CHARACTERISTICS OF THERMOMETRIC MATERIAL $Lu_{1-x}Sc_xNiSb$

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Abstract. The results of modeling the properties of the semiconductor solid solution $Lu_{1-x}Sc_xNiSb$, x=0–0.10, which is a promising thermometric material for the manufacture of sensitive elements of thermocouples, are presented. Modeling of the electronic structure of $Lu_{1-x}Sc_xNiSb$ was performed by the Korringa-Kohn-Rostoker (KKR) method in the approximation of coherent potential and local density and by the full-potential method of linearized plane waves (FLAPW). KKR simulations were performed using the AkaiKKR software package in the local density approximation for the exchange-correlation potential with parameterization Moruzzi, Janak, Williams. The Elk software package was used in the FLAPW calculations.

To check the limits of the existence of the thermometric material $Lu_{1-x}Sc_xNiSb$ by the KKR method, the change of the values of the period of the unit cell $a(x)$ in the range x=0–0.10 was calculated. It is established that the substitution of Lu atoms in the crystallographic position 4*a* by Sc atoms is accompanied by a decrease in the values of the unit cell period $a(x)$ $Lu_{1-x}Sc_xNiSb$. This behavior of $a(x)$ $Lu_{1-x}Sc_xNiSb$ is since the atomic radius Sc (r_{Sc}=0.164 nm) is smaller than that of Lu (r_{Lu}=0.173 nm). In this case, structural defects of neutral nature are generated in $Lu_{1-x}Sc_xNiSb$, because the atoms Lu ($5d^16s^2$) and Sc ($3d^14s^2$) are located in the same group of the Periodic Table of the Elements and contain the same number of *d*-electrons.

To study the conditions for obtaining thermometric material $Lu_{1-x}Sc_xNiSb$, x=0–0.10, and to establish the energy feasibility of its formation in the form of a continuous solid solution, modeling of thermodynamic characteristics in the approximation of harmonic oscillations of atoms within the DFT density functional theory. The low values of the enthalpy of mixing $\Delta H_{mix}(x)$ and the nature of the dependence behavior indicate the energy expediency of substitution in the crystallographic position 4*a* of Lu atoms for Sc atoms and the existence of a solid substitution solution for the studied samples $Lu_{1-x}Sc_xNiSb$, x=0–0.10.

To understand the mechanisms of electrical conductivity of the thermometric material $Lu_{1-x}Sc_xNiSb$, x=0–0.10, various models of crystal and electronic structures of the basic semiconductor LuNiSb are considered. Assuming that the crystal structure of $Lu_{1-x}Sc_xNiSb$ is ordered (crystallographic positions are occupied by atoms according to the MgAgAs structural type), the Elk software package was used to model the DOS electronic state density distribution for LuNiSb and $Lu_{0.875}Sc_{0.125}NiSb$. It is shown that in the LuNiSb compound the Fermi level ε_F lies in the middle of the band gap ε_g, and the bandwidth is ε_g=190.5 meV. DOS simulations for the ordered variant of the $Lu_{0.875}Sc_{0.125}NiSb$ crystal structure show a redistribution of the density of DOS electronic states and an increase in the band gap ε_g. In this case, the Fermi level ε_F, as in the case of LuNiSb, lies in the middle of the band gap ε_g, and the generated structural defects are neutral.

The DOS calculation for the disordered variant of the crystal structure of the LuNiSb compound was performed using a model that can be described by the formula $Lu_{1+y}Ni_{1-2y}Sb$. In this model, the Lu atoms partially move to the 4*c* position of the Ni atoms, and in this position, a vacancy (y) occurs simultaneously. Moreover, as many Lu atoms additionally move to the 4*c* position of Ni atoms, so many vacancies arise in this position. In this model of the crystal structure of the LuNiSb compound and the absence of vacancies (y=0), the calculation of the DOS electronic state density distribution indicates the presence of the band gap ε_g, and the Fermi level ε_F lies near the valence band ε_V. In the model of the structure of the LuNiSb compound at vacancy concentrations y=0.01, the DOS calculation also shows the presence of the band gap ε_g, and the Fermi level ε_F still lies near the valence band ε_V. Since Ni atoms make the greatest contribution to the formation of the conduction band ε_C, even at a concentration of y=0.02, the DOS calculation shows that the Fermi level ε_F now lies near the conduction band ε_C. This means that the main carriers of the electric current of the LuNiSb compound at y=0.02 are electrons, which does not correspond to the results of experimental studies.

Based on the above model of the disordered crystal structure of the LuNiSb compound, the density distribution of DOS electronic states was calculated for the disordered variant of the crystal structure of the thermometric material $Lu_{1-x}Sc_xNiSb$, which is described by the formula $Lu_{1-x+y}Sc_xNi_{1-2y}Sb$. In this model of the $Lu_{1-x}Sc_xNiSb$ crystal structure, the calculation of the DOS electronic state density distribution shows the presence of a band gap ε_g, in which small energy levels ("tail tails") are formed, which overlap with the zones of continuous energies. In this case, the Fermi level ε_F is localized at low energy levels, which makes it impossible to accurately determine the depth from the Fermi level ε_F. The proposed model is correct only for a small number of impurity Sc atoms since the partial occupation of the 4*c* position of Ni atoms by Lu atoms significantly deforms the structure with its subsequent decay. The results of experimental studies of the kinetic, energy, and magnetic properties of the thermometric material $Lu_{1-x}Sc_xNiSb$ will show the degree of adequacy of the proposed model.

Key words. Electric conductivity, Thermopower coefficient, Fermi level.

1. Introduction

In [1–5], a study of a new class of semiconductor thermoelectric materials based on RNiSb compounds (R – Y, Gd–Lu), which have high efficiency in converting thermal energy into electricity, was initiated. Interest in thermometric materials based on RNiSb is due to both high and reproducible values of the thermopower coefficient $\alpha(T)$ and electrical resistance $\rho(T)$ in a wide temperature range. This is what makes these materials one of the most promising and researched.

Thermoelectric materials based on RNiSb compounds (R – Er, Lu) [4, 5] were obtained by doping with Zr or Sc atoms by substituting rare earth metal atoms in the crystallographic position 4*a*. This was accompanied by the generation of structural defects of the donor or neutral nature, which allowed for optimizing the values of the thermopower coefficient $\alpha(T,x)$, thermal conductivity $\kappa(T,x)$, and specific conductivity $\sigma(T,x)$. Thus, doping (Er, Lu) of NiSb with Zr atoms ($4d^2 5s^2$) [4, 5] led to the following changes in crystal and electronic structures:

– substitution at position 4*a* of Er or Lu atoms for Zr atoms generates structural defects of donor nature because Zr has a larger number of *d*-electrons than, for example, the Lu atom ($5d^1 6s^2$). In this case, an impurity donor zone $\varepsilon_D{}^1$ appears in the band gap ε_g;

– occupation of vacancies in position 4*a* by Zr atoms simultaneously eliminates structural defects of acceptor nature and generates defects of donor nature and donor zone $\varepsilon_D{}^2$.

In the case of doping ErNiSb with Sc atoms ($3d^1 4s^2$), no donor level was formed in the $Er_{1-x}Sc_xNiSb$ semiconductor, because Er and Sc atoms are located in the same group of the Periodic Table of the Elements. Instead, the occupation of vacancies by Sc atoms in position 4*a* creates defects of donor nature with the appearance of an impurity donor zone $\varepsilon_D{}^2$ in the band gap ε_g.

The paper presents the results of modeling the structural, thermodynamic, and energy characteristics of the thermometric material $Lu_{1-x}Sc_xNiSb$ obtained by doping the basic semiconductor LuNiSb with Sc atoms by substituting Lu atoms. The obtained results will allow to clarify the spatial arrangement of atoms in the units of the unit cell, as well as to identify the mechanisms of electrical conductivity to determine the conditions for the synthesis of thermosensitive materials with maximum efficiency of thermal energy conversion into electricity. In addition, the process of optimizing the characteristics of thermometric materials $Lu_{1-x}Sc_xNiSb$ will be predictable.

2. Disadvantages

Studies of thermometric materials based on the basic semiconductor RNiSb have established their high sensitivity to heat treatment (temperature and duration of annealing).

3. Aim of the Work

To establish the mechanism of formation of structural defects in the thermometric material $Lu_{1-x}Sc_xNiSb$, x=0–0.10, which will identify the mechanisms of electrical conductivity and determine the conditions of their synthesis with the maximum values of electrical resistance and thermopower coefficient.

