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Peculiarities of structural, electrokinetic, energetic, and magnetic properties semiconductive solid solution $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$

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The structural, electrokinetic, energetic, and magnetic properties of the new semiconductive solid solution $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$, $x=0-0.10$, were studied. It was shown that V atoms could simultaneously occupy different crystallographic positions in different ratios, generating structural defects of acceptor and donor nature. This creates corresponding acceptor and donor bands in the bandgap ε_g of $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$. The mechanism of the formation of two acceptor bands with different depths of occurrence has been established: a small acceptor band ε_A^2 , formed by defects due to the substitution of Ni atoms by V ones in the 4c position, and band ε_A^1 , generated by vacancies in the LuNiSb structure. The ratio of the concentrations of generated defects determines the position of the Fermi level ε_F and the conduction mechanisms. The investigated solid solution $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$ is a promising thermoelectric material.

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

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Introduction

The presented work continues the program of finding new thermoelectric materials based on half-Heusler phases (space group $F\bar{4}3m$ [1]). It is known that thermoelectric materials based on half-Heusler phases have high efficiency in converting thermal energy into electrical energy. The thermoelectric figure of merit Z for some samples of solid solutions reaches values of $ZT \sim 1.4$ at a temperature of $T=800$ K [2], which corresponds to the best characteristics of thermoelectric materials based on tellurides, clathrates, skutterudites, etc. ($Z=\alpha^2 \cdot \sigma / \kappa$, where σ – electrical conductivity, α – coefficient of thermopower, and κ – thermal conductivity) [3].

The study of the structural, electrokinetic, energetic, and magnetic properties of semiconductive substitutional solid solutions based on half-Heusler phases, in particular, based on RNiSb ($R = \text{Y, Gd} - \text{Lu}$) compounds [4-11], allows us to understand the nature of processes of charges transport. After all, the optimization of the electrokinetic

characteristics of thermoelectric materials to increase the efficiency of the conversion of thermal energy into electrical energy is carried out by appropriate doping of half-Heusler phases with donor and/or acceptor impurities [12].

It was shown in Refs. [1, 4-11] that the crystal structure of half-Heusler RNiSb phases is defective. Vacancies are present in crystallographic positions 4a of R atoms and 4c of Ni atoms, which are structural defects of an acceptor nature. The presence of vacancies creates a corresponding acceptor band ε_A^1 in the band gap ε_g of RNiSb , which is indicated by positive values of the thermopower coefficient $\alpha(T)$. Understanding the peculiarities of the spatial arrangement of atoms in the nodes of the unit cell of half-Heusler RNiSb phases, in particular, the degree of occupancy of crystallographic positions, allows us to understand the processes of transformation of crystal and electronic structures and the mechanisms of electrical conductivity during the formation of solid solutions.

Thus, the introduction of Sc atoms ($3d^14s^2$) into the structure of the half-Heusler LuNiSb phase by substituting Lu atoms ($5d^16s^2$) in the $4a$ position simultaneously generates various structural defects in $\text{Lu}_{1-x}\text{Sc}_x\text{NiSb}$, $x = 0-0.10$ [9]. Since Lu and Sc atoms are located in the same group of the Periodic System of chemical elements, the substitution of Lu atoms by Sc atoms in position $4a$ generates structural defects of a neutral nature. In the event that Sc atoms occupy vacancies in position $4a$, structural defects of the acceptor nature caused by the vacancies are eliminated, and defects of the donor nature are generated, and the corresponding donor band ε_D^2 appears. Moreover, at concentrations $x \geq 0.07$, the number of donors in $\text{Lu}_{1-x}\text{Sc}_x\text{NiSb}$ grows ~ 2 times faster than in the range $x = 0-0.07$. However, at all concentrations, the Fermi level ε_F lies in the band gap ε_g near the valence band ε_v , and holes are the main current carriers. Occupation of vacancies by Sc atoms is also accompanied by a slight increase in the lattice parameter $a(x)$ $\text{Lu}_{1-x}\text{Sc}_x\text{NiSb}$.

