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Experimental studies of a new thermoelectric material based on semiconductor solid solution $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$

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The structural, electrokinetic, and energetic properties of the $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$ semiconductor solid solution, obtained by introducing of Al atoms into the structure of the TiNiSn half-Heusler phase by substituting Ti atoms in the crystallographic position $4a$, were studied. It is shown that in the range of concentrations $x = 0-0.01$, Al atoms mainly replace Ni atoms in the $4c$ position, generating acceptor states. It was established that at temperatures $T = 80-160$ K, the ratio of concentrations of ionized acceptor and donor states in $n\text{-Ti}_{1-x}\text{Al}_x\text{NiSn}$, $x = 0-0.04$, is unchanged, but the concentration of donors is greater. At higher temperatures, $T \geq 250$ K, deep donor states that existed in $n\text{-TiNiSn}$ as a result of "a priori doping" of the semiconductor are ionized. An additional mechanism for the generation of donor states in $n\text{-Ti}_{1-x}\text{Al}_x\text{NiSn}$ when the tetrahedral voids of the structure are partially occupied by Al atoms was revealed. The concentration ratio of the generated donor-acceptor states determines the position of the Fermi level ε_F and the conductivity mechanisms of $n\text{-Ti}_{1-x}\text{Al}_x\text{NiSn}$. The studied semiconductor solid solution is a promising thermoelectric material.

Keywords: Semiconductor, Electric conductivity, thermopower coefficient, Fermi level.

Received 03 August 2023; Accepted 21 February 2024.

Introduction

Thermoelectric materials based on half-Heusler phases (structure type MgAgAs , space group $F\bar{4}3m$ [1]) have a high efficiency of converting thermal energy into electrical energy [2]. The formation of substitution solid solutions based on half-Heusler semiconductor phases MNiSn ($M = \text{Ti, Zr, Hf}$) allows to purposefully change the values of specific electrical conductivity σ , thermopower coefficients α and thermal conductivity κ and to obtain high values of thermoelectric factor Z ($Z = \alpha^2 \cdot \sigma / \kappa$) [3]. In turn, understanding the mechanisms of electrical conductivity of solid solutions based on half-Heusler phases is decisive in the process of optimizing the kinetic characteristics of semiconductor thermoelectric materials to increase the efficiency of converting thermal energy into electrical energy by changing the impurity concentration [2, 4].

In the proposed work, a new semiconductor solid solution $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$ is obtained by substituting Ti atoms

($3d^24s^2$) for Al atoms ($3d^23p^1$) in the crystallographic position $4a$ of the TiNiSn compound, which should generate structural defects of an acceptor nature in the crystal (the Al atom has a smaller number of electrons on the outer shells than Ti). The study of the structural, kinetic and energetic properties of the $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$ solid solution will allow us to understand the nature of the electrical conductivity mechanism, which will make the process of obtaining a thermoelectric material manageable and predictable.

Previous structural studies of the TiNiSn half-Heusler phase established the disordering of its crystal structure, which consists in the existence of a statistical mixture of Ti and Ni atoms in the crystallographic position of Ti atoms ($4a$). It is shown that $\sim 0.5\%$ of Ti atoms are replaced by Ni in position $4a$, and the compound is described by the formula $(\text{Ti}_{0.995}\text{Ni}_{0.005})\text{NiSn}$ [5]. Partial occupation by Ni atoms ($3d^84s^2$) of crystallographic position $4a$ of Ti atoms generates structural defects of the donor nature in the crystal, since the Ni atom has a greater number of d -electrons than the Ti atom. Calculations of the distribution

of the density of electronic states (DOS) showed that the TiNiSn compound is a semiconductor of the electronic conductivity type. At the same time, small donor states of two types appear in the band gap ε_g of the semiconductor. Shallow donor states (donor band ε_D^1) are located near the bottom of the conduction band ε_C and overlap with its edge, forming a "tail" of the density of states. Deeper donor states (donor band ε_D^2) are ionized at temperatures $T \geq 250$ K.

Calculations also showed that the band gap ε_g of n -TiNiSn is sensitive to the concentration of Ni atoms in the 4a position of Ti atoms. For the disordered version of the $(\text{Ti}_{1-x}\text{Ni}_x)\text{NiSn}$ structure, the values of $\varepsilon_g(x)$ decrease from $\varepsilon_g(x=0) \approx 320$ meV to $\varepsilon_g(x=0.01) \approx 120$ meV. Kinetic, energy, and magnetic studies of the n -TiNiSn phase agree with the results of the electronic structure modeling [5]. Therefore, the nature of "a priori doping" of the TiNiSn half-Heusler phase by donors is related to defects in its crystal structure as a result of partial, up to 0.5 at. %, substitution of Ti atoms with Ni atoms in position 4a.

