MECHANISM OF CONDUCTIVITY IN n-ZrNiSn INTERMETALLIC SEMICONDUCTOR DOPED WITH YTTRIUM ACCEPTOR IMPURITY

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The X-ray diffraction and phase analyses have been used to determine the crystal structure of the ZrNiSn intermetallic semiconductor (the half-Heusler alloy) highly doped by substituting Y atoms for Zr ones. The corresponding electronic structure has been calculated. The temperature and concentration dependences of the resistivity and the thermopower coefficient of the substitutional solid solution $Zr_{1-x}Y_xNiSn$ have been studied in the temperature interval from 80 to 380 K. A conductivity transition of the insulator–metal type caused by a change of the relative arrangement of the Fermi level and the percolation level in the valence band due to the variation of the compensation degree in $Zr_{1-x}Y_xNiSn$ has been observed. A correlation between the magnetic susceptibility and the electric conductivity of $Zr_{1-x}Y_xNiSn$ has been demonstrated.

1. Introduction

This work continues our researches aimed at the search and the optimization of thermoelectric materials, which is related to a fine control over their properties on the basis of the interrelation between the crystalline structure and the properties [1–5]. To achieve high values of the thermoelectric figure of merit of thermoelectric substances, it is necessary to obtain a semiconductor with high electroconductivity, large thermopower, and low heat conductivity. The coexistence of such properties, which are closely related to one another, in one alloy is a rare phenomenon, which considerably narrows the regions of search for such materials. Among a variety of semiconductor phases, which are proposed for the fabrication of thermoelectric materials, intermetallic semiconductors of the MgAgAs structural type (ST) (the so-called half-Heusler alloys) dominate [6].

The results of researches of intermetallic semiconductors MeNiSn (Me = Ti, Zr, Hf), which were carried out at various research laboratories including the ours, testify that electrons are the majority current carriers in those phases at $T \geq 4.2$ K, and the temperature dependences of the specific electroresistance and the thermopower coefficient evidence for the presence of noncontrollable donor impurities in them. In the overwhelming majority of works known to us, the procedure of producing such semiconductors consists in alloying the mixture of initial components in an electroarc furnace followed by a fast noncontrolled cooling of the melt. Such a technology makes alloys partially amorphous [7], which gives rise to the emergence of a structural disordering and local deformations in crystallites of polycrystalline specimens and, as a consequence, leads to a modulation of continuous energy bands. In a strongly doped semiconductor, owing to fluctuations of the substantial concentration of charged impurities, the energy scheme looks like that shown in work [8].

Doping semiconductors of the MgAgAs ST to considerable concentrations of charged impurities (10^{19}–10^{21} cm^{-3}) is known to increase their thermoelectric figure of merit. Therefore, it is of interest to study the influence of the doping of intermetallic semiconductor ZrNiSn with acceptor impurities—in particular, the substitution of Zr $4d^25s^2$ atoms by Y ($4d^15s^2$) ones—on its physical properties.

2. Research Results and Their Discussion

The specimens of $Zr_{1-x}Y_xNiSn$ solid solution alloys ($x = 0 - 0.25$) were fabricated by the method of electroarc melting of initial components in the purified argon environment. The homogenizing annealing of specimens was carried out in evacuated quartz ampoules at 1070 K for 1000 h and was followed by their quenching in cold water. The research of the crystal structure was carried out by analyzing the data arrays for experimental intensities obtained on a DRON-2.0M diffractometer (Fe Kα-radiation). The lattice parameters were calculated making use of the CSD software package [9].

The specific electroresistance ρ and the Seebeck coefficient α relative to copper were measured in the temperature interval 80–380 K, whereas the magnetic susceptibility χ at room temperature. The measurement techniques of the physical properties concerned are described in work [10]. The calculation of the distribution of the electron density of states in the whole concentration interval of a $Zr_{1-x}Y_xNiSn$ solid solution was carried out in the framework of self-consistent Korringa–Kohn–Rostoker method and in the coherent potential approximation (KKR–CPA–LDA) [11, 12].

For the first time, the influence of the substitution of Zr atoms by Y ones in the ZrNiSn compound was studied in work [13]. It was demonstrated that such a doping gives rise to the change of the Seebeck coefficient sign and the transformation of the conductivity type from semiconducting to metallic one. However, only three homogeneous alloys of a solid solution $Zr_{1-x}Y_xNiSn$ were studied in the cited work, which did not allow the measurement results to be analyzed in full.