In the case of introducing into the structure of the half-Heusler LuNiSb phase, the lowest concentration of Zr atoms ($4d^25s^2$), $x = 0.01$, the behavior of the electrokinetic characteristics is fundamentally different than when Sc atoms are introduced [10, 11]. The metallic (non-activation) nature of the behavior of the temperature dependences of the resistivity $\rho(T,x)$ and the negative values of the thermopower coefficient $\alpha(T,x)$ of $\text{Lu}_{1-x}\text{Zr}_x\text{NiSb}$ at all concentrations of Zr atoms indicate that the Fermi level ε_F crossed the percolation level of the conduction band ε_c . This behavior of electrokinetic and energetic properties is caused by the following changes in the crystal and electronic structures:

- substitution of Lu atoms by Zr atoms in the $4a$ position generates structural defects of the donor nature, which is associated with a higher number of d -electrons of Zr. At the same time, a donor band ε_D^1 appears in the band gap ε_g ;

- occupation of vacancies in position $4a$ by Zr atoms simultaneously eliminates structural defects of the acceptor nature generated by the vacancies and generates defects of the donor nature and the donor band ε_D^2 . Occupation of vacancies by Zr atoms is also accompanied by a slight increase in the parameter of the unit cell $a(x)$ of $\text{Lu}_{1-x}\text{Zr}_x\text{NiSb}$ samples.

In this context, it seems interesting to study when V atoms ($3d^34s^2$) will be introduced into the structure of the half-Heusler LuNiSb phase by replacing Lu atoms in the $4a$ position. *A priori*, as in the case of $\text{Lu}_{1-x}\text{Zr}_x\text{NiSb}$ [10, 11], we expected the generation of only donor defects in the $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$ structure, $x=0-0.10$, since the V atom has a higher number of d -electrons than Lu. On the other hand, the atomic radius of V ($r_V=0.134$ nm) is much smaller than that of Lu ($r_{Lu}=0.173$ nm) and close to the atomic radius of Ni ($r_{Ni}=0.125$ nm). This may be a precondition for more complex structural changes in $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$, associated with the possible partial occupation by V atoms of the $4c$ position by occupation of vacancies and/or replacement of Ni atoms. The latter can lead to the generation of defects of an acceptor nature, which will be reflected in the experiment by positive values of the thermopower coefficient $\alpha(T,x)$. In the case of $\text{Lu}_{1-x}\text{Sc}_x\text{NiSb}$ and $\text{Lu}_{1-x}\text{Zr}_x\text{NiSb}$ solid solutions, it was impossible to occupy the crystallographic position $4c$ with atoms of impurities Sc

($r_{Sc}=0.164$ nm) and Zr ($r_{Zr}=0.160$ nm) due to a significant difference with the atomic radius of Ni.

The following results of the study of the structural, electrokinetic, energetic, and magnetic properties of the semiconductive solid solution $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$, $x = 0-0.10$, will allow us to establish the factors that have a decisive influence on the crystal and electronic structures. The latter will make it possible to model and obtain thermoelectric materials with high efficiency in converting thermal energy into electrical energy.

I. Methods and materials

$\text{Lu}_{1-x}\text{V}_x\text{NiSb}$ solid solution samples, $x=0.01-0.10$, were prepared by arc-melting a batch of components weighed with an accuracy of ± 0.001 g in an electric arc furnace with a tungsten electrode (cathode) in purified argon atmosphere under a pressure of 0.1 kPa on a copper water-cooled bottom (anode). For homogenization, the obtained alloys were sealed in vacuumed (up to 1.0 Pa) quartz ampoules and annealed in muffle electric furnaces with temperature control with an accuracy of ± 10 K at a temperature of 1073 K for 720 h, followed by quenching in cold water. For X-ray phase analysis, diffraction data were obtained on a STOE STADI-P powder diffractometer (Cu $K\alpha_1$ radiation). Structural characteristics of $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$ samples were calculated using the Fullprof program package [13]. Control of the chemical and phase composition of the samples was carried out using energy dispersive X-ray spectroscopy (EDRS) (scanning electron microscope Tescan Vega 3 LMU). Measurements of the temperature dependences of the electrical resistivity $\rho(T,x)$ of $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$ were carried out by the two-probe method in the temperature range of 80–400 K on samples in the form of rectangular parallelepipeds measuring $\sim 1.0 \times 1.0 \times 5$ mm³. The values of the thermopower coefficient were measured using the potentiometric method relative to copper. Measurements of the voltage drop on the samples were carried out in different directions of the electric current [2] to reduce the influence of “parasitic” effects at the contact points, as well as the influence of a possible p - n transition. The specific magnetic susceptibility χ of $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$ samples was measured by the relative Faraday method at a temperature of 293 K in magnetic fields up to 10 kOe.

II. Study of the structural properties of $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$

X-ray phase analysis of the samples $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$, $x = 0-0.10$, indicated the absence of traces of impurity phases, except for the main phase, which is indexed in the structure type MgAgAs [1]. According to microprobe analysis data, the concentration of atoms on the surface of $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$ samples corresponds to the initial composition of the charge.