In this context, it seems interesting to study when Al atoms will be introduced into the structure of the TiNiSn half-Heusler phase by replacing Ti atoms in the 4a position. A priori, we expected the generation in $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$ of only defects of an acceptor nature and the appearance in the band gap ε_g , along with the existing donor states (bands ε_D^1 and ε_D^2), acceptor states (bands ε_A^1). At low concentrations of Al atoms, this will lead to an increase in the degree of compensation of the semiconductor, an increase in the specific resistance $\rho(x,T)$, and at higher concentrations – a change in the sign of the thermopower coefficient $\alpha(x,T)$ from negative to positive, while the holes will become the main current carriers.

The following results of the study of the structural, kinetic and energy properties of the $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$ semiconductor solid solution 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 a high efficiency of converting thermal energy into electrical energy [2, 4].

I. Research methods

The synthesis of $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$ solid solution samples ($x = 0-0.10$) was performed by the method of electric arc melting of a charge of compact metals (weighing accuracy ± 0.001 g) in a purified argon atmosphere (spongy Ti was used as a getter). For homogenizing annealing, the synthesized alloys were sealed in vacuumed quartz ampoules and annealed at a temperature of 1073 K for 720 hours, followed by quenching in cold water without breaking the ampoule. X-ray phase analysis of annealed alloys was carried out based on X-ray powder patterns obtained on a DRON-4.0 powder diffractometer ($\text{FeK}\alpha$ -radiation). Crystallographic parameters of $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$ samples were calculated using the WinCSD program [6].

The method of energy dispersive X-ray spectroscopy (EDRS) (scanning electron microscope Tescan Vega 3 LMU) was used to confirm the chemical and phase composition of the samples and determine the content of

components in the phases. Measurements of the temperature dependences of the specific electrical resistivity $\rho(T,x)$ and the thermopower coefficient $\alpha(x,T)$ of $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$ samples, cut in the form of rectangular parallelepipeds of size $\sim 1.0 \times 1.0 \times 5$ mm³, were carried out by the two-probe method in the temperature range 80–400 K. Measurements of the values of the thermopower coefficient were carried out by the potentiometric method relative to copper. Measurements of the voltage drop on the samples were carried out in different directions of the electric current to reduce the influence of "parasitic" effects at the contact points, as well as the influence of a possible p - n transition [2].

II. Study of the structural properties of $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$

X-ray phase analysis of the obtained $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$ samples proved the absence of traces of impurity phases with Al concentrations of $x=0-0.04$, except for the main phase, which is indexed in the structure type MgAgAs [1] (Fig. 1a). At higher concentrations of Al atoms, $x > 0.04$, additional reflections appear on the powder patterns, which were identified as inclusions of the AlNi phase (structure type CsCl), and the $\text{Ti}_{0.94}\text{Al}_{0.06}\text{NiSn}$ sample contains, in addition to the AlNi phase, impurity Sn reflections (Fig. 1a). According to the results of the X-ray spectral analysis, the concentration of atoms on the surface of the $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$ samples, $x = 0-0.04$, corresponds to the initial composition of the charge (Fig. 2a). As shown in fig. 2b, c, according to the results of EDRS analysis, $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$ samples at concentrations $x > 0.04$ also contain inclusions of the AlNi phase ($\text{Ti}_{0.95}\text{Al}_{0.05}\text{NiSn}$) or two impurity phases AlNi and Sn ($\text{Ti}_{0.94}\text{Al}_{0.06}\text{NiSn}$). In addition, the X-ray spectral analysis showed the unchanged concentration of Ni atoms in the $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$ samples with Al content of $x > 0.04$. Based on the results of X-ray phase and X-ray spectral analyses, further studies were performed for $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$ samples with compositions of $x = 0-0.04$.

X-ray structural studies of $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$ solid solution samples, $x = 0-0.04$, due to insignificant concentrations of impurity Al atoms did not allow to reveal the ordering of the crystal structure of the half-Heusler phase, which was characteristic when, for example, Dy, Y, Sc V, So, Su, Ga, In atoms were introduced into the structure [2]. On the other hand, structural studies of $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$ samples, $x = 0-0.04$, established the complex behavior of the lattice parameter $a(x)$ with increasing concentration of Al atoms (Fig. 1b). Since the atomic radius of Al ($r_{\text{Al}} = 0.143$ nm) is close to that of Ti ($r_{\text{Ti}} = 0.146$ nm), we expected a slight decrease in the values of the lattice parameter $a(x)$ of $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$ when replacing Ti atoms with Al in the 4a position. However, the result turned out to be diametrically opposed to what was expected: for concentrations $x = 0-0.04$, the values of $a(x)$ $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$ increase. This behavior of $a(x)$ $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$ suggests that the Al atoms introduced into the matrix of the half-Heusler phase of TiNiSn can simultaneously, in different ratios, partially occupy both different crystallographic positions and the tetrahedral voids of the structure, which make up

