# MEASURING TRANSDUCERS

## RESEARCH OF THERMOMETRIC MATERIAL $Er_{1-x}Sc_xNiSb$.
## I. MODELLING OF PERFORMANCES

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**Abstract.** Automated The results of modeling performances of the semiconductor solid solution $Er_{1-x}Sc_xNiSb$ are presented, which can be a promising thermometric material for the manufacture of sensitive elements of thermoelectric and electroresistive thermocouples. Fullprof Suite software was used to model the crystallographic characteristics of the $Er_{1-x}Sc_xNiSb$ thermometric material. Modeling of the electronic structure of $Er_{1-x}Sc_xNiSb$ was performed by Coring-Kon-Rostocker methods in the approximation of coherent potential and local density using the exchange-correlation potential Moruzzi-Janak-Williams and Linear Muffin-Tin Orbital in the framework of DFT density functional theory. The Brillouin zone was divided into 1000 $k$-points, which were used to model energetic performances by calculating 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) was used in the representation of the linear MT orbital in the representation of plane waves. The accuracy of calculating the position of the Fermi level was $\varepsilon_F \pm 6$ meV.

To verify the existence of a continuous solid solution, $Er_{1-x}Sc_xNiSb$ substitution, the change in the values of the period of the unit cell $a$ ($x$) was calculated within the framework of the DFT density functional theory in the range $x = 0–1.0$. It is presented that the calculated and experimentally obtained dependences of the period of the unit cell $a(x)$ $Er_{1-x}Sc_xNiSb$ are almost parallel, which confirms the correctness of the used tools and the obtained modeling results.

To research the possibility of obtaining thermometric material $Er_{1-x}Sc_xNiSb$ in the form of a continuous solid solution was performed modeling of thermodynamic calculations in the approximation of harmonic oscillations of atoms in the theory of DFT density functional for a hypothetical solid solution $Er_{1-x}Sc_xNiSb$, $x = 0–1.0$. It is shown that the change in the values of free energy $\Delta G(x)$ (Helmholtz potential) passes through the minimum at the concentration $x \approx 0.1$ for all temperatures of possible homogenizing annealing of the samples, indicating the solubility limit of Sc atoms in the structure of the ErNiSb compound. The presence of this minimum indicates that the substitution of Er atoms for Sc atoms in the ErNiSb compound is energetically advantageous only up to the concentration of impurity atoms Sc, $x \approx 0.1$. At higher concentrations of Sc atoms, $x > 0.10$, stratification occurs (spinoidal phase decay). It is shown that modeling of the mixing entropy behavior S even at a hypothetical temperature $T = 4000$ K shows the absence of complete solubility of Sc atoms in $Er_{1-x}Sc_xNiSb$.

To model the energetic and kinetic performances of the semiconductor thermometric material $Er_{1-x}Sc_xNiSb$, particularly the behavior of the Fermi level $\varepsilon_F$ , bandgap width $\varepsilon_g$ the distribution of the density of electronic states (DOS) and the behavior of its electrical resistance $\rho(x, T)$ is calculated for an ordered variant of the structure in which the Er atoms in position 4$a$ are replaced by Sc atoms. It is shown that the ErNiSb compound is a semiconductor of the electronic conductivity type, in which the Fermi level is located near the level of the conduction band $\varepsilon_C$ . The modeling showed that at higher concentrations of Sc atoms, the number of generated acceptors exceeds the concentration of uncontrolled donors, and the concentration of free holes exceeds the concentration of electrons. Under these conditions, the Fermi level $\varepsilon_F$ approaches, and then the level of the valence band $\varepsilon_V$ $Er_{1-x}Sc_xNiSb$ crosses: the dielectric-metal conductivity transition occurs. The experiment should change the sign of the thermo-EMF coefficient $\alpha(x, T)$ $Er_{1-x}Sc_xNiSb$ from negative to positive, and the intersection of the Fermi level $\varepsilon_F$ and the valence band $\varepsilon_V$ changes the conductivity from activating to metallic: on the dependences $\ln(\rho(1/T))$ the activation sites disappear, and the values of resistivity $\rho$ increase with temperature.