The X-ray phase and structural analyses of the studied specimens of a solid solution $Zr_{1-x}Y_xNiSn$ showed that they are single-phase ones, except for alloys with the compositions $Zr_{0.90}Y_{0.10}NiSn$ and $Zr_{0.75}Y_{0.25}NiSn$, which contain insignificant admixtures of another phase, with the $Zr_{0.90}Y_{0.10}NiSn$ specimen including much more such impurities than the $Zr_{0.75}Y_{0.25}NiSn$ one does. The parameters of crystal lattices for all fabricated specimens, which were specified according to diffractometry measurements by the powder method, are quoted in the table.

As follows from the table, the lattice constant of the substitutional solid solution $Zr_{1-x}Y_xNiSn$ monotonously grows, when the atoms with a smaller dimension ($r_{Zr} = 0.160$ nm) are substituted by larger ones ($r_Y = 0.180$ nm). Taking into account that Y is an acceptor relative to Zr, and the substitution takes place, most probably, at the crystallographic positions of Zr atoms, such a substitution is equivalent to the introduction of defects with acceptor nature into the semiconductor. In this case, the concentration of such defects changes proportionally to the concentration of Y in $Zr_{1-x}Y_xNiSn$ alloys.

Crystallographic, electrophysical, and magnetic characteristics of solid solution alloys $Zr_{1-x}Y_xNiSn$

Alloy	a, nm	ε_1^ρ, meV	ε_3^ρ, meV	$\chi, 10^{-6}$ cm^3/g
ZrNiSn	0.61076	28.9	1.6	0.07
$Zr_{0.98}Y_{0.02}NiSn$	0.61157	52.20	2.2	0.077
$Zr_{0.95}Y_{0.05}NiSn$	0.61178	17.30	1.38	0.148
$Zr_{0.92}Y_{0.08}NiSn$	0.61222	11.96	–	0.339
$Zr_{0.90}Y_{0.10}NiSn$	0.61261	–	–	0.621
$Zr_{0.88}Y_{0.12}NiSn$	0.6124 [13]	6.63	–	0.348 [13]
$Zr_{0.80}Y_{0.20}NiSn$	0.61448	–	–	0.510
$Zr_{0.75}Y_{0.25}NiSn$	0.61526	–	–	0.590

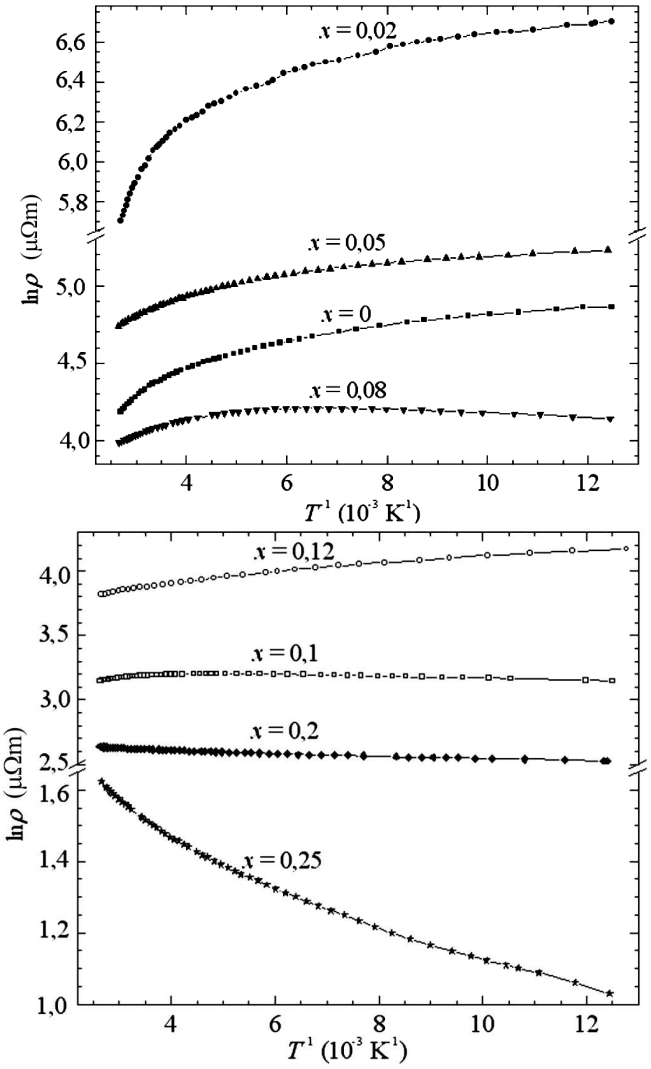

Fig. 1. Temperature dependences of the specific electroresistance of alloys of a solid solution $Zr_{1-x}Y_xNiSn$

