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V.A. Romaka<sup>1,2</sup>, P. Rogl<sup>3</sup>, Yu.V. Stadnyk<sup>4</sup>, L.P. Romaka<sup>4</sup>, R.O. Korzh<sup>2</sup>,  
D. Kaczorowski<sup>5</sup>, V.Ya. Krayovskyy<sup>2</sup>, O.I. Lakh<sup>6</sup>

<sup>1</sup>Ya. Pidstryhach Institute for Applied Problems of Mechanics and Mathematics National Academy of Sciences of Ukraine, 3-b, Naukova Str., Lviv, 79060, Ukraine;

<sup>2</sup>National University "Lvivska Polytechnika", 12, S. Bandera Str., Lviv, 79013, Ukraine;

<sup>3</sup>Institut für Physikalische Chemie, Universität Wien, 42, Währinger Str., Wien, A-1090, Österreich;

<sup>4</sup>Ivan Franko National University of Lviv, 6, Kyryla and Mefodiya Str., 79005, Lviv, Ukraine;

<sup>5</sup>Institute of Low Temperature and Structural Research Polish Academy of Sciences, 2, Okólna Str., Wrocław, 50-422, Poland;

<sup>6</sup>Closed JSC V.I. Lakh "NVO "Thermoprylad", 3, Naukova Str., Lviv, 79060, Ukraine

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## STRUCTURAL, ENERGY AND KINETIC CHARACTERISTICS OF $Hf_{1-x}Lu_xNiSn$ THERMOELECTRIC MATERIAL

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*The crystal and electronic structures, the temperature and concentration dependencies of resistivity, the Seebeck coefficient and magnetic susceptibility of  $Hf_{1-x}Lu_xNiSn$  thermoelectric material were studied in the range  $T = 80 \div 400$  K,  $N_A^{Lu} \approx 1.9 \cdot 10^{20} \text{ cm}^{-3}$  ( $x = 0.01$ )  $\div 1.9 \cdot 10^{21} \text{ cm}^{-3}$  ( $x = 0.10$ )  $H \leq 10$  T. The mechanisms of a simultaneous generation of donor- and acceptor-nature defects in a crystal were established. They change the compensation degree of semiconductor material and determine the mechanism of conduction predicted by the  $Hf_{1-x}Lu_xNiSn$  electronic structure calculations.*

**Key words:** electronic structure, resistivity, the Seebeck coefficient.

### Introduction

Interest in thermoelectric materials based on intermetallic semiconductors  $n\text{-ZrNiSn}$ ,  $n\text{-HfNiSn}$ ,  $n\text{-TiNiSn}$  and  $p\text{-TiCoSb}$ , crystallized as structural type  $MgAgAs$  (space group  $F\bar{4}3m$ ) [1] is caused by simultaneously high values of the electric conductivity and the Seebeck coefficient, which assures high efficiency of thermal into electric energy conversion and makes these semiconductor materials some of the most studied thermoelectric materials [2, 3]. This paper, contributing to further research into the effect of heavy doping of  $MgAgAs$  ( $N_{A,D} \sim 10^{19} \div 10^{21} \text{ cm}^{-3}$ ) semiconductors making them heavily doped and strongly compensated [4] on the change in structural, energy, kinetic and magnetic characteristics, studies thermoelectric material  $Hf_{1-x}Lu_xNiSn$  obtained by doping  $n\text{-HfNiSn}$  with atoms of rare-earth  $Lu$  metal.

These investigations are caused by the fact that optimization of thermoelectric material parameters to obtain maximum values of thermoelectric figure of merit depends on a series of factors, in particular, carrier concentration, scattering mechanisms, thermal conductivity, etc., and one of the methods of such optimization is doping of semiconductor with donor and/or acceptor impurities [5].

### Investigation procedures

The object to be investigated included crystalline structure, electron density distribution (DOS), electrokinetic and energy characteristics of  $Hf_{1-x}Lu_xNiSn$ . The samples were synthesized in the

laboratory of Institute for Physical Chemistry, Vienna University. The *X*-ray structural analysis with employment of Fullprof program [6] was used to obtain the values of  $Hf_{1-x}Lu_xNiSn$  crystal lattice periods. The data arrays obtained by the powder method (diffractometer Guinier-Huber image plate system,  $CuK\alpha_1$ -radiation;  $8^\circ \leq 2\theta \leq 100^\circ$ ) were used for the calculation of structural characteristics. The chemical and phase compositions of samples were controlled by scanning electron microscope (SEM, Zeiss Supra 55VP) and microprobe analyzer (EPMA, energy-dispersive *X*-ray analyzer). The electronic structure calculations were performed by the Korringa-Kohn-Rostoker (KKR) methods in coherent potential approximation (CPA) and local density approximation (LDA) [7]. For the calculations use was made of lattice constant values on *k*-net of size  $10 \times 10 \times 10$  and parametrization type of Moruzzi-Janak-Williams exchange-correlation potential [8]. The width of energy window covered by the loop is 16 eV. The number of energy values for the calculation of DOS was 1000. The accuracy of calculation of the Fermi level position was  $\pm 8$  meV. The temperature and concentration dependences of the electrical resistivity ( $\rho$ ) and the Seebeck coefficient ( $\alpha$ ) were measured with respect to copper and magnetic susceptibility ( $\chi$ ) by the Faraday method of  $Hf_{1-x}Lu_xNiSn$  samples in the ranges:  $T = 80 \div 400$  K,  $N_A^{Lu} \approx 1.9 \cdot 10^{20} \text{ cm}^{-3}$  ( $x = 0.01$ )  $\div 1.9 \cdot 10^{21} \text{ cm}^{-3}$  ( $x = 0.10$ ) and magnetic field induction  $H \leq 10$  T.

### Research on structural features of $Hf_{1-x}Lu_xNiSn$

The microprobe analysis of the concentration of atoms on the surface of  $Hf_{1-x}Lu_xNiSn$  samples has shown their conformity to the initial charge compositions, which is one of the experimental proofs of a predicted substitution of *Hf* atoms by *Lu* atoms. In turn, the *X*-ray phase and structural analyses have shown that all  $Hf_{1-x}Lu_xNiSn$  samples up to the composition  $x = 0.35$  inclusive have no traces of other phases (Fig. 1, inset). The research has also confirmed the result of [9] as regards the disorder of *n-HfNiSn* crystal structure which consists in partial, up to  $\sim 1\%$ , occupation by *Ni* ( $3d^84s^2$ ) atoms of crystallographic position  $4a$  of *Hf* ( $5d^26s^2$ ) atoms, which generates donor-nature structural defects in a crystal, and electrons are major current carriers. As was expected, replacement of smaller-size *Hf* atoms ( $r_{Hf} = 0.158$  nm) by larger-size *Lu* atoms ( $r_{Lu} = 0.173$  nm) leads to increase in the values of  $Hf_{1-x}Lu_xNiSn$  unit cell period (Fig. 1).

