

MECHANISMS OF CONDUCTIVITY IN AN n -ZrNiSn INTERMETALLIC SEMICONDUCTOR HEAVILY DOPED WITH Co. 2. ELECTRON STRUCTURE CALCULATIONS

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The electron structure of a ZrNiSn intermetallic semiconductor heavily doped with an acceptor impurity (by substituting Co atoms for Ni ones) has been calculated. The density of states at the Fermi level has been demonstrated to oscillate depending on the acceptor impurity concentration.

1. Introduction

This work completes the study of mechanisms of electroconductivity in an intermetallic semiconductor n -ZrNiSn heavily doped with a $\text{Co}(3d^74s^2)$ acceptor impurity which is introduced into the semiconductor and substitutes $\text{Ni}(3d^84s^2)$ atoms. The study was started in work [1]. We did not succeed there in explaining the results of experimental researches obtained for the temperature dependences of the specific resistance, the thermoelectric power, and the magnetic susceptibility of the semiconductor solid solution $\text{ZrNi}_{1-x}\text{Co}_x\text{Sn}$ in the framework of either the acceptor or donor impurity band model proposed in works [2–5]. Therefore, while analyzing the corresponding experimental results, a number of assumptions were made. In particular, we assumed that two impurity bands — the controllable acceptor and uncontrollable donor ones — exist simultaneously in the energy gap of this compound, and that the reconstruction of impurity bands stimulated by the variation of the acceptor impurity concentration may proceed following certain mechanisms. Those assumptions gave rise to a nonmonotonic variation

of the density of states at the Fermi level, $N(E_F)$, as the impurity concentration changed. In work [1], we associated this result with the variations of the compensation degree of the semiconductor solid solution $\text{ZrNi}_{1-x}\text{Co}_x\text{Sn}$, the dimensions of impurity bands, and the arrangement of the latter with respect to the tops of continuous energy bands [6] depending on the Co acceptor impurity concentration. In $\text{ZrNi}_{1-x}\text{Co}_x\text{Sn}$, provided that the acceptor impurity concentrations correspond to compositions $x \leq 0.6$, the Fermi level E_F becomes fixed at one of the Coulomb gaps of impurity bands; therefore, the reconstruction of impurity bands should result in a nonmonotonic drift of E_F . In work [1], we referred such a drift of the Fermi level to the indirect influence of a nonmonotonic variation of the energy ε_1 needed for the charge carriers to be activated from E_F into the continuous energy bands. The corresponding experimental result was a starting point for the assumptions made in work [1].

We associated a conductivity transition of the insulator–metal type discovered in n -ZrNiSn, which occurs if the concentration of acceptor impurity introduced into this substance increases up to the values that correspond to $\text{ZrNi}_{1-x}\text{Co}_x\text{Sn}$ compositions $x > 0.06$, with a possible transition of E_F first onto the mobility edge of the valence band (E_V) and then (at $x > 0.08$) into the valence band itself. If this assumption is correct, the insulator–metal conductivity transition is the Anderson one [7].

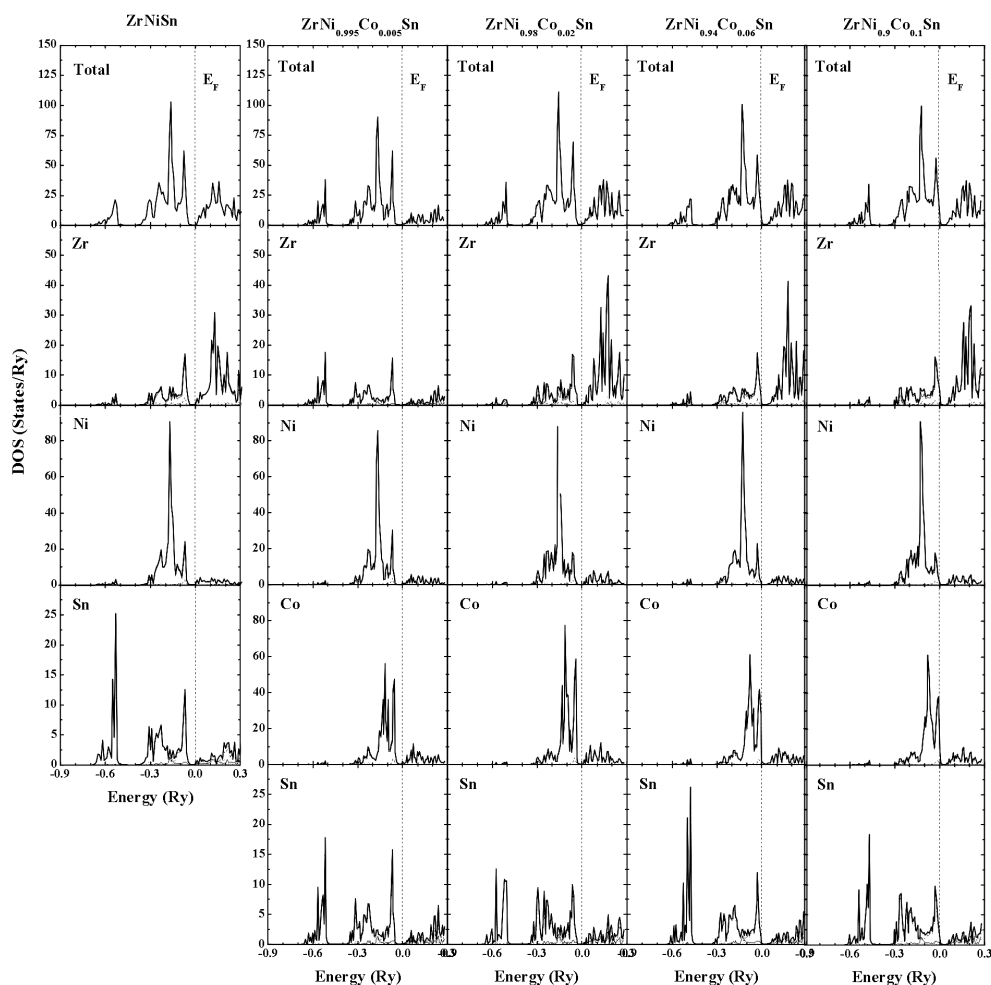


Fig. 1. Component-wise and total distributions of the density of states in ZrNiSn at various concentrations of the Co acceptor impurity

Thus, by studying the variation of the electron structure of the intermetallic semiconductor $\text{ZrNi}_{1-x}\text{Co}_x\text{Sn}$, it is possible to deny or confirm the assumptions made in paper [1], which is the main purpose of this work.

2. Results of Electron Structure Calculations and Their Discussion

The electron structure of the $\text{ZrNi}_{1-x}\text{Co}_x\text{Sn}$ solid solution was calculated in the framework of the Green's function methods and in the Korringa–Kohn–Rostoker coherent potential approximation (KKR-CPA-LDA) [8]. The crystalline potential and the electron charge density were selected to be spherically symmetric inside a sphere and constant in the intermediate region (the “muffin-tin” method). In intermetallic semiconductors with the

MgAgAs-type structure, only three of four possible atomic positions with $43m$ symmetry are occupied. To increase the packing factor in a Wigner–Seitz cell, we introduced an extra empty sphere around the fourth, unoccupied position. The radii of nonoverlapping spheres were selected to achieve the maximal filling of the Wigner–Seitz cell. The total density of states (DOS) and separate partial contributions from every atom and its electron shells with $l_{\max} = 2$ were calculated. The iteration procedure of finding the self-consistent solution was carried out until the difference between the values of potential in consequent iterations became smaller than 10^{-4} Ry.

In Fig. 1, the results of calculations of the electron density distribution are presented for each of the $\text{ZrNi}_{1-x}\text{Co}_x\text{Sn}$ components, as well as the total distribution for various x values. From this figure,

it follows that the ZrNiSn compound ($x = 0$) is a narrow-gap semiconductor. This conclusion agrees with the results of theoretical calculations carried out in the framework of the pseudo-potential [9], KKR [10], and KKR-CPA-LDA [11, 12] methods and with the experimental results quoted in work [1] and other literature sources.

From Fig. 1, it is also evident that the Fermi level is located in the energy gap, near the bottom of the conduction band. Such an arrangement of E_F is characteristic of impurity semiconductors with the electron type of conductivity and is caused by the energy levels which are created by donor impurities. Just such an arrangement of E_F in ZrNiSn governs the electron type of conductivity of the latter within the studied temperature interval; the sign of the thermoelectric power coefficient is accordingly negative, which was also observed in experiment [1].

The substitution of Ni atoms by Co ones within the investigated interval of the acceptor impurity concentration, which corresponded to compositions $0 \leq x \leq 0.1$ of the ZrNi_{1-x}Co_xSn solution, practically does not change the magnitude of the gap between the conduction and the valence band, which is also in agreement with experimental results [1] (in contrast to the conclusions made in works [12, 13]). In so doing, the Fermi level becomes shifted toward lower energies (in the valence band direction). At the acceptor impurity concentration that corresponds to the ZrNi_{1-x}Co_xSn composition value of $x \approx 0.15$, E_F crosses the energy gap midpoint and continues to drift toward the valence band. This means that the overcompensation of the semiconductor should take place, the latter should become a semiconductor with the hole type of conductivity, and the thermoelectric power coefficient should change its sign from negative to positive. This conclusion has also found its experimental evidence in work [1].

The fact that the Fermi level in ZrNi_{1-x}Co_xSn at $x < 0.06$ is located in the semiconductor energy gap, being fixed at the Coulomb gap of either of the impurity bands, means that the conductivity in this substance can be determined by the activation of electrons (holes) from the impurity donor (acceptor) band into the conduction (valence) one (with the activation energy ε_1), the hopping conductivity (with the activation energy ε_2) through the impurity band (until the Mott transition, i.e. a transition “insulator—metal” of the conductivity through the impurity band [7], occurs), and the conductivity of free charge carriers. At the acceptor impurity concentrations that

correspond to the ZrNi_{1-x}Co_xSn compositions $x > 0.06$, the impurity acceptor band merges with the mobility edge of the valence band, which the Fermi level is fixed at. Provided that the acceptor impurity concentrations correspond to the compositions $x \geq 0.08$, the Fermi level falls within the valence band, so that the conductivity of the semiconductor is governed by free holes and has a metallic character, i.e. the conductivity transition “insulator—metal” takes place. The experimental results completely confirm the conclusion that several activation and band mechanisms of conductivity are relevant to the n -ZrNiSn semiconductor heavily doped with Co acceptor impurities [1].

From this viewpoint, we recall that the Anderson transition occurs if the quantity $\Delta E = E_V - E_F$ changes its sign in the course of the ZrNi_{1-x}Co_xSn solid solution composition variation [7]. The comparison of the results obtained both in this work and in work [1] allows us to assert the following:

- (i) at low temperatures, the solid solution ZrNi_{1-x}Co_xSn with $x \leq 0.01$ is a compensated semiconductor, the level E_F is fixed at the Coulomb gap of the donor impurity band, the conductivity is determined by both the activation of electrons from the impurity donor band into the conduction one and the hopping conductivity through the impurity donor band, and $E_V - E_F < 0$;
- (ii) at low temperatures, ZrNi_{1-x}Co_xSn with x in the composition interval $0.02 \leq x \leq 0.04$ is a compensated semiconductor, E_F is fixed at the Coulomb gap of the acceptor impurity band, the conductivity is determined by both the activation of holes from the donor impurity band into the valence one and the hopping conduction through the acceptor impurity band, and $E_V - E_F < 0$;
- (iii) the conductivity of ZrNi_{1-x}Co_xSn at $x \geq 0.08$ is determined by free holes in the valence band, it has a metallic character, the level E_F is located in the valence band, and $E_V - E_F > 0$.

