DIELECTRIC—METAL TRANSITION DURING A CHANGE OF THE COMPOSITION OF A HIGHLY DOPED AND COMPENSATED $TiCo_{1-x}Ni_xSb$ SOLID SOLUTION: THE ROLE OF DONOR IMPURITIES

V.A. ROMAKA,[1,2], YU.V. STADNYK[3], M.G. SHELYAPINA[4], D. FRUCHART[5], V.F. CHEKURIN[1], L.P. ROMAKA[3], A.V. TKACHUK[3]

UDC 621.315.592

[1]**Ya. Pidstryhach Institute of Applied Problems of Mechanics and Mathematics, Nat. Acad. Sci. of Ukraine**
(3b, Naukova Str., Lviv 79060, Ukraine),

[2]**National University "Lvivs'ka Politekhnika"**
(12, Bandera Str., Lviv 79013, Ukraine),

[3]**Ivan Franko Lviv National University**
(6, Kyryl and Mefodii Str., Lviv 79005, Ukraine; e-mail: stadnyk_ yuriy@franko.lviv.ua),

[4]**V.A. Fock Institute of Physics of the St.-Petersburg National University**
(1, Ul'yanovskaya Str., Petrodvorets, St.-Petersburg 198504, Russia),

[5]**Laboratoire de Cristallographie, CNRS**
(BP 166, Grenoble 38042, Cedex 9, France)

The role of the impurity donor band in the conductivity of a highly doped and compensated TiCoSb semiconductor is determined. The electronic structure of a $TiCo_{1-x}Ni_xSb$ semiconductor solid solution is calculated. The model of the reconstruction of the impurity band of the TiCoSb semiconductor under its doping by donor impurities is proposed. The theoretically predicted and experimentally verified transition from the activated conductivity to the metallic one during a change of the composition of a $TiCo_{1-x}Ni_xSb$ solid solution is interpreted as the Anderson transition.

1. Introduction

The presented research, which continues the study of the dopant influence on the electrophysical properties of inter-metallic compounds of the structural type MgAgAs, in particular, semiconductors (M^1,M^2)(Co,Ni)(Sn,Sb), where M^1=Ti, Zr, Hf and M^2=Sc, Y, La, Tm, Lu, V, Nb, Ta, shows an important role of the impurity energy levels in the conductivity of these semiconductors. This conclusion is based on the analysis of our theoretical and experimental results and on the known theoretical and experimental investigations of the electronic and crystal structure, specific electric resistance, Hall and Seebeck coefficients, optical properties, specific heat, electron paramagnetic resonance spectra, magnetization, and magnetic susceptibility of pure M^1NiSn and M^1CoSb and doped semiconductors (the solid solutions on their basis)[1—11].

The study of the influence of acceptor impurities of various concentrations, from $N_A = 3.5 \times 10^{20}$ cm^{-3} to $N_A = 5.3 \times 10^{21}$ cm^{-3}, on the kinetic phenomena in n−ZrNiSn and the calculation of the electron density distribution in $Zr_{1-x}Sc_xNiSn$ allowed us to propose, for the first time, a model of the reconstruction of the acceptor impurity band upon the doping of the semiconductor by acceptor impurities. The predicted dielectric-metal transition in the conductivity, which is the Anderson transition, was also observed experimentally [12, 13]. In [14], a new approach was developed for the interpretation of the experimental results for highly doped and compensated semiconductors of the structural type MgAgAs. This approach takes into account simultaneously the properties of highly doped and compensated semiconductors [15] and a local disorder of the crystal structure, especially those of semiconductor solid solutions [16].

The determination of a position of the Fermi level, (E_F), and the variation of its position in the TiCoSb semiconductor by means of doping are the important practical problems, because this semiconductor is one of the most investigated and promising thermoelectric materials [17—19].

Structural disorders in compounds of the MgAgAs type [20] and the disorders caused by fluctuations of the concentration of charged impurities (with concentrations $10^{19} \div 10^{21}$ cm^{-3}) [15] are responsible for the appearance of impurity levels in the forbidden gap, as well as of localized states separated by the mobility edge in the continuous energy band [16]. This has an essential influence on the kinetic properties of a semiconductor. In order to separate the phenomena related to the impurity band, we carried out the calculation of the electronic structure of $TiCo_{1-x}Ni_xSb$ using the Green function method in the coherent potential approximation [21].

In this work, we study the influence of donor impurities on the kinetic characteristics of semiconductors with a structure of the MgAgAs type. We investigate the electric conductivity, Seebeck coefficient, and magnetic susceptibility of TiCoSb compound doped by donor impurities of various concentrations. These dopants replace Co ($3d^74s^2$) by Ni ($3d^84s^2$) and create the solid solution of substitution $TiCo_{1-x}Ni_xSb$. In the experiments, the donor concentration was changed from $N_D = 1.9 \times 10^{20}$ cm^{-3} ($x = 0.01$) to $N_D = 3.8 \times 10^{21}$ cm^{-3} ($x = 0.2$).

2. Experimental Technique

The samples of the $TiCo_{1-x}Ni_xSb$ solid solution were prepared by the method of electric arc fusion of the original elements on a copper water-cooled substrate in the refined argon atmosphere. The alloys underwent the homogenizing annealing at 1070 K during 720 h in the vacuumized quartz ampoules. The x-ray phase analysis was carried out with the use of diffractometers DRON-2.0 (FeK_α radiation) and HZG-4A (CuK_α radiation).

The lattice parameters and the details of the crystal structure were calculated with the use of the software CSD [22]. The electric resistance ρ, Seebeck coefficient S with respect to copper, and magnetic susceptibility χ (Faraday method) were measured in the temperature range 80÷380 K.

3. Calculation of the Electronic Structure of the $TiCo_{1-x}Ni_xSb$ Solid Solution

Figure 1 shows the calculated electron density distributions for each component of the $TiCo_{1-x}Ni_xSb$ solid solution and the total distribution for various values of x. It can be seen that the TiCoSb and TiNiSb compounds, which present the extremes in the solid solution concentrations, are the narrow-band semiconductors. This conclusion is consistent as with the experimental data, as with the theoretical calculations by the pseudo-potential method [5]. The difference between these two compounds is that the Fermi level lies in the band gap in TiCoSb and in the conduction band in TiNiSb. Accordingly, the TiCoSb conductance is of the activation type and is determined mainly by the concentration ratio of donor and acceptor impurities, while the conductivity of TiNiSb has a metallic character and is determined by electrons of the conduction band.

Figure 1 shows also that the electron density above the Fermi level is determined mainly by the d-states of Ti, while the electron density in the valence band is determined by the d-states of Co or Ni that overlap with the d-states of Ti and p-states of Sb. Already at $x = 0.1$, the Fermi level falls into the conduction band. The increase in x is accompanied by the Fermi level drift further in the depth of the conduction band. In this case, we observe a decrease of the intensity peaks in the valence band at –0.14 and –0.006 Ry (for TiCoSb) which belong to the d-states of Co and Ni, respectively. A new peak at –0.22 Ry below the Fermi level, which is related to the increase of the d-states of Ni, becomes more distinctive and dominates at $x = 0.9$. In this case, the conductance of $TiCo_{1-x}Ni_xSb$ has a metallic character. Thus, the replacement of Co by Ni in the $TiCo_{1-x}Ni_xSb$ semiconductor solid solution leads to the transition of the conductance from activated to metallic.

The state density calculation at the Fermi level shows (Fig. 2, insertion) that, for small x (small donor impurity concentrations), the state density at the Fermi level is determined by the d-electrons of Ti with the essential contribution of the d-states of Co. With increase in x, the main contribution comes from the d-electrons of Ni.

4. Experimental Investigations of $TiCo_{1-x}Ni_xSb$

The x-ray phase analysis confirms that all investigated samples of the $TiCo_{1-x}Ni_xSb$ solid solutions with $x = 0 \div 0.1$ are singe-phase and are crystallized in a structure of the MgAgAs type (spatial group $F\bar{4}3m$). The more detailed investigations of the crystal structure of the phases of the compositions $TiCo_{0.99}Ni_{0.01}Sb$ and $TiCo_{0.95}Ni_{0.05}Sb$ show that the atom distribution in the samples corresponds to a structure of MgAgAs type, in which positions 4(a) 0 0 0 are statistically occupied by Ni and Co atoms.

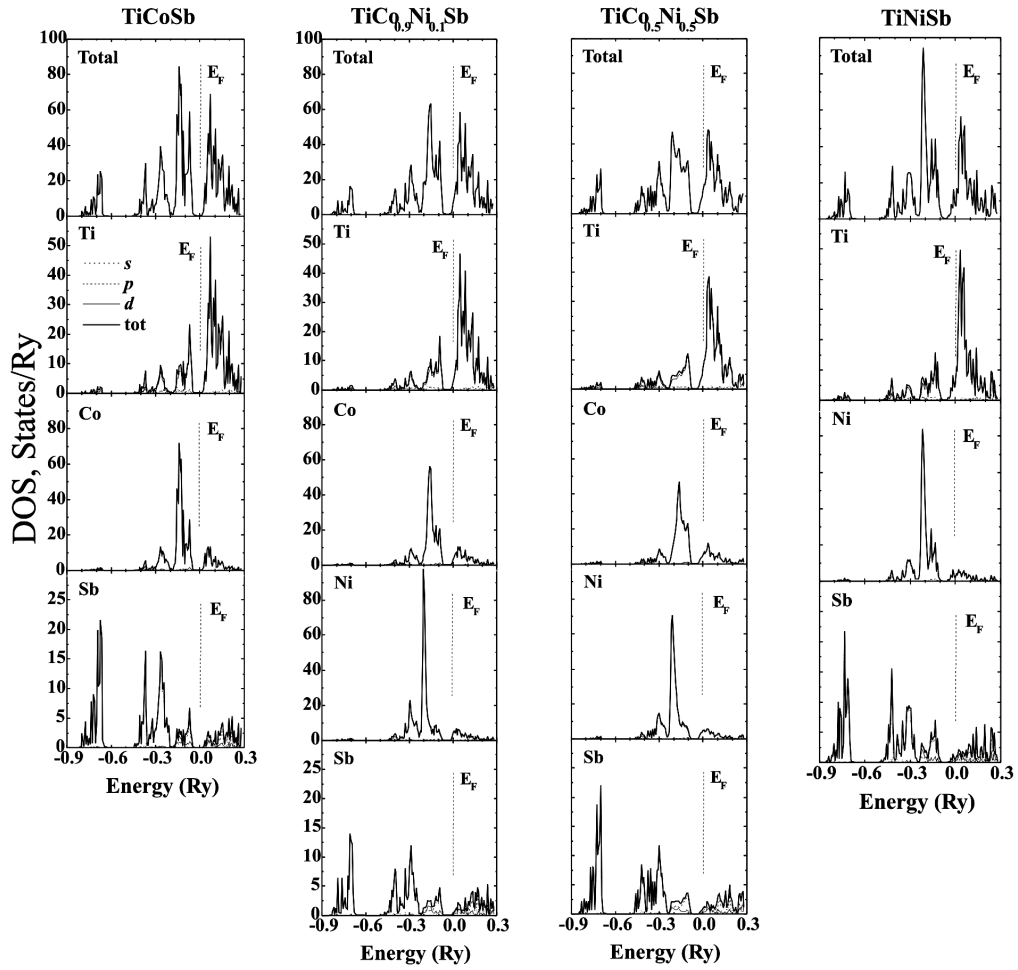

Fig. 1. Component and total state density distributions in the $_{1-x}\mathrm{Ni}_x\mathrm{Sb}$ semiconductor solid solution

The dependences $\ln\rho(1/T)$ for $\mathrm{TiCo}_{1-x}\mathrm{Ni}_x\mathrm{Sb}$ with $x \leq 0.01$ are typical of semiconductors (see Fig. 3). At $x > 0.01$, the activation parts of these curves disappear, and the functions represent the metallic conductance. On the plot of $\ln\,\rho(1/T)$ for TiCoSb, one can distinguish the regions of the high- and low-temperature activation conductivity. The first of these regions is related to the electron activation from the Fermi level, which is situated in the Coulomb gap of the impurity band, to the non-localized states of the conduction band (ε_1). The second region is attributed to the activation at the mobility edge E_C of the conductive band (ε_2). Calculations show that $\varepsilon_1 \approx$176 meV and $\varepsilon_2 \approx 9$ meV for TiCoSb ($x = 0$).

Figure 4 shows that the Seebeck coefficient changes with temperature nonlinearly. This behavior, $S(T)$, nontypical of classical semiconductors is due to the high concentration of impurities ($\sim 10^{20}$ cm^{-3}) [24]. Such a behavior was observed in ZrNiSn semiconductors compensated and highly doped by acceptor impurities [25,26]. For the sample with $x = 0$, the value of S at $T < 100$ K is positive (Figs. 2 and 4) and is negative at higher temperatures as for all other samples in the measured temperature range. The sign change for the Seebeck coefficient from positive to negative shows that the studied sample of TiCoSb contains uncontrolled impurities and has the hole type of conductance. Here, we should mention that all investigated samples were single-phase according to the x-ray analysis, which means that this method did not provide a precise measurement of the amount of impurities which, in turn, have an essential influence on the semiconductor properties.

Doping the semiconductor with donor impurities with the concentration $N_D = 1.9 \times 10^{20}$ cm^{-3} ($x = 0.01$) leads to the reconstruction of the impurity band as a

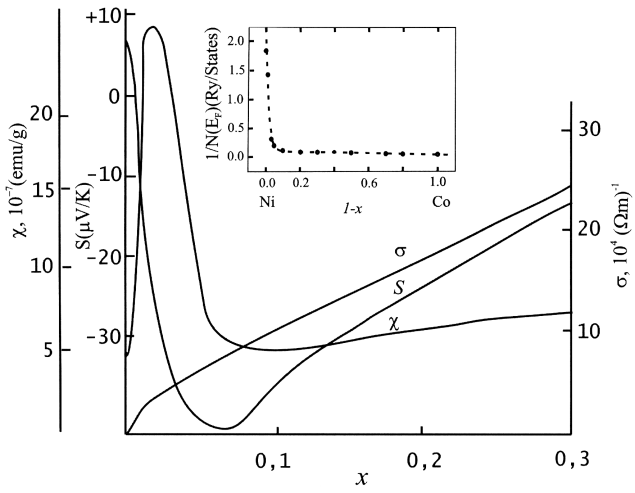

Fig. 2. Conductivity σ (*1*), Seebeck coefficient S (*2*), magnetic susceptibility χ (*3*), and the calculated state densities at the Fermi level (insert) versus the composition of $TiCo_{1-x}Ni_xSb$ at 80 K

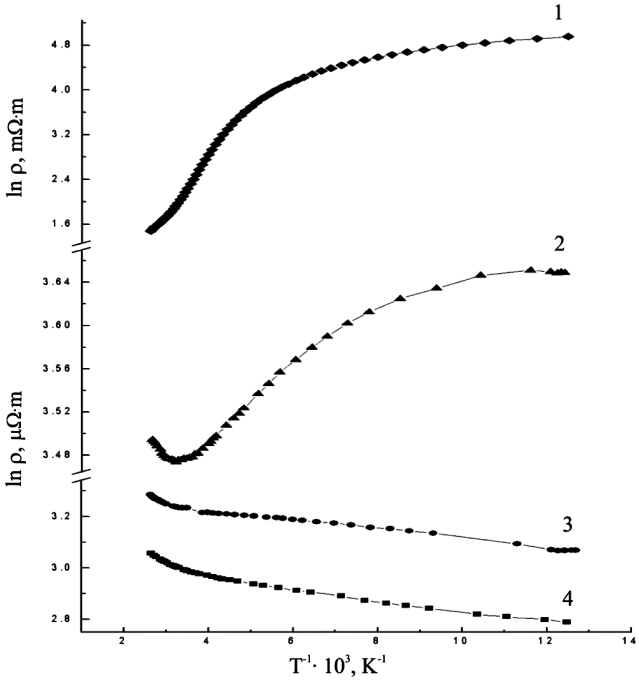

Fig. 3. Specific electric resistance ρ of $TiCo_{1-x}Ni_xSb$ as a function of temperature for various x: *1* — 0; *2* — 0.01; *3* — 0.03; *4* — 0.05

result of the change of a compensation degree of the semiconductor. The latter should result in the change of the Fermi level position, the size of the band, and its position with respect to the maxima of the continuous energy bands and in the change of the conductance mechanisms of the semiconductor. At the full

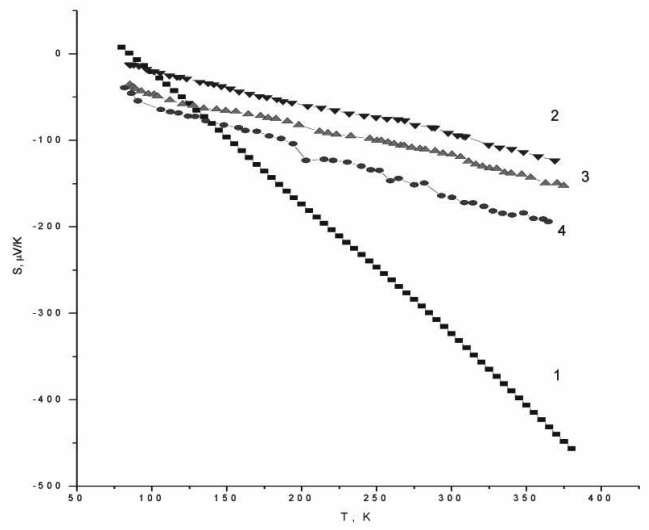

Fig. 4. Seebeck coefficient S for $TiCo_{1-x}Ni_xSb$ versus temperature for various x: *1* — 0; *2* — 0.01; *3* — 0.03; *4* – 0.05

compensation of the semiconductor, the Fermi level is located at the bottom of the impurity band, and it will move under overcompensation (the further increase in x) within the impurity band towards the conduction band [15]. The decrease of the activation energy ε_2 from 9 meV ($x = 0$) to 3.5 meV ($x = 0.01$) indicates an increase of the electron localization radius and a shift of the Fermi level with respect to the mobility edge of the conduction band E_C due to a change of the compensation degree of the semiconductor. As follows from Fig. 2, in this concentration range ($x = 0 \div 0.05$), we observe the weaker dependence $\chi(x)$ ($\chi \sim N(E_F)$ for Pauli paramagnetics) and the increase in $S(x)$ ($S \sim k_BT/E_F$). Because all investigated samples are Pauli paramagnetics, the observed correlation in $S(x)$ and $\chi(x)$ in the concentration range $N_D = (1.9 \div 9.5)\times10^{20}$ cm^{-3} ($x = 0.01 \div 0.05$) indicates a decrease in the state density at the Fermi level, which is due firstly to a change of the compensation degree of the semiconductor and to its following overcompensation from the *p*- to *n*-type conductivity. This causes the Fermi level shift from the bottom of the impurity band towards the conduction band (in the case of a strong compensation of the *n*-type semiconductor), up to the top of this band (in the case of a weak compensation) as the donor impurity concentration increases [15]. We can assