PHYSICS AND CHEMISTRY OF SOLIDSTATE
V. 18, № 2 (2017) P. 187-193
DOI: 10.15330/pcss.18.2.187-193

ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 18, № 2 (2017) С. 187-193

УДК 537.311.322

ISSN 1729-4428

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Investigation of Band Structure of $ZrNiSn_{1-x}Ga_x$ Semiconductor Solid Solution

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The mechanism of simultaneous generation of donor-acceptor pairs in $ZrNiSn_{1-x}Ga_x$ semiconductor solid solution is established. The modeled distribution of atoms in the crystal lattice of $ZrNiSn_{1-x}Ga_x$ showed that the speed of movement of Fermi level ε_F, obtained from the band structure calculations is in agreement with experimental extracted from $\ln\rho(1/T)$ dependencies. It is shown that with substitution of Sn ($5s^25p^2$) with Ga ($4s^24p^1$) atoms in 4*b* crystallographic site both acceptor and donor (vacancies in 4*b* site) defects are generated.
Keywords: crystal and electronic structures, conductivity, thermopower coefficient.

Article acted received 31.03.2017; accepted for publication 05.06.2017.

Introduction

The study of the electrokinetic and energy state characteristics of *n*-ZrNiSn [1] and *n*-TiNiSn [2] intermetallic semiconductors doped by Ga acceptor impurity introduced by substitution for the Sn atoms revealed the appearance of the considerable number of the electrons with unknown origin mechanism, the concentration of which increases with increasing of Ga content. Structural studies did not reveal any structural defects of donor nature in $ZrNiSn_{1-x}Ga_x$ and $TiNiSn_{1-x}Ga_x$, which could be a source of electrons, since their concentration lies beyond the limit of the accuracy of X-ray method. At the same time, the crystal structure refinements of $ZrNiSn_{1-x}Ga_x$ and $TiNiSn_{1-x}Ga_x$ [1, 2] showed that substitution of Sn atoms by Ga (Fig. 1) ordered their crystal structure: all the atoms occupied their own crystallographic site in accordance with the MgAgAs structure type [3].

It worth to note that the crystal structures of ZrNiSn and TiNiSn compounds are disordered due to partial up to about 1 % occupation of Zr(Ti) ($4d^25s^2$) atoms by Ni ($3d^84s^2$) atoms in the 4*a* atomic positions [4]. It leads to generation of the structural defects with donor nature ("a priori doping") caused by higher number of *d*-electrons in the Ni atoms, and the donor impurity levels ε_D^1 appear in the band gap. Taking into account that the Ga ($4s^24p^1$) atom has one *p*-electron less than Sn ($5s^25p^2$) atom, the substitution of Sn atom by Ga atom generates acceptor defect in the 4*b* site that lead to an appearance of the acceptor impurity levels in the band gap, which in a significant number of impurities formed extended impurity acceptor band ε_A.

Since the electrokinetic study of $ZrNiSn_{1-x}Ga_x$ and $TiNiSn_{1-x}Ga_x$ [1, 2] showed that at the temperatures $T = 80$ K and $T > 250$ K the sign of the thermoelectric coefficient remained negative for all concentrations of Ga impurity atoms, the authors suggested that simultaneously acceptor defects and donor defects as vacancies in 4*b* position of Sn atoms, i.e. donor-acceptor pairs, were generated. The additional investigations, especially, studies of electronic structure are necessary to confirm this supposition.

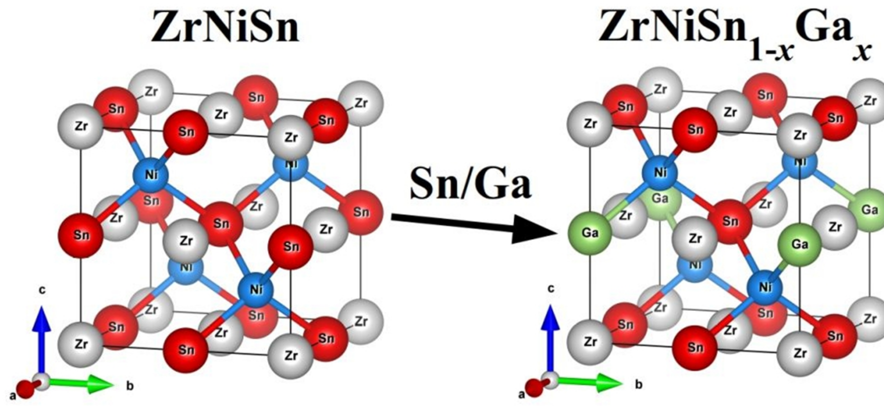

Fig. 1. Model of transformation of the ZrNiSn crystal structure to $ZrNiSn_{1-x}Ga_x$ (MgAgAs structure type, space group *Fm*-43*m*).

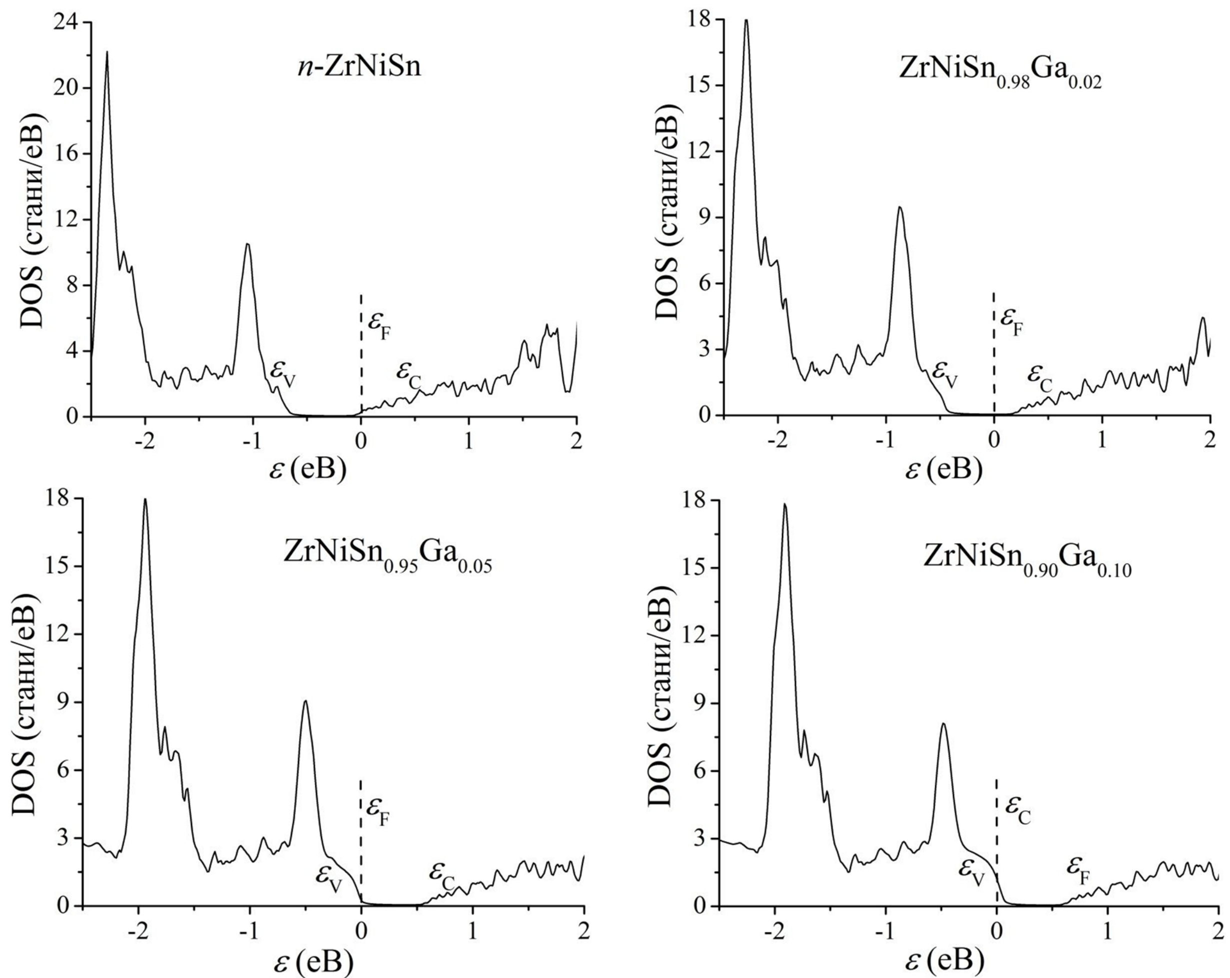

Fig. 2. Calculated distribution of the density of electronic states DOS of $ZrNiSn_{1-x}Ga_x$ due to substitution of Sn atoms by Ga.