**Key words:** Electric conductivity; Thermopower coefficient; Fermi level.

## 1. Introduction

A new class of thermometric materials with high efficiency of conversion of thermal energy into electric are semiconductor solid substitution solutions based on basic semiconductors RNiSb where $R$ is a rare earth metal (structural type MgAgAs, spatial group $F\bar{4}3m$ ). The combination of high values of the coefficient of thermo-EMF $\alpha$ and the specific conductivity $\sigma$ is the starting point for obtaining materials with stable and reproducible thermometric performances in the temperature range 4.2÷1073 K.

A comprehensive study of the structural, energetic, and kinetic performances of basic semiconductors RNiSb was conducted in [1]. It is found out that the crystal structure of these compounds is defective. However, the accuracy of X-ray methods of studying the structure lies outside the concentration of structural defects and does not allow the identification of them. That is why in [1] for studying the features of the structure of the LuNiSb semiconductor was used the method of optimizing the crystal structure model, the essence of which is to compare the results of calculating the density distribution of electronic states (DOS) and physical properties. After all, ***the adequacy*** of the results of DOS calculation and experimental studies of the energetic performances of the semiconductor by default assumes that the model of its crystal structure is ***adequate*** to the spatial arrangement of atoms in a real crystal. Therefore, the results of modeling the electronic structure in comparison with the results of kinetic and energetic performances allow us to obtain information about the structure, which is not available to X-ray research methods. The authors [1] proposed for the basic semiconductor LuNiSb a variant of the spatial arrangement of atoms in the unit cell, which provides for the following filling of positions: Ni (4*c*) = 92.65 % Ni + 1.35 % Lu + 6 % *Vac*; Lu (4*a*) = 100 % Lu; Sb (4*b*) = 100 % Sb. Structural defects of LuNiSb in the form of vacancies in positions 4*a* and 4*c* generate structural defects of acceptor nature.

The presence of a significant number of defects in RNiSb semiconductors causes a complex mechanism of structural changes during their doping. Thus, the authors of [1] suppose that the introduction of Zr atoms ($4d^25s^2$) into the structure of the ErNiSb compound by substituting Er atoms in position 4*a* ($5d^06s^2$) is also accompanied by the simultaneous partial occupation of the 4*c* position of Ni atoms by impurity atoms ($3d^84s^2$). As a result, the semiconductor $Er_{1–x}Zr_xNiSb$ simultaneously generates structural defects of donor nature at position 4*a* (Zr has more *d*-electrons than Er) and acceptor defects at position 4*c* (Ni has more 3*d*-electrons than Zr). In this case, the energy states of the donor and acceptor zones appear in the $Er_{1–x}Zr_xNiSb$ bandgap, which determines the conduction mechanisms.

The study of a solid solution of $Tm_{1-x}Sc_xNiSb$ in the concentration range ($x$ = 0–1) showed that the substitution of Tm atoms for Sc does not change the type of the main current carriers and the holes remain the main carriers of electricity [2]. Below we return to the analysis of the results of this work. In turn, the authors [2] found that the compound ScNiSb, which is on the opposite side of the supposedly solid solution of substitution $Tm_{1–x}Sc_xNiSb$ ($x$ = 1), is a semiconductor of the hole conductivity type, and the values of the Thermo-EMF coefficient $\alpha$ ($\alpha$ = 240 μV/K) are maximum at temperatures $T \approx 450$ K. According to the authors [2], vacancies in the Ni (4*c*) position are responsible for the hole conductivity type ScNiSb, which generate defects of acceptor nature.