The temperature dependences of the specific electroresistance, $\ln\rho\,(1/T)$, which are exhibited in Fig. 1, are typical of highly doped semiconductors. The high- and low-temperature sections of the dependences $\ln\rho\,(1/T)$ were used to determine the activation energies ε_1^ρ and ε_3^ρ, respectively (see the table). The activation energy ε_1^ρ monotonously decreases with increase in the Y content in $Zr_{1-x}Y_xNiSn$ from $x = 0.02$ to $x = 0.12$. This reduction is associated with the approach of the Fermi

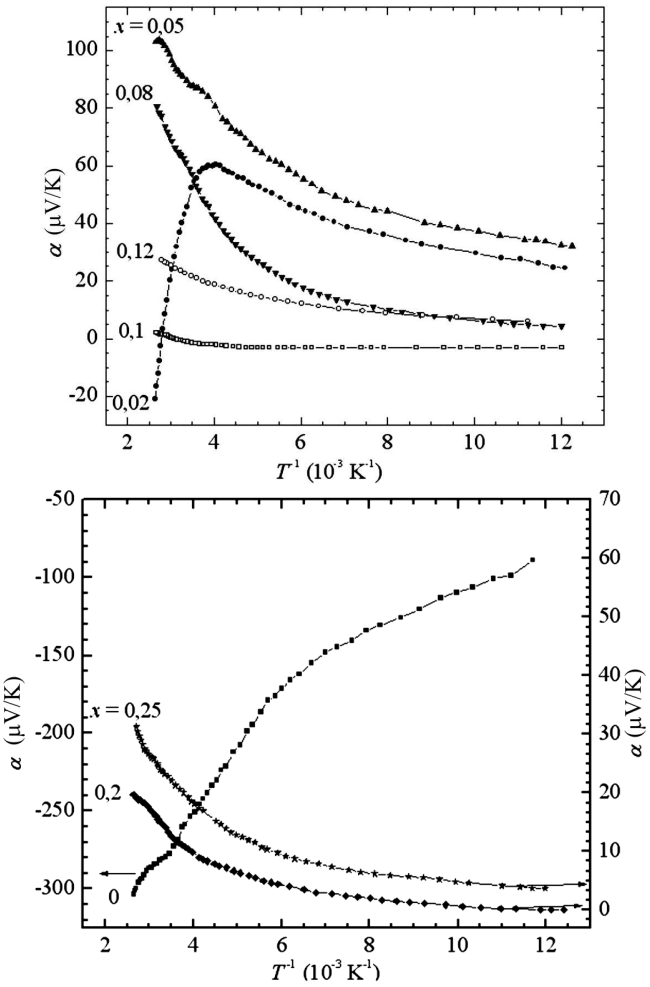

Fig. 2. Temperature dependences of the Seebeck coefficient for alloys of a solid solution $Zr_{1-x}Y_xNiSn$

level to the valence band edge in the given concentration interval. At higher concentrations of acceptor-type defects (up to $x = 0.2$), the activation sections disappear from the dependences $\ln \rho\,(1/T)$ (Fig. 1), and the transition insulator–metal is observed. The absence of activation sections in the dependences $\ln \rho\,(1/T)$ at low temperatures for specimens with $x = 0.08$ and 0.10 testifies to a considerable contribution of the hopping mechanism to the electroconductivity. The presence of the extremum in the concentration dependence $\varepsilon_1^{\rho}(x = 0.02)$ does not testify to a nonmonotonic change of the Fermi level position, because, at $x = 0$, the activation of electrons into the conduction band takes place (it is evidenced by the negative sign of the Seebeck coefficient), whereas it is the activation of holes into the valence band at $x \geq 0.02$. In other words, the inclusion of Y atoms into the crystal structure of ZrNiSn is accompanied by a monotonous drift of the Fermi level toward the valence band. Such a character of the dependence $\varepsilon_1^{\rho}\,(x)$, which reflects a variation in the Fermi level position, and the monotonous increase of the lattice parameter due to the growth of the concentration of Y atoms in a solid solution $Zr_{1-x}Y_xNiSn$ are the evidence that Y atoms occupy the crystallographic positions of Zr ones.