It is known that to calculate the electron energy in the first Brillouin zone it is necessary to know the distribution of atoms in crystallographic sites (or their absence – vacancies) in the unit cell. On the other hand the negligible structural changes lead to changes of the local symmetry and distribution of the density of electronic states. In this case the closeness of the calculated density of electronic states and results of experimental study of energy state characteristics of semiconductive material provides that the model of its crystal structure corresponds to spatial distribution of atoms in crystalline substance. The calculations of electronic structure in comparison with the results, for example, of kinetic and energy state characteristics give an opportunity to obtain information about the real crystal structure, which is inaccessible by X-ray methods.

Therefore, the aim of the present work is calculation of electronic structure of $ZrNiSn_{1-x}Ga_x$ for different variants of spatial atoms distribution in the unit cell or their absence (vacancies) to choice such variant of distribution of atoms or existent vacancies for which the calculated behavior of fundamental parameters of electronic structure for semiconductive solid solution will coincide with those obtained by electrokinetic study [1].

I. Experimental details

The calculations of electronic structure of semiconductive $ZrNiSn_{1-x}Ga_x$ solid solution were carried out using the Korringa-Kohn-Rostoker (KKR) method in the coherent potential approximation (CPA) and local density approximation (LDA) [5] and LMTO based on Density Functional Theory DFT. The experimental values of the lattice parameter [1] on the *k*-grid equal to 10×10×10 *k*-points and type of parametrization of exchange-cross-correlation potential Moruzzi-Janak-Williams [6] were used. The width of energy window was equal to 16 eV, and exactness of calculation of the Fermi level position ε_F was equal ±8 meV for 1000 energy values.

II. Investigation of electronic structure for $ZrNiSn_{1-x}Ga_x$ with consideration of substitution of Sn for Ga

To predict the behavior of the Fermi level ε_F, band gap ε_g and electrokinetic characteristics for $ZrNiSn_{1-x}Ga_x$ the calculation of the density of electronic states (DOS) was performed (Fig. 2). Taking into account the results of the structural study [1] according to which doping of ZrNiSn structure by Ga atoms at the $0 \leq x \leq 0.01$ concentration range led to its ordering where Zr atoms replaced Ni atoms in the 4*a* site ("healing" of structural defects) the calculation DOS was carried out for ordered variant of structure with substitution of Sn atoms for Ga atoms.

As seen in Fig. 2, the Fermi level ε_F (dotted line) of *n*-ZrNiSn semiconductor is located near the bottom of conduction band, which is characteristic of the semiconductors with electron type of conductivity and corresponds to the results of electrokinetic studies [1]. Upon introduction into *n*-ZrNiSn the least accessible in experiment concentrations of Ga acceptor impurity the degree of compensation of semiconductor increases and the Fermi level ε_F begins to drift from the conduction band ε_C to the middle of the band gap.

In this context it is necessary to note that at $0 < x \leq 0.1$ concentration range of Ga an additional structural factor will affect on the motion rate of the Fermi level ε_F from the edge of conduction band in direction to the middle of the band gap, because the ordering of crystal structure of $ZrNiSn_{1-x}Ga_x$ accompanied with restructuring of electronic structure. Thus, if the donor levels ε_D^1 exist in the band gap of *n*-ZrNiSn as a result of structure disordering [3], then its ordering (displacement of Ni from Zr position (4*a*)) leads to decreasing of donor number and elimination of donor band ε_D^1. In this case two factors effect on degree of compensation and position of the Fermi level at concentration range of Ga atoms $0 < x \leq 0.1$:

a) occupation of impurity Ga atoms the crystallographic position 4*b* of Sn atoms generates the structural defects of acceptor nature, concentration of which increases linearly;

b) introduction of Ga atoms orders the structure of $ZrNiSn_{1-x}Ga_x$ and decreases the number of defects of donor nature because Ni atoms leave the position 4*a* of Zr atoms.