The research presents the results of modeling the structural, thermodynamic, energetic, and kinetic performances of the thermometric material $Er_{1–x}Sc_xNiSb$ obtained by doping the basic semiconductor ErNiSb with Sc atoms by replacing Er atoms (4*a*). The obtained results allow us to specify the spatial arrangement of atoms (or their absence) in the units of the unit cell $Er_{1–x}Sc_xNiSb$, as well as to identify the mechanisms of electrical conductivity to determine the conditions of synthesis of thermosensitive materials with maximum efficiency of thermal energy conversion.

## 2. Disadvantages

Research of thermometric materials based on the basic semiconductor RNiSb [1] has established their high sensitivity to heat treatment (temperature and duration of annealing).

## 3. Research Objective

To establish the mechanism of formation of structural defects in the thermometric material $Er_{1-x}Sc_xNiSb$, which allows to identify the mechanisms of electrical conductivity and determine the conditions of their synthesis to obtain maximum efficiency of conversion of thermal energy into electricity.

## 4. Research Methods

Simulation of the crystallographic characteristics of the thermometric material $Er_{1–x}Sc_xNiSb$ was performed using the program Fullprof Suite [3]. Modeling of the electronic structure of $Er_{1–x}Sc_xNiSb$ was performed by Coring-Kon-Rostocker (KKR) methods in the approximation of coherent potential (CPA) and local density (LDA) [4] using the exchange-correlation potential of Moruzzi-Janak-Williams [5] and LMTO Line Muffin-Tin Orbital) in the framework of the theory of DFT density functional. The Brillouin zone was divided into 1000 *k*-points, which were used to model energetic performances by calculating 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) was used in the representation of the linear MT orbital in the representation of plane waves. The LDA approximation with MJW parameterization was also used as the exchange-correlation potential. The accuracy of calculating the position of the Fermi level $\varepsilon_F \pm 6$ meV.

## 5. Modeling of structural performances of thermometric material $Er_{1-x}Sc_xNiSb$

To test the existence of a continuous solid solution of $Er_{1–x}Sc_xNiSb$ substitution (ScNiSb compound also crystallizes in *CT* MgAgAs), the change in the values of the unit cell period $a(x)$ was calculated within the framework of the DFT density functional theory in the range $x$ = 0–1.0 (Fig. 1, curve 1). For comparison with the calculated values of the period $a(x)$ in Fig. 1, curve 2, the experimental results of the values of the cell period *a* for ErNiSb and ScNiSb semiconductors, taken in [1, 2], are also presented. We can see that the calculated and experimentally obtained dependences of the period of the unit cell $a(x)$ $Er_{1-x}Sc_xNiSb$ are almost parallel, which confirms the correctness of the tools used and the obtained simulation results.

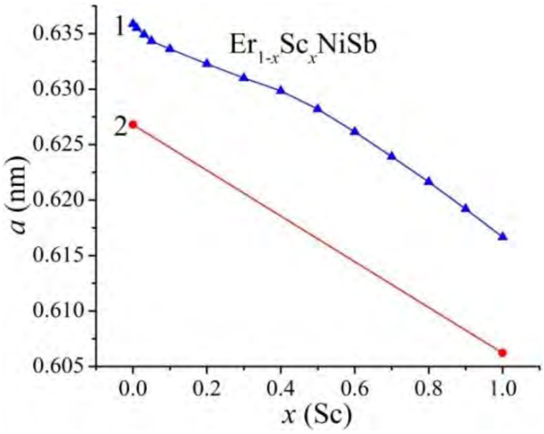


*Fig. 1. Changing the values of the period of the unit cell of the thermometric material* $Er_{1-x}Sc_xNiSb$*: 1 – calculated, 2 – from [1, 2]*

The question may arise, why parallel dependences $a(x)$ $Er_{1-x}Sc_xNiSb$, and not coinciding?