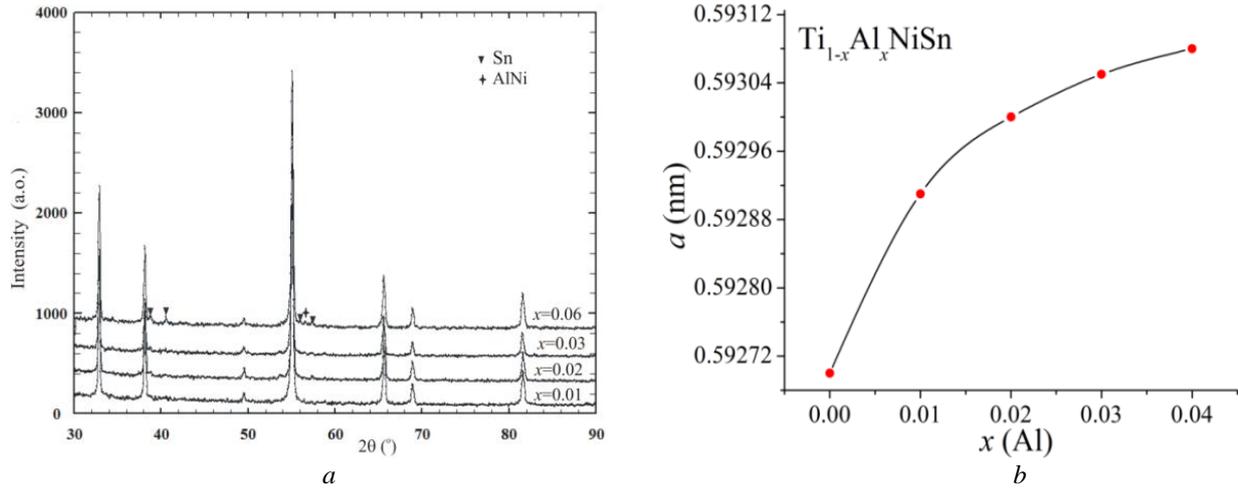


Fig. 1. X-ray powder patterns of samples (a) and variation of the lattice parameter $a(x)$ (b) of $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$.

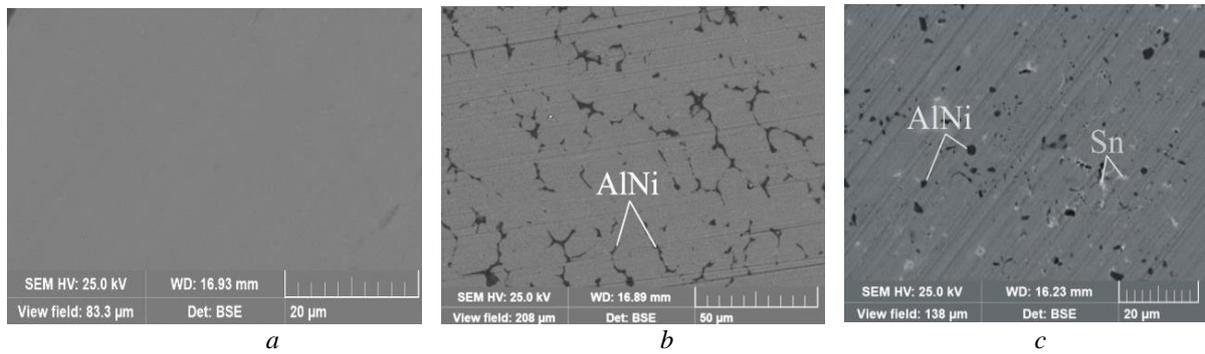


Fig. 2. Microphotographs of samples $\text{Ti}_{0.98}\text{Al}_{0.02}\text{NiSn}$ (a), $\text{Ti}_{0.95}\text{Al}_{0.05}\text{NiSn}$ (b) and $\text{Ti}_{0.94}\text{Al}_{0.06}\text{NiSn}$ (c).

~24% of the volume of an unit cell [2]. Taking into account the fact that the atomic radius of Ni ($r_{\text{Ni}}=0.124$ nm) is the smallest among the components of the $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$ solid solution ($r_{\text{Sn}}=0.162$ nm), the increase of the lattice parameter $a(x)$ in the concentration range $x=0-0.04$ can be associated with Al atoms occupying crystallographic position $4c$ of Ni atoms, as well as tetrahedral voids of the structure.