Refinement of  $Hf_{1-x}Lu_xNiSn$  crystalline structure by powder method with a simultaneous refinement of isotropic parameters of atomic substitution and occupancy of crystallographic position of *Hf* ( $4a$ ) has shown that the lowest value of coefficient of nonconformity between a model of crystalline structure and an array of Bragg reflections ( $R_{Br} = 2.7\%$ ) was obtained for a model where the occupancy of position of *Hf*(*Lu*) atoms for  $x \geq 0.01$  is 100%. In other words, *Lu* atoms introduced into the structure put in order crystalline structure of  $Hf_{1-x}Lu_xNiSn$  semiconductor, which creates prerequisites for preparation of material with unambiguous and predicted kinetic characteristics.

Note the availability of two linear areas on the dependence  $a(x)$   $Hf_{1-x}Lu_xNiSn$ :  $0 \leq x \leq 0.01$  and  $x \geq 0.03$ . Such, at first sight, minor peculiarity of  $a(x)$  behaviour is typical of all previously studied related  $Zr_{1-x}R_xNiSn$  solid solutions (*R* is rare-earth metal) [10] and served as additional proof of the correctness of proposed model of *n-HfNiSn* crystalline structure [9]. Indeed, if in the output structure of *HfNiSn* compound the positions of *Hf* atoms are partially occupied by smaller-size *Ni* atoms [1], then on doping of semiconductor with atoms of rare-earth metal on the area  $0 \leq x \leq 0.01$  there is a displacement of smaller-size *Ni* atoms ( $r_{Ni} = 0.124$  nm) by *Lu* atoms of considerably larger size (by  $\sim 40\%$ ). At impurity concentrations  $x \geq 0.01$  all *Ni* atoms will be displaced from the position of *Hf* atoms, and *Hf* atoms will be substituted by *Lu* atoms, where the difference in atomic radii is

considerably smaller. In that case the amplitude of change in the values of  $Hf_{1-x}Lu_xNiSn$  unit cell period in the areas  $0 \leq x \leq 0.01$  and  $x \geq 0.03$  will be different; in the former case this change will be greater, as evidenced by a larger slope of dependence  $a(x)$ , which is only possible with displacement of smaller-size  $Ni$  atoms from the position of larger-size  $Hf$  atoms.

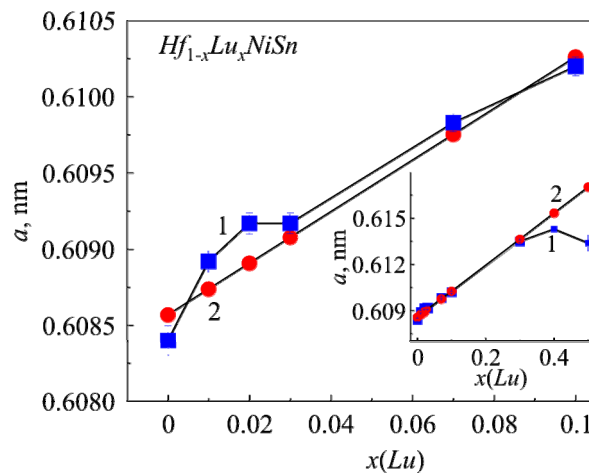


Fig. 1. Change in the values of unit cell period  $a(x)$  of  $Hf_{1-x}Lu_xNiSn$ : 1 – experiment; 2 – calculation.

Proceeding from the assumption that doping of  $n$ - $HfNiSn$  with  $Lu$  atoms is accompanied by crystal structure ordering, and  $Lu$  impurity atoms displace  $Hf$  atoms from position  $4a$ , we calculated a change in the values of unit cell period (Fig. 1, curve 2). In the calculations we assumed that the initial compound  $HfNiSn$  is ordered, that is, all the atoms occupy only their own crystallographic positions. Exactly for this reason the calculated value of unit cell period for the initial compound  $HfNiSn$  is larger than the experimental one, as long as in a real compound, as we mentioned before,  $\sim 1\%$  of  $Hf$  atoms are displaced by smaller-size  $Ni$  atoms. Comparison of the calculated and experimental values of unit cell period of  $Hf_{1-x}Lu_xNiSn$  (Fig. 1) vividly demonstrates structural changes that we investigated in the refinement of crystal structure by powder method.

The process of semiconductor crystal structure ordering on doping with  $Lu$  atoms, apart from structural peculiarities, contributes essentially to electron density redistribution. Thus, if in the initial compound  $HfNiSn$  there are donor-nature structural defects as a result of displacement of up to  $\sim 1\%$  of  $Hf$  atoms by smaller-size  $Ni$  atoms, the process of semiconductor doping with  $Lu$  atoms and ordering its crystal structure is accompanied, on the one hand, by the reduction of the number of donor-nature structural defects, since  $Ni$  atoms leave the position of  $Hf$  atoms (“healing” of donor-nature structural defects in position  $4a$ ). On the other hand, since  $Lu$  ( $5d^16s^2$ ) atom possesses one  $5d$ -electron less than  $Hf$  atom, such doping will generate acceptor-nature structural defects in a crystal.

Thus, doping of  $n$ - $HfNiSn$  with the atoms of rare-earth metal  $Lu$  by substitution of  $Hf$  atoms is accompanied by crystal structure ordering and makes it resistant to temperature and time changes, which is a necessary condition of possible material use for production of sensitive elements of thermal converters. Moreover, such ordering is accompanied by a simultaneous reduction of the number of donor-nature defects ( $Ni$  atoms in position  $4a$  of  $Hf$  atoms) and increase in the number of acceptor-nature structural defects ( $Lu$  atoms in position  $4a$  of  $Hf$  atoms), which must lead to a change in semiconductor compensation degree and the type of major current carriers as a result of a change in the ratio of donor- and acceptor-nature defects.