X-ray structural studies of the $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$ solid solution, $x=0-0.10$, exhibited the complex behavior of the unit cell parameter $a(x)$ with an increasing concentration of V atoms (Fig. 1). Based on the fact that the atomic radius of Lu significantly exceeds that of V, it was logical

to expect a decrease in the values of the unit cell parameter $a(x)$ $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$ when replacing Lu atoms with V atoms in the $4a$ position. However, as can be seen from Fig. 1, in the concentration range $x=0-0.03$, the values of $a(x)$ for $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$ increase, pass through a maximum, and rapidly decrease at $x>0.03$. By the way, we observed a similar behavior of the unit cell parameter $a(x)$ in the $\text{Lu}_{1-x}\text{Zr}_x\text{NiSb}$ solid solution [10, 11] (Fig. 1, inset). The presence of maximum on the dependence $a(x)$ of $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$ (Fig. 1) allows us to assume that the V atoms introduced into the matrix of the half-Heusler LuNiSb phase can simultaneously, in different ratios, partially occupy both different crystallographic positions and tetrahedral voids of the structure which make up $\sim 24\%$ of the volume of a unit cell [2].

Since the atomic radius of Ni ($r_{\text{Ni}} = 0.124$ nm) is the smallest among the components of the $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$ solid solution ($r_{\text{Sb}}=0.159$ nm), the increase in the unit cell parameter $a(x)$ in the concentration range $x = 0-0.03$ can be caused by only partial occupation by V atoms crystallographic position $4c$, and also vacancies in position $4a$. In the case of substitution of Ni atoms ($3d^84s^2$) by V atoms ($3d^34s^2$) in $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$, structural defects of an acceptor nature are generated, since the V atom contains fewer d -electrons. At the same time, an additional acceptor band ε_A^2 will appear in the band gap of $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$. On the other hand, the possible occupation of vacancies in position $4c$ by V atoms will also lead to an increase in the values of the lattice parameter $a(x)$ for $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$. At the same time, the structural defect of the acceptor nature (vacancy) and the corresponding acceptor band ε_A^1 disappear. Atom V, occupying a vacancy in position $4c$, generates a structural defect of the donor nature. Therefore, the semiconductor $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$, $x = 0-0.03$, will simultaneously contain donors and acceptors, and their ratio during ionization will determine the sign of the thermopower coefficient $\alpha(x, T)$ and the type of the main current carriers.

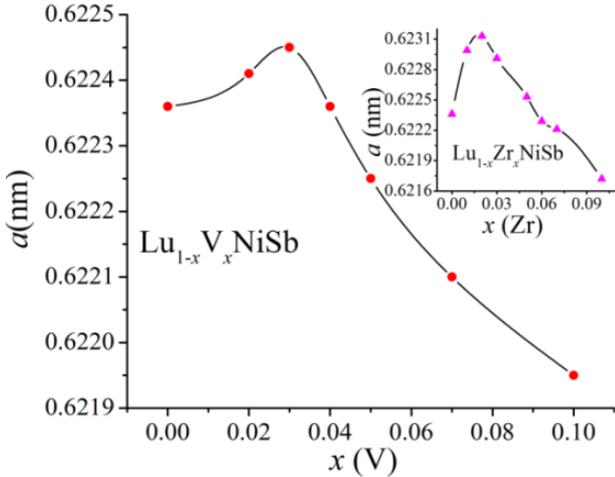


Fig. 1. Variation of the unit cell parameter $a(x)$ with increasing impurity content in $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$ and $\text{Lu}_{1-x}\text{Zr}_x\text{NiSb}$ [11] (upper inset).

A decrease in the values of the unit cell parameter $a(x)$ $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$, which occurs at $x > 0.03$ (Fig. 1), can be caused only by the occupation of crystallographic position $4a$ by V atoms. At the same time, structural defects of a

donor nature will be generated in the crystal both during the substitution of Lu atoms and the occupation of vacancies. The latter eliminates the structural defect in the form of a vacancy and the corresponding acceptor band. The maximum on the dependence $a(x)$ of $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$ at a concentration of $x \approx 0.03$ is the result of two competing processes in the structure of the semiconductor, associated with the simultaneous occupation of crystallographic positions $4c$ and $4a$ by V atoms in different ratios.