The fact is that the simulation of the change in the values of the period $a(x)$ $Er_{1-x}Sc_xNiSb$ (Fig. 1, curve 1) is carried out for an ordered variant of the structure for 100 % occupation of the atoms of their crystallographic positions. Instead, the results of previous studies of ErNiSb and ScNiSb compounds [1, 2] showed the existence of a significant number of vacancies in many crystallographic positions, which significantly deforms the structure and reduces the interatomic distances in the real crystal. For this reason, in Fig. 1 there is no coincidence of the calculated and experimentally obtained dependences $a(x)$ $Er_{1-x}Sc_xNiSb$.

The formation of the semiconductor thermometric material $Er_{1-x}Sc_xNiSb$ by substituting Er atoms at position 4*a* for Sc is accompanied by changes in both the crystal structure and the electron structure. After all, the introduction of Sc atoms ($3d^14s^2$) into the structure of the ErNiSb compound by substituting Er atoms in position 4*a* is first accompanied by the occupation of existing vacancies in this position by Sc atoms. This will reduce the number of vacancies and structural defects of acceptor nature, which will significantly change the electronic structure of the semiconductor. On the other hand, the substitution of Er atoms ($5d^06s^2$) for Sc ($3d^14s^2$) should generate structural defects of donor nature, because the Sc atom contains more *d*-electrons on the outer electron 3*d*-shell than the Er atom.

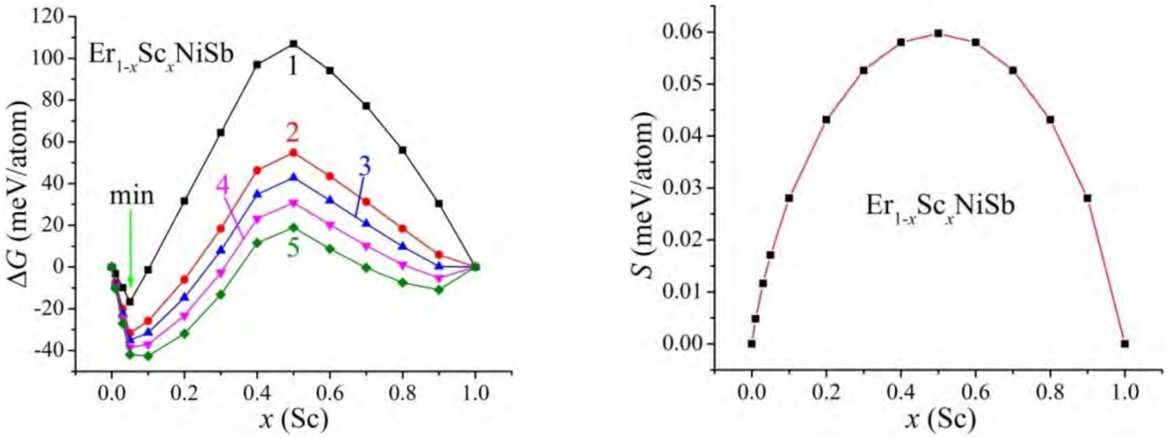
Therefore, the results of modeling the structural performances of the semiconductor thermometric material $Er_{1-x}Sc_xNiSb$ suggest the orderliness of its crystal structure.

## 6. Modeling of thermodynamic performances of thermometric material $Er_{1-x}Sc_xNiSb$

*A priori*, based on the assumption that ErNiSb and ScNiSb compounds crystallize in the same structural type of MgAgAs, it was suggested that there may be a continuous solid solution of $Er_{1-x}Sc_xNiSb$ (100 % substitution in the structure of compounds of Er atoms on Sc and vice versa). Indirectly, the possibility of the existence of a continuous solid solution of $Er_{1-x}Sc_xNiSb$ was indicated by a rather smooth change in the calculated values of the period of the unit cell $a(x)$ (Fig. 1). After all, the ability to synthesize a continuous solid solution of $Er_{1-x}Sc_xNiSb$ allows obtaining a wide range of thermometric materials with a smooth and predictable change in its kinetic performances.