### Research on the electron structure of $Hf_{1-x}Lu_xNiSn$

To predict the behaviour of the Fermi level  $\varepsilon_F$ , the energy gap  $\varepsilon_g$  and the kinetic characteristics of  $n$ - $HfNiSn$  doped with  $Lu$  atoms, the electron density distribution (DOS) of  $Hf_{1-x}Lu_xNiSn$ ,  $0 \leq x \leq 0.10$  was calculated (Fig. 2 a). Taking into account the results of structural research, namely that introduction of  $Lu$  atoms into  $HfNiSn$  compound puts in order its crystal structure, the calculation of DOS was performed for the case of ordered structure variant.

As mentioned above, introduction of  $Lu$  atoms into the structure of  $HfNiSn$  compound is attended by generation of acceptors. In that case, doping of  $n$ - $HfNiSn$  semiconductor by the lowest concentrations of acceptor impurity can be expected to be attended by increase in semiconductor compensation degree [6].

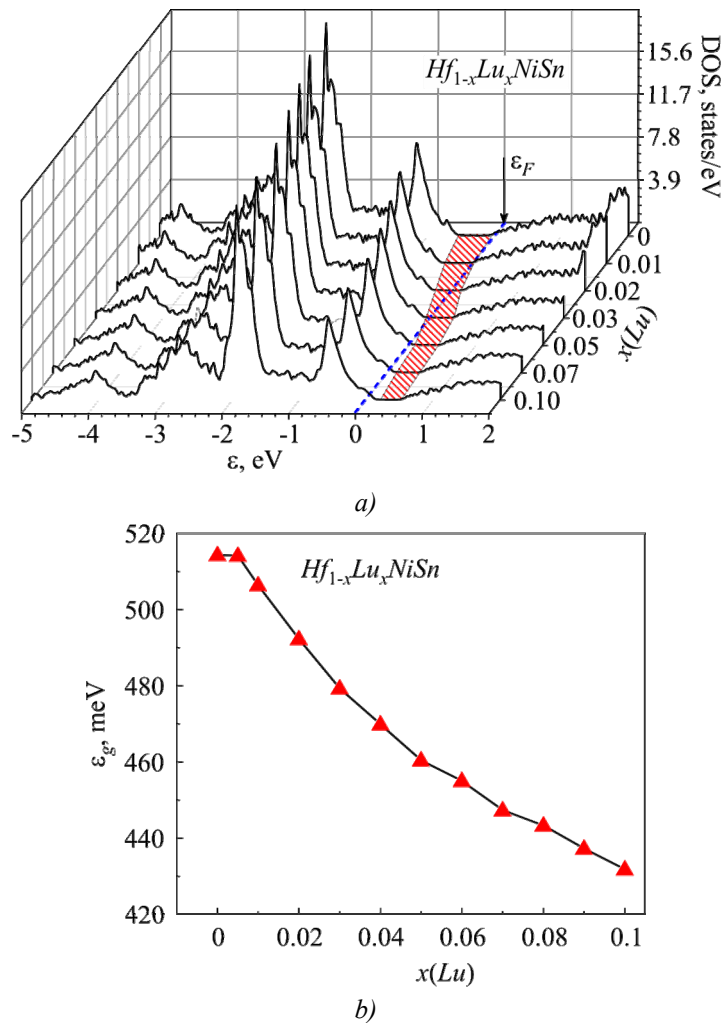


Fig. 2. Calculation of the electronic density of states DOS (a) and change in the values of energy gap  $\varepsilon_g$  (b) of  $Hf_{1-x}Lu_xNiSn$ .

As can be seen from Fig. 2 a, on introducing into  $n$ - $HfNiSn$  the least attainable in the experiment concentrations of  $Lu$  acceptor impurity, the Fermi level  $\varepsilon_F$  starts drifting from conduction band from which it was spaced  $\sim 81.3$  meV [9], to the mid of the energy gap  $\varepsilon_g$  (hatched area in Fig. 2 a), and then to valence band which will be crossed at certain  $Lu$  concentrations. Crossing by the Fermi level  $\varepsilon_F$  of the mid energy gap and its further motion towards valence band will change semiconductor conduction type, and holes will become major current carriers. In that case further doping of now

*p*-type semiconductor with acceptors must be accompanied by a decrease in compensation degree.

Apart from the drift caused by a change in semiconductor compensation degree, there is also a reduction in the values of energy gap  $\varepsilon_g$  (Fig. 2 *b*) from the values of  $\varepsilon_g(x=0) = 514.3$  meV and  $\varepsilon_g(x=0.05) = 460.4$  meV to  $\varepsilon_g(x=0.10) = 431.8$  meV. The predicted behaviour of the Fermi level  $\varepsilon_F$  is accompanied by interesting processes of change in DOS values on the Fermi level (Fig. 3 *a*, curve 2). Thus, doping of *n*-*HfNiSn* semiconductor with *Lu* acceptor impurities will expectedly result in the reduction of DOS on the Fermi level, and the minimum of dependence  $g(\varepsilon_F)$  corresponds to crossing by the Fermi level the mid energy gap of semiconductor. At concentrations of *Lu* impurity, when the Fermi level will cross the mid energy gap and approach the valence band, there will be a predicted growth of DOS on the Fermi level.

The above results of calculations of change in the electron density distribution and, in particular, the density of states on the Fermi level, agree with the results of experimental measurement of the magnetic susceptibility  $\chi$  of  $Hf_{1-x}Lu_xNiSn$  (Fig. 3 *a*, curve 1). Investigations have shown that  $Hf_{1-x}Lu_xNiSn$ ,  $x > 0.01$  semiconductors are Pauli paramagnetics whose magnetic susceptibility is determined exclusively by the electron gas and is proportional to the density of states on the Fermi level. As can be seen from Fig. 3 *a*, curve 1, dependence  $\chi(x)$  has a plateau in the concentration area  $x = 0.02 \div 0.03$  which we attribute, as shown by calculations, exactly to a change in the density of states on the level of  $g(\varepsilon_F)$ . In this context it should be noted that basic semiconductor *n*-*HfNiSn* is not Pauli paramagnetic, but a weak diamagnetic, as testified by the negative values of magnetic susceptibility:  $\chi(x=0) = -0.082$  cm<sup>3</sup>/g [11]. So, the alleged growth of dependence  $\chi(x)$  in the concentration area  $x = 0 \div 0.02$  cannot be attributed to increase in DOS on the Fermi level.

