

Crystal and electronic structures of an intermetallic semiconductor ZrNiSn heavily doped with an Y impurity $(N_{\rm A}^{\rm Y} \approx 3.8 \times 10^{20} \div 4.8 \times 10^{21} \ {\rm cm^{-3}})$ have been studied. It is shown that the doping of *n*-ZrNiSn is accompanied by the ordering of a crystal structure. Impurity atoms occupy the positions of Zr atoms only, generating acceptor-type defects. By detecting the conductivity transition "dielectric-metal," the existence range of a solid solution Zr_{1-x}Y_xNiSn and the dependences between the solid solution concentration, on the one hand, and the direction and the rate of Fermi level drift, on the other hand, have been established.

1. Introduction

Intermetallic semiconductors MNiSn (M = Ti, Zr, Hf), p-TiCoSb, and RNiSb (R is a rare-earth metal) belong to thermoelectric substances that are intensively studied in the world research centers. The topic of those researches is the transformation of thermal energy into electric one, and the application of semiconductors mentioned above should make this process economically justified [1], which is evidenced, in particular, by high values of the thermoelectric figure of merit Z. In particular, in work [2], the value $ZT \ge 1.7$ was obtained for n-ZrNiSn at T = 700 K.

Previous researches have shown that the process of intermetallic semiconductor doping is not always predictable. It depends on both the kind of a dopant and the features of a crystal structure in the undoped semiconductor. It turned out that only 90.0% of the Zr atom positions and 91.6% of the Ni atom positions in n-ZrNiSn are occupied by corresponding atoms. That is, the situation of the so-called local amorphization of semiconductor is realized [3]. As a consequence, in the course of intermetallic semiconductor doping, impurity atoms have an opportunity to occupy different vacant crystallographic positions simultaneously. For instance, when doping *n*-ZrNiSn, e.g., with Mn $(3d^54s^2)$ or Fe $(3d^64s^2)$ impurity atoms [4], the dopant atoms simultaneously and in different ratios occupy both the vacant positions of Ni $(3d^84s^2)$ atoms, generating acceptor-type defects in the crystal, and the vacant positions of Zr $(4d^25s^2)$ atoms, generating donor-type defects. At the same time, if *n*-ZrNiSn is doped with Dy $(5d^06s^2)$ impurity atoms, the latter occupy only the crystallographic positions of Zr atoms, generating acceptor-type defects [5]. In this case, the substitution process is accompanied, besides the defect generation, by a considerable deformation of the crystal lattice. At certain impurity concentrations, which were coined the threshold of solid solution existence [6], the crystal lattice is destroyed owing to stress-induced deformations.

Taking the local amorphization of intermetallic semiconductors into account—in particular, the occupation degree of crystallographic positions—is also important for the calculations of the electron density of states (DOS) and the spectral bands, which should provide the adequacy of such theoretical results to those of experimental studies.

In this context, the results concerning doping n-ZrNiSn with Y atoms, the radius of which, $r_{\rm Y} = 0.1801$ nm, exceeds the radii of all impurities that were studied by us earlier, are of interest. In this paper, which is the first part of the work, we report the results of both X-ray diffraction researches and the calculations of the electronic structure of a semiconductor solid solution $Zr_{1-x}Y_xNiSn$. The results of electro-transport researches will be the subject of another paper. The techniques of specimen fabrication, the regimes of ho-



Fig. 1. Evolution of the MgAgAs-type structure in a $Zr_{1-x}Y_xNiSn$ solid solution: (a) evolution of an elementary cell, (b) evolution of the electron concentration

mogenizing annealing, the procedure of calculation of the crystal structure [7] and the electronic structure in the framework of the relativistic method of linear combination of MT-orbitals (LMTO) [8], making use of the "LMTART 6.20" software package, are presented in work [3].

2. Researches of the $Zr_{1-x}Y_xNiSn Crystal Structure$

To detect the presence of individual phases, to determine the crystal structure, and to calculate important crystallographic parameters, we used x-ray diffraction methods of researches. For the precise refinement of the elementary cell constants and the determination of crystallographic parameters - atomic coordinates, thermal parameters, occupancies of crystallographic positions - we used data arrays obtained on an HZG-4a automatic diffractometer with a source of $CuK\alpha$ -radiation and a step-by-step registration of reflection intensities. The diffractometer scanning was carried out following the Bragg-Brentano geometry. All calculations dealing with the deciphering of data obtained with the use of the powder method [7] and the refinement of a crystal structure were carried out on the personal computer; the Rietveld method and the CSD program [9] were applied. The xray phase and structural analyses showed that the studied $Zr_{1-x}Y_xNiSn$ specimens were single-phase (the MgAgAs-type structure, the $F\bar{4}3m$ spatial group): the x-ray diffraction patterns of Bragg reflections did not include reflections that could be identified with uncontrollable phases. The Bragg factor $R_{\rm Br}$ of a mismatch between the results given by the crystal structure model and the experimental x-ray reflections from $Zr_{1-x}Y_xNiSn$ crystallographic planes did not exceed 4%, and, in the case of $Zr_{0.92}Y_{0.08}NiSn$, $R_{Br} = 2.2\%$. In addition, the refinement of the crystal structure showed that the doping of *n*-ZrNiSn with the Y impurity is accompanied by the ordering of the semiconductor crystal structure, the 100%-occupation of the right system of points (RSP) of Zr(Y) and Ni atoms (see Table). The results obtained allowed us to construct a model of atomic arrangement over the lattice sites of the $Zr_{1-x}Y_xNiSn$ elementary cell (Fig. 1,*a*). An analogy with the cases of the doping of *n*-ZrNiSn with Dy acceptor impurities [5], which also resulted in the structural defect "healing", suggests itself.

Figure 2,*a* illustrates how the constants of the $Zr_{1-x}Y_xNiSn$ elementary cell monotonously grow with increase of the concentration of atoms (Y) with larger dimensions. The calculations of the crystal structure also testified that the interatomic distances Ni–Zr(Y), Sn–Ni, and Sn–Zr(Y) are shorter than the sum of corresponding atomic radii ($r_{Ni} = 0.1246$ nm, $r_{Sn} = 0.1623$ nm, and $r_{Zr} = 0.1602$ nm), which evidences for the presence of the covalent component in chemical bonds and explains the semiconducting properties of $Zr_{1-x}Y_xNiSn$.

The analysis of the electron density maps of ZrNiSn compound (Fig. 1,b) revealed some extra maxima between Ni and Sn atoms which indicate a partial covalence of the bond between Ni and Sn atoms. One can also see that Zr atoms are additionally bound with Sn ones, though much more weakly than in the case of the Ni–Sn bond. It is worth noting that no similar maxima were revealed between Ni and Zr atoms. The base compound also demonstrated a strong reduction of the Ni–Zr distance. It can be explained by the fact that Zr atoms are attracted to Sn ones more strongly, and the latter, in their turn, form a hard tetrahedral framework around Ni atoms.

As follows from Fig. 2,b, the growth of the Y atom content in the $Zr_{1-x}Y_xNiSn$ structure is accompanied by an increase of the relative diminishing δ of the distance in the Ni-Zr(Y) and Sn-Zr(Y) atomic pairs, whereas this parameter decreases for the Sn-Ni pair. In other words, interatomic distances between different atoms in the $Zr_{1-x}Y_xNiSn$ structure change differently. For instance, the Sn-Ni interatomic distance changes in such a way that it approaches that between isolated atoms, which is a straightforward proof of a reduction of the covalent component fraction in $Zr_{1-x}Y_xNiSn$. The reduction of the covalent bond fraction is accompanied by an increase of the Sn-Ni interatomic distances, which induces an increase of the elementary cell constants, as is illustrated in Fig. 2, b. At the same time, the tendency for the Ni-Zr(Y) and Sn-Zr(Y) interatomic distances to change (Fig. 2,b; curves 1 and 3) evidences for an enhancement of the covalent bond fraction between those atoms, which should bring about a reduction of the elementary cell constants for $Zr_{1-x}Y_xNiSn$. However, as follows from Fig. 2,a, the value of lattice spacing a(x)only grows.

Hence, it follows from the aforesaid that the substitution of Zr atoms by Y ones in *n*-ZrNiSn is accompanied by elementary cell distortions: a compressive deformation takes place in the directions Ni–Zr(Y) and Sn–Zr(Y), and a tensile one in the direction Sn–Ni. Figure 2,*b* also exhibits the result of approximation (the dashed line) of the relative distance reduction in the range $x = 0 \div 0.38$, which was made according to the method of work [8]. We can predict that the substitution of Zr atoms by Y ones in the $Zr_{1-x}Y_x$ NiSn structure will not invoke the change of the crystal lattice type, while x < 0.38. At the other content end of the $Zr_{1-x}Y_x$ NiSn solid solution, when Zr atoms are completely replaces by Y ones, the compound YNiSn (the structural type TiNiSi, the *Pnma* spatial group) is realized.