For investigation of the possibility of obtaining thermometric material $Er_{1-x}Sc_xNiSb$ in the form of a continuous solid solution, modeling of thermodynamic calculations in the approximation of harmonic oscillations of atoms within the theory of DFT density functional for a hypothetical solid solution $Er_{1-x}Sc_xNiSb$, $x = 0 – 1.0$ was performed (Fig. 2, *a*). We can see that the change in the values of free energy $\Delta G(x)$ (Helmholtz potential) passes through the minimum at a concentration of $x \approx 0.1$ for all temperatures of possible homogenizing annealing of the samples, indicating the solubility limit of Sc atoms in the structure of the ErNiSb compound. The presence of this minimum indicates that the substitution of Er atoms for Sc atoms in the ErNiSb compound is energetically advantageous only up to the concentration of impurity atoms Sc, $x \approx 0.1$.

Therefore, the results of modeling the behavior of the Gibbs thermodynamic potential $\Delta G(x)$ $Er_{1-x}Sc_xNiSb$ suggest that there is no unlimited solubility of Sc atoms in the structure of the basic semiconductor ErNiSb, and the concentration of impurity atoms Sc, $x \approx 0.1$, is the limit of the existence of solid solution substitution when Sc atoms occupy the crystallographic position 4*a*. At higher concentrations of Sc atoms, $x > 0.10$, stratification occurs (spinoidal phase decay). In this case, experimental studies of the distribution of components, chemical, and phase compositions of the samples indicate the alleged existence of a solid solution, but this statement will be false. Interestingly, the simulations of the mixing entropy behavior S (Fig. 2, *b*) even at a hypothetical temperature $T = 4000$ K show the absence of complete solubility of Sc atoms in $Er_{1-x}Sc_xNiSb$.



*a* *b*

*Fig. 2. Change in the values of the Gibbs thermodynamic potential ΔG (x) at different temperatures: 1 – T = 0 K, 2 – T = 873 K, 3 – T = 1073 K, 4 – T = 1273 K, 5 – T = 1473 K (a) and the entropy of mixing of S components (b) in* $Er_{1-x}Sc_xNiSb$

In this context, it is advisable to return to the results of experimental studies of such a semiconductor solid solution $Tm_{1-x}Sc_xNiSb$ [2]. It seems to us that the lack of thermodynamic studies of the related solid solution $Tm_{1-x}Sc_xNiSb$ did not allow the authors [2] to correctly position the objects of study. Aiming to obtain a thermoelectric material with high values of thermoelectric figure of merit $Z$ ($Z = \alpha^2 \cdot \sigma/\kappa$, where $\alpha$ is the coefficient Thermo-EMF, $\sigma$ is the specific electrical conductivity, $\kappa$ is the coefficient of thermal conductivity) in [2] partially achieved this goal in samples $Tm_{1-x}Sc_xNiSb$, $x \geq 0.25$, reducing the value of the thermal conductivity $\kappa$. However, the case of $Tm_{1-x}Sc_xNiSb$, $x \geq 0.25$, is very similar to the method of obtaining thermoelectric materials by pressing and sintering the powder, when the values $\kappa$ also decrease $Tm_{1-x}Sc_xNiSb$, $x \geq 0.25$, which leads to an increase in the thermoelectric factor Z. However, these are completely different stories that have nothing to do with *solid substitution solution.*

## 7. Modeling of energetic and kinetic performances of thermometric material $Er_{1-x}Sc_xNiSb$

For modeling the energetic and kinetic performances of the semiconductor thermometric material $Er_{1-x}Sc_xNiSb$, particularly the behavior of the Fermi level $\varepsilon_F$, the bandgap $\varepsilon_g$, the distribution of the density of electronic states (DOS) was calculated (Fig. 3) and the behavior of its electrical resistance $\rho(x, T)$. For an ordered variant of the structure in which the Er atoms in position 4*a* are replaced by Sc atoms. As can be seen from Fig. 3, the ErNiSb compound is a semiconductor of the electronic conductivity type, in which the Fermi level $\varepsilon_F$ (dotted line) is located near the level of the conduction band $\varepsilon_C$.