Thus, the conductivity transition insulator—metal, which was experimentally observed in work [1], is the Anderson transition.

We also calculated the density of states in ZrNi_{1-x}Co_xSn at the Fermi level $N(E_F)$ which is mainly determined by the density of states of d -electrons of Co atoms. It follows from Fig. 2 that the doping of ZrNiSn with acceptor impurities (the replacement of Ni atoms by Co ones) brings about a nonmonotonic dependence of the quantity $1/N(E_F)$ on the acceptor impurity concentration. The result obtained is different if n -ZrNiSn (n -TiNiSn) is doped with acceptor impurities by substituting Sc atoms for Zr (Ti) ones, or if p -TiCoSb

is doped with donor impurities by substituting Ni or Cu atoms for Co ones; in this case, the dependences of the quantity $1/N(E_F)$ on the impurity concentration are monotonic [2–5, 14].

The reduction of the energy ε_1 of activation (first from the Fermi level located in the donor impurity band into the conduction one and then from the Fermi level located in the acceptor impurity band into the valence one), which accompanies the increase of the acceptor impurity concentration and was experimentally observed for ZrNiSn in work [1], cannot be explained by a monotonous drift of the Fermi level from the donor impurity band to the valence one and its consequent entering into the latter. The results of calculations testify that, in the ZrNi_{1-x}Co_xSn case, the monotonous drift of E_F across the donor impurity band from its bottom to top takes place only within the acceptor impurity concentration interval which corresponds to compositions $x = 0.005 \div 0.01$, when the transition from the strong compensation case ($1 - K \ll 1$, where $K = N_A/N_D$) to the weak compensation one ($K \ll 1$), takes place [6]. For the acceptor impurity concentrations that correspond to ZrNi_{1-x}Co_xSn compositions, $x > 0.02$, the level E_F also drifts monotonically across the acceptor impurity band. Hence, if the concentration of the acceptor impurity increases, the density of states at the Fermi level will monotonously change in both the donor and acceptor impurity bands. The monotonicity will be violated in the case of the semiconductor overcompensation from the *n*- to *p*-type of conductivity, i.e. if the E_F level transfers from the donor impurity band to the acceptor impurity one [2–6].

The results, which are presented in Fig. 2, evidence for a nonmonotonic dependence of the density of states at the Fermi level on the acceptor impurity concentration. They are in agreement with the nonmonotonous (oscillating) variations of the activation energy ε_1 , the thermoelectric power factor, and the specific electroresistance ρ in Co-doped *n*-ZrNiSn ($\rho \sim 1/N(E_F)$). Our calculations also confirm the model of a reconstruction of the donor and acceptor impurity bands in intermetallic *n*-ZrNiSn under the doping of the latter with acceptor impurities, which was proposed in work [1].

We would like to attract attention to the results and conclusions of works [11, 13, 14, 16]. In works [13, 14], a reduction of the activation energy that accompanied the growth of the acceptor or donor impurity concentration in ZrNiSn (the replacement of Sn atoms by In or Sb ones [13], and Zr atoms by Ce ones [14]) was experimentally