This tendency can also be clearly seen on the electron density map for a specimen with the composition

T a b l e 1. Distribution and thermal vibration parameters of atoms in the crystal structure of $Zr_{0.92}Y_{0.08}NiSn$ $(a = 0.612220 \text{ nm}, R_{Br} = 2.2 \%)$

Atoms	RSP	x/a	y/b	z/c	$B_{\rm iso} \times 10^2, {\rm nm}^2$
Zr^*	4b	0	0	0	0.68(5)
Ni**	4c	1/4	1/4	1/4	0.37(4)
Sn	4a	1/2	1/2	1/2	0.65(4)

N o t e: Occupation degree of atomic positions:

 $^*\mathrm{Zr}(\mathrm{Y}){=}\;0.92$ Zr(Y); $^{**}\mathrm{Ni}{=}\;0.1$ Ni

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Fig. 2. Variations of the lattice spacing (a) and the relative reduction of interatomic distances (b) in the $\operatorname{Zr}_{1-x} Y_x \operatorname{NiSn}$ crystal structure: (1) Ni–Zr(Y), (2) Sn–Ni, (3) Sn–Zr(Y)

x = 0.1 (Fig. 1,b), where the number of maxima decreases between Ni and Sn atoms and increases between Zr(Y) and Sn ones. This means that the covalent bond becomes weaker between Ni and Sn atoms and stronger between Zr(Y) and Sn ones. Such a variation can make semiconducting properties of $Zr_{1-x}Y_xNiSn$ worse, when the Y concentration increases. A reduction of the Ni-Zr(Y) distance is caused by a stronger attraction of Y atoms to the strong tetrahedral framework built by Sn atoms, inside which a strongly bound Ni atom is located. At a certain concentration of Y atoms (x = 0.38), when the relative reductions of Zr(Y)–Sn and Ni–Sn distances become identical (Fig. 2, b, the point of intersection between dependences 2 and 3), the structural type MgAgAs ceases to exist and transforms into a more stable one of the TiNiSi type.

Hence, the doping of the intermetallic semiconductor n-ZrNiSn with an acceptor Y impurity is accompanied



Fig. 3. Electron densities of states (DOS) in $\rm Zr_{0.98}Y_{0.02}NiSn$ and YNiSn

by the ordering of the crystal structure. Y atoms substitute only the crystallographic positions of Zr atoms and generate acceptor-type defects. It makes possible to predict the concentration and the type of impurities in $Zr_{1-x}Y_xNiSn$ in the range $x = 0 \div 0.38$. The last circumstance should allow the control over the basic physical regularities of the transformation functions of *n*-ZrNiSnbased thermoelectric substances.

3. Calculation of the $Zr_{1-x}Y_xNiSn$ Electron Structure

To predict the behavior of the Fermi level ($\varepsilon_{\rm F}$), the electroconductivity, and the thermopower coefficient at the doping of the intermetallic semiconductor *n*-ZrNiSn with an Y impurity, we calculated the electron density of states (Fig. 3) and the band spectrum (Fig. 4) in the $\Gamma - K$ symmetry directions of the Brillouin zone of this compound (Fig. 5). The result obtained for ZrNiSn coincides with that of work [10]. Namely, it follows that ZrNiSn is a narrow-gap semiconductor, the electron den-



Fig. 4. Band structures in $Zr_{0.98}Y_{0.02}NiSn$ and YNiSn

sity of states above the Fermi level is mainly determined by *d*-states of Zr atoms, whereas the valence band is determined by *d*-states of Ni ones, which overlap with *d*-states of Zr and *p*-states of Sn atoms. The Fermi level is located in the energy gap near the bottom of the conduction band. Hence, electrons are the majority charge carriers in such a semiconductor, and the sign of the thermopower coefficient is negative. In the temperature dependences of the resistivity and the thermopower coefficient, there should be activation sections associated with both the hopping conductivity between localized states in the conduction band and the activation of electrons from the Fermi level onto a percolation level in the conduction band.