4. Research methods

Calculations of the electronic structure, density of states (DOS), electron localization function (ELF), thermodynamic characteristics, and optimization of the crystal structure parameters of the $Lu_{1-x}Sc_xNiSb$, x=0–0.10, thermometric material were performed using the Korringa-Kohn-Rostoker (KKR) method in the Coherent Potential Approximation (CPA) and Local Density Approximation (LDA) approximation, as well as the full potential method of linearized plane waves (FLAPW). KKR simulations were performed using AkaiKKR software packages [6] in the local density approximation for the exchange-correlation potential with parameterization Moruzzi, Janak, Williams [7]. Elk software package was used for FLAPW modeling [8]. The simulation was performed for a 10×10×10 *k*-grid in both the LDA and generalized gradient (GGA) approximations. The Brillouin zone was divided into 1000 *k*-points, which were used both to calculate the Bloch spectral function (band energy spectrum) and the density of electronic states.

5. Modeling of structural and thermodynamic characteristics of $Lu_{1-x}Sc_xNiSb$

Simulation of the change in the values of the period of the unit cell $a(x)$ of the thermometric material $Lu_{1-x}Sc_xNiSb$, x=0–0.10, was performed by the KKR method (software package AkaiKKR [6]) and allows to predict changes in its electronic structure. After all, the behavior of the kinetic characteristics of the thermometric material $Lu_{1-x}Sc_xNiSb$ (specific resistivity and thermopower coefficient) is determined by its electronic structure. In addition, this simulation shows the solubility limits of Sc atoms in the matrix of the basic semiconductor LuNiSb, which allows us to estimate the concentration of generated acceptors and donors in $Lu_{1-x}Sc_xNiSb$, as well as to establish the mechanism of electrical conductivity.

As the simulation results show, the substitution of Lu atoms in the crystallographic position 4*a* by Sc atoms is accompanied by a decrease in the values of the period of the unit cell $a(x)$ $Lu_{1-x}Sc_xNiSb$ at concentrations x=0–0.10 (Fig. 1, curve 1). The obtained result is understandable because the atomic radius Sc (r_{Sc}=0.164 nm) is smaller than that of Lu (r_{Lu}=0.173 nm). In this case, structural defects of neutral nature are generated in the semiconductor thermometric material $Lu_{1-x}Sc_xNiSb$, because the atoms Lu ($5d^1 6s^2$) and Sc ($3d^1 4s^2$) are located in the same group of the Periodic Table of the Elements and contain the same number of external *d*-electrons.

Modeling of thermodynamic characteristics for the thermometric material $Lu_{1-x}Sc_xNiSb$, x=0–0.10, in the approximation of harmonic oscillations of atoms in the framework of the DFT density functional theory allows establishing the energy feasibility of the existence of a solid substitution solution. In Fig. 1, curve 2, the results of modeling by the KKR method of the change in the enthalpy of mixing $\Delta H_{mix}(x)$ $Lu_{1-x}Sc_xNiSb$, x=0–0.10, are given. The nature of the dependence behavior and low values of the enthalpy of mixing $\Delta H_{mix}(x)$ show the energy feasibility of the existence of a solid substitution solution for the studied samples $Lu_{1-x}Sc_xNiSb$, x=0–0.10.

Thus, the results of modeling the period of the unit cell a(x) and the enthalpy of mixing $\Delta H_{mix}(x)$ of the thermometric material $Lu_{1-x}Sc_xNiSb$, x=0–0.10, allow us

to assert the energy expediency of substituting Lu atoms for Sc atoms in the crystallographic position 4*a*.

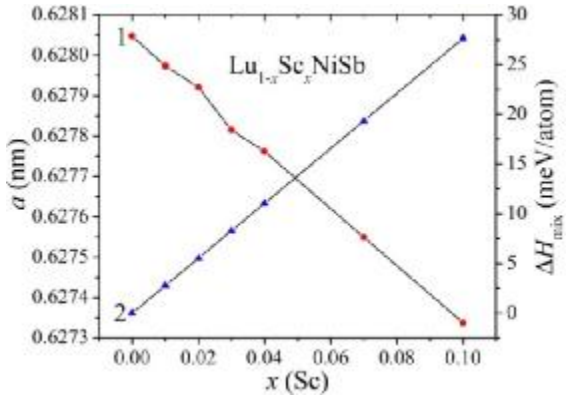

Fig. 1. Simulation by the AkaiKKR method of changes in the values of the period of the unit cell a(x) (1) and the enthalpy of mixing ΔH_{mix} (2) of the thermometric material $Lu_{1-x}Sc_xNiSb$

6. Modeling of energy characteristics of $Lu_{1-x}Sc_xNiSb$

Important parameters characterizing the results of doping the basic semiconductor LuNiSb with Sc atoms to obtain the thermometric material $Lu_{1-x}Sc_xNiSb$ are the behavior of the Fermi level ε_F, the band gap ε_g and the zones of continuous energies. Assuming that the crystal structure of $Lu_{1-x}Sc_xNiSb$ is ordered (crystallographic positions are occupied by atoms following the structural type of MgAgAs [1]), using the Elk software package [8], the DOS electronic state density distribution was modeled. (Fig.2), as an example, shows the results of DOS modeling for the basic semiconductor LuNiSb and thermometric material $Lu_{0.875}Sc_{0.125}NiSb$.

