute value (Fig. 1a).

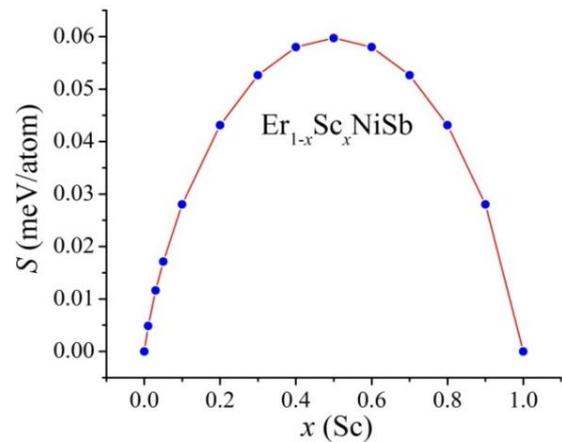
The formation of a semiconducting  $\text{Er}_{1-x}\text{Sc}_x\text{NiSb}$  solid solution by substitution of Er atoms by Sc in  $4a$  position is accompanied by changes in both the crystal structure and the electronic structure. The introduction of Sc atoms into the structure of the ErNiSb compound by substituting Er atoms in position  $4a$  is first accompanied by the occupation of the available vacancies in this position by the Sc atoms. This will reduce the number of structural defects of acceptor nature and change the electronic structure of the semiconductor. We can assume that the occupation of vacancies in  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$  by Sc atoms will lead to the ordering of the crystal structure of the semiconductor.

Carrying out thermodynamic calculations in the approximation of harmonic oscillations of atoms within the theory of density functional DFT (Fig. 1b) was the next step in establishing the possibility of the existence of a continuous  $\text{Er}_{1-x}\text{Sc}_x\text{NiSb}$  substitutional solid solution,  $x = 0 - 1.0$ . After all, our X-ray diffraction studies of phase equilibria in ternary systems of the rare earth metals, transition  $d$ -metals with tin, and antimony have shown the importance of verifying the existence of substitutional solid solutions by other methods.

A priori, based on the conclusions of studies of the related solid solution  $\text{Tm}_{1-x}\text{Sc}_x\text{NiSb}$ ,  $x = 0 - 1.0$ , [9, 10], as well as the results of both structural studies in the concentration range  $x = 0 - 0.10$  [8] and modeling of the lattice parameter variation  $a(x)$  of  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$  in the concentration range  $x = 0 - 1.0$  (Fig. 1a), we assumed the existence of a continuous solid solution. The proximity of the physicochemical properties of rare earth metals Tm and Er was not least the basis for such assumptions. However, the results of modeling the variation of free energy  $\Delta G(x)$  for  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$ ,  $x = 0 - 1.0$ , at different temperatures (Fig. 1b) revealed the falsity of our previous assumptions about the possibility of continuous dissolution of Sc atoms in the structure of ErNiSb compound.

We can see from Fig. 1b that the dependence of the free energy  $\Delta G(x)$  for  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$  in the concentration range  $x = 0 - 0.10$  decreases at all investigated temperatures, showing the energy expediency of forming a substitutional solid solution where Er atoms are substituted by Sc in the crystallographic position  $4a$ .

As seen from Fig. 1b the dependence of the free energy  $\Delta G(x)$  of  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$  at all simulation temperatures passes through a minimum near the concentration  $x \approx 0.10$ , and then increases, now indicating the energy inefficiency and substitution of Er atoms by Sc. Therefore, the results of modeling the  $\Delta G(x)$  behavior show that at higher concentrations of Sc atoms,  $x > 0.10$ , there is stratification (spinoidal phase decomposition). It should be noted that the diffraction pattern of the synthesized  $\text{Er}_{0.88}\text{Sc}_{0.12}\text{NiSb}$  sample contains traces of additional phase. It is interesting that even at a hypothetical temperature  $T = 4000$  K, the calculated entropy of mixing  $S(x)$  shows the absence of complete solubility of Sc atoms in  $\text{Er}_{1-x}\text{Sc}_x\text{NiSb}$  up to the Sc content  $x = 1.0$  (Fig. 2).