In the case of substitution of Ni atoms ($3d^84s^2$) for Al atoms ($3d^23p^1$) in $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$ structural defects of an acceptor nature are generated since the Al atom contains fewer d -electrons. At the same time, in the band gap ε_g of the semiconductor $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$, next to the acceptor band ε_A^1 , which could have arisen when Ti atoms ($3d^24s^2$) were replaced by Al atoms, the acceptor band ε_A^2 will appear. In the event that Al atoms occupy the tetrahedral voids of the structure, defects of the donor nature are generated, and another donor band will appear in the band gap ε_g . As a result, the semiconductor $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$, $x=0-0.04$, will be heavily doped and compensated, simultaneously contain donor and acceptor states, and their ratio will determine the type of main current carriers [7].

Given the small concentrations of Al in $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$ and the accuracy of X-ray structural studies, we could not identify the causes of structural transformations of the solid solution. The given considerations regarding changes in the structure based on the behavior of the parameter of the unit cell $a(x)$ are of an evaluative nature. The results of the study of the kinetic and energy properties of $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$, $x=0-0.04$, should clarify the conclusions regarding possible changes in the structure of

the semiconductor. On this basis, it will be possible in the future to model crystal and electronic structures as close as possible to the real state of matter, which will be the basis for optimizing the kinetic properties of the thermoelectric material by choosing doping conditions [4].

III. Study of kinetic and energetic properties of $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$

In Fig. 3 shows the temperature dependences of the specific electrical resistivity $\ln(\rho(1/T,x))$ and the thermopower coefficient $\alpha(1/T,x)$ of the $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$ semiconductor solid solution, $x=0-0.04$. At all $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$ concentrations, the temperature dependences $\ln(\rho(1/T,x))$ and $\alpha(1/T,x)$ have high-temperature activation regions (Fig. 3), indicating the location of the Fermi level ε_F in the band gap ε_g . Since at all temperatures the sign of the thermopower coefficient $\alpha(1/T,x)$ is negative, the main electric current carriers of $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$ are electrons, and the Fermi level ε_F is closer to the conduction band ε_C . Therefore, all $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$ samples are doped and compensated semiconductors of the electronic conductivity type [7]. The obtained result does not correspond to previous expectations regarding the type of conductivity but is consistent with the conclusions of structural studies.

The temperature dependences $\ln(\rho(1/T,x))$ of $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$ (Fig. 3) can be described by the well-known

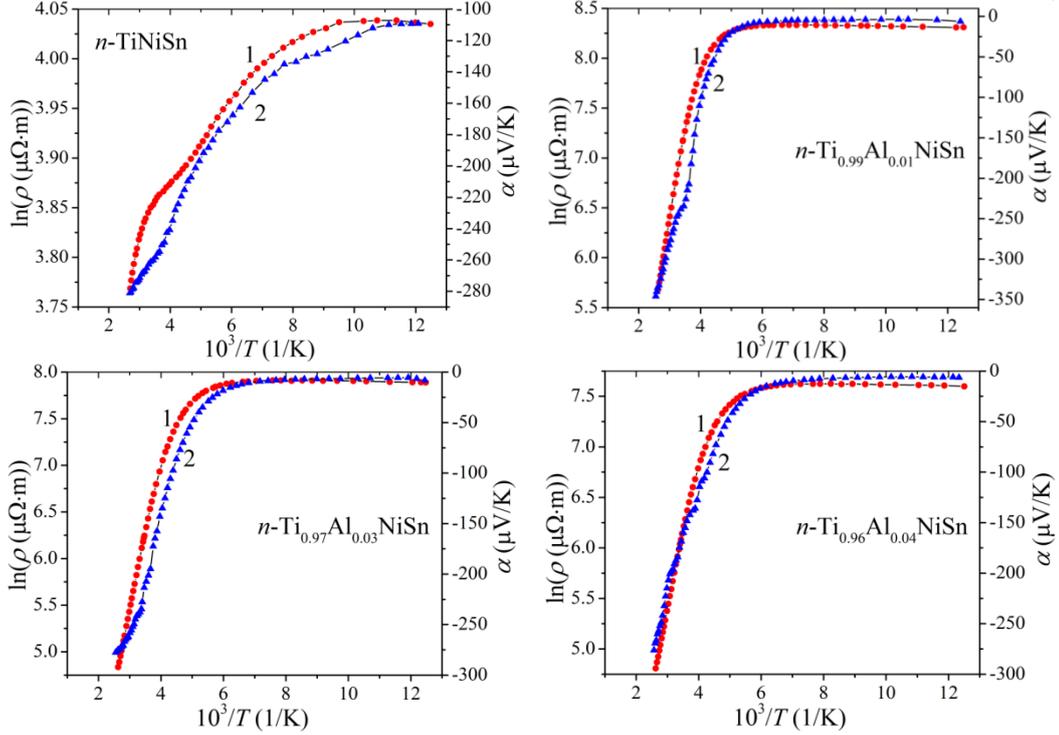


Fig. 3. Temperature dependences of specific electrical resistance $\ln(\rho(1/T,x))$ (1) and thermopower coefficient $\alpha(1/T,x)$ (2) of $n\text{-Ti}_{1-x}\text{Al}_x\text{NiSn}$ samples.