At higher concentration of Ga impurity the Fermi level ε_F will cross the middle of the band gap ($x \approx 0.025$) and will move to the valence band which will cross it at Ga concentration $x \approx 0.05$, i.e. the insulator-metal transition of conduction realized (Anderson transition) [7]. At such concentration of Ga impurity the type of conduction of semiconductor change, the halls become the main charge carriers and the compensation degree of

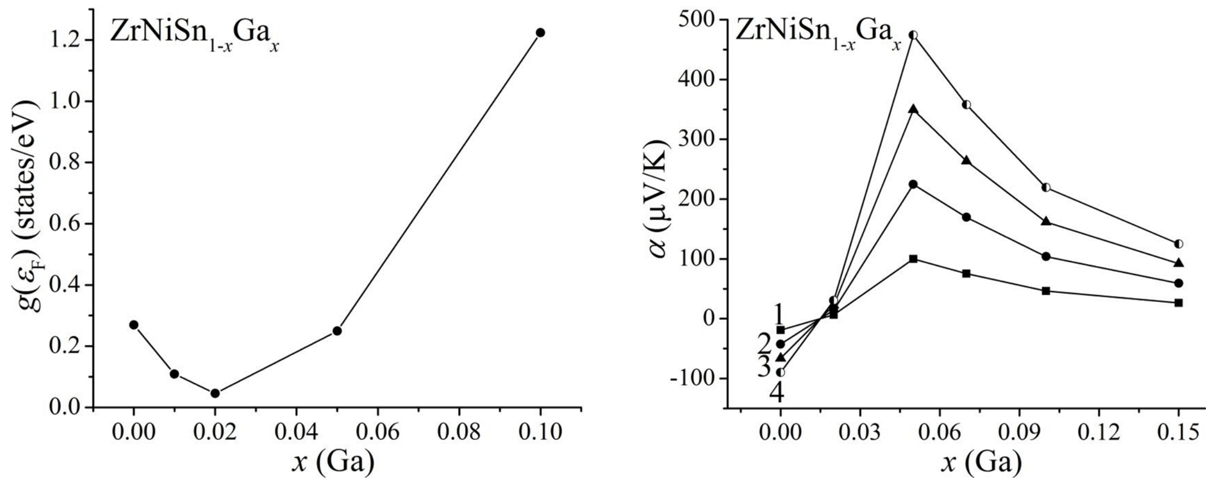

Fig. 3. Calculated variation of the density of electronic states at Fermi level $g(\varepsilon_F)$ (***a***) and thermopower coefficient (***b***) of $ZrNiSn_{1-x}Ga_x$ at different temperatures: 1 – 80 K; 2 – 160 K; 3 – 250 K; 4 – 380 K.