**Fig. 2.** Variation of the entropy of mixing  $S(x)$  of the components for  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$ .

It should be understood that experimental studies of the distribution of components, chemical and phase compositions of the samples may indicate the hypothetical existence of a continuous substitutional solid solution. However, to confirm the conclusion about the real lack of complete solubility of Sc in the ErNiSb compound, we need to use other research tools, which we did.

The increase of temperature in the modeling of free energy  $\Delta G(x)$  is accompanied by a slight drift of the dependence minimum in the region of higher concentrations (Fig. 1b), reaching maximum values at  $T = 1473$  K. Such behavior of the free energy  $\Delta G(x)$  of  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$  indicates that the concentration  $x \approx 0.10$  is the solubility limit of Sc atoms in the structure of ErNiSb compound (limit of existence of  $\text{Er}_{1-x}\text{Sc}_x\text{NiSb}$  substitutional solid solution) when Sc atoms occupy the  $4a$  crystallographic position of Er atoms. Therefore, it is energetically inefficient and impossible to obtain a continuous substitutional solid solution  $\text{Er}_{1-x}\text{Sc}_x\text{NiSb}$ ,  $x = 0 - 1.0$ . On the other hand, this result shows that the data of experimental studies of  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$  at concentrations  $x = 0 - 0.10$ , and the conclusions made are correct, because exactly the substitutional solid solution

was studied [8].

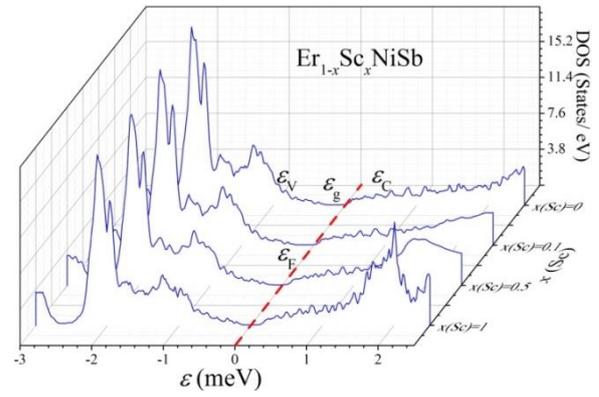
In this context, it is advisable to return to the results of experimental studies of the related semiconductor  $p$ - $\text{Tm}_{1-x}\text{Sc}_x\text{NiSb}$  [9, 10]. Aiming to obtain a thermoelectric material with high values of the figure of merit  $Z$  ( $Z = \alpha^2 \sigma / \kappa$ , where  $\alpha$  is the thermopower coefficient,  $\sigma$  is the electrical conductivity,  $\kappa$  is the thermal conductivity coefficient), the authors [9, 10] partially achieved this goal in samples  $\text{Tm}_{1-x}\text{Sc}_x\text{NiSb}$ ,  $x \geq 0.25$ , reducing the value of the thermal conductivity  $\kappa$ . The smooth change of the lattice parameter  $a(x)$  indirectly indicated the possibility of the existence of a continuous  $\text{Tm}_{1-x}\text{Sc}_x\text{NiSb}$  solid solution. After all, it is attractive to be able to synthesize a continuous  $\text{Tm}_{1-x}\text{Sc}_x\text{NiSb}$  solid solution, which allows obtaining a line of thermoelectric materials with a predicted change of characteristics. The decrease of the thermal conductivity  $\kappa$  can be due to the spinoidal phase decomposition, which is an ideal mechanism for the phonons scattering by nanoparticles at the boundaries of the phase fields.