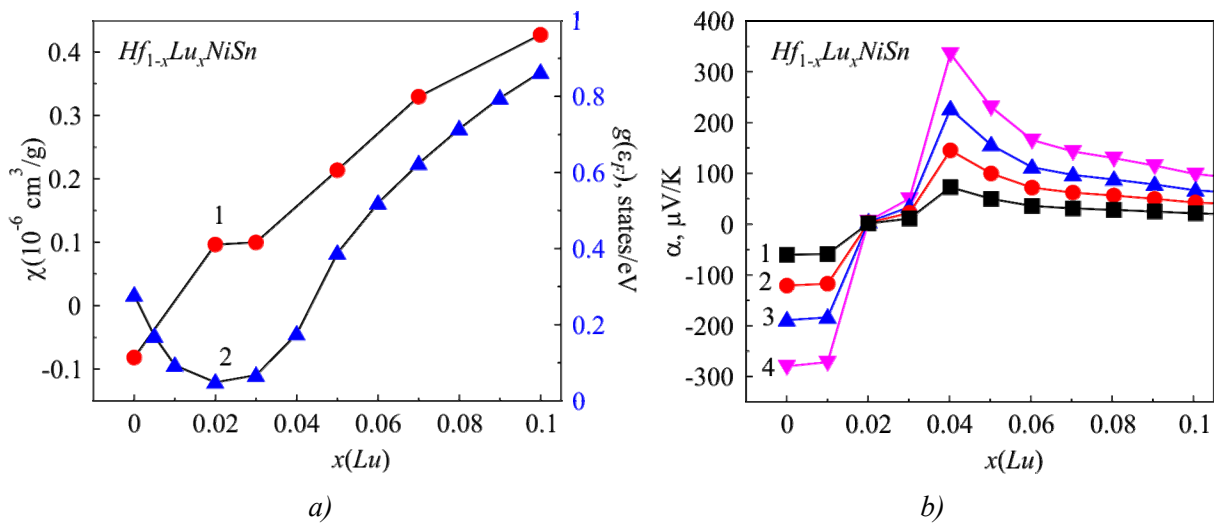


Fig. 3. Change in the values of magnetic susceptibility  $\chi$  (curve 1) and density of states on the Fermi level  $g(\varepsilon_F)$  (curve 2) (a) and the Seebeck coefficient  $\alpha$  (calculation) (b) of  $Hf_{1-x}Lu_xNiSn$  at the temperatures: 1 – 80 K; 2 – 160 K; 3 – 250 K; 4 – 380 K.

Having calculated the electronic structure of  $Hf_{1-x}Lu_xNiSn$  thermoelectric materials, we obtained the mechanism for prediction of the kinetic characteristics of a semiconductor, in particular, the Seebeck coefficient, the electric resistivity, etc. For the calculation of the Seebeck coefficient  $\alpha$  as a working formula the relationship [12] was used:

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

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

As an example, Fig. 3 b shows a change in the values of the Seebeck coefficient  $\alpha(x)$  of  $Hf_{1-x}Lu_xNiSn$  at different temperatures. Changing the concentration of *Lu* atoms, we can purposefully obtain in thermoelectric material both positive and negative high values of the Seebeck coefficient and conductivity, which serves one of the conditions for obtaining high values of thermoelectric figure of merit.

Thus, the results of calculation of the density of electronic states of  $Hf_{1-x}Lu_xNiSn$  based on the results of structural investigations confirm the predicted acceptor nature of structural defects generated in a crystal on substitution of *Hf* atoms by *Lu*. The results of experimental research presented below will show the conformity of calculated results to real processes in thermoelectric material.

### Research on the electrokinetic and energy characteristics of $Hf_{1-x}Lu_xNiSn$

The temperature dependences of electric resistivity  $\rho$  and the Seebeck coefficient  $\alpha(1/T)$  for the samples of  $Hf_{1-x}Lu_xNiSn$ ,  $0 \leq x \leq 0.1$  are shown in Fig. 4. The dependences  $\ln(\rho(1/T))$  and  $\alpha(1/T)$  are typical for doped and compensated semiconductors with high- and low-temperature activation areas, which is indicative of the presence in them of several activation conductivity mechanisms. From the activation areas of dependences  $\ln(\rho(1/T))$  we calculated the values of activation energies from the Fermi level  $\varepsilon_F$  to percolation level of conduction band (valence band)  $\varepsilon_1^p$  and electron jumps  $\varepsilon_3^p$  in the states with energies close to the Fermi level  $\varepsilon_F$ , and from the activation areas of dependences  $\alpha(1/T)$  – the values of activation energies  $\varepsilon_1^\alpha$  and  $\varepsilon_3^\alpha$ , which yield, respectively, the values of modulation amplitude of continuous energy bands and small-scale fluctuation of heavily doped strongly compensated semiconductors [13].

