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FEATURES OF STRUCTURAL, ENERGY AND KINETIC CHARACTERISTICS OF *TiNiSn$_{1-x}$Ga$_x$* THERMOELECTRIC MATERIAL

The crystal and electronic structures, the temperature and concentration dependences of resistivity and the Seebeck coefficient of TiNiSn$_{1-x}$Ga$_x$ were investigated in the range of T = 80 – 400 K, x = 0.02 – 0.15. It was shown that doping of n-TiNiSn with Ga impurity atoms led to the generation in the crystal of acceptor structural defects at occupation by Ga atoms of 4b sites of Sn atoms, and donor defects as vacancies in the Sn atomic sites. The mechanism of conductivity of TiNiSn$_{1-x}$Ga$_x$ thermoelectric material was established.

Key words: electronic structure, resistivity, thermo-power coefficient.

Introduction

One of the methods for producing thermoelectric materials with high efficiency of thermal into electric energy conversion is generation in the crystal of donor and or acceptor structural defects, which under certain conditions changes the Seebeck coefficient and electric resistivity values [1].

Research on *n-TiNiSn* based thermoelectric materials prepared by substitution of *Sn* atoms has shown a complicated mechanism of impurity introduction into semiconductor structure. Thus, in the case of substitution of *Sn* ($5s^25p^2$) atoms by *In* ($5s^25p^1$) in *TiNiSn$_{1-x}$In$_x$* crystal there is simultaneous generation of both acceptor (*In* atom has less *p*-electrons than *Sn* atom) and donor structural defects through generation of vacancies in the crystallographic position *4b* of *Sn* atoms [2]. In so doing, the Fermi level ε_F remained near the conduction band, as evidenced by the negative values of the Seebeck coefficient. The absence of change in the Seebeck coefficient sign from negative to positive also took place in the case of *TiNiSn$_{1-x}$Al$_x$* [3], where the generation of acceptors was expected, since *Al* ($3s^23p^1$), just as In, possesses less *p*-electrons as compared to *Sn*.

The paper presents the results of research on the effect of *Ga* ($4s^24p^1$) doping impurity on the change in crystalline structure, distribution of the density of electronic states (DOS), electrokinetic and energy characteristics of *TiNiSn$_{1-x}$Ga$_x$*, which will make it possible to reveal the features of electric conductivity mechanism and develop ways for optimization of material parameters for getting maximum values of thermoelectric figure of merit [4].

Investigation procedures

The *TiNiSn$_{1-x}$Ga$_x$* samples were synthesized in the laboratory of Institute for Physical Chemistry, Vienna University. The X-ray structural analysis (powder method) was used to obtain the data arrays (diffractometer Guinier-Huber image plate system, *CuK*α_1), and Fullprof program [5] was employed for the calculation of structural characteristics. The chemical and phase compositions of the samples were controlled by microprobe analyzer (EPMA, energy-dispersive X-ray analyzer). The electronic structure calculations were performed by the Korringa-Kohn-Rostoker (KKR) method in coherent potential approximation (CPA) and local density approximation (LDA) [6] with the use of Moruzzi-Janak-Williams exchange-correlation potential [7]. The accuracy of calculating the position of the Fermi level ε_F is ± 8 meV. The temperature and concentration dependences of the electrical resistivity (ρ) and the Seebeck coefficient (α) were measured with respect to copper in the temperature range *T* = 80 ÷ 400 K, in the samples of *TiNiSn$_{1-x}$Ga$_x$*, *x* = 0.01 ÷ 0.10 ($N_A^{Ga} \approx 1.9 \cdot 10^{20}$ cm^{-3} ÷ $2.9 \cdot 10^{21}$ cm^{-3}).

Research on the crystalline structure of *TiNiSn$_{1-x}$Ga$_x$*

A microprobe analysis of the concentration of atoms on the surface of *TiNiSn$_{1-x}$Ga$_x$* samples has shown their conformity to the initial charge compositions, and X-ray phase and structural analyses have revealed no traces of other phases on X-ray diffraction patterns. As long as the atomic radius of *Ga* (r_{Ga} = 0.141 nm) is smaller than that of *Sn* (r_{Sn} = 0.162 nm), the monotonous decrease in the values of unit cell period *a(x)* of *TiNiSn$_{1-x}$Ga$_x$* served one of the arguments in favour of substitution of *Sn* atoms by *Ga* atoms (Fig. 1, curve 1).

Refinement of *TiNiSn$_{1-x}$Ga$_x$* crystalline structure by the powder method has confirmed the result of [8] as regards crystal structure disorder of *n-TiNiSn* (*x* = 0), the key point of which lies in a partial, up to ~ 1 %, occupancy by *Ni* atoms of the crystallographic position 4*a* of *Ti* atoms, and the semiconductor formula can be written as (*Ti$_{1-z}$Ni$_z$)NiSn*, *z* ≤ 0.01. If it is remembered that *Ni* ($3d^8 4s^2$) atom possesses a larger number of *d*-electrons than *Ti* ($3d^2 4s^2$) atom, donor structural defects are created in the crystal ("a priori" doping with donors [8]), and electrons are the majority carriers.