It seems to us that the lack of thermodynamic studies of the related  $\text{Tm}_{1-x}\text{Sc}_x\text{NiSb}$  solid solution did not allow the authors [9, 10] to correctly characterize the objects of research, because it is difficult to detect stratification (spinoidal decomposition of phase) only by X-ray diffraction studies. The fact that in the case of  $\text{Tm}_{1-x}\text{Sc}_x\text{NiSb}$ ,  $x \geq 0.25$ , an increase of the figure of merit  $Z$  was obtained, resembled the method of obtaining efficient thermoelectric materials by pressing and sintering the powder, when the  $\kappa$  values also decreased, leading to an increase of  $Z$  values. These are positive aspects, but they have nothing to do with the substitutional solid solution.

### III. Modeling of the energetic characteristics for ordering structure of $p$ - $\text{Er}_{1-x}\text{Sc}_x\text{NiSb}$

Refinement of the crystal structure of  $p$ - $\text{Er}_{1-x}\text{Sc}_x\text{NiSb}$ ,  $x = 0 - 0.10$ , by powder method with a simultaneous refinement of the isotropic parameters of atomic displacement and occupancy of the crystallographic position  $4a$  due to the low concentration of impurity Sc atoms did not reveal the disorder of the structure at which other Sc atoms would occupy tetrahedral voids of the structure, which make up  $\sim 24\%$  of the volume of the unit cell of the  $\text{MgAgAs}$  structure type [7]. Therefore, the distribution of density of electronic states (DOS) was calculated for the case of an ordered structure variant for modeling the behavior of the Fermi level  $\varepsilon_F$ , the band gap  $\varepsilon_g$  and electrokinetic characteristics of the hypothetical continuous solid solution  $\text{Er}_{1-x}\text{Sc}_x\text{NiSb}$ ,  $x = 0 - 1.0$ , (Fig. 3).

As seen from Fig. 3, the  $\text{ErNiSb}$  compound is an electronic conductivity type semiconductor in which the Fermi level  $\varepsilon_F$  is located near the percolation level of the conduction band  $\varepsilon_C$ . Such location of the Fermi level  $\varepsilon_F$  in  $\text{ErNiSb}$  implies obtaining in experimental studies negative values of the thermopower coefficient  $\alpha(T, x)$ . It



**Fig. 3.** Calculated distribution of density of electronic states DOS for ordered crystal structure of  $\text{Er}_{1-x}\text{Sc}_x\text{NiSb}$ ,  $x = 0 - 1$ .

is worth noting that the DOS simulation result for the  $\text{ErNiSb}$  compound does not correspond to the experimental results [8], where the values of the thermopower coefficient at all temperatures had positive values, in particular,  $\alpha_{80\text{K}} = 10.81 \mu\text{V/K}$  and  $\alpha_{380\text{K}} = 120.88 \mu\text{V/K}$ , and free holes were the main carriers of current.

DOS calculations for the ordered variant of the structure of the  $\text{Er}_{1-x}\text{Sc}_x\text{NiSb}$  solid solution showed that the substitution of Er atoms by Sc atoms in the  $\text{ErNiSb}$  compound of the electron type of conductivity generates a structural defect of neutral nature in the crystallographic position  $4a$ . Such doping is also accompanied by a decrease of the band gap  $\varepsilon_g$ , and the Fermi level  $\varepsilon_F$  slightly deviates from the percolation level of the conduction band  $\varepsilon_C$ , which should provide negative values of the thermopower coefficient  $\alpha(T, x)$  in the experiment. However, experimental studies of the  $\text{Er}_{1-x}\text{Sc}_x\text{NiSb}$  solid solution,  $x = 0 - 0.1$ , [8] and the  $\text{ScNiSb}$  compound [10] showed positive values of the thermopower coefficient  $\alpha(T, x)$  at all concentrations and temperatures.

Thus, the calculations of the electronic structure of  $\text{Er}_{1-x}\text{Sc}_x\text{NiSb}$  for the ordered variant of the crystal structure, when considering only the substitution of Er atoms by Sc atoms, which generates structural defects of neutral nature in the crystal, is not consistent with the results of electrokinetic studies [8]. Obviously, there is a more complex mechanism of simultaneous generation of structural defects of different nature in the semiconducting solid solution  $\text{Er}_{1-x}\text{Sc}_x\text{NiSb}$ , which does not allow to predict the characteristics and obtain thermoelectric material with high efficiency of conversion of thermal energy into electricity.