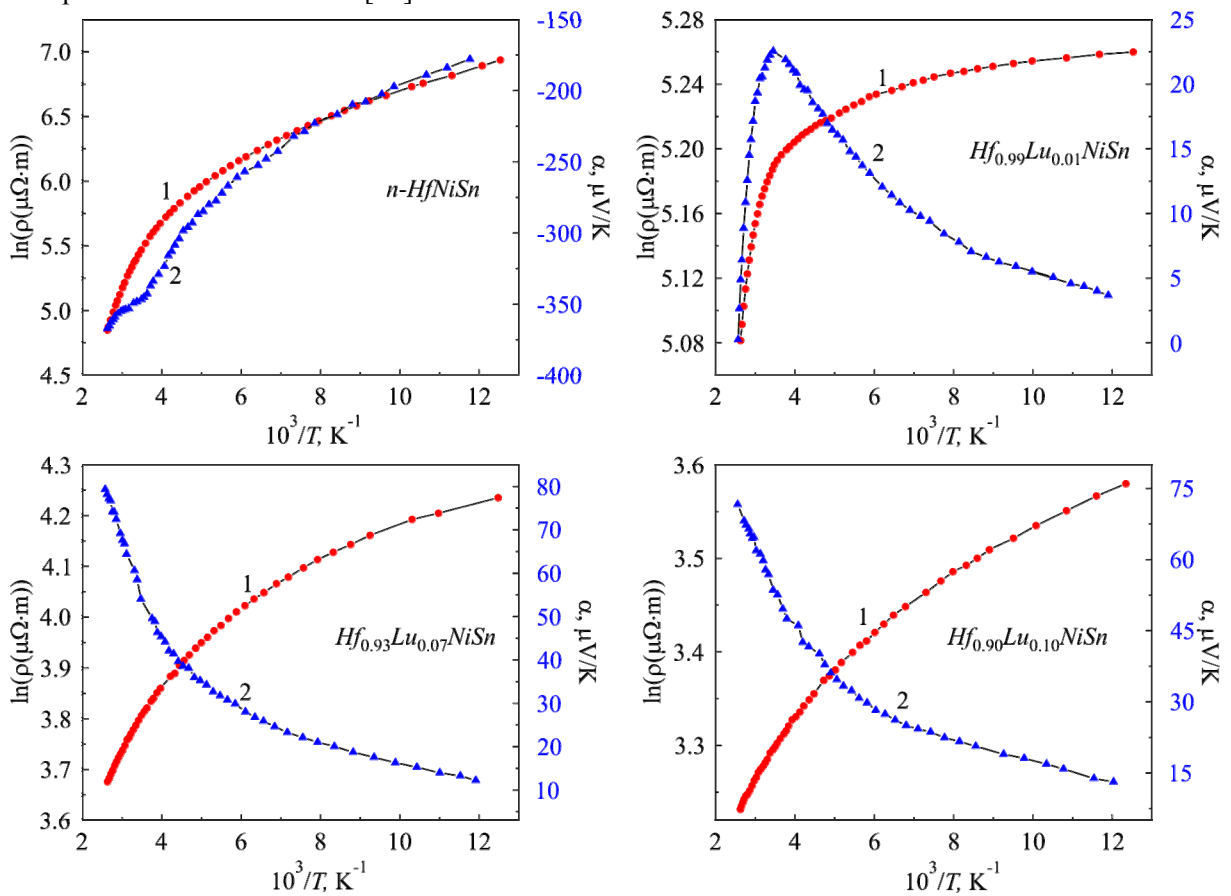


Fig. 4. Temperature dependences of resistivity  $\rho$  (1) and the Seebeck coefficient  $\alpha$  (2) of  $Hf_{1-x}Lu_xNiSn$ .

As is shown in Figs. 4 and 5 b, the Seebeck coefficient of  $Hf_{1-x}Lu_xNiSn$ ,  $x = 0$ , has negative values, and electrons are the main current carriers. This is a well known and expected result related to donor nature of structural defects of  $n-HfNiSn$  semiconductor [1].

Introduction to  $HfNiSn$  compound of the lowest concentration of  $Lu$  atoms leads to a change in conduction type of  $Hf_{1-x}Lu_xNiSn$  semiconductor: at  $x \geq 0.01$  the values of the Seebeck coefficient become positive over the entire temperature range, indicating that the Fermi level is now closer to the valence band than to conduction band (Fig. 4 and 5 b). Such a behavior of the Fermi level had been anticipated by the calculations of semiconductor electron structure and results from the appearance in a crystal of acceptor-nature structural defects at introduction of  $Lu$  atoms.

The fact that  $Lu$  atoms introduced into  $HfNiSn$  compound result in generation in a crystal of acceptor-nature structural defects is shown by the dependences of change in the values of electric resistivity over the entire temperature and concentration ranges (Fig. 5 a). Thus, introduction of the lowest in the experiment concentration of  $Lu$  atoms is accompanied by a drastic reduction in the values of electric resistivity, for instance, at 80 K, from the values of  $\rho(x = 0) = 1029.1 \mu\Omega \cdot m$  to  $\rho(x = 0.01) = 192.4 \mu\Omega \cdot m$  and  $\rho(x = 0.1) = 35.9 \mu\Omega \cdot m$ . The point is that the concentration of acceptors generated in a crystal on introducing the lowest concentration of  $Lu$  ( $x = 0.01$ ) is too high, and we jump over the concentration gap whereby the Fermi level would move from the edge of conduction band to the mid of the energy gap, which would be attended by growth in the electric resistivity values due to a reduction of density of states on the Fermi level in the  $n$ -type semiconductor doped with acceptors.

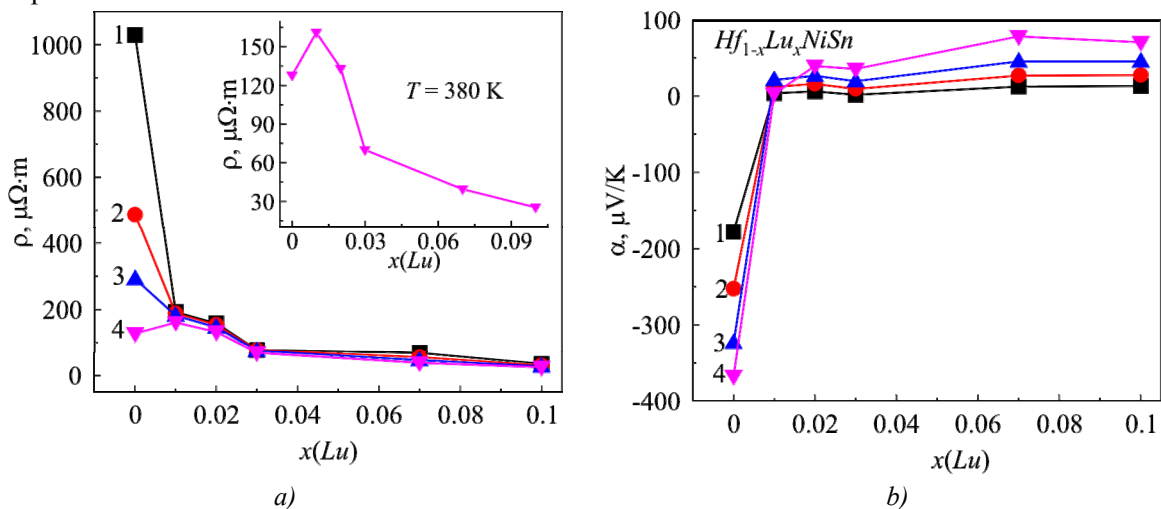


Fig. 5. Change in the values of resistivity  $\rho(x)$  (a) and the Seebeck coefficient  $\alpha(x)$  (b)  $Hf_{1-x}Lu_xNiSn$  at the temperatures: 1 – 80 K; 2 – 160 K; 3 – 250 K; 4 – 380 K.

We draw attention to the fact of appearance of maximum on the dependence  $\rho(x)$  at a temperature of  $T = 380$  K (Fig. 5 a). A similar picture of maximum  $\rho(x)$  displacement to the area of high impurity concentrations was observed in [11, 14] on doping of  $n-HfNiSn$  with acceptor impurities  $Rh$  and  $Co$ . This effect was explained by generation in a crystal of acceptor-nature defects concurrently with donor-nature structural defects whose ionization occurs at higher temperatures.