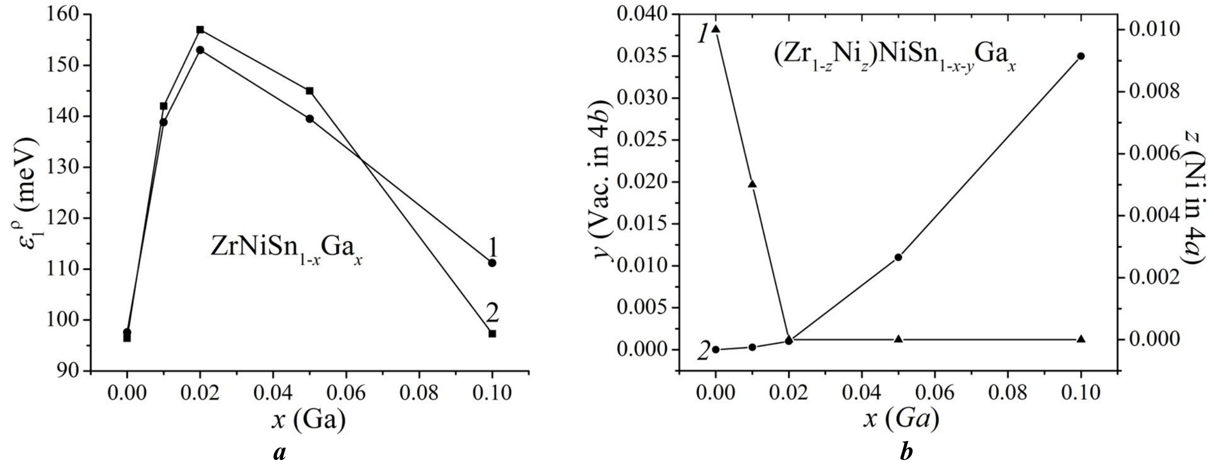

Fig. 4. Experimental (1) and calculated (2) concentration dependencies of the energy activation ε_1^{ρ} from the Fermi level to edge of the conduction band (***a***) and dynamics of concentration variation of Ni atoms (z) in 4a position of Zr atoms and vacancies (y) in 4b position of Sn atoms (2) (b) for $ZrNiSn_{1-x}Ga_x$.

p-$ZrNiSn_{1-x}Ga_x$ at $x > 0.025$ decreases.

The predicted behavior of the Fermi level ε_F is accompanied with interesting behavior of the density of states at Fermi level $g(\varepsilon_F)$ (Fig. 3, a). Doping of n-ZrNiSn by Ga acceptor impurity leads to decreasing of $g(\varepsilon_F)$ values, and minimum of $g(\varepsilon_F)$ dependence at $x \approx 0.025$ corresponds to the crossing by the Fermi level ε_F of the middle of the band gap for $ZrNiSn_{1-x}Ga_x$. At Ga concentrations, when the Fermi level ε_F crosses the middle of the band gap and be approached to the valence band ε_V the density of states at the Fermi level $g(\varepsilon_F)$ starts to increase.

The calculation of the electronic structure of the $ZrNiSn_{1-x}Ga_x$ solid solution allow to predict its electrokinetic characteristics, in particular, behavior of the thermopower coefficient, electrical resistivity, etc. The values of the thermopower coefficient were calculated according to the following formula [7]:

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

The variation of the thermopower coefficient values $\alpha(x)$ for $ZrNiSn_{1-x}Ga_x$ at different temperatures, for example, is shown in Fig. 3, b. As seen, at different Ga concentration we can obtain for the semiconductive solid solution high positive and negative values of the thermopower coefficient, which is the one of the conditions to achive high values of the thermoelectric power factor.

The calculations DOS, $g(\varepsilon_F)$ and $\alpha(x)$ for $ZrNiSn_{1-x}Ga_x$ described above were performed with supposition that the classic substitutional solid solution was realized, which allowed only one structural change such as substitution of Sn atom for Ga. In this way the unit cell of the $ZrNiSn_{1-x}Ga_x$ solid solution, and as result, the reverse unit cell of Vigner-Seitz, which is the first Brillouin zone was constructed and for which the calculation of the electron energy was carried out.

Comparative analysis of the experimental study of the electrokinetic and energy state characteristics of the semiconductive solid solution $ZrNiSn_{1-x}Ga_x$ [1] and described above calculation of its electronic structure shows the row of the fundamental contradictions. The presence of high-temperature activation parts in the $\ln\rho(1/T)$ dependences for all $ZrNiSn_{1-x}Ga_x$ samples shows that the Fermi level ε_F is located in the band gap, from which the thermal activation of carriers to the continuous energy band takes place. At the same time the DOS calculations for $ZrNiSn_{1-x}Ga_x$ (Fig. 2) predict a crossing of the top of the valence band ε_V by the Fermi level ε_F and insulator-metal transition of conduction at Ga concentration $x \approx 0.05$. Assuming that in $ZrNiSn_{1-x}Ga_x$ only one structural change, namely substitution of Sn atom for Ga atom was realized, at the concentration of the acceptor impurity Ga, for example, $x = 0.15$ ($N_A^{Ga} \approx 3\cdot10^{21}$ cm^{-3}) the Fermi level ε_F exactly could cross the valence band. Actually, there is a logical question what restrains crossing by the Fermi level ε_F of the valence band and metallization of conduction at such giant concentrations of impurity and hold the Fermi level ε_F to remain in the band of forbidden energies, representing the compensation degree of $ZrNiSn_{1-x}Ga_x$?