It could be concluded that for the results of modeling the electronic structure of  $\text{Er}_{1-x}\text{Sc}_x\text{NiSb}$  and, in particular, the direction and motion rate of the Fermi level  $\varepsilon_F$  to be close and consistent with the position of the Fermi level  $\varepsilon_F$  calculated from high-temperature parts of  $\ln(\rho(I/T))$  dependences [8], it is necessary to make significant changes in the spatial arrangement of atoms in the nodes of the unit cell of a semiconducting solid solution. For solving this problem, we applied the optimization method of the crystal structure model based on the results of the calculation of the electronic structure and physical

properties of  $\text{Er}_{1-x}\text{Sc}_x\text{NiSb}$  [8].

#### IV. Optimization of the crystal and electronic structures of $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$

It is known that to calculate the energy of an electron in the first Brillouin zone, it is necessary to know the spatial arrangement of atoms (or their absence - vacancies) in the nodes of the unit cell. On the other hand, the smallest structural changes affect the local symmetry and distribution of density of electronic states DOS. Therefore, the adequacy of DOS results, in particular, the Fermi energy behavior and the dynamics of Fermi level motion, obtained from experimental studies, assumes that the model of the crystal structure of the semiconductor is as close as possible to the real one.

Having the experimental results of the drift rate of the Fermi level  $\varepsilon_F$  as the activation energy  $\varepsilon_1^p(x)$  from the Fermi level to the percolation level of the valence band  $\varepsilon_V$  of  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$  [8] (Fig. 4a, insert), we sought the degree of compensation of semiconductor (ratio of the structural defects of donor and acceptor nature), which will define the direction and motion rate of the Fermi level  $\varepsilon_F$ , maximally close to the activation energy  $\varepsilon_1^p(x)$ .

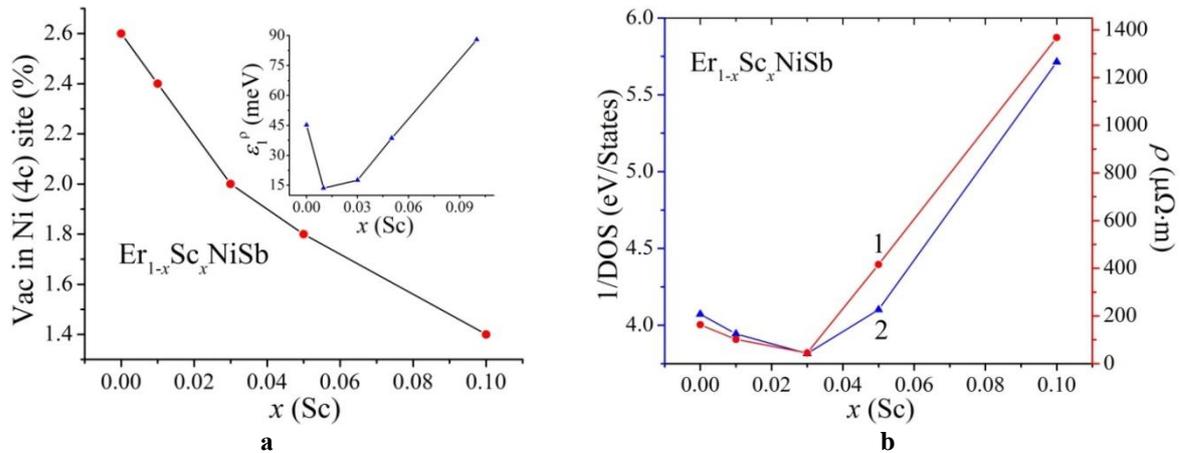
Calculations of the density distribution of electronic states DOS were performed for almost all variants of the location of atoms in the nodes of the unit cell, and the occupancy of all positions by their own and/or foreign atoms, as well as the existence of vacancies in them. It turned out that the most acceptable variant for the  $\text{ErNiSb}$  compound is one that assumes the presence of vacancies in the crystallographic positions 4a and 4c of the Er and Ni atoms, respectively. Exactly the presence of vacancies in the crystallographic positions 4a and 4c that generate structural defects of acceptor nature, which is consistent with the results of the experiment and explains the hole conductivity type of  $p\text{-ErNiSb}$  [8]. Moreover, the number of vacancies in the position Er (4a) is twice less than the number of vacancies in the Ni position (4c) (Fig. 4a). This ratio is maintained for the  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$  semiconductor,

which is also consistent with the results of the experiment [8].