The obtained result of modeling the electronic structure of the basic semiconductor ErNiSb does not agree with the results of experimental studies [1] when positive values of the Thermo-EMF coefficient $\alpha(T)$ were obtained at all investigated temperatures. The question may arise as to the correctness of the method used to model the electronic structure of the semiconductor when in the calculations, we took into account only the outer electronic shells of all atoms of solid solution $Er_{1-x}Sc_xNiSb$, as well as the results of experimental studies [1]. After all, thermometric materials based on basic RNiSb semiconductors have a high sensitivity to heat treatment modes (temperature and duration of annealing). On the other hand, the inconsistency of the results of experimental studies of the basic ErNiSb semiconductor and modeling of the electronic structure may be caused by the disorder of its crystal structure, when partial atoms of non-crystallographic positions are possible. According to the obtained result, this issue requires additional experimental and theoretical studies.

At higher concentrations of Sc atoms, the number of generated acceptors exceeds the concentration of uncontrolled donors, and the concentration of free holes exceeds the concentration of electrons. Under these conditions, the Fermi level $\varepsilon_F$ approaches, and then the level of the valence band $\varepsilon_V$ $Er_{1-x}Sc_xNiSb$ crosses: the dielectric-metal conductivity transition occurs. The experiment should change the sign of the Thermo-EMF coefficient $\alpha(x, T)$ $Er_{1-x}Sc_xNiSb$ from negative to positive, and the intersection of the Fermi level and the valence band $\varepsilon_V$ changes the conductivity from activation to metallic: on the dependences $\ln(\rho(1/T))$ the activation sites disappear, and the values of resistivity $\rho$ will increase with temperature. The results of kinetic and energetic studies of $Er_{1-x}Sc_xNiSb$ show the correspondence of these calculations to real processes in the semiconductor.