expression (1) [7]:

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

where the first high-temperature term describes the activation of current carriers $\varepsilon_1^\rho(x)$ from the Fermi level ε_F into the conduction band ε_C , and the second, low-temperature term, describes the jump conduction $\varepsilon_3^\rho(x)$ with energies close to the Fermi level ε_F . The temperature dependence of the thermopower coefficient $\alpha(1/T,x)$ $n\text{-Ti}_{1-x}\text{Al}_x\text{NiSn}$ (Fig. 3) is described by formula (2) [8]:

$$\alpha = \frac{k_B}{e} \left(\frac{\varepsilon_1^\alpha}{k_B T} - \gamma + 1 \right), \quad (2)$$

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 regions of the dependence $\alpha(1/T,x)$. The authors [9] showed that in heavily doped and compensated semiconductors, the values of the activation energies $\varepsilon_1^\alpha(x)$ and $\varepsilon_3^\alpha(x)$ are proportional to the amplitude of the large-scale fluctuation of the continuous energy bands and the small-scale fluctuation. The amplitude of the band modulation indicates the degree of compensation of the semiconductor.

The absence in the $n\text{-Ti}_{1-x}\text{Al}_x\text{NiSn}$ samples, as well as in the base semiconductor $n\text{-TiNiSn}$, of the mechanism of jump ε_3^ρ -conductivity at low temperatures and the presence of activation of electrons $\varepsilon_1^\rho(x)$ from the Fermi level ε_F to the conduction band ε_C at high temperatures indicates the presence in the band gap ε_g of two types of donors. Some donor states merge with the bottom of the

conduction band ε_C , forming a tail, and therefore the values of specific electrical resistivity ρ at low temperatures increase with increasing temperature (Fig. 3). In doped and compensated semiconductors, the metallization of low-temperature conductivity occurs under the condition that the energy gap between the position of the Fermi energy ε_F and the flow level of continuous energy bands is smaller than $k_B T$ [7]. At higher temperatures, current carriers are activated from other donor states, deeply located in the band gap ε_g , which are manifested by activation regions on the temperature dependences of the specific electrical resistivity $\ln(\rho(1/T,x))$ and the thermopower coefficient $\alpha(1/T,x)$ of $n\text{-Ti}_{1-x}\text{Al}_x\text{NiSn}$.

Using formulas (1) and (2), the depth of the Fermi level ε_F was calculated and the change in the degree of compensation of the semiconductor was estimated by calculated values of the amplitude of the large-scale fluctuation of the continuous energy bands $\varepsilon_1^\alpha(x)$ (Fig. 4). In the $n\text{-TiNiSn}$ semiconductor at high temperatures, the depth of the Fermi level ε_F relative to the percolation level of conduction band ε_C is $\varepsilon_1^\rho = 16.9$ meV, and the amplitude of the large-scale fluctuation of continuous energy band is $\varepsilon_1^\alpha = 26.3$ meV. The values of the activation energies calculated by us for $n\text{-TiNiSn}$ coincide with those obtained earlier [5].

Doping $n\text{-TiNiSn}$ with the lowest concentration of Al atoms in the experiment is accompanied by a rapid (by an order of magnitude) departure of the Fermi level ε_F from the conduction band ε_C and a location in the band gap ε_g at a distance of $\varepsilon_1^\rho(x = 0.01) = 167.7$ meV (Fig. 4). Thus, the position of the Fermi level ε_F can be changed only by doping of the semiconductor of the electronic conduction type with acceptor impurities. As it was shown above, Al atoms will act in $n\text{-Ti}_{1-x}\text{Al}_x\text{NiSn}$ as an acceptor impurity

and generate acceptor states in the band gap ε_g in two cases:

- a) in case of replacement of Ni atoms ($3d^84s^2$) by Al atoms ($3d^23p^1$) in crystallographic position 4c;
- b) in the case of substitution of Ti atoms ($3d^24s^2$) with Al atoms in crystallographic position 4a.

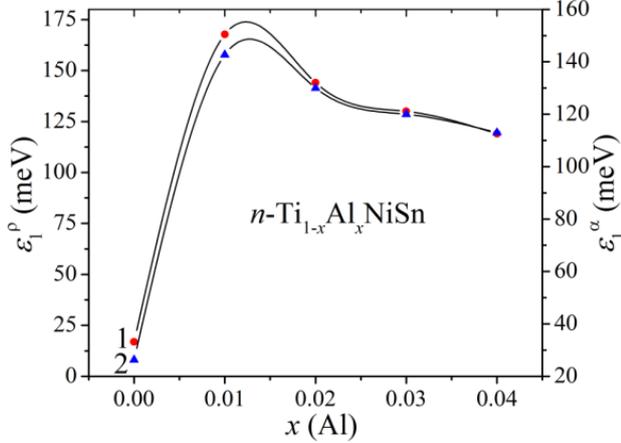


Fig. 4. Change in values of activation energies $\varepsilon_1^p(x)$ (1) and $\varepsilon_1^a(x)$ (2) for $n\text{-Ti}_{1-x}\text{Al}_x\text{NiSn}$.