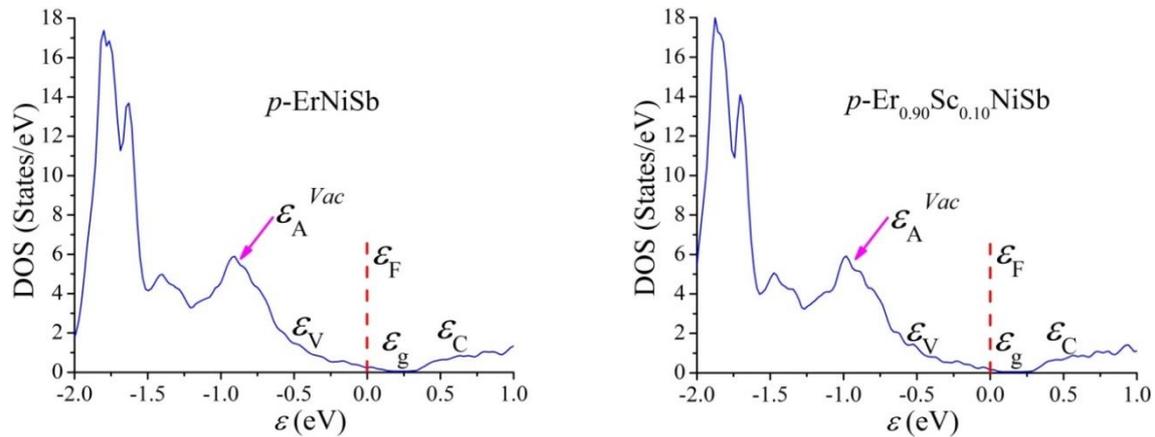
Having obtained the mechanism of generating structural defects in the  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$  semiconductor, we can model the behavior of its electrokinetic characteristics. As an example, the experimentally obtained dependence of the resistivity  $\rho(x, T)$  of  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$  [8] versus the concentration of Sc impurity atoms at  $T = 80$  K is shown in Fig. 4b (curve 1), which varies by the same law as the value of  $1/\text{DOS}(\varepsilon_F)$  (curve 2) obtained by simulation, which by its nature is proportional to the electrical resistivity ( $1/\text{DOS}(\varepsilon_F) \sim \rho$ ).

Thus, the agreement between the results of experimental studies of the electrokinetic and energetic characteristics of the  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$  semiconductor and the results of modeling these characteristics under the simultaneous existence of vacancies in the crystallographic positions of Er (4a) and Ni (4c) atoms was obtained. In addition, the number of vacancies in position 4a is twice less than the number of vacancies in position 4c.

In turn, vacancies in the crystallographic positions of Er (4a) and Ni (4c) atoms of  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$  are structural defects of acceptor nature, which generate in the semiconductor at least two acceptor bands  $\varepsilon_A^{Er}$  and  $\varepsilon_A^{Ni}$  of different capacity and location depth relative to the percolation level of the valence band  $\varepsilon_V$ . Doping  $p\text{-ErNiSb}$  by introducing into the structure of Sc impurity atoms by substitution of Er atoms in position 4a is also accompanied by the occupation of vacancies by Sc atoms and reducing their number. The Sc atom, occupying the vacancy, participates in the formation of the valence band and the conduction band of the  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$  semiconductor and now acts as a source of free electrons. We can also assume that the introduction of Sc atoms into the structure of the  $\text{ErNiSb}$  compound is accompanied by the process of ordering the structure of  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$ , and Ni atoms occupy vacancies in position 4c. This process also, however, two times slower, leads to a decrease in the concentration of structural defects of acceptor nature. In this case, Ni atoms, giving away valence electrons, now act as donors.