Structural investigations have also shown that introduction of *Ga* atoms puts into order crystalline structure of *TiNiSn$_{1-x}$Ga$_x$* ("heals" structural defects): *Ni* atoms leave the position of *Ti* (4 *a*) atoms. Moreover, structural changes contribute to the redistribution of the electronic density of states. Thus, if donor structural defects exist in *n-TiNiSn* as a result of displacement of up to ~ 1 % of *Ti* atoms by *Ni* atoms [8], then ordering of *TiNiSn$_{1-x}$Ga$_x$* structure is accompanied, on the one hand, by the reduction in the number of donors – *Ni* leaves the position of *Ti*.

On the other hand, as long as *Ga* atom has one *p*-electron less than *Sn* atom, the acceptor structural defects are generated in the crystal. In this case, doping of *n-TiNiSn* semiconductor of electron with the lowest concentrations of the acceptor impurity will increase the compensation ratio (the ratio between donors and acceptors) [1, 9]. At concentrations when *Ni* atoms leave position 4 *a* of *Ti* atoms, the concentration of acceptors in the crystal will increase, the type of majority carriers must change and the compensation ratio will decrease. It is important to note that ordering of *TiNiSn$_{1-x}$Ga$_x$* structure makes it stable, and the kinetic characteristics become reproducible during thermal cycling.

At the same time, contrary to expectations, simulation of change in the values of unit cell period *a(x)* of *TiNiSn$_{1-x}$Ga$_x$* in case of occupation by *Ga* atoms of crystallographic position 4 *b* of *Sn* atoms a decrease in the values of *a(x)* takes place faster (Fig. 1, curve 2) than the experiment gives (Fig. 1, curve 1).
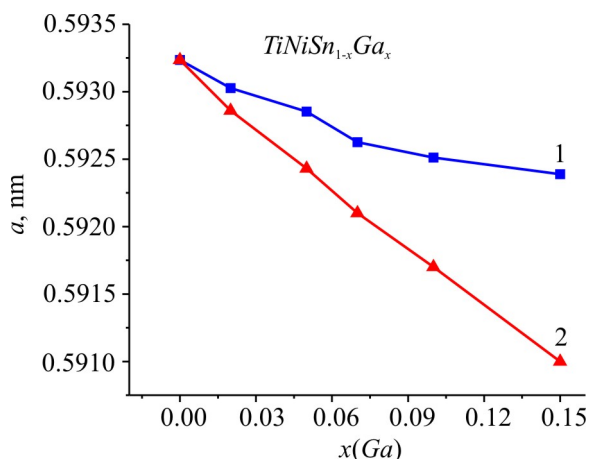
Fig. 1. Change in the values of unit cell period of TiNiSn$_{1-x}$Ga$_x$:
1 – experiment, 2 – calculation.

On the basis of the obtained it can be assumed that changes that took place in the structure of TiNiSn$_{1-x}$Ga$_x$ cannot be identified by X-ray investigation methods, however, they contribute to redistribution of the electronic density of states and, as a result, of crystal properties.

Research on the electronic structure of TiNiSn$_{1-x}$Ga$_x$

The density of electronic states (DOS) was calculated for simulation of electric conductivity mechanisms, the behaviour of the Fermi level ε_F, the energy gap ε_g of TiNiSn$_{1-x}$Ga$_x$. As long as doping of n-TiNiSn with Ga atoms puts into order crystalline structure, calculation of DOS was performed for the case of ordered structure version (Fig. 2). From Fig. 2 it is seen that on introduction into n-TiNiSn of Ga acceptor impurity, the Fermi level ε_F starts drifting from the bottom of the conduction band ε_C, spaced ~ 16.9 meV from it [8], toward the valence band ε_V, to cross it at $x \approx 0.04$.

The drift of the Fermi level ε_F from the conduction band edge ε_C to the valence band ε_V also means a change in the ratio of TiNiSn$_{1-x}$Ga$_x$ majority carriers. Thus, for the concentrations of TiNiSn$_{1-x}$Ga$_x$, $x < 0.02$, when the Fermi level ε_F is between the conduction band ε_C and the midgap ε_g, electrons are the majority carriers. In this case, doping of n-TiNiSn semiconductor of electron conductivity type with the lowest concentrations of acceptors will be accompanied by increase in the compensation ratio [1, 9]. In turn, at $x > 0.02$ and up to crossing of the valence band ε_V by the Fermi level ε_F holes are the majority carriers. In this case, doping of p-type semiconductor with acceptors must lead to a reduction of compensation ratio. Besides, crossing of the valence band by the Fermi level ε_F will also cause a change from the activation to metal conduction mechanism of TiNiSn$_{1-x}$Ga$_x$ (the dielectric-metal transition which is referred to as the Anderson transition [9]).