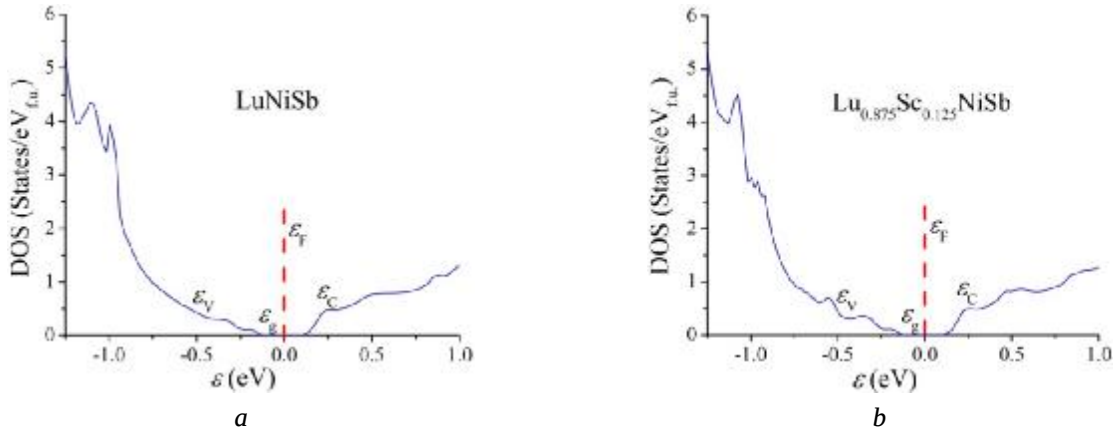

*Fig. 2. Simulation of the density distribution of DOS electronic states for the ordered variant of the crystal structure LuNiSb **(a)** and $Lu_{0.875}Sc_{0.125}NiSb$ **(b)***

From Fig. 2*a* we can see that in LuNiSb the Fermi level ε_F (dotted line) lies in the middle of the band gap ε_g, and its width is ε_g=190.5 meV. This Fermi level ε_F the arrangement is characteristic of intrinsic semiconductors [9]. The results of DOS modeling for the ordered variant of the crystal structure $Lu_{0.875}Sc_{0.125}NiSb$ show the redistribution of the density of electronic DOS states (Fig. 2*b*) and the increase in the band gap ε_g. In this case, the Fermi level ε_F, as in the case of LuNiSb, lies in the middle of the band gap ε_g, and the generated structural defects are neutral because the atoms Lu and Sc are located in the same group of the Periodic Table of the Elements.

On the other hand, the results of experimental studies of LuNiSb [5] showed that this compound is a semiconductor of the hole-type conductivity, and the main carriers of electric current are free holes. In this case, the Fermi level ε_F is located near the valence band ε_V. Therefore, the DOS modeling for the ordered variant of the LuNiSb and $Lu_{0.875}Sc_{0.125}NiSb$ structure does not correspond to the results of the experiment. In this context, we can note that the results of electrokinetic studies of LuNiSb [5] formed the basis of the model of its crystal structure, the essence of which is the presence of vacancies in positions 4*a* and 4*c* of Lu and Ni atoms.

The discrepancy between the results of experimental LuNiSb studies and the modeling of the electronic structure for the ordered model of its crystal structure indicates its disorder. Thus, in the crystal structure of the LuNiSb compound, there is a partial occupation of atoms of foreign positions, and it is also possible to have vacancies in different crystallographic positions. After all, in the case of doping LuNiSb with impurities, the degree of occupancy of the crystallographic positions of atoms will determine the mechanism of generating structural defects and energy levels in the band gap ε_g.