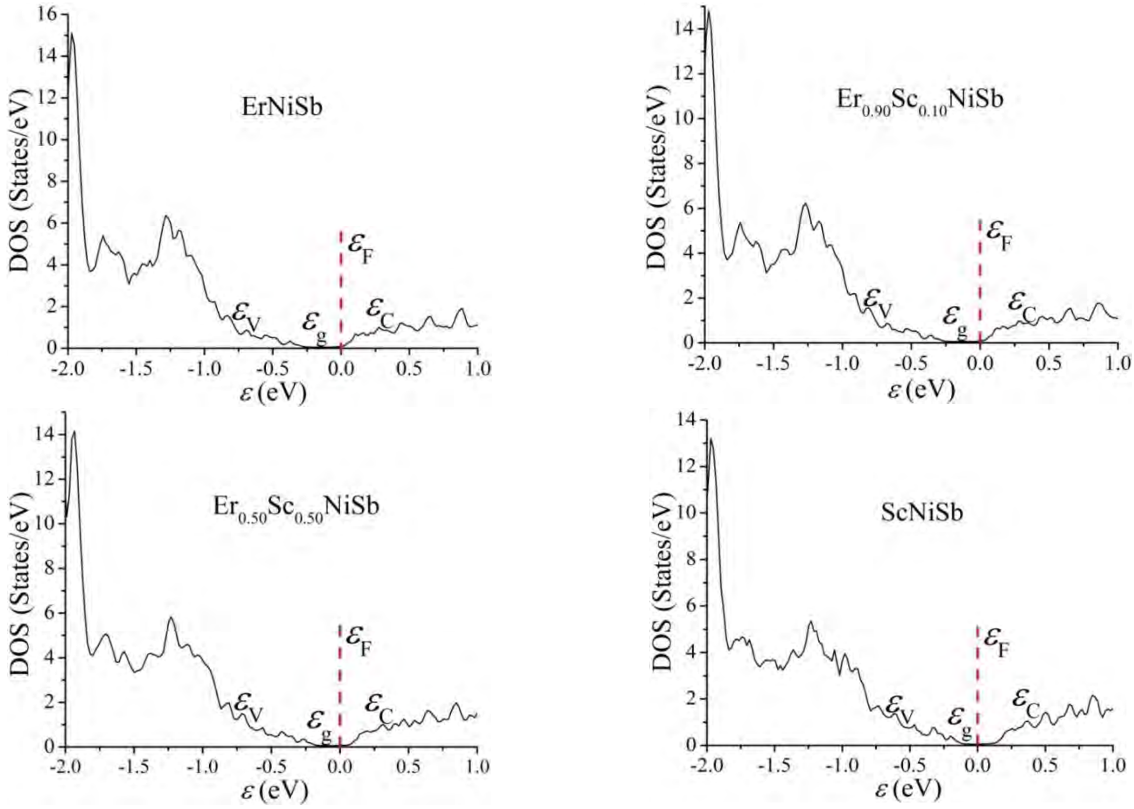


*Fig. 3. Calculation of the density distribution of electronic states DOS* $Er_{1-x}Sc_xNiSb$ *for an ordered variant of the structure*

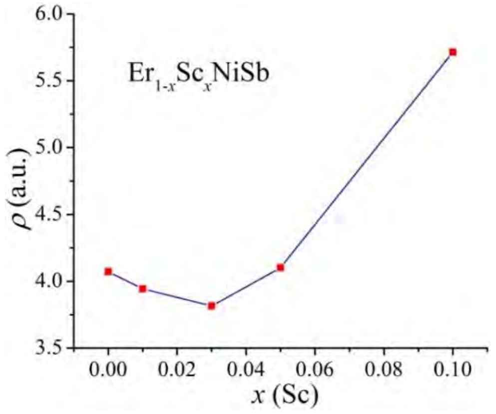


*Fig. 4. Calculation of change of values resistivity* $\rho$ $Er_{1-x}Sc_xNiSb$

As can be seen from Fig. 3, the substitution of Er atoms for Sc generates structural defects of acceptor nature in the semiconductor, and even at the lowest concentrations of impurity Sc atoms the Fermi level $\varepsilon_F$ begins to drift from the conduction band $\varepsilon_C$ to the depth of the bandgap $\varepsilon_g$. In a hypothetical semiconductor with the composition $Er_{0.50}Sc_{0.50}NiSb$, the Fermi level $\varepsilon_F$ is located near the middle of the bandgap $\varepsilon_g$, indicating its maximum compensation when the concentrations of ionized acceptors and donors are close. In the experiment, the approximation of the Fermi level $\varepsilon_F$ to the middle of the bandgap $\varepsilon_g$ should be accompanied by a sharp increase in the values of resistivity $\rho(x, T)$ $Er_{1-x}Sc_xNiSb$, as the number of free electrons decreases due to their capture by acceptors.

Calculating the electronic structure of the thermometric material $Er_{1-x}Sc_xNiSb$, we can also provide modeling the behavior of its electrical resistance $\rho(x, T)$ (Fig. 4), since the values of $\rho(x, T)$~1/DOS. We can see that at the concentration of impurity atoms Sc, $x > 0.03$, the values of electrical resistance increase rapidly, which can be used for the manufacture of electro resistive means of temperature measurement.

## 8. Conclusions

Modeling of structural, thermodynamic, energetic, and kinetic performances of thermosensitive material $Er_{1-x}Sc_xNiSb$ for the case of ordered crystal structure showed that in the semiconductor are generated as structural defects of acceptor nature, the concentration of which increases with increasing content of Sc atoms. The investigated $Er_{1-x}Sc_xNiSb$ solid solution is a promising thermometric material but requires detailed experimental studies, which is the subject of our next work.

## 9. Gratitude

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## 10. Conflict of interests

The authors declare that there is no financial or other possible conflict related to this work.

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