Other discrepancy between the experimental results and calculated electronic structure of $ZrNiSn_{1-x}Ga_x$ concerns to the behavior of the thermopower coefficient $\alpha(x)$. Study of the temperature and concentration dependencies of the thermopower coefficient for $ZrNiSn_{1-x}Ga_x$, for example, at temperature 80 K showed [1] that sign of the thermopower coefficient $\alpha(x)$ was negative for all concentrations and electrons were the main carriers of current. However, the calculations of the density of electronic states (Fig. 2) predict that the Fermi level ε_F will cross the middle of the band gap and will be approached to the valence band ε_V at concentration $x > 0.025$. It results in appearance and increasing of concentration of the free holes as the main carriers of current, which corresponds to the positive values of thermopower coefficient $\alpha(x)$. The calculation of the variation of the thermopower coefficient values $\alpha(x)$ at different temperatures also indicates about the change of the main carriers of current (Fig. 3, b).

Thus, the electronic structure calculations for ordered variant of the $ZrNiSn_{1-x}Ga_x$ crystal structure with substitution of Sn atom for Ga which generates in crystal the structural defects of acceptor nature are not consistent with the results of the electrokinetic studies [1].

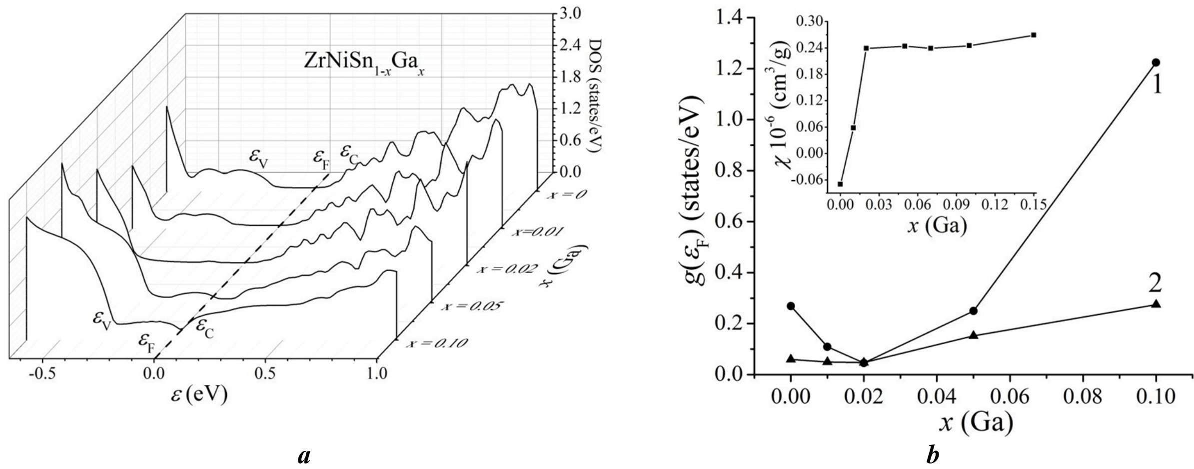

Fig. 5. Calculated distribution of the density of electronic states with taking into account the generation of donor-acceptor pairs in $ZrNiSn_{1-x}Ga_x$ (***a***) and the density of electronic states at Fermi level $g(\varepsilon_F)$ (***b***): 1 – with generation of acceptors; 2 – with generation of donor-acceptor pairs. Insert ***b***: variation of the magnetic susceptibility values $\chi(x)$ of $ZrNiSn_{1-x}Ga_x$ at the temperature 300 K.

Obviously, the semiconductive $ZrNiSn_{1-x}Ga_x$ solid solution has more complex mechanism of simultaneous generation of structural defects of acceptor and donor nature.

It can be stated that for agreement of the calculated electronic structure of $ZrNiSn_{1-x}Ga_x$, in particular, of the direction and motion rate of the Fermi level ε_F with position of the Fermi level ε_F calculated from high temperature regions of $\ln\rho(1/T)$ dependencies [1], it is necessary to make the principal changes in distribution of the atoms in the sites of unit cell for semiconductive solid solution. To decide this problem we will use the method of optimisation of crystal structure model based on the calculated electronic structure and physical properties of $ZrNiSn_{1-x}Ga_x$ [8].

III. Mechanism of generation of donor-acceptor pairs in $ZrNiSn_{1-x}Ga_x$

To decide indicated problem the calculation of the density of electronic states (DOS) was carried out practically for all variants of the distribution of atoms in the unit cell, occupancy of the crystallographic positions by own and/or other atoms and the presence of vacancies. From the experimental results of the drift rate of the Fermi level ε_F as activation energy $\varepsilon_1^{\rho}(x)$ for $ZrNiSn_{1-x}Ga_x$ (Fig. 4, *a*, curve 1) the compensation degree (correlation between structural defects of donor and acceptor nature) which will set the motion rate of the Fermi level maximally near to $\varepsilon_1^{\rho}(x)$ was found.

The results of the dynamics of change of all structural defects upon high doping of *n*-ZrNiSn by Ga acceptor impurity, which provides proximity of the calculated motion rate of the Fermi level ε_F (Fig. 4, *a*, curve 2) and motion rate obtained from high temperature regions of lnρ (1/*T*) dependencies (Fig. 4, *a*, curve 1) within the calculation errors is shown in Fig. 4, *b*. It turned out that the most acceptable is a variant of distribution of atoms in ordered, but deformed structure with such changes:

a) crystal structure of *n*-ZrNiSn is disordered (local amorphization) caused by partial occupation (up to ~1 %, $z \approx 0.01$) of Zr atoms by Ni atoms in 4*a* position, which generates the structural defects with donor nature in semiconductor (formula of semiconductor is $(Zr_{1-z}Ni_z)NiSn$)) [4];

b) introduction of Ga atoms orders the structure and reduces the number of the structural defects with donor nature: Ni atoms leave the 4*a* site of Zr atoms ($z \to 0$), and formula of the semiconductive solid solution should be written as $(Zr_{1-z}Ni_z)NiSn_{1-x}Ga_x$;

c) occupation of the crystallographic position 4*b* of Sn atoms by Ga impurity atoms generates the structural defects with acceptor nature;

d) generation and increasing of vacancies number (*y*) in 4*b* position of Sn atoms (final formula is $(Zr_{1-z}Ni_z)NiSn_{1-x-y}Ga_x$).

In this context we can note that simultaneous generation of the donor-acceptor pairs provides the principle of electrical neutrality in 4*b* position and structure stability of the solid solution.

Based on obtained results of the atomic distribution with taking into account the generation of the donor-acceptor pairs in $ZrNiSn_{1-x}Ga_x$ the calculation of the density of electronic states (DOS) which adequately represented the compensation degree of semiconductive solid solution was performed (Fig. 5, a). As seen in Fig. 5*a*, the Fermi level ε_F of $ZrNiSn_{1-x}Ga_x$ insignificantly changed its position relative to the conduction band edge that corresponded to the negative values of the thermopower coefficient and agreed with results of the electrokinetic studies [1].

The calculation of the variation of the density of electronic states at Fermi level $g(\varepsilon_F)$ for $ZrNiSn_{1-x}Ga_x$ taking into account the generation of the donor-acceptor pairs (Fig. 5, *b*, curve 2) differs significantly from those in the case of generation only the crystal defects with acceptor nature in crystal (Fig. 5, *b*, curve 1). As seen, the density of electronic states at Fermi level $g(\varepsilon_F)$ in the case of generation the donor-acceptor pairs varies more

slowly than in the case of generation in semiconductor only the defects with acceptor nature (substitution of Sn by Ga). These calculations correspond to the results of the kinetic studies of $ZrNiSn_{1-x}Ga_x$ [1].