However, only in the case of replacement of Ni atoms with Al atoms in the 4c position, the parameter of unit cell $a(x)$ of $n\text{-Ti}_{1-x}\text{Al}_x\text{NiSn}$ will increase, as indicated by the results of structural studies (Fig. 1b). We will recall that if Ti atoms are replaced by Al atoms, the unit cell parameter $a(x)$ will decrease slightly. Therefore, we can assume that at concentrations $x = 0 - 0.01$ in $n\text{-Ti}_{1-x}\text{Al}_x\text{NiSn}$, the rate of generation of acceptor states is greater than the rate of generation of donor states.

On the other hand, the negative values of the thermopower coefficient $\alpha(1/T, x)$ of $n\text{-Ti}_{0.99}\text{Al}_{0.01}\text{NiSn}$ indicate that the concentration of the generated acceptor states is insufficient to change the type of the main current carriers. At the same time, the Fermi level ε_F in $n\text{-Ti}_{0.99}\text{Al}_{0.01}\text{NiSn}$ did not cross the middle of the band gap ε_g and is located closer to the conduction band ε_C than to the valence band ε_V . If we assume that all Al atoms introduced into the structure of the half-Heusler phase ($x=0.01$) will displace Ni atoms from the crystallographic position 4c, then the concentration of generated defects of the acceptor nature would be \sim twice higher than the concentration of defects of the donor nature ($y = 0.005$) in the base semiconductor $n\text{-TiNiSn}$ with "a priori doping" [5]. Then the main carriers would be holes. Since electrons remain the main current carriers in $n\text{-Ti}_{0.99}\text{Al}_{0.01}\text{NiSn}$, there is another mechanism for generating donor states in the semiconductor, in addition to "a priori doping", which has not yet been identified.

From Fig. 4, it can be seen that in the concentration part $x = 0 - 0.01$, the activation energy of electrons $\varepsilon_1^p(x)$ from the Fermi level ε_F to the percolation level of conduction band ε_C increases almost linearly. This makes it possible to determine the speed of movement of the Fermi level ε_F from the conduction band ε_C into the depth of the band gap ε_g , which is $\Delta\varepsilon_F/\Delta x \approx 16.9$ meV/%Al.

Another important evidence of the generation of acceptor states in $n\text{-Ti}_{0.99}\text{Al}_{0.01}\text{NiSn}$ is a \sim 5-fold increase in the degree of compensation of the semiconductor, as

indicated by a rapid increase in the amplitude of the large-scale fluctuation of the continuous energy bands $\varepsilon_1^a(x=0.01) = 142.7$ meV (in $n\text{-TiNiSn}$ $\varepsilon_1^a = 26.3$ meV) (Fig. 4).

At an even higher concentration of Al atoms ($x = 0.02$), the Fermi level ε_F begins to reverse in the direction of the conduction band ε_C and in the $n\text{-Ti}_{0.98}\text{Al}_{0.02}\text{NiSn}$ semiconductor it is located at a distance $\varepsilon_1^p(x = 0.02) = 144.1$ meV from the edge of the conduction band (Fig. 4). That is, in $n\text{-Ti}_{0.98}\text{Al}_{0.02}\text{NiSn}$, the rate of generation of donor states now exceeds the rate of generation of acceptor states. Since the concentration of donor states during "a priori doping" of $n\text{-TiNiSn}$ is a constant value, the reverse movement of the Fermi level ε_F to the conduction band ε_C in $n\text{-Ti}_{0.98}\text{Al}_{0.02}\text{NiSn}$ can only cause the appearance of donor states of unknown origin. This trend of change in the ratio of generated donors and acceptors persists even at higher concentrations of Al atoms, and the Fermi level continues to drift in the direction of the conduction band

ε_C : $\varepsilon_1^p(x = 0.03) = 130.1$ meV, and $\varepsilon_1^p(x = 0.04) = 119.2$ meV (Fig. 4).

An increase of the rate of generation of donors over acceptors in the $n\text{-Ti}_{1-x}\text{Al}_x\text{NiSn}$ semiconductor of electronic conduction type naturally leads to a decrease in the degree of compensation. This is evidenced by the results of the calculated values of the amplitude of the large-scale fluctuation of the continuous energies bands from $\varepsilon_1^a(x = 0.02) = 130.2$ meV to $\varepsilon_1^a(x = 0.03) = 120.1$ meV and $\varepsilon_1^a(x = 0.04) = 113.3$ meV (Fig. 4).