Therefore, structural studies of the semiconductive solid solution $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$, $x=0-0.10$, indicate that V atoms can simultaneously occupy different crystallographic positions in different ratios, generating at the same time structural defects of a donor and/or acceptor nature.

The above considerations regarding the changes in the structure of the $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$ solid solution based on the behavior of the unit cell parameter $a(x)$ are of an evaluative nature, since the accuracy of X-ray structural studies does not allow to unambiguously identify the causes of these changes. The results of the study of the electrokinetic, energetic and magnetic properties of $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$, $x = 0-0.10$, presented below, will complement the results of structural studies, which will allow modeling of crystal and electronic structures as close as possible to the real state of the substance.

III. Study of electrokinetic, energetic and magnetic properties of $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$

The temperature dependences of the electrical resistivity $\ln(\rho(1/T, x))$ and the thermopower coefficient $\alpha(1/T, x)$ of the $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$ solid solution, $x = 0-0.10$, are shown in Fig. 2. At all concentrations of $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$, high-temperature activation parts are presented on the temperature dependences $\ln(\rho(1/T, x))$ and $\alpha(1/T, x)$ (Fig. 2). This is evidence that the investigated samples are doped and compensated semiconductors [14]. The presence of high-temperature activation on the dependences $\ln(\rho(1/T, x))$ of $\text{Lu}_{1-x}\text{Sc}_x\text{NiSb}$ indicates the location of the Fermi level ε_F in the band gap ε_g . For samples with concentrations $x = 0-\leq 0.07$, the Fermi level ε_F lies near the valence band ε_V , as indicated by the positive values of the thermopower coefficient α at high temperatures (Fig. 2). At concentrations $x > 0.07$, the Fermi level ε_F moved to the conduction band ε_C , which is indicated by the negative values of the thermopower coefficient α at all temperatures.

The temperature dependences $\ln(\rho(1/T, x))$ of $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$ (Fig. 2) can be described by the well-known expression (1) [14]:

$$\rho^{-1}(T) = \rho_1^{-1} \exp\left(-\frac{\varepsilon_1^p}{k_B T}\right) + \rho_3^{-1} \exp\left(-\frac{\varepsilon_3^p}{k_B T}\right) \quad (1)$$

where the first high-temperature term describes the activation of current carriers $\varepsilon_1^p(x)$ from the Fermi level ε_F into the valence band ε_V , and the second, low-temperature term, describes the jump conduction $\varepsilon_3^p(x)$ with energies