**Fig. 4.** Dynamics of vacancy concentration variation in position 4c of Ni atoms (a); experimental at  $T=80$  K (1) and calculated (2) variation of the electrical resistivity values (b) for  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$ . Insert in Fig. a: variation of activation energy values  $\varepsilon_1^p$  from the Fermi level  $\varepsilon_F$  to the percolation level of the valence band  $\varepsilon_V$  of  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$  [8].



**Fig. 5.** Calculated distribution of density of electronic states DOS for  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$  in the presence of vacancies in the crystallographic positions  $4a$  and  $4c$ .

As an example, the results of calculations of the density distribution of electronic states DOS for  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$  are shown in Fig. 5, which adequately reflects its compensation degree. As seen from Fig. 5, the Fermi level  $\varepsilon_F$  in  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$  at all impurity concentrations  $x$  slightly changes its location relative to the percolation level of the valence band  $\varepsilon_V$ , which corresponds to positive values of the thermopower coefficient  $\alpha(T, x)$  obtained in the experiment [8].

## Conclusions

By modeling the change of the free energy  $\Delta G(x)$  values, the energy expediency of the existence of a substitutional  $\text{Er}_{1-x}\text{Sc}_x\text{NiSb}$  solid solution up to the concentration  $x \approx 0.10$  was established. At higher Sc concentrations,  $x > 0.10$ , there is stratification (spinoidal decomposition of phase). It was shown that in the structure of the  $p\text{-ErNiSb}$  semiconductor there are vacancies in positions  $4a$  and  $4c$  of Er and Ni atoms, respectively, generating structural defects of acceptor nature. The

number of vacancies in position  $4a$  is twice less than in position  $4c$ . This proportion remains for  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$ . Doping of  $p\text{-ErNiSb}$  by Sc atoms due to substitution of Er atoms is accompanied by both replacing of Er atoms and occupying of vacancies by them in position  $4a$ . In this case, Ni atoms occupy vacancies in position  $4c$ , which can be accompanied by the process of ordering the structure of  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$ . Occupation of vacancies by Sc and Ni atoms leads to increasing the concentration of free electrons, enlarging the compensation degree of the semiconductor, which changes the position of the Fermi level  $\varepsilon_F$  and the mechanisms of electrical conductivity.

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## Моделювання структурних та енергетичних параметрів напівпровідника $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$

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Моделюванням зміни значень вільної енергії  $\Delta G(x)$  (потенціал Гельмгольца) встановлено енергетичну доцільність існування твердого розчину заміщення  $\text{Er}_{1-x}\text{Sc}_x\text{NiSb}$  до концентрації  $x \approx 0.10$ . За більших концентрацій Sc,  $x > 0.10$ , має місце розшарування (спіноїдальний розпад фази). Показано, що у структурі напівпровідника  $p\text{-ErNiSb}$  присутні вакансії у позиціях  $4a$  та  $4c$  атомів Er та Ni, відповідно, генеруючи структурні дефекти акцепторної природи. Число вакансій у позиції  $4a$  є вдвічі меншою, ніж у позиції  $4c$ . Дана пропорція збережена і для  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$ . Легування  $p\text{-ErNiSb}$  домішкою Sc шляхом заміщення атомів Er супроводжується також зайняттям ними вакансій у позиції  $4a$ . При цьому атоми Ni займають вакансії у позиції  $4c$ , що може супроводжуватися процесом упорядкування структури  $p\text{-Er}_{1-x}\text{Sc}_x\text{NiSb}$ . Зайняття атомами Sc та Ni вакансій приводить до збільшення концентрації вільних електронів, росту ступеню компенсації напівпровідника, що змінює положення рівня Фермі  $\epsilon_F$  та механізми електропровідності.

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