The substitution of Zr by Y atoms does not change the observed shape of the electron density distribution, in accordance with a strong hybridization among all el-

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ements. The doping of *n*-ZrNiSn with an Y impurity is accompanied by a drift of the Fermi level toward the valence band, which should result in a change of the majority charge carriers—electrons instead of holes, so that the experimental thermopower coefficient would change its sign. Experiments would also testify to a reduction of the energy of activation from the Fermi level onto the valence band mobility edge, when the Fermi level approaches the valence band top. Our calculations of the density of states at the Fermi level testify that, provided the Y impurity concentration is low, the density of states is determined by *d*-electrons of Zr atoms, with a contribution made by *d*-states of Ni ones. If the concentration of Y atoms increases, the contribution made by their *d*-electrons becomes dominant.

The intersection between the Fermi level and the percolation level in the valence band of $\operatorname{Zr}_{1-x} \operatorname{Y}_x \operatorname{NiSn}$ should take place at $x \approx 0.135$ and should be accompanied by the conductivity transition insulator-metal, which is the Anderson transition, because the Fermi level enters into the continuous energy band of the semiconductor [11]. The Anderson transition is known to occur, when the composition of the $\operatorname{Zr}_{1-x} \operatorname{Y}_x \operatorname{NiSn}$ solid solution changes in such a manner that the difference $\Delta \varepsilon = \varepsilon_V - \varepsilon_F$ changes its sign. The comparison between corresponding calculation results allows us to assert that (i) in *n*-ZrNiSn, ε_F is located in the energy gap, so that $\varepsilon_V - \varepsilon_F < 0$; and (ii) in $\operatorname{Zr}_{1-x} \operatorname{Y}_x \operatorname{NiSn}$, $\varepsilon_V - \varepsilon_F > 0$, if $x \geq 0.135$.

To obtain additional proofs that the impurity concentration affects the stability of the crystal structure of the intermetallic semiconductor $\operatorname{Zr}_{1-x} Y_x \operatorname{NiSn}$, we calculated the electron density distribution and the band structure for the YNiSn compound, which implements the state of complete substitution of Zr atoms in $\operatorname{Zr}_{1-x} Y_x \operatorname{NiSn}$ by Y ones (Figs. 3 and 4, respectively). Calculations were carried out for the $\Gamma - R$ symmetry directions of the Brillouin zone. From the given results, it follows that there is no energy gap between the bands, and the Fermi level is fixed at the density peak of valence *d*-electrons. We may draw conclusion that the YNiSn compound is a metal, and the character of its electroconductivity is non-activation (metallic).

Hence, the introduction of the acceptor Y impurity into the crystal structure of n-ZrNiSn is accompanied by a redistribution of the electron density, the monotonous motion of the Fermi level from the conduction band edge to the valence band, and its drift in the continuous energy band. At the Y impurity concentrations, when the Fermi level is located below the percolation level in the

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Fig. 5. Brillouin zone of $Zr_{0.98}Y_{0.02}NiSn$

conduction band or the valence band, the mechanism of hopping conductivity takes place in $Zr_{1-x}Y_xNiSn$.

4. Conclusions

Thus, the doping of *n*-ZrNiSn with Y allows one to obtain thermoelectric substances with preassigned properties and to control their thermometric characteristics, which will make it possible to create thermoelements with a maximal thermoelectric figure of merit.

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МЕХАНІЗМ ДЕФЕКТОУТВОРЕННЯ У СИЛЬНОЛЕГОВАНОМУ АТОМАМИ Y *n*-ZrNiSn. І. ДОСЛІДЖЕННЯ КРИСТАЛІЧНОЇ ТА ЕЛЕКТРОННОЇ СТРУКТУРИ

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Резюме

Досліджено кристалічну та електронну структури інтерметалічного напівпровідника *n*-ZrNiSn, сильнолегованого домішкою Y ($N_A^X \approx 3,8\cdot 10^{20}$ –4,8·10²¹ см⁻³). Показано, що легування *n*-ZrNiSn супроводжується упорядкуванням кристалічної структури, атоми домішки займають лише позиції атомів Zr, генеруючи дефекти акцепторної природи. Встановлено область існування твердого розчину Zr_{1-x}Y_xNiSn, залежності між концентрацією домішки та напрямом і швидкістю дрейфу рівня Фермі, переходом провідності діелектрик–метал.

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