The temperature dependences of the thermoelectric coefficient for the studied specimens of a solid solution $Zr_{1-x}Y_xNiSn$ are depicted in Fig. 2. The figure demonstrates that even the lowest yttrium concentrations in $Zr_{1-x}Y_xNiSn$ bring about the change of the α-sign, which testifies to the change of the type of majority current carriers which define the character of the semiconductor electroconductivity—from the electron- (in the ternary ZrNiSn) to hole-type one (in $Zr_{1-x}Y_xNiSn$ alloys with $x < 0.02$)—and is a result of the interplay between the concentrations of controllable acceptor defects and uncontrollable donor ones, i.e. the compensation degree. We may assert that the Fermi level is located near the conduction band bottom at $x = 0$, so that electrons are the majority current carriers. Near the valence band top at $x = 0.02$, the majority current carriers are holes. Figure 2 also shows that the Seebeck coefficient for the $Zr_{0.90}Y_{0.10}NiSn$ specimen is negative practically in the whole temperature interval. Such a behavior of the quantity $\alpha\,(1/T)$ can be associated with the fact that, as was shown above, alloy $Zr_{0.90}Y_{0.10}NiSn$ includes impurities of another phase. That is, the concentration of uncontrollable donor impurity is higher in comparison with those in other solid solution specimens, so that the available concentration of the acceptor impurity is insufficient for the overcompensation of the semiconductor. The conclusion drawn above is confirmed by the results of measurements for alloy $Zr_{0.88}Y_{0.12}NiSn$, which is close by composition to $Zr_{0.90}Y_{0.10}NiSn$, taken from work [13] (Figs. 1 and 2). Namely, the corresponding thermopower is positive within the whole studied temperature interval. It should be noted that alloy $Zr_{0.88}Y_{0.12}NiSn$ did not contain impurities of other phases [13].

As was in the cases of doping the intermetallic semiconductor p-TiCoSb with Ni acceptor impurities [14] or n-ZrNiSn with scandium ones [5], the Anderson transition is also realized in $Zr_{1-x}Y_xNiSn$, and it occurs when the composition of a solid solution changes so much that the quantity $\Delta E = (E_V - E_F)$ changes its sign [8]. Really, at low temperatures, $Zr_{1-x}Y_xNiSn$ with $x = 0$ is a compensated semiconductor with the electron type of conductivity, and its Fermi level is fixed in the donor band. At $0.02 \leq x \leq 0.12$, the Fermi level is located near

the valence band top, and $E_V - E_F < 0$. In $Zr_{1-x}Y_xNiSn$ with $x > 0.20$, the conductivity is defined by free holes in the valence band, the Fermi level is located in the valence band, and $E_V - E_F > 0$.

By values of the magnetic susceptibility measured at room temperature (see the table), the specimens of a solid solution $Zr_{1-x}Y_xNiSnZr$ can be characterized as Pauli paramagnets. The magnetic susceptibility of Pauli paramagnets is known to be proportional to the density of states at the Fermi level ($\chi \propto N(E_F)$), i.e. the behavior of the dependence $\chi(x)$ correlates with the concentration dependence of the electroconductivity. The monotonic increase of χ with the yttrium concentration (the acceptor-type defects) in a solid solution $Zr_{1-x}Y_xNiSn$, which is caused by the reconstruction of impurity bands and the increase of the density of states at the Fermi level, agrees well with the corresponding behaviors of the specific electroresistance and the Seebeck coefficient. The fact that the value of χ for the $Zr_{0.90}Y_{0.10}NiSn$ specimen is larger than that for the $Zr_{0.88}Y_{0.12}NiSn$ one completely correlates with their electrophysical characteristics and follows from the results of crystallographic researches, which was emphasized above.

Solid substitutional solutions can be considered as systems with a composition disorder, in which the band and localized states are possible, provided that there exists a periodic crystalline structure. Important is the fact that the translational topology—in other words, the structure periodicity—is preserved in such alloys, as it occurs in $Zr_{1-x}Y_xNiSn$ solid solutions, where the crystal structure persists in every alloy. The available mathematical methods allow the calculations of the electron density of states for partially disordered alloys to be carried out. We studied the influence of the heavy doping with the acceptor Y impurity on the electronic structure of ZrNiSn. In Fig. 3, the calculated densities of states in undoped and doped ZrNiSn semiconductors are shown. In the latter case, the semiconductor is supposed to be doped with the acceptor yttrium impurity by substituting Zr atoms by Y ones. In ZrNiSn, the Fermi level is located in the energy gap. When Zr atoms are progressively substituted by Y ones, the Fermi level shifts toward lower energies (toward the valence band) and then penetrates into the band. The results of theoretical calculations of the density of states in a solid solution alloys $Zr_{1-x}Y_xNiSn$ agree with experimental ones in that the type of majority current carriers changes, and the conductivity type transforms from the activation to metallic one.

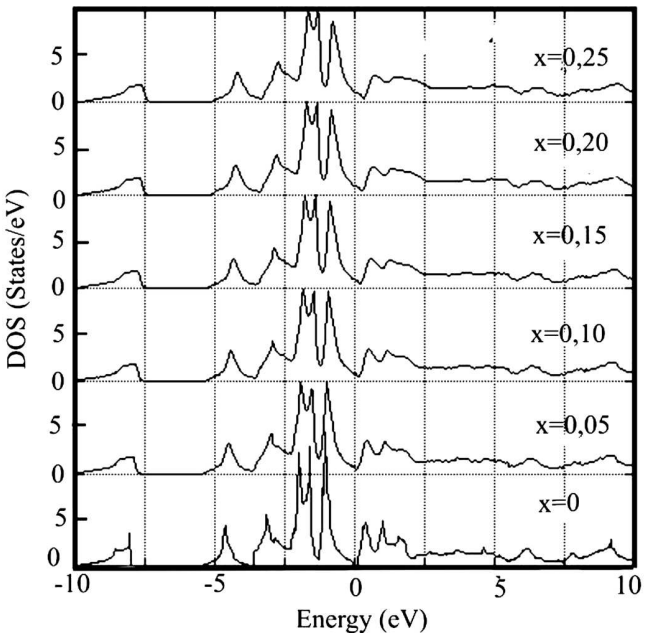

Fig. 3. Total density of electron states in alloys of a solid solution $Zr_{1-x}Y_xNiSn$

3. Conclusions

According to the results of our researches, we may assert that

– yttrium atoms play the role of acceptor-type impurities in a substitutional solid solution $Zr_{1-x}Y_xNiSn$;

– the substitution of Zr atoms by Y ones leads to the overcompensation of the semiconductor and a shift of the Fermi level toward the valence band; the observed insulator–metal transition in the n-ZrNiSn semiconductor is the Anderson transition;

– the coincidence of the results of theoretical calculations and the experimental ones testifies to the adequacy of the model proposed for the description of the band structure in a substitutional solid solution $Zr_{1-x}Y_xNiSn$.

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МЕХАНІЗМИ ПРОВІДНОСТІ ІНТЕРМЕТАЛІЧНОГО НАПІВПРОВІДНИКА *n*-ZrNiSn, ЛЕГОВАНОГО АКЦЕПТОРНОЮ ДОМІШКОЮ Y

Ю. Стадник, А. Горинь, Е.К. Хліл, Д. Фрушарт, Ю. Гореленко, Л. Ромака

Р е з ю м е

Методами рентгеноструктурного та рентгенофазового аналізів визначено кристалічну структуру інтерметалічного напівпровідника ZrNiSn, сильнолегованого акцепторною домішкою шляхом заміщення атомів Zr на Y, та здійснено розрахунок електронної структури. Досліджено температурні та концентраційні залежності питомого електроопору та коефіцієнта термо-ерс сплавів твердого розчину заміщення $Zr_{1-x}Y_xNiSn$ у температурному інтервалі 80–380 K. Виявлено перехід провідності діелектрик–метал в $Zr_{1-x}Y_xNiSn$, зумовлений зміною взаємного розташування рівнів Фермі та протікання валентної зони внаслідок зміни ступеня компенсації напівпровідника. Показано взаємозв'язок між магнітною сприйнятливістю та провідністю в $Zr_{1-x}Y_xNiSn$.