So what is the nature of these structural defects of the donor nature, which give rise to new donor states in the band gap of ε_g $n\text{-Ti}_{1-x}\text{Al}_x\text{NiSn}$?

The analysis of the behavior of the concentration dependences of the specific electrical resistivity $\rho(x, T)$ and the thermopower coefficient $\alpha(x, T)$ of $n\text{-Ti}_{1-x}\text{Al}_x\text{NiSn}$ at different temperatures (Fig. 5) complements the results obtained above and the conclusions drawn, which allows us to identify the nature of these donor became.

An increase of the specific electrical resistivity $\rho(x, T)$ of $n\text{-Ti}_{1-x}\text{Al}_x\text{NiSn}$ in the concentration range $x = 0 - 0.01$ is possible in n -type semiconductor only if the concentration of free electrons decreases. This reason is the generation of acceptors in the semiconductor that capture electrons, which increases the degree of compensation of the semiconductor (Fig. 4). After all, the higher modulation amplitude of the continuous energy bands $\varepsilon_1^a(x)$, the higher the degree of compensation of the semiconductor [7].

The results of the kinetic and energy properties of $n\text{-Ti}_{1-x}\text{Al}_x\text{NiSn}$, $x = 0 - 0.01$, not only agree with the conclusions of structural studies, but also clarify them. In particular, when analyzing the features of structural changes in $n\text{-Ti}_{1-x}\text{Al}_x\text{NiSn}$, it was shown that the increase of the unit cell parameter $a(x)$ in the concentration range $x = 0 - 0.01$ can cause only partial occupation of the 4c position of Ni atoms by Al atoms. At the same time, acceptors are generated in the semiconductor, and their concentration should be \sim twice higher than the concentration of donors in $n\text{-TiNiSn}$. However, the sign of the thermopower coefficient $\alpha(x, T)$ of $n\text{-Ti}_{0.99}\text{Al}_{0.01}\text{NiSn}$ remains negative.

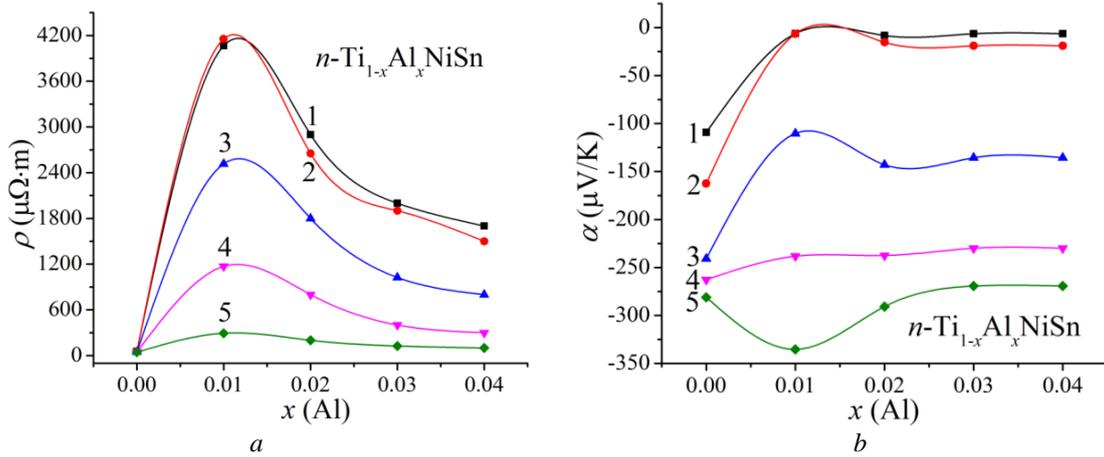


Fig. 5. Change in specific electrical resistivity values $\rho(x, T)$ (a) and the thermopower coefficient $\alpha(x, T)$ (b) for $n\text{-Ti}_{1-x}\text{Al}_x\text{NiSn}$ at different temperatures: 1 – $T=80$ K; 2 – $T=160$ K; 3 – $T=250$ K; 4 – $T=300$ K; 5 – $T=380$ K.

At the concentration $x = 0.01$, an extremum appears in the dependence of the specific electrical resistivity $\rho(x, T)$ of $n\text{-Ti}_{0.99}\text{Al}_{0.01}\text{NiSn}$. The appearance of an extremum on the dependence $\rho(x, T)$ is the result of a change in the ratio of ionized acceptors and donors present in the semiconductor.