The results of the investigation of the magnetic susceptibility χ for $ZrNiSn_{1-x}Ga_x$ (insert in Fig. 5, *b*) appeared to be interesting and confirmed expounded conclusion about simultaneous generation in the solid solution the structural defects of acceptor and donor nature. Performed studies showed that the $ZrNiSn_{1-x}Ga_x$ samples, $x > 0.01$, are Pauli paramagnets, magnetic susceptibility χ of which is determined exceptionally by electron gas and is proportional to the density of states at the Fermi level $g(\varepsilon_F)$. As seen in Fig. 5, *b*, $\chi(x)$ dependence at $x > 0.03$ rapidly changes slope, goes on a plateau and remains virtually unchanged up to $x = 0.15$. It means that increasing of the concentration of the acceptor impurity and possible increasing of the free holes practically do not change the $g(\varepsilon_F)$ values for the $ZrNiSn_{1-x}Ga_x$ semiconductive solid solution. This behavior of $\chi(x)$ (χ~$g(\varepsilon_F)$) is possible only at appearance in the $ZrNiSn_{1-x}Ga_x$ the *charge carriers* of opposite sign with concentration close to holes concentration as a result of the generation of donor-acceptor pairs, that cause invariability of the density of states at Fermi level $g(\varepsilon_F)$. It's noted, that *n*-ZrNiSn semiconductor is weak diamagnet that is evidenced by negative values of the magnetic susceptibility: $\chi(x = 0) = -0.07$ cm^3/g. Therefore, the growth of the $\chi(x)$ dependence at the concentration range $x = 0$ - 0.01 cannot be explained by increasing of $g(\varepsilon_F)$ values.

Conclusions

Thus, using the method of optimization of the crystal structure model based on the calculated electronic structure and physical properties for $ZrNiSn_{1-x}Ga_x$ allows us to establish the mechanism of simultaneous generation of the structural defects with acceptor and donor nature (donor-acceptor pairs) which change the compensation degree and obtain the electrical conduction mechanism of material. Investigated $ZrNiSn_{1-x}Ga_x$ semiconductive solid solution is a perspective thermoelectric material and ordering of the crystal structure provides the stability and reproducibility of the characteristics.

The work was supported by the Ministry of Education and Science of Ukraine (grants No. 0115U003257 and 0114U005464).

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[1] L.P. Romaka, V.A. Romaka, Yu.V. Stadnyk, P.-F. Rogl, V.Ya. Krayovskyy, A.M. Horyn, Z.M. Rykavets, PCSS 18(1), 41 (2017).
[2] V.A. Romaka, P. Rogl, L.P. Romaka, Yu.V. Stadnyk, V.Ya. Krayovskyy, D. Kaczorowski, A.M. Horyn, Journal of Thermoelectricity (3), 24 (2016).
[3] V.V. Romaka, L.P. Romaka, V.Ya. Krayovskyy, Yu.V. Stadnyk, Stannides of rare earth and transition metals Станіди рідкісноземельних та перехідних металів (Lvivska Politekhnika, Lviv, 2015).
[4] V.V. Romaka, P. Rogl, L. Romaka, Yu. Stadnyk, A. Grytsiv, O. Lakh, V. Krayovsky, Intermetallics 35, 45 (2013).
[5] M. Schruter, H. Ebert, H. Akai, P. Entel, E. Hoffmann, G.G. Reddy, Phys. Rev. B 52, 188 (1995).
[6] V.L. Moruzzi, J.F. Janak, A.R. Williams, Calculated electronic properties of metals (Pergamon Press, NY, 1978).
[7] N.F. Mott, E.A. Davis, Electron processes in non-crystalline materials (Clarendon Press, Oxford, 1979).
[8] V.A. Romaka, V.V. Romaka and Yu.V. Stadnyk, Intermetallic Semiconductors: Properties and Applications (Lvivsk. Politekhnika, Lviv, 2011).

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Дослідження електронної структури напівпровідникового твердого розчину $ZrNiSn_{1-x}Ga_x$

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Встановлена природа механізму генерування донорно-акцепторних пар у напівпровідниковому твердому розчині $ZrNiSn_{1-x}Ga_x$. Показано, що при зайнятті атомом Ga ($4s^2 4p^1$) позиції $4b$ атомів Sn ($5s^2 5p^2$) одночасно генеруються як структурні дефекти акцепторної природи, так і донорної (донорно-акцепторні пари) у вигляді вакансій у позиції $4b$. Знайдено таке просторове розташування атомів в елементарній комірці $ZrNiSn_{1-x}Ga_x$, коли швидкість руху рівня Фермі ε_F, отримана з розрахунків розподілу густини електронних станів DOS, співпадає з експериментально встановленою з температурних залежностей питомого електроопору $\ln\rho(1/T)$.

Ключові слова: кристалічна і електронна структури, електропровідність, коефіцієнт термо-ерс.