The proof of the fact that the Fermi level crossed the mid of the energy gap and is moving exactly in the direction of valence band on doping of  $n-HfNiSn$  with  $Lu$  atoms is a behaviour of the dependence of the Seebeck coefficient  $\alpha(x)$  of  $Hf_{1-x}Lu_xNiSn$  (Fig. 5 b). Thus, the values of the Seebeck coefficient, for instance, at 80 K, vary from the values of  $\alpha(x = 0) = -178.1 \mu VK^{-1}$  to  $\alpha(x = 0.01) = 3.7 \mu VK^{-1}$  and  $\alpha(x = 0.1) = 13.2 \mu VK^{-1}$ , which testifies to a change in the type of major

current carriers in  $Hf_{1-x}Lu_xNiSn$  – from electrons at  $x = 0$  to holes at  $x \geq 0.01$ .

We also focus on the behaviour of dependence of the Seebeck coefficient  $\alpha(x)$  of  $Hf_{1-x}Lu_xNiSn$  at  $T = 380$  K. The value of the Seebeck coefficient at temperature  $T = 380$  K varied with a change in concentration of  $Lu$  impurity atoms at follows: from  $\alpha(x = 0) = -367.2 \mu\text{VK}^{-1}$  to  $\alpha(x = 0.01) = 0.2 \mu\text{VK}^{-1}$  and  $\alpha(x = 0.02) = 39.4 \mu\text{VK}^{-1}$ . We can see that at concentration  $Hf_{1-x}Lu_xNiSn$ ,  $x = 0.01$  and temperature  $T = 380$  K the concentrations of ionized acceptors and donors became practically the same, as indicated by the Seebeck coefficient value close to zero. This result completely agrees with the nature of behaviour of  $\rho(x)$  at temperature  $T = 380$  K exactly in the region of acceptor concentrations  $x = 0.01$ . And this, in turn, also points to the fact of appearance in a crystal of donors by so far unknown mechanism on doping with acceptor impurity.

Therefore, the two experimental results, namely change in the values of electric resistivity  $\rho(x)$  and the Seebeck coefficient  $\alpha(x)$  of  $Hf_{1-x}Lu_xNiSn$  point to the presence in a crystal of a complicated mechanism of generation of structural defects of both acceptor and donor nature.

In this context it is interesting to follow the nature of change in the energy characteristics of  $Hf_{1-x}Lu_xNiSn$ , obtained from the experimental research (Fig. 6), from which it can be also concluded that introduction of  $Lu$  impurity atoms into the structure of  $HfNiSn$  compound is accompanied by generation of both acceptor- and donor-nature structural defects. Thus, from Fig. 6 a it is seen that doping of semiconductor results in the reduction of the values of activation energy  $\varepsilon_1^p(x)$ . It is important to explain that the value of energy  $\varepsilon_1^p(x)$  for undoped semiconductor  $n\text{-HfNiSn}$  reflects the energy gap between the position of the Fermi level  $\varepsilon_F$  and the edge of conduction band. At the same time, the values of activation energy  $\varepsilon_1^p(x)$  for the lowest and all succeeding concentrations of  $Lu$  atoms reflect the energy gap between the Fermi level position and the edge of valence band. The fact that the value of activation energy  $\varepsilon_1^p(x = 0)$  fits in the dependence  $\varepsilon_1^p(x)$  is quite casual.

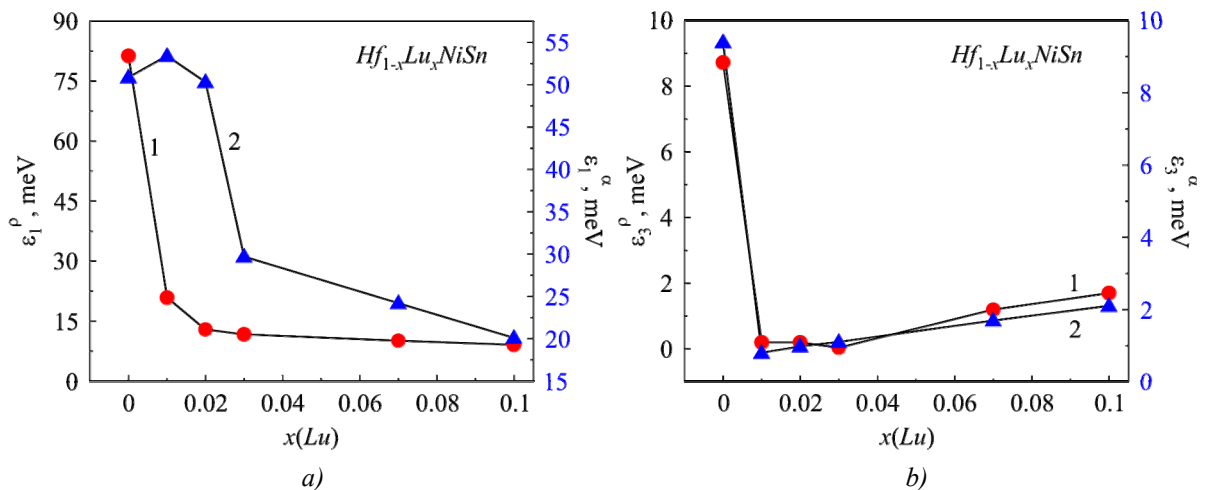


Fig. 6. Change in the values of activation energies  $\varepsilon_1^p(x)$  (1) and  $\varepsilon_1^\alpha(x)$  (2) (a) and  $\varepsilon_3^p(x)$  (1) and  $\varepsilon_3^\alpha(x)$  (2) (b)  $Hf_{1-x}Lu_xNiSn$ .

The nature of behaviour of  $\varepsilon_1^p(x)$  implies the following interesting peculiarity. We can see that starting from the concentration of  $Lu$  impurity  $x = 0.01$  to  $x = 0.10$  the rate of motion of the Fermi level  $\varepsilon_F$  to the edge of valence band each time is reduced and is as follows: in the concentration area  $x = 0.01 \div 0.02$  the rate of motion is  $\Delta\varepsilon_F/\Delta x = 8 \text{ meV}/\%Lu$ , in the area  $x = 0.02 \div 0.03$  the rate of motion is  $\Delta\varepsilon_F/\Delta x = 1.2 \text{ meV}/\%Lu$ , in the area  $x = 0.03 \div 0.07$  the rate of motion is  $\Delta\varepsilon_F/\Delta x = 0.4 \text{ meV}/\%Lu$  and



in the area  $x = 0.07 \div 0.10$  the rate of motion is  $\Delta\varepsilon_F/\Delta x = 0.3$  meV/%Lu. In connection with the above values of drift velocity of the Fermi level  $\varepsilon_F$  in various concentration areas of Lu impurity atoms, quite a logical question arises. As long as we increase the concentration of Lu acceptor impurities by the linear law, which generate in a crystal the acceptor-nature structural defects by the same law, then why does the Fermi level not move by the same law to the edge of valence band? Which serves the restraining factor of such motion, and the dependence resembles the exponent?

Answering this question, it is logical to assume that apart from acceptors, donors are also generated in a crystal, whose generation velocity increases with increasing concentration of Lu atoms introduced into a crystal. This conclusion coincides with that made from the nature of electric resistance and the Seebeck coefficient behaviour.

On the other hand, simultaneous generation in a crystal with different velocity of donor- and acceptor-nature structural defects will be attended by a change in semiconductor compensation factor, as well as by a change in modulation amplitude of continuous energy bands of heavily doped strongly compensated semiconductor by the law that reflects the ratio of ionized acceptors and donors in a crystal. Fig. 6 a shows a change in the values of activation energy  $\varepsilon_1^\alpha(x)$  which is proportional to modulation amplitude of continuous energy bands  $Hf_{1-x}Lu_xNiSn$ . We can see that in the case of undoped semiconductor  $n-HfNiSn$  the modulation amplitude is  $\varepsilon_1^\alpha(x=0) = 50.9$  meV. Introduction into  $n$ -type semiconductor of the lowest in the experiment concentration of Lu impurity that corresponds to composition  $x = 0.01$  is accompanied by increase in semiconductor compensation factor, as indicated by the value of modulation amplitude  $\varepsilon_1^\alpha(x=0.01) = 53.4$  meV. Moreover, at concentration  $x = 0.01$  the type of semiconductor conductivity is changed, namely holes become major current carriers.

Adding to now  $p$ -type  $Hf_{1-x}Lu_xNiSn$  semiconductor,  $x = 0.01$ , of Lu acceptor impurity naturally reduces the degree of compensation, that is, the difference in the number of ionized acceptors and donors will be increased. This effect is reflected in the reduction of modulation amplitude values of  $\varepsilon_1^\alpha(x=0.02) = 50.3$  meV, and a maximum appears on the dependence  $\varepsilon_1^\alpha(x)$ . It is clear that further doping of  $p$ -type semiconductor with acceptor impurity will only reduce the compensation factor, and the value of modulation amplitude of continuous energy bands will be reduced as well (Fig. 6 a). As long as we monotonously increase acceptor concentration in a semiconductor, where holes are major current carriers, it would be quite logical to expect the same reduction in the values of modulation energy of continuous energy bands of  $Hf_{1-x}Lu_xNiSn$ . However, as is seen from Fig. 6 a, a change in the values of  $\varepsilon_1^\alpha(x)$  dependence for the cases of  $x > 0.01$  does not follow the linear law, but reminds the case of  $\varepsilon_1^p(x)$ , indicating simultaneous generation, along with acceptors, of donors by unknown mechanisms.

Changes in the values of hopping conductivity activation energy  $\varepsilon_3^p(x)$  and activation energy  $\varepsilon_3^\alpha(x)$  of  $Hf_{1-x}Lu_xNiSn$  (Fig. 6 b) also point to generation in a crystal of donor-nature defects by unknown mechanism. And indeed, a monotonous increase in the number of acceptor-nature defects in  $p$ -type semiconductor was to cause a reduction in the values of activation energy of hopping conduction  $\varepsilon_3^p(x)$ , as long as electron localization radius would have to be reduced. However, in the experiment, starting from concentration  $x \geq 0.03$ , we observe increased values of activation energy of hopping conductivity from the values of  $\varepsilon_3^p(x=0.03) = 0.04$  meV to  $\varepsilon_3^p(x=0.07) = 1.2$  meV and  $\varepsilon_3^p(x=0.1) = 1.7$  meV. Such a behaviour of hopping conductivity activation energy  $\varepsilon_3^p(x)$  is possible only in the presence of donors, which increases electron localization radius [4].

Increase in the values of modulation amplitude of small-scale fluctuation from the values of  $\varepsilon_3^\alpha(x=0.01) = 0.8$  meV to  $\varepsilon_3^\alpha(x=0.07) = 1.7$  meV and  $\varepsilon_3^\alpha(x=0.1) = 2.1$  meV is also possible only under condition of generation of donors alongside with acceptors, which will change semiconductor

compensation degree. It can be predicted that with a certain number of acceptors the rate of donor generation will be the same as that of acceptors and even greater, which will again change semiconductor compensation degree.

Thus, the results of kinetic investigations of  $Hf_{1-x}Lu_xNiSn$  allow speaking about a complex mechanism of a simultaneous generation in a crystal of acceptor- and donor-nature structural defects on introducing atoms of rare-earth metal  $Lu$  into the structure of  $HfNiSn$  compound by substitution of  $Hf$  atoms. Such a mechanism will be proposed below.

### Refinement of the crystal and electron structures of $Hf_{1-x}Lu_xNiSn$

In [1] we proposed a procedure for getting information on crystal structure which is unavailable when using  $X$ -ray investigation methods. The essence of this procedure lies in seeking for such spatial arrangement of atoms in the nodes of semiconductor crystal lattice that provides the adequacy of the results of calculation of electron structure distribution and the results obtained from the experimental research, in particular, a change in the Fermi level position.

Using binding to numerical values of activation energy  $\varepsilon_1^p$  from the Fermi level to the level of percolation of valence band of  $Hf_{1-x}Lu_xNiSn$ , we sought for a compensation factor that would provide experimentally established velocity of the Fermi level motion shown in Fig. 7 a, curve 1. Calculations of DOS were performed for various variants of atoms arrangement in the nodes of unit cell, and the degree of occupancy of crystallographic position of  $Hf_{1-x}Lu_xNiSn$  by intrinsic or extrinsic atoms. It turned out that the most acceptable variant of atoms arrangement foresees the appearance of vacancies in the position of  $Sn$  atoms (4 b). In this case compound formula will change for  $Hf_{1-x}Lu_xNiSn_{1-y}$ , and crystalline structure will remain ordered. The dynamics of change in the concentration of vacancies in crystallographic position 4 b of  $Sn$  atoms in  $Hf_{1-x}Lu_xNiSn_{1-y}$  is shown in Fig. 7 b. The velocity of the Fermi level motion towards the valence band is shown in Fig. 7 a, curve 1, which within the limits of calculation errors coincides with the results of motion of the Fermi level (Fig. 7 a, curve 2), obtained from the temperature dependences of electric resistivity (Fig. 4).

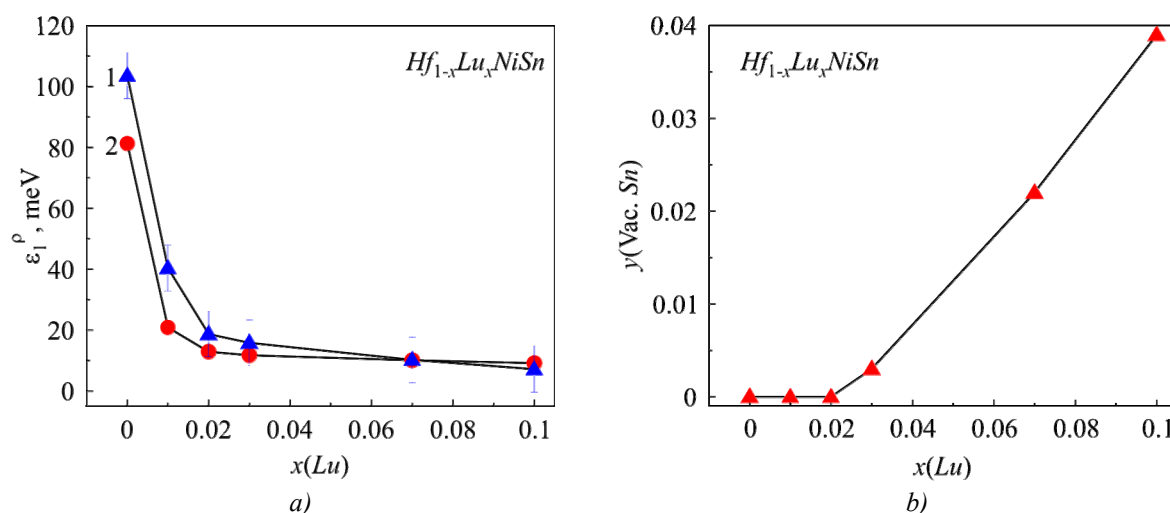


Fig. 7. Calculated (1) and experimentally obtained (2) dependence of activation energy  $\varepsilon_1^p$  (a) in  $Hf_{1-x}Lu_xNiSn$  and dynamics of change in the concentration of vacancies in crystallographic position of  $Sn$  (b).

## Conclusions

Thus, as a result of a comprehensive research on crystal and electron structures, the electrokinetic and magnetic characteristics of intermetallic semiconductor  $n-HfNiSn$ , heavily doped with the atoms of rare-earth metal  $Lu$ , the mechanisms of simultaneous generation in a crystal of acceptor- and donor-nature structural defects have been established that change thermoelectric material compensation factor and determine the mechanisms of electric conductivity.

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## References

1. V.A. Romaka, V.V. Romaka, and Yu.V. Stadnyk, *Intermetallic Semiconductors: Properties and Applications* (Lviv, Lvivska Polytechnika, 2011), 488 p.
2. T.M. Tritt, M.A. Sabramanian, Thermoelectric Materials, Phenomena, and Applications: A Bird's Eye View, *MRS Bulletin* **31** (3), 188 – 198 (2006).
3. G.S. Nolas, J. Poon, and M. Kanatzidis, Recent Developments in Bulk Thermoelectric Materials, *MRS Bulletin* **31** (3), 199 – 205 (2006).
4. B.I. Shklovsky, A.L. Efros, *Electronic Properties of Doped Semiconductors* (Moscow: Nauka, 1979), 416 p.
5. L.I. Anatychuk, *Thermoelements and Thermoelectric Devices* (Kyiv: Naukova Dumka, 1979), 768 p.
6. T. Roisnel, J. Rodriguez-Carvajal, WinPLOTR: a Windows Tool for Powder Diffraction Patterns Analysis, *Mater. Sci. Forum, Proc. EPDIC7* **378-381**, 118 – 123 (2001).
7. 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).
8. V.L. Moruzzi, J.F. Janak, and A.R. Williams, *Calculated Electronic Properties of Metals* (NY: Pergamon Press, 1978), 348 p.
9. V.V. Romaka, P. Rogl, L. Romaka, Yu. Stadnyk, A. Grytsiv, O. Lakh, and V. Krajovsky, Peculiarities of Structural Disorder in Zr- and Hf- Containing Heusler and Half-Heusler Stannides, *Intermetallics* **35**, 45 – 52 (2013).
10. V.A. Romaka, D. Fruchart, E.K. Hlil, R.E. Gladyshevskii, D. Gignoux, V.V. Romaka, B.S. Kuzhel, and R. Krayjvskii, Features of an Intermetallic  $n-ZrNiSn$  Semiconductor Heavily Doped with Atoms of Rare-Earth Metals, *Semiconductors* **44** (3), 293 – 302 (2010).
11. V.A. Romaka, P. Rogl, V.V. Romaka, Yu.V. Stadnyk, E.K. Hlil, V.Ya. Krajovsky, and A.M. Horyn, Features of Conduction Mechanisms in  $n-HfNiSn$  Semiconductor Heavily Doped with Rh Acceptor Impurity, *Semiconductors* **47** (9), 1145 – 1152 (2013).
12. N. Mott, T. Davis, *Electronic Processes in Noncrystalline Substances* (Moscow: Mir, 1982), 368 p.
13. V.A. Romaka, Yu.V. Stadnyk, V.V. Romaka, D. Fruchart, Yu.K. Gorelenko, V.F. Chekurin, and A.M. Horyn, Features of Electrical Conductivity in the  $n-ZrNiSn$  Intermetallic Semiconductor Heavily Doped with the In Acceptor Impurity, *Semiconductors* **41** (9), 1041 – 1047 (2007).
14. V.A. Romaka, P. Rogl, Yu.V. Stadnyk, V.V. Romaka, E.K. Hlil, V.Ya. Krayovskii, and A.M. Horyn, Features of the Conduction Mechanisms of the  $n-HfNiSn$  Semiconductor Heavily Doped with the Co Acceptor Impurity, *Semiconductors* **46** (9), 1106 – 1113 (2012).

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