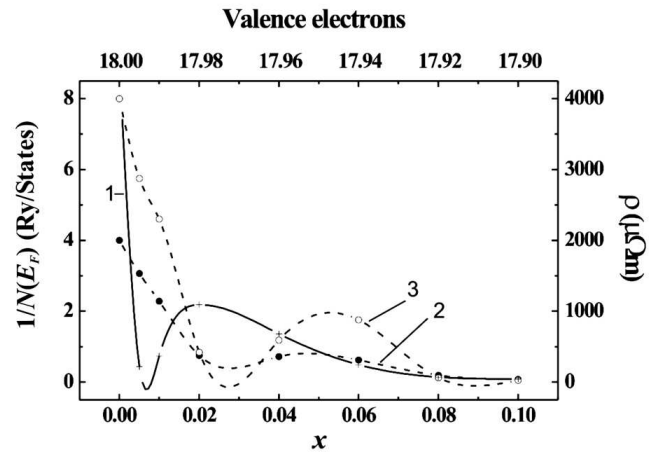


Fig. 2. Dependences of the quantity $1/N(E_F)$ (1) and the specific electroresistance ρ at temperatures of 80 (2) and 300 K (3) on the acceptor impurity concentration x for the intermetallic compound *n*-ZrNiSn

observed. This fact allowed the authors of works [13, 14] to make an assumption about a reduction of the energy gap width in ZrNiSn semiconductors down to its complete collapse as the concentration of acceptor or donor impurities increases.

Our calculations (see Fig. 1) and the results of works [1–5, 15] contradict the conclusions of works [13, 14]. Our researches testify that the reduction of the activation energy, which accompanies the increase of the acceptor impurity concentration in ZrNiSn, is not associated with the reduction of the energy gap width down to its complete disappearance, but is related to the variation of the semiconductor compensation degree and, as a consequence, to the motion of the Fermi level, which is fixed at the Coulomb gap of the impurity band, toward that or another continuous energy band (depending on the impurity type), with its subsequent entering into either of the continuous energy bands (Fig. 1), and with the transition of the conductivity type from the activation to metallic one [1–5, 15].

In addition, the results of our calculations and our interpretation of experimental results contradict the conclusions of works [11, 16]. The calculation of the electron structure of the intermetallic compound TiCoSn [11], whose composition lies at the opposite – with respect to intermetallic semiconductor TiNiSn – end of the Ni–Co composition interval of the TiNi_{1-x}Co_xSn solid solution, shows that the states of the conduction and valence bands in TiCoSn are separated by an energy gap, and the magnitudes of energy gaps in TiNiSn [11] and TiCoSn [11, 16] differ slightly. In other words,

TiNiSn and TiCoSn are typical semiconductors. The only difference between their electron structures is that the level E_F falls within the energy gap in TiNiSn, while it is located deeply in the valence band in TiCoSn, which is characteristic of intermetallic semiconductors heavily doped with acceptor impurities [1–5, 15]. However, the authors of works [11, 16], ignoring the results of their own calculations and taking into account only the metallic type of the TiCoSn conductivity, classified this intermetallic compound as a metal. Although such a statement was made on the basis of experimental results, it contradicts both the results of calculations of the TiCoSn electron structure and our results. Therefore, we consider it as erroneous.

Thus, the calculations of the electron structure of the intermetallic semiconductors ZrNiSn heavily doped with Co evidence for the correctness of the assumptions made in work [1] about the nonmonotonic dependence of the density of states at the Fermi level on the acceptor impurity concentration, the engagement of two impurity bands — the donor and acceptor ones — in the semiconductor conductivity, and the classification of the conductivity type change as the Anderson transition.

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МЕХАНІЗМИ ПРОВІДНОСТІ ІНТЕРМЕТАЛІЧНОГО НАПІВПРОВІДНИКА n -ZrNiSn, СИЛЬНОЛЕГОВАНОГО АКЦЕПТОРНОЮ ДОМІШКОЮ Co. 2. РОЗРАХУНОК ЕЛЕКТРОННОЇ СТРУКТУРИ

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Резюме

Здійснено розрахунок електронної структури інтерметалічного напівпровідника ZrNiSn, сильнолегованого акцепторною домішкою шляхом заміщення атомів Ni на Co. Виявлено осцилюючий характер залежності щільності станів на рівні Фермі від концентрації акцепторної домішки.