Calculation of the electronic density of states for TiNiSn$_{1-x}$Ga$_x$ allows predicting its kinetic characteristics, in particular, the behaviour of the Seebeck coefficient $\alpha(x, T)$ at different temperatures (Fig. 3). Below is given the working formula used for the calculation of $\alpha(x, T)$ [9]:

$$\alpha(x, T) = \frac{2\pi^2}{3} \frac{k_B^2 T}{e} \left(\frac{d}{d\varepsilon} \ln g(\varepsilon_F) \right) ,$$

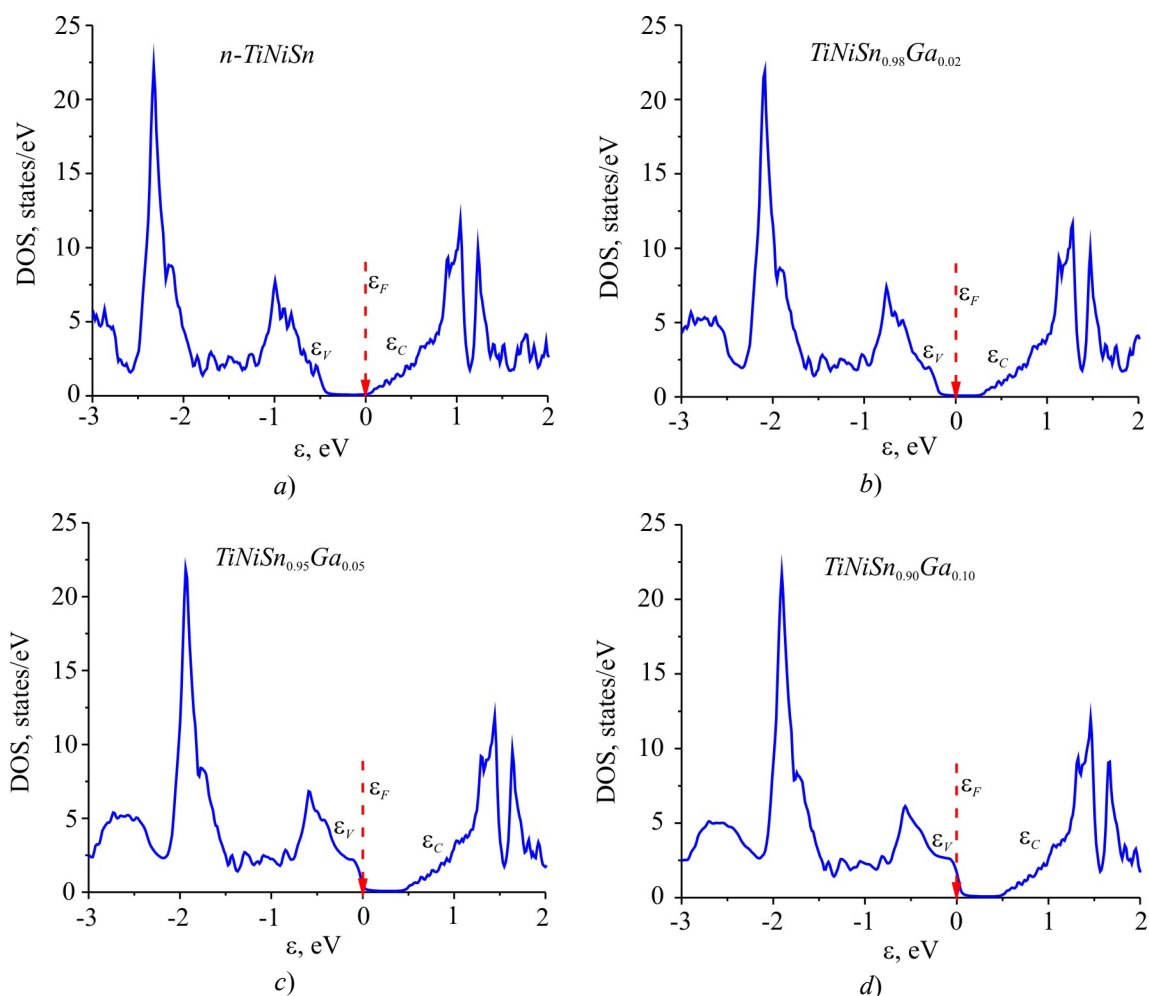where $g(\varepsilon_F)$ is the density of states at the Fermi level.

Fig. 2. Calculation of the electronic density of states for TiNiSn$_{1-x}$Ga$_x$.

From Fig. 3 it is seen that at different concentrations of *Ga* one can obtain in thermoelectric material high values of the Seebeck coefficient of both signs, assuring high values of thermoelectric figure of merit [4].
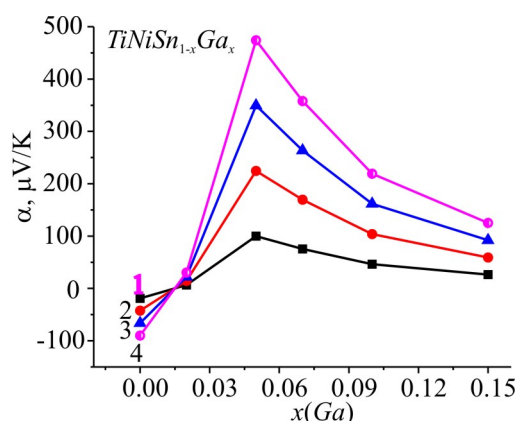

Fig. 3. Changes in the values of the Seebeck coefficient of TiNiSn$_{1-x}$Ga$_x$ at the temperatures:
1 – 80 K; 2 – 180 K; 3 – 280 K; 4 – 380 K.