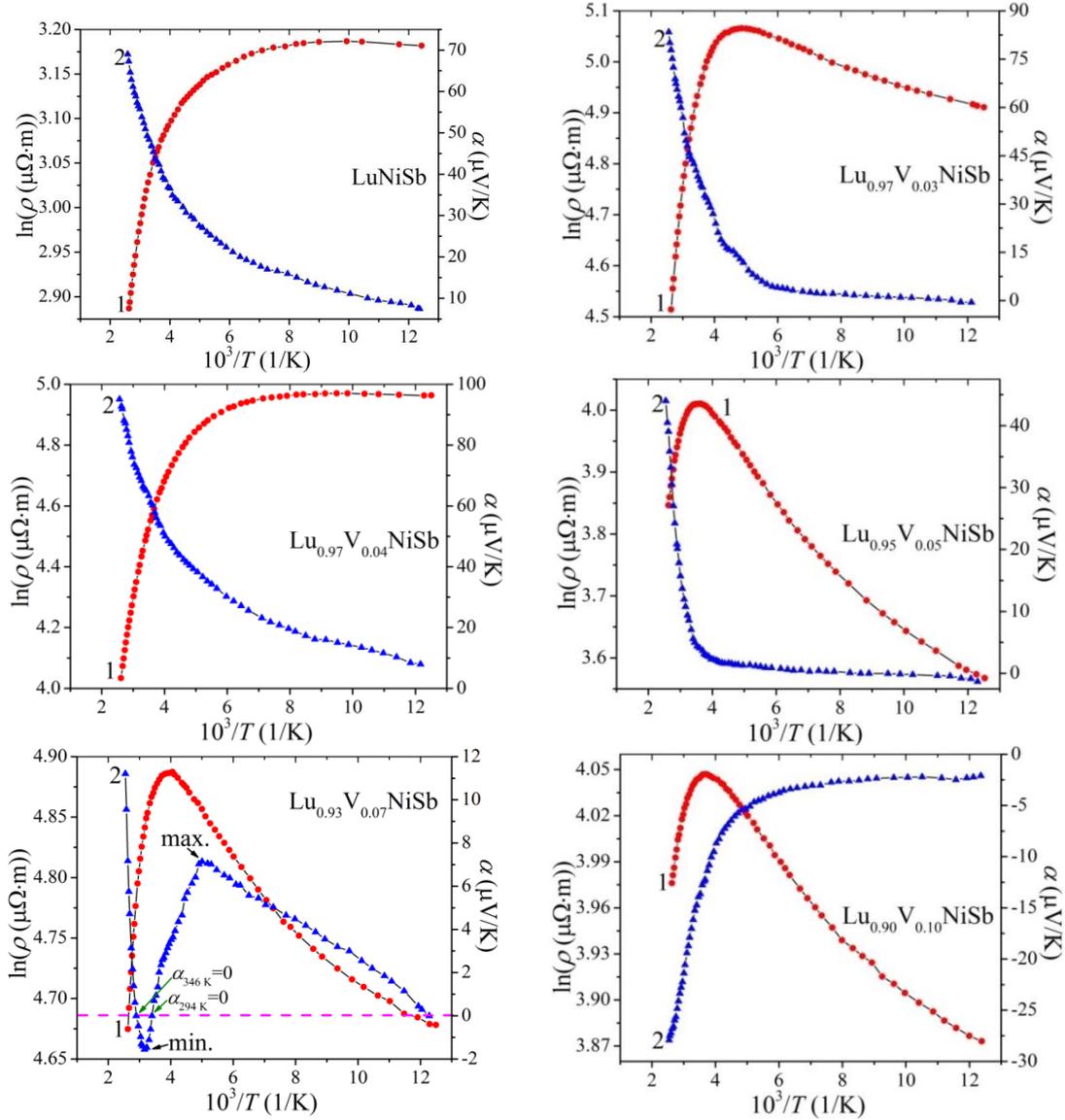


Fig. 2. Temperature dependences of specific electrical resistivity $\ln(\rho(1/T,x))$ (1) and thermopower coefficient $\alpha(1/T,x)$ (2) of $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$.

close to the Fermi level ε_F . The temperature dependence of the thermopower coefficient $\alpha(1/T,x)$ for $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$ (Fig. 2) is described by formula (2) [15]:

$$\alpha = \frac{k_B}{e} \left(\frac{\varepsilon_F^\alpha}{k_B T} - \gamma + 1 \right) \quad (2)$$

where γ is a parameter that depends on the nature of the scattering mechanism. Based on formula (2), the values of activation energies $\varepsilon_1^\alpha(x)$ and $\varepsilon_3^\alpha(x)$ were calculated from the high- and low-temperature activation parts of the dependence $\alpha(1/T,x)$. In Ref. [12], it was established that the values of the activation energies $\alpha(1/T,x)$ are proportional to the amplitude of the large-scale fluctuation of the continuous energy bands and the small-scale fluctuation of the doped and compensated semiconductor. The compensation degree of semiconductor is evaluated by the modulation amplitude of the bands.

The existence of the hopping ε_3^p -conductivity mechanism at low temperatures in the LuNiSb samples indicates the presence of a significant number of ionized acceptors in the semiconductor (positive values of the

thermopower coefficient α) and compensating donors of unknown origin, which actually ensures carrier jumps in localized states in the vicinity of the Fermi energy ε_F . In this case, the Fermi level ε_F in LuNiSb is at a distance of 10.2 meV from the percolation level of the valence band ε_V (Fig. 3). At the same time, a feature of the temperature dependences of the electrical resistivity $\ln(\rho(1/T,x))$ for all doped samples ($x > 0$) of $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$ is the absence of low-temperature activation parts, i.e. the hopping ε_3^p -conductivity mechanism. We can see that in the samples $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$, $x > 0$, at low temperatures, the values of electrical resistivity ρ increase with increasing temperature (Fig. 2), which is characteristic of a metallic type of conductivity.

In doped and compensated semiconductors, the metallization of low-temperature conductivity indicates the closeness of the Fermi energy ε_F and the percolation level of continuous energy bands [14]. In the case of $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$ doped samples, $x=0.01-0.07$, this energy proximity facilitates the ionization of acceptors and the appearance of a significant number of free holes in the