The DOS calculation for the disordered variant of the crystal structure of the LuNiSb compound was performed using the model we proposed in the DOS calculations for the YNiSb compound [4]. A model of the structure of the LuNiSb compound, which can be

described by the formula $Lu_{1+y}Ni_{1-2y}Sb$, is considered. In this model, the Lu atoms partially move to the 4*c* position of the Ni atoms, and in this position, a vacancy (*y*) occurs simultaneously. Moreover, as many Lu atoms additionally move to the 4*c* position of Ni atoms, so many vacancies arise in this position. That is, if the atoms of Lu at the amount of *y*=0.01 move to the position 4*c* of the atoms of Ni, then there are additional vacancies with a concentration of 0.01. Therefore, in position 4c of Ni atoms is Ni – 0.98, Lu – *y*=0.01, Vac – *y*=0.01.

In this model of the crystal structure of the LuNiSb compound, in the absence of vacancies (*y*=0), the calculation of the DOS electronic state density distribution shows the presence of the band gap ε_g, and the Fermi level ε_F lies near the valence band ε_V (Fig. 3). Under such conditions, we obtain positive values of the thermopower coefficient $\alpha(T,x)$ LuNiSb at all investigated temperatures.

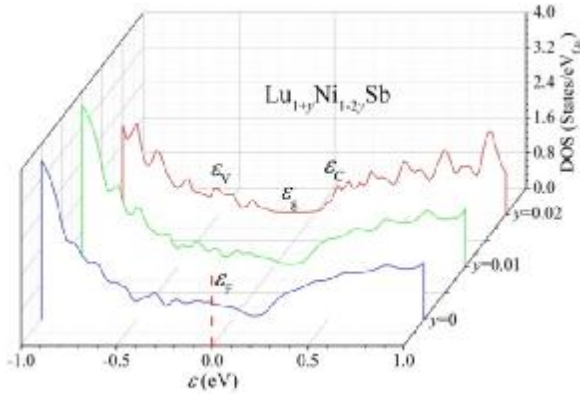

Fig. 3. Calculation of the density distribution of electronic states of DOS for the disordered variant of the crystal structure of the basic semiconductor LuNiSb

In the model of the structure of the LuNiSb compound at vacancy concentrations *y*=0.01, the DOS calculation also shows the presence of the band gap ε_g, and the Fermi level ε_F still lies near the valence band ε_V (Fig. 3). Since Ni atoms make the greatest contribution to the formation of the conduction band ε_C, even at concentration *y*=0.02 the DOS calculation shows (Fig. 3) that the Fermi level ε_F now lies near the conduction band ε_C. This means that the main carriers of the electric current of the compound LuNiSb are electrons, which does not correspond to the results of experimental studies [5].

Based on the model of the crystal structure of the LuNiSb compound considered above, the density distribution of DOS electronic states was calculated for the disordered variant of the crystal structure of the $Lu_{1-x}Sc_xNiSb$ thermometric material (Fig. 4). A model of the structure of a semiconductor solid solution $Lu_{1-x+y}Sc_xNi_{1-2y}Sb$ is considered, in which at position 4*a* the Lu atoms are replaced by Sc atoms. In addition, the Lu atoms partially move to the 4*c* position of the Ni atoms, and in this position, a vacancy (*y*) arises at the same time. Moreover, as many Lu atoms additionally move to the 4*c* position of Ni atoms, so many vacancies arise in this position. In this model of the crystal structure of the thermometric material $Lu_{1-x}Sc_xNiSb$, the calculation of the density distribution of the electronic states of DOS shows the presence of the band gap ε_g. At the same time there is a large number of structural defects of donor and acceptor nature, in particular:

– substitution at position 4*a* of Lu atoms for Sc atoms generates defects of neutral nature because Lu and Sc atoms contain the same number of external *d*-electrons;

– occupation of vacancies in position 4*a* by Sc atoms simultaneously eliminates in the forbidden zone ε_g the structural defect of acceptor nature and the corresponding acceptor zone. This creates structural defects in the donor nature and the corresponding donor zone.

– occupation of vacancies by Sc atoms in position 4*c* of Ni atoms simultaneously eliminates structural defects of acceptor nature and the corresponding acceptor zone, and in the forbidden zone ε_g a structural defect of donor nature is formed and a donor zone appears.

Thus, in the band gap ε_g $Lu_{1-x}Sc_xNiSb$, small energy levels ("tail tails") are formed, which overlap with the zones of continuous energies. This makes it difficult to determine the actual band gap ε_g. The Fermi level ε_F is localized at low energy levels, which makes it impossible to determine the depth from the Fermi level ε_F (activation energy of holes from the Fermi level ε_F to the valence band ε_V).

This model is correct only for a small number of impurity atoms Sc because even partial occupation of the position 4*c* of Ni atoms by Lu atoms significantly deforms the structure with its subsequent decay. The disadvantage of this model is also the generation of a significant number of energy levels in the band gap ε_g, which intersect with the zones of continuous energies and fix the Fermi level ε_F. This makes it difficult to determine the actual band gap ε_g.

The results of experimental studies of the kinetic, energy, and magnetic properties of the thermometric material $Lu_{1-x}Sc_xNiSb$ will show the degree of adequacy of the proposed disordered model of the crystal structure to the real structure of the semiconductor. However, this is the task of the next study.

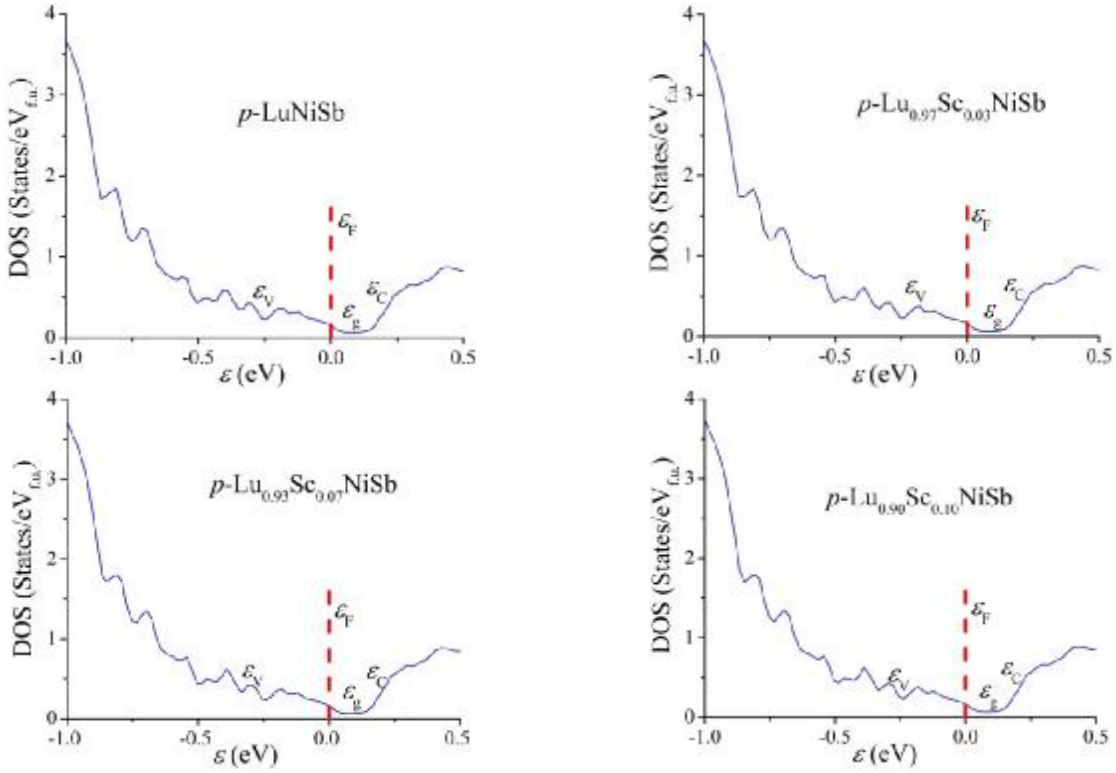

Fig. 4. Simulation of the density distribution of electronic states of DOS for the disordered variant of the crystal structure $Lu_{1-x}Sc_xNiSb$

7. Conclusions

As a result of modeling the structural, thermodynamic, and energy properties of the $Lu_{1-x}Sc_xNiSb$ thermometric material obtained by doping the LuNiSb compound with Sc atoms by substituting Lu atoms in the crystallographic position 4*a*, the complex nature of structural changes was established. It is shown that, depending on the concentration of Sc atoms, they can occupy different crystallographic positions in the $Lu_{1-x}Sc_xNiSb$ semiconductor matrix, which leads to different rates of generation of structural defects of acceptor and donor nature. The ratio of the concentrations of the existing defects of donor and acceptor nature determines the position of the Fermi level ε_F and the conduction mechanisms in $Lu_{1-x}Sc_xNiSb$. The investigated solid solution $Lu_{1-x}Sc_xNiSb$ is a promising thermometric material.

8. Gratitude

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9. Conflict of interest

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

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