The nature of the change in the values of specific electrical resistivity $\rho(x, T)$ and thermopower coefficient $\alpha(x, T)$ of $n\text{-Ti}_{1-x}\text{Al}_x\text{NiSn}$ at different temperatures is extremely interesting. From Fig. 5, it can be seen that for all studied concentrations ($x = 0\text{--}0.04$), the dependences of the specific electrical resistivity $\rho(x, T)$ and the thermopower coefficient $\alpha(x, T)$ at temperatures $T=80$ and $T=160$ K practically overlap each other. This shows that at temperatures $T = 80\text{--}160$ K, the concentration ratio of ionized acceptor and donor states in $n\text{-Ti}_{1-x}\text{Al}_x\text{NiSn}$ is unchanged, but the concentration of donors is greater. And only with an increase of temperature, $T \geq 250$ K, the amplitude of the extremum on the dependence of $\rho(x, T)$ rapidly decreases, the total conductivity of semiconductors increases, indicating an increase in the concentration of free electrons.

So what is their nature?

Paradoxically, at first view, the concentration of free electrons increases as the concentration of Al atoms (as if an acceptor impurity) increases, which is indicated by the negative sign of the thermopower coefficient $\alpha(x, T)$ of $n\text{-Ti}_{1-x}\text{Al}_x\text{NiSn}$. The fact that the values of $\rho(x, T)$ and $\alpha(x, T)$ significantly decrease at temperatures $T \geq 250$ K indicates the ionization of a group of donor states (ϵ_D^2 bands) located much deeper. These donor states (ϵ_D^2 bands) existed in $n\text{-TiNiSn}$ as a result of "a priori doping" of the semiconductor [4]. Ionization of these states is a source of free electrons, which increases the electrical conductivity of the semiconductor. And an additional mechanism for increasing the concentration of donor states in $n\text{-Ti}_{1-x}\text{Al}_x\text{NiSn}$ can only be the occupation of the tetrahedral voids of the structure by Al atoms, which generate structural defects of the donor nature [2].

Conclusions

According to the results of a comprehensive study of the structural, kinetic, and energy properties of the semiconductor solid solution $\text{Ti}_{1-x}\text{Al}_x\text{NiSn}$, obtained by introducing Al atoms into the structure of the TiNiSn half-Heusler phase by substituting Ti atoms in the $4a$ position, a complex nature of structural changes was revealed. It is shown that in the concentration range $x = 0\text{--}0.01$, Al atoms mainly replace Ni atoms in the $4c$ position, generating acceptor states. It was established that at temperatures $T=80\text{--}160$ K, the concentration ratio of ionized acceptor and donor states in $n\text{-Ti}_{1-x}\text{Al}_x\text{NiSn}$, $x=0\text{--}0.04$, is unchanged, but the concentration of donors is greater. At higher temperatures, $T \geq 250$ K, deep donor states that existed in $n\text{-TiNiSn}$ as a result of "a priori doping" of the semiconductor are ionized. An additional mechanism for the generation of donor states in $n\text{-Ti}_{1-x}\text{Al}_x\text{NiSn}$ when the tetrahedral voids of the structure are partially occupied by Al atoms was revealed. The concentration ratio of the generated donor-acceptor states determines the position of the Fermi level ϵ_F and the conductivity mechanisms of $n\text{-Ti}_{1-x}\text{Al}_x\text{NiSn}$. The studied semiconductor solid solution is a promising thermoelectric material.

The work was carried out within the framework of the Ministry of Education of Ukraine (grant No 0124U000989) and with the partial support of the Simons Foundation (Award Number: 1290588).

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Експериментальні дослідження нового термоелектричного матеріалу на основі напівпровідникового твердого розчину $Ti_{1-x}Al_xNiSn$

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Досліджено структурні, електрокінетичні та енергетичні властивості напівпровідникового твердого розчину $Ti_{1-x}Al_xNiSn$, отриманого уведенням до структури пів-Гейслерової фази $TiNiSn$ атомів Al шляхом заміщення у кристалографічній позиції 4a атомів Ti. Показано, що на ділянці концентрацій $x = 0-0.01$ атоми Al, в основному, заміщають у позиції 4c атоми Ni, генеруючи акцепторні стани. Встановлено, що за температур $T = (80-160)$ К співвідношення концентрацій іонізованих акцепторних та донорних станів у $n-Ti_{1-x}Al_xNiSn$, $x = 0-0.04$, є незмінним, однак концентрація донорів є більшою. За вищих температур, $T \geq 250$ К, відбувається іонізація глибоких донорних станів, які існували в $n-TiNiSn$ як результат «априорного легування» напівпровідника. Виявлено додатковий механізм генерування донорних станів у $n-Ti_{1-x}Al_xNiSn$ при частковому зайнятті атомами Al тетраедричних пустот структури. Співвідношення концентрацій генерованих донорно-акцепторних станів визначає положення рівня Фермі ϵ_F та механізми провідності $n-Ti_{1-x}Al_xNiSn$. Досліджений напівпровідниковий твердий розчин є перспективним термоелектричним матеріалом.

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