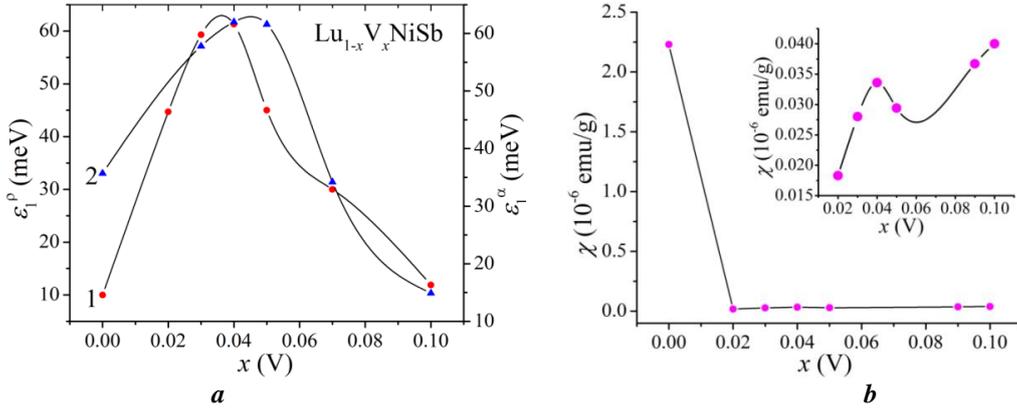


Fig. 3. Variation of activation energies $\varepsilon_1^p(x)$ (1) and $\varepsilon_1^\alpha(x)$ (2) (a), and specific magnetic susceptibility $\chi(x)$ (b) of $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$.

valence band ε_V , which causes the overlap of the wave functions of impurity states near the Fermi energy ε_F .

Using the terminology of the traditional approach to describe semiconductors, let's rephrase what has been said: the ε_A^2 acceptor band, generated by defects due to the substitution of Ni atoms by V ones, intersects with the ε_V valence band, forming a "tail" that leads to the metallization of conductivity.

At higher temperatures, holes are activated from the Fermi level ε_F , which is now fixed by another acceptor band ε_A^1 , generated by vacancies in the structure of the half-Heusler LuNiSb phase. This acceptor band is located deep in the band gap ε_g and the high-temperature activation parts of $\ln(\rho(1/T, x))$ for $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$ reflect the process of hole activation exactly from the acceptor band ε_A^1 . And if in LuNiSb the depth of the Fermi level ε_F relative to the percolation level of the valence band ε_V is ~ 10.2 meV, then, for example, in the semiconductor $\text{Lu}_{0.98}\text{V}_{0.02}\text{NiSb}$ it is about 45 meV (Fig. 3a).

As seen from Fig. 3a, in the concentration range $x = 0-0.03$, the hole activation energy $\varepsilon_1^p(x)$ from the Fermi level ε_F to the percolation level of the valence band ε_V increases almost linearly. This makes it possible to determine the motion rate of the Fermi level ε_F from the valence band ε_V , which is $\Delta\varepsilon_F/\Delta x \approx 16.4$ meV/%V. At concentrations $x \geq 0.07$, the motion rate of the Fermi level ε_F to the percolation level of the conduction band ε_C (negative values of the thermopower coefficient α) is $\Delta\varepsilon_F/\Delta x \approx 6.1$ meV/%V.

The temperature dependence of the thermopower coefficient $\alpha(1/T, x)$ of the semiconductor $\text{Lu}_{0.93}\text{V}_{0.07}\text{NiSb}$ (Fig. 2) revealed two acceptor bands with different depths of occurrence in the band gap ε_g , as well as a donor band, the existence of which we assumed based on results of structural studies. The growth of the thermopower coefficient dependence $\alpha(1/T, x)$ in the temperature range $T = 80-190$ K shows that donors are generated in the semiconductor $\text{Lu}_{0.93}\text{V}_{0.07}\text{NiSb}$ even at low temperatures. The presence of an extremum (maximum) on the dependence $\alpha(1/T, x)$ at $T \approx 190$ K indicates that the growth rate of the concentration of ionized donors is greater than the rate of increase in the concentration of ionized acceptors. Obviously, the depletion of the ε_A^1 acceptor band, generated by vacancies in the structure of the half-Heusler LuNiSb phase, takes place. Such dynamics of growth in the concentration of ionized donors

leads to a change in the sign of the thermopower coefficient $\alpha(1/T, x)$ at $T \approx 294$ K, and the growth of negative values of the thermopower coefficient in the range $T = 294-316$ K indicates a change of type of semiconductor conductivity, when free electrons become the main carriers.