Thus, the results of calculation of the electronic density of states for *TiNiSn$_{1-x}$Ga$_x$*, based on structural research data, prove the acceptor nature of generated defects. The results of research on the kinetic characteristics of *TiNiSn$_{1-x}$Ga$_x$* will show the degree of conformity of such calculations to real processes occurring in material.

Research on the electrokinetic and energy characteristics of *TiNiSn₁₋ₓGaₓ*

The temperature dependences of resistivity $\ln\rho(1/T)$ and the Seebeck coefficient $\alpha(1/T)$ for *TiNiSn₁₋ₓGaₓ* are presented in Fig. 4. From the high-temperature activation areas of $\ln\rho(1/T)$ dependences the activation energy from the Fermi level ε_F to the bands of continuous energies ε_1^ρ was calculated, and from the same $\alpha(1/T)$ dependences – the activation energies ε_1^α yielding the value of modulation amplitude of continuous energy bands for heavily doped compensated semiconductor [1, 9].

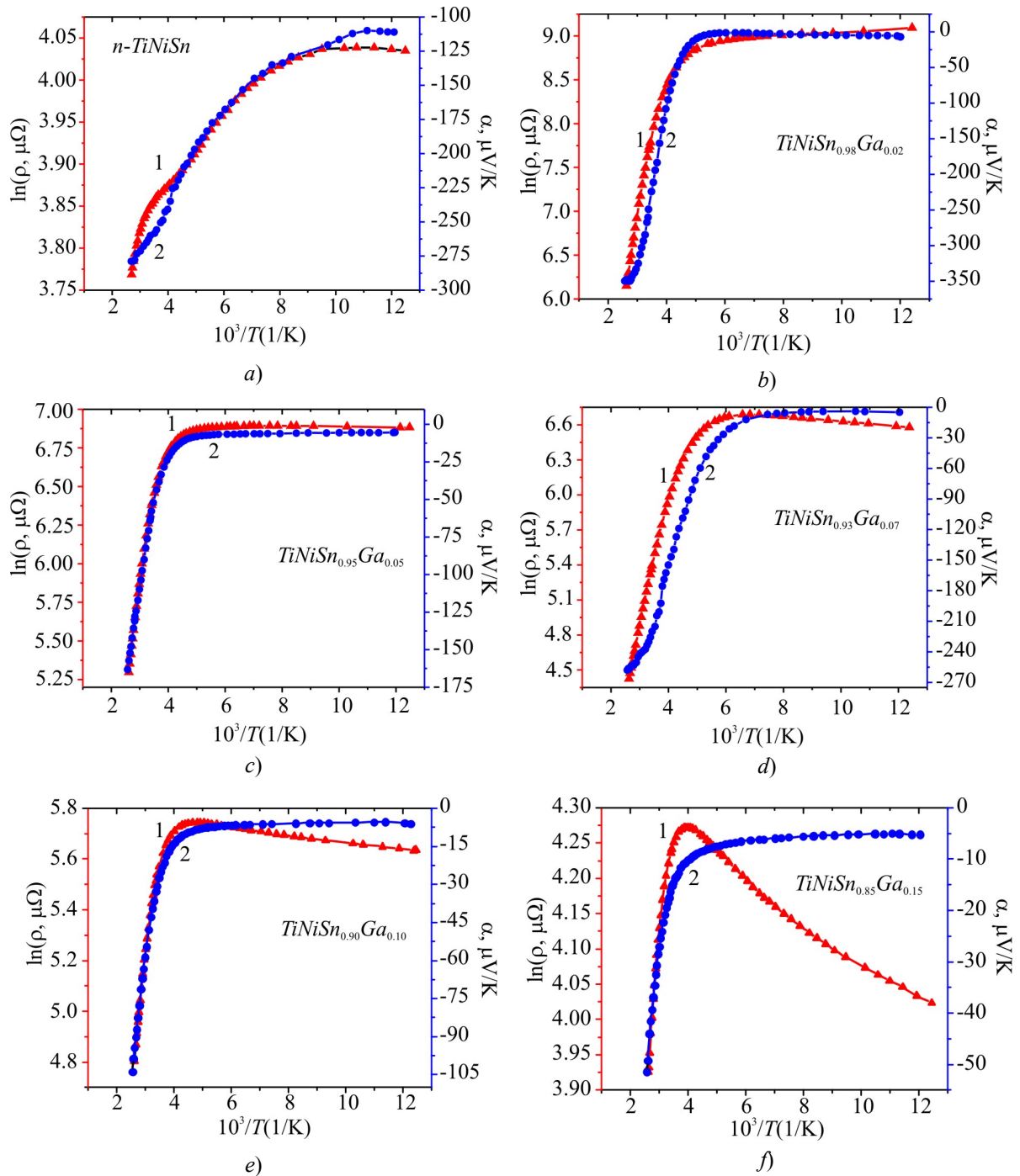*Fig. 4. Temperature dependences of the electric resistivity and the Seebeck coefficient of TiNiSn₁₋ₓGaₓ.*

As is seen from Fig. 4, for all compositions of *TiNiSn$_{1-x}$Ga$_x$* samples on the dependences $\ln\rho(1/T)$ there are high-temperature activation areas, which points to the arrangement of the Fermi level ε_F in the energy gap, from where carriers are activated to continuous energy bands. The result obtained contradicts to the results of calculations of DOS (Fig. 2) which predicted crossing by the Fermi level ε_F of the valence band and conductivity metallization at concentration *Ga* $x \approx 0.04$.