The minimum on the dependence of $\alpha(1/T, x)$ at the temperature $T \approx 316$ K indicates the beginning of ionization of acceptor states ε_A^2 , generated by defects in the replacement of Ni atoms with atoms V and depletion of donor states. Repeated complete compensation of the semiconductor $\text{Lu}_{0.93}\text{V}_{0.07}\text{NiSb}$ occurs at $T \approx 346$ K when the sign of the thermopower coefficient changes from negative to positive. At the same time, at temperatures $T > 346$ K, the holes again become the main current carriers.

The absence at low temperatures of the hopping ε_3^p -conductivity mechanism in $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$, $x > 0.07$, indicates the location of the Fermi level ε_F at a distance of $k_B \cdot T$ from the percolation level of the conduction band ε_C (negative values of the thermopower coefficient $\alpha(1/T, x)$). This leads to an overlap of the wave functions of the impurity states near the Fermi energy ε_F . In the semiconductor $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$, $x > 0.07$, a high concentration of free electrons appears due to the simplified ionization of generated donors as a result of the corresponding structural transformations.

Experimental studies of the magnetic susceptibility $\chi(x)$ showed that the samples of both the LuNiSb compound and the $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$ solid solution at all concentrations are Pauli paramagnets (Fig. 3b). In this case, the similarity of the behavior of the dependences of the resistivity $\rho(x, T)$, the thermopower coefficient $\alpha(x, T)$ (Fig. 4b) and the magnetic susceptibility $\chi(x)$ (Fig. 3b) is clear and associated with a change in the density of states at the Fermi level $g(\varepsilon_F)$.

The behavior of the concentration dependences of the electrical resistivity $\rho(x, T)$ and the thermopower coefficient $\alpha(x, T)$ of $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$ at different temperatures is interesting and informative (Fig. 4). An increase of the electrical resistivity $\rho(x, T)$ in the concentration range $x = 0-0.03$ in a semiconductor of p -type conductivity is possible only if the concentration of free holes decreases. This reason is the generation of donors in the semiconductor that capture holes. This leads to an increase

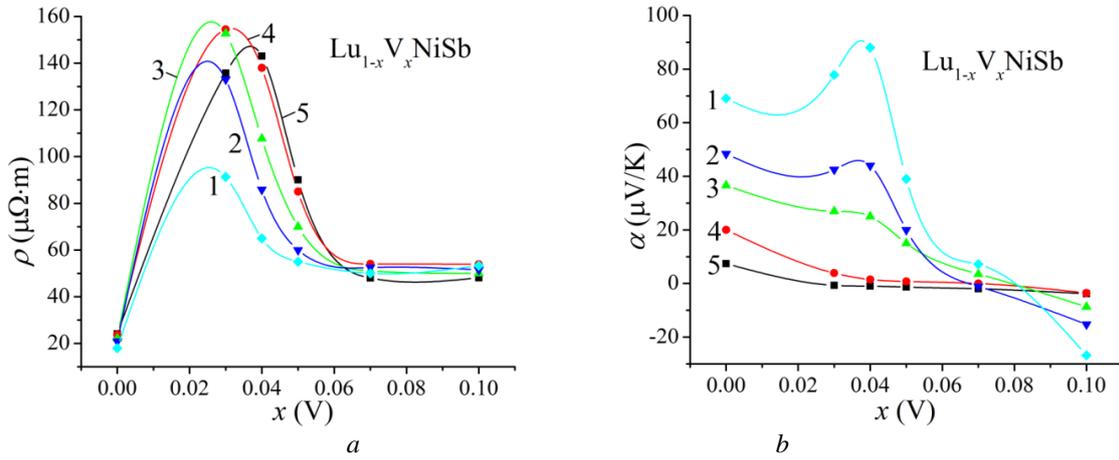


Fig. 4. Variation of the electrical resistivity $\rho(x, T)$ (a) and the thermopower coefficient $\alpha(x, T)$ (b) of $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$ at different temperatures: 1 – $T=380$ K; 2 – $T=300$ K; 3 – $T=250$ K; 4 – $T=160$ K; 5 – $T=80$ K.

in the compensation degree of the semiconductor, as indicated by the behavior of the activation energy $\varepsilon_1^\alpha(x)$, calculated from the high-temperature part of the dependencies $\alpha(1/T, x)$ of $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$ (Fig. 3a, curve 2). At higher modulation amplitude of the continuous energy bands $\varepsilon_1^\alpha(x)$, the higher compensation degree of the semiconductor was observed [14]. We can see that in the concentration range $x=0-0.03$, the values of the activation energy $\varepsilon_1^\alpha(x)$ increase, and the reason is the appearance of donors in the semiconductor.

The results of the electrokinetic and energetic properties of $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$ in the concentration range $x=0-0.03$ are consistent and clarify the conclusions of the structural studies. Thus, based on an analysis of the structural characteristics of $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$, it was established that the increase of the lattice parameter $a(x)$ in the concentration range $x=0-0.03$ can be caused by the only partial occupation of the $4c$ position by V atoms. Since donors are generated in the semiconductor in this case, V atoms in the concentration range $x=0-0.03$ occupy vacancies in position $4c$ (substitution of Ni atoms generates acceptors). At the same time, as follows from the behavior of the thermopower coefficient $\alpha(x, T)$, the concentration of acceptors dominates the concentration of generated donors.

At a concentration $x=0.04$ and temperature of 80 K, an extremum appears on the dependence of the electrical resistivity $\rho(x, T)$, which shifts with increasing temperature to the region of lower concentrations of V atoms. The appearance of an extremum on the $\rho(x, T)$ dependence is the result of changes in the ratio of ionized acceptors and donors available in the semiconductor. The fact that as the temperature increases, the maximum on the $\rho(x, T)$ dependence shifts to the region of lower concentrations of V atoms is understandable, since the increase of temperature simplifies the ionization of acceptors and donors and the increase in the concentration of free carriers. We can assume that at all temperatures in semiconductors $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$, $x > 0.03$, such concentration of free carriers of both types appears that even with a slight increase of the compensation degree up to $x \approx 0.05$ (Fig. 3a, curve 2) the total conductivity of semiconductors increases rapidly and continues up to concentration $x=0.07$.

Since the semiconductor $\text{Lu}_{0.93}\text{V}_{0.07}\text{NiSb}$ simultaneously contains significant concentrations of electrons and holes and is heavily doped and compensated, with an increase of the concentration of V atoms ($x > 0.07$), the type of main carriers changes from holes to electrons (Fig. 3b), however, high concentrations of free electrons provide high conductivity, which has little effect on the change in the values of electrical resistivity $\rho(x, T)$ at all temperatures (Fig. 3a).

Therefore, studies of the electrokinetic, energetic, and magnetic properties of the $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$ solid solution, $x=0-0.10$, confirm the conclusions of structural studies regarding the simultaneous occupation of V atoms in different ratios of crystallographic positions $4a$ and $4c$, generating at the same time structural defects of a donor and/or acceptor nature. Understanding the mechanism of structural transformations in $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$ will make it possible to model and obtain thermoelectric materials with high efficiency in converting thermal energy into electrical energy.

Conclusions

According to the results of a complex study of the structural, electrokinetic, energetic, and magnetic properties of the semiconductive solid solution $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$, obtained by introducing V atoms into the structure of the LuNiSb compound by substitution of Lu atoms in the crystallographic position $4a$, a complicated character of structural changes was revealed. It is shown that V atoms can simultaneously occupy different crystallographic positions in different ratios, generating structural defects of acceptor and donor nature. This gives rise to the corresponding acceptor and donor bands in the band gap ε_g of $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$. The mechanism of the formation of two acceptor bands with different depth of occurrence in $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$ has been established: a small acceptor band ε_A^2 , formed by defects upon the substitution of Ni atoms by V in the $4c$ position, and band ε_A^1 , generated by vacancies in the structure of the half-Heusler LuNiSb phase. The ratio of the concentrations of generated defects determines the position of the Fermi level ε_F and the conduction mechanisms. The investigated solid solution $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$ is a promising thermoelectric

material.

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Особливості структурних, електрокінетичних, енергетичних та магнітних властивостей напівпровідникового твердого розчину $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$

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Досліджено структурні, електрокінетичні, енергетичні та магнітні властивості нового напівпровідникового твердого розчину $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$, $x = 0-0.10$. Показано, що атоми V можуть одночасно у різних співвідношеннях займати різні кристалографічні позиції, генеруючи структурні дефекти акцепторної та донорної природи. Це породжує у забороненій зоні ϵ_g $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$ відповідні акцепторні та донорні зони. Встановлено механізм формування двох акцепторних зон з різною глибиною залягання: дрібна акцепторна зона ϵ_{A^2} , утворена дефектами при заміщенні у позиції 4c атомів Ni на V, та зона ϵ_{A^1} , породжена вакансіями у структурі LuNiSb . Співвідношення концентрацій генерованих дефектів визначає положення рівня Фермі ϵ_F та механізми провідності. Досліджений твердий розчин $\text{Lu}_{1-x}\text{V}_x\text{NiSb}$ є перспективним термоелектричним матеріалом.

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