Introduction to *n-TiNiSn* of the lowest in the experiment concentration of *Ga* atoms by substitution of *Sn* is accompanied with a drastic increase in the values of electric resistivity $\rho(x)$ (Fig. 5 *a*), for instance, at 80 K, from the values of $\rho(x = 0) = 56.5$ μΩ·m to $\rho(x = 0.02) = 8885.2$ μΩ·m. Such behaviour of $\rho(x)$ at different temperatures (Fig. 5 *a*) is a manifestation of the above described structural feature of semiconductor which accounts for a simultaneous reduction of free electrons by two mechanisms: (1) – decreasing the number of donors, when *Ni* atoms leave position 4*a* of *Ti* atoms ("healing" of donor-nature defects) and (2) – "freezing out" of free electrons to acceptor band generated at occupation by *Ga* atoms of the position of *Sn* atoms. Exactly the reduction in the concentration of free electrons *n* leads to increase in the values of electric resistivity, since $\rho \sim 1/n$.
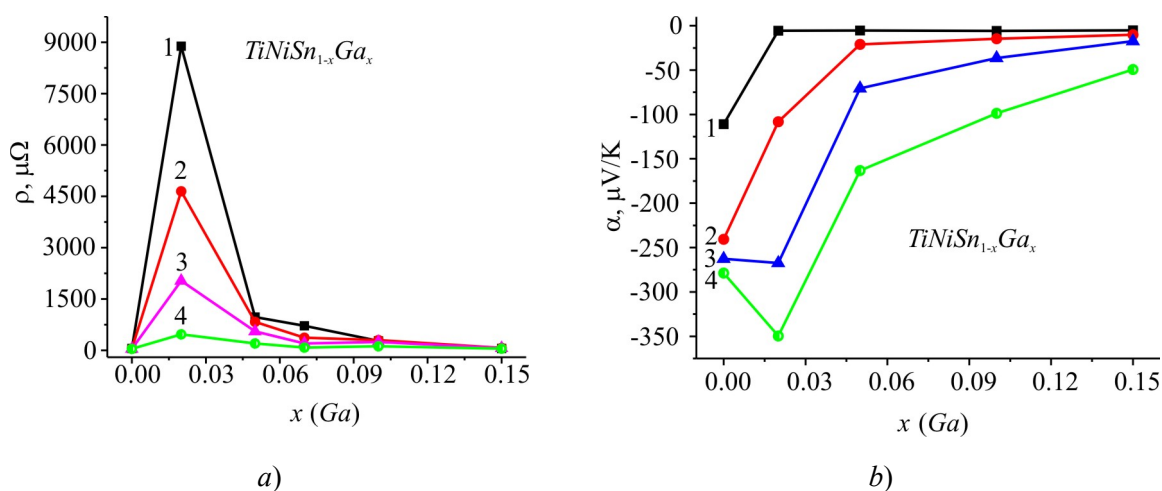

Fig. 5. Change in the values of the electric resistivity ρ(x) (a) and the Seebeck coefficient α(x) (b) of TiNiSn$_{1-x}$Ga$_x$ at the temperatures: 1 – 80 K; 2 – 160 K; 3 – 250 K; 4 – 380 K.

The presence of an extreme point on the dependence $\rho(x, T)$ at $x = 0.02$ (Fig. 5a) and the reduction of electric resistivity values of *TiNiSn$_{1-x}$Ga$_x$* at higher concentrations of *Ga* impurity atoms, for instance, at 80 K, from the values of $\rho(x = 0.05) = 975.3$ μΩ·m to $\rho(x = 0.10) = 280.1$ μΩ·m and $\rho(x = 0.15) = 55.9$ μΩ·m points to a drastic increase in the crystal of free carriers. *A priori*, based on the results of calculation of *TiNiSn$_{1-x}$Ga$_x$* electronic structure, such free carriers must be holes which will determine the electric conductivity of thermoelectric material.

However, the behaviour of the Seebeck coefficient of *TiNiSn$_{1-x}$Ga$_x$* $\alpha(x)$ (Fig. 4) and $\alpha(1/T)$ (Fig. 5 *b*) proved to be unexpected. Thus, the negative values of the Seebeck coefficient of *n-TiNiSn* (or, in the other form, *Ti$_{1-z}$Ni$_z$)NiSn*) are understandable and related to "a priori doping" of semiconductor with donors generated at occupation by *Ni* atoms of up to ~ 1 % ($z \approx 0.01$) of positions of *Ti* atoms [8].

In turn, in the sample of *TiNiSn$_{1-x}$Ga$_x$*, $x = 0.02$, the concentration of *Ga* acceptor impurity exceeds that of available donors ($y \approx 0.01$) in *n-TiNiSn* ("a priori" doping), and the state of strong compensation is realized when the Fermi level ε_F must be arranged a little lower than the midgap ε_g. At the same time, the negative values of the Seebeck coefficient at $x = 0.02$ testify (Fig. 4, 5 *b*) that the concentration of generated acceptors at the substitution of *Sn* atoms by *Ga* atoms is lower than the

concentration of donors, hence the Fermi level ε_F is fixed by the impurity donor band (above the midgap). It turns out that the concentration of donors ($z \approx 0.01$) in $TiNiSn_{1-x}Ga_x$, $x = 0.02$, exceeds the concentration of acceptors, though it should be the other way round. Moreover, in all the samples of $TiNiSn_{1-x}Ga_x$, $x \geq 0.02$, the values of the Seebeck coefficient remained negative and, for instance, at temperature 80 K they changed from the values of $\alpha(x = 0) = -110.9$ µV/K to $\alpha(x = 0.02) = -5.7$ µV/K anda $\alpha(x = 0.15) = -5.2$ µV/K and temperature 380 K from the values of $\alpha(x = 0.02) = -349.7$ µV/K to $\alpha(x = 0.15) = -49.3$ µV/K. The negative values of the Seebeck coefficient of $TiNiSn_{1-x}Ga_x$ for all compositions and temperatures under study indicate that electrons continue to remain the majority carriers in the crystal. Such behaviour of the Seebeck coefficient of $TiNiSn_{1-x}Ga_x$ reminds the behaviour of kinetic characteristics in the case of introduction into n-$TiNiSn$ of other p-elements In and Al [2, 3].

This result does not correspond to the results of calculations of DOS in $TiNiSn_{1-x}Ga_x$ performed for the ordered structure version. In such a case, only acceptor defects had to be generated in the crystal. The behaviour of the Seebeck coefficient (Fig. 4, 5 b) shows that donor defects are also generated in $TiNiSn_{1-x}Ga_x$ by the unknown mechanism and the concentration of donors exceeds the concentration of generated acceptors.

In this context it is interesting to trace the character of change in the energy characteristics of $TiNiSn_{1-x}Ga_x$ obtained from the experimental investigations of the temperature dependences of resistivity $\ln\rho(1/T)$ and the Seebeck coefficient $\alpha(1/T)$ (Fig. 6). Taking into account that the value of the Seebeck coefficient points to electrons as the majority carriers in $TiNiSn_{1-x}Ga_x$, the high-temperature activation areas on the dependences $\ln\rho(1/T)$ and $\alpha(1/T)$ reflect a complicated process of simultaneous thermal throw of electrons from the impurity donor area to the conduction band and of holes to the valence band. In so doing, the concentration component of free electrons exceeds that for holes.
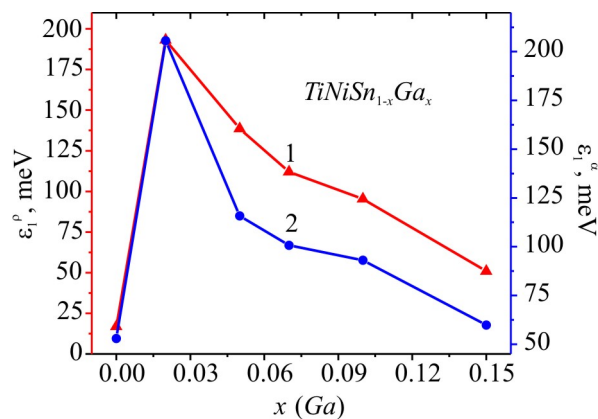

Fig. 6. Change in the values of activation energy $\varepsilon_1^\rho(x)$ (1) and $\varepsilon_1^\alpha(x)$ (2) of TiNiSn₁₋ₓGaₓ.

A drastic increase in the values of activation energy ε_1^ρ from 16.9 meV for $x = 0$ to $\varepsilon_1^\rho(x = 0.02) = 193.2$ meV clearly shows that the Fermi level ε_F moves toward the midgap and became essentially distant from the bottom of the conduction band. Such behaviour of the Fermi level ε_F can be only caused by the appearance in $TiNiSn_{1-x}Ga_x$ crystal of acceptors that trap free electrons, reducing their concentration, which increases the compensation ratio of semiconductor (the ratio between acceptors and donors). From the linear behaviour of $\varepsilon_1^\rho(x)$ in the concentration area $x = 0 - 0.02$ it can be argued that the Fermi level ε_F moves from the edge of conduction band at a rate of $\Delta\varepsilon_F/\Delta x = 88.2$ meV/% Ga. The obtained result is logical, since the concentration of Ga impurity grows by the linear law, and the acceptor defects are generated in $TiNiSn_{1-x}Ga_x$ by the same law.

However, further increase in the concentration of Ga atoms in $TiNiSn_{1-x}Ga_x$, $x > 0.02$ leads to a decrease in the values of activation energy ε_1^ρ (Fig. 6), which points to a reverse motion of the

Fermi level ε_F now toward the conduction band, as long as the values of the Seebeck coefficient remain negative (Fig. 4, 5 *b*). Thus, the values of activation energy ε_1^{ρ} decrease from $\varepsilon_1^{\rho}(x = 0.05) = 138.6$ meV to $\varepsilon_1^{\rho}(x = 0.10) = 95.4$ meV and $\varepsilon_1^{\rho}(x = 0.15) = 50.9$ meV, and the rate of motion of the Fermi level ε_F in the concentration area $x = 0.10 - 0.15$ is $\Delta\varepsilon_F/\Delta x = 8.5$ meV/% *Ga*. From the obtained result it follows that despite generation of a large number of acceptors in the crystal ($p = 2.9 \cdot 10^{21}$ cm^{-3} for $x = 0.15$), the concentration of electrons is larger. This raises the question as to the mechanism of generation in the crystal of donors that are the source of free electrons.

The simultaneous generation in the crystal of the donor and acceptor structural defects is accompanied by a change in the compensation ratio, as well a change in the modulation amplitude of continuous energy bands of heavily doped compensated semiconductors [1,9] according to the law reflecting the ratio between ionized acceptors and donors. A change in the values of activation energy $\varepsilon_1^{\alpha}(x)$ which is proportional to the modulation amplitude of continuous energy bands of *TiNiSn₁₋ₓGaₓ* and reflects the compensation ratio of semiconductor [1, 9] seems to be interesting. From Fig. 6 it is seen that for *n-TiNiSn* the modulation amplitude is $\varepsilon_1^{\alpha}(x = 0) = 52.9$ meV, and introduction into *n*-type semiconductor of the lowest in the experiment concentration of *Ga* impurity drastically increases the compensation ratio, pointing to the appearance of defects of the opposite sign – acceptors, as evidenced by increase in the values of the modulation amplitude $\varepsilon_1^{\alpha}(x = 0.02) = 205.6$ meV. In so doing, electrons remain the majority carriers, which corresponds to the behaviour of the activation energy of $\varepsilon_1^{\rho}(x)$ *TiNiSn₁₋ₓGaₓ*.

Further increase in the concentration of *Ga* atoms in *TiNiSn₁₋ₓGaₓ*, $x > 0.02$ is accompanied by the decrease in the values of activation energy $\varepsilon_1^{\alpha}(x)$ from $\varepsilon_1^{\alpha}(x = 0.05) = 115.8$ meV to $\varepsilon_1^{\alpha}(x = 0.10) = 93.03$ meV and $\varepsilon_1^{\alpha}(x = 0.15) = 59.8$ meV, pointing to the reduction of compensation ratio, which can be only possible on condition of electrons appearing in a crystal by the hitherto unknown mechanism whose total concentration exceeds the concentration of generated holes.

Thus, the results of structural investigations (the behaviour of unit cell period $a(x)$) and kinetic investigations (the negative values of the Seebeck coefficient) of *TiNiSn₁₋ₓGaₓ* semiconductor material enable us to speak of a complicated mechanism for the simultaneous generation in the crystal of the acceptor and donor structural defects on introduction of *Ga* atoms into the structure of *TiNiSn* compound by the substitution of *Sn* atoms. Note that no such defects have been revealed by structural investigations of *TiNiSn₁₋ₓGaₓ*, as long as their concentration is beyond the accuracy of X-ray investigation methods.

Refinement of crystalline and electronic structures of *TiNiSn₁₋ₓGaₓ*

For the identification of structural defects in *TiNiSn₁₋ₓGaₓ* the method proposed in [1] was employed. The electronic structure of *TiNiSn₁₋ₓGaₓ* was calculated for different variants of atoms arrangement in the unit cell sites and for a different degree of occupancy of crystallographic positions of all atoms by proper or foreign atoms (Fig. 7).

We sought for such spatial arrangement of atoms in the unit cell (or their vacancies) of *TiNiSn₁₋ₓGaₓ* (the ratio between the donor and acceptor defects – compensation ratio), when the calculated rate and character of motion of the Fermi level ε_F will agree with the experimentally obtained numerical values of activation energy $\varepsilon_1^{\rho}(x)$ from the Fermi level ε_F to the edge of the conduction band. It turned out that the most acceptable version of atoms arrangement in *TiNiSn₁₋ₓGaₓ* provides for the emergence of vacancies in position (4 *b*) of *Sn* atoms whose concentration grows with increase in the number of *Ga* atoms.
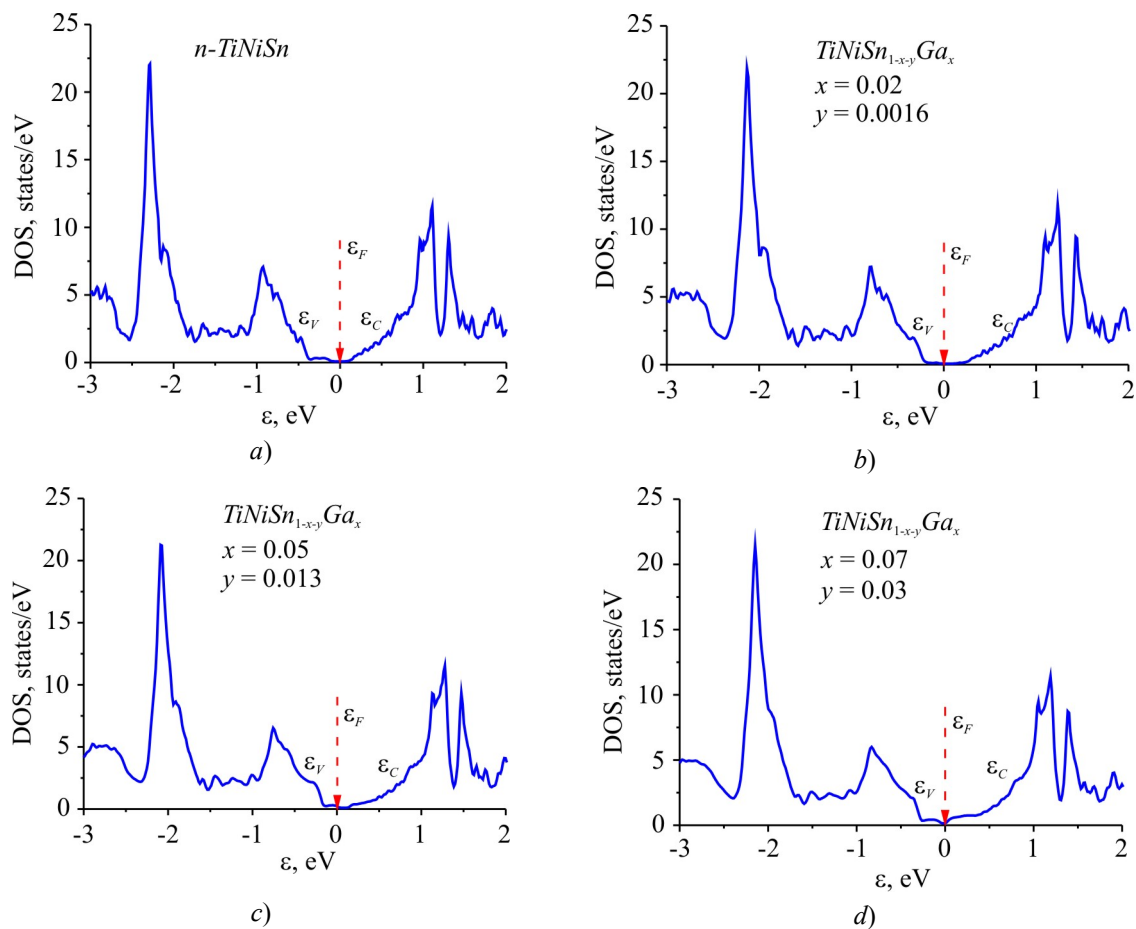
Fig. 7. Refined calculation of the electronic density of states of TiNiSn$_{1-x}$Ga$_x$.

In this case the formula of thermoelectric material can be written as *TiNiSn$_{1-x-y}$*, where *y* is concentration of vacancies in position (4 *b*) of *Sn* atoms. Based on the new results of the spatial arrangement of atoms in *TiNiSn$_{1-x}$Ga$_x$* crystalline structure, more refined calculations were made of the electronic density of states distribution (Fig. 7) and, specifically, the density of states at the Fermi level $g(\varepsilon_F)$ that are consistent with the experimental results.

Conclusions

Thus, as a result of integrated research on the structural, energy and kinetic characteristics of *n-TiNiSn* intermetallic semiconductor heavily doped with *Ga* atoms, the mechanisms for the simultaneous generation in the crystal of the acceptor and donor structural defects have been identified that change the compensation ratio of thermoelectric material. The obtained results made it possible to reveal the features of electric conductivity mechanism at different concentrations and to develop ways for optimization of material parameters for getting maximum values of thermoelectric figure of merit [4].

References

1. V.A.Romaka, V.V.Romaka, and Yu.V.Stadnyk, *Intermetallic Semiconductors: Properties and Application* (Lviv:Lvivska Polytechnika, 2011), 488 p.

2. Yu.V.Stadnyk, V.A.Romaka, Peculiarities of Electric Conductivity Mechanisms of Semiconductor Solid Solution *TiNiSn$_{1-x}$In$_x$*, *J.Thermoelectricity* 1, 43 – 51 (2007).

3. L.P.Romaka, Yu.V.Stadnyk, A.M.Goryn, Yu.K.Gorelenko, and Skolozdra, *MgAgAs* Structure Type Solid Solutions as a New Thermoelectric Material, *Proc.16th Intern. Conf. Thermoelectrics* (Dresden, Germany, 1997, 516 – 519).

4. L.I.Anatychuk, *Thermoelements and Thermoelectric Devices* (Kyiv: Naukova Dumka, 1979), 768 p.

5. T.Roisnel, J.Rodriguez-Carvajal, WinPLOTR: a Windows Tool for Powder Diffraction Patterns Analysis, *Mater. Sci. Forum, Proc. EPDIC7*, **378 – 381**, 118 – 123 (2001).

6. M.Schruter, H.Ebert, H.Akai, P.Entel, E.Hoffmann, and G.G.Reddy, First-Principles Investigations of Atomic Disorder Effects on Magnetic and Structural Instabilities in Transition-Metal Alloys, *Phys. Rev. B* **52**, 188 – 209 (1995).

7. V.L.Moruzzi, J.F.Janak, and A.R.Williams, *Calculated Electronic Properties of Metals* (NY: Pergamon Press, 1978), 348 p.

8. V.A.Romaka, P.Rogl, V.V.Romaka, E.K.Hlil, Yu.V.Stadnyk, and S.M.Budgerak, Features of «a priori» Heavy Doping of the *n-TiNiSn* Intermetallic Semiconductor, *Semiconductors* 45, 850 – 856 (2011).

9. B.I.Shklovsky, *Electron Properties of Doped Semiconductors* (Moscow: Nauka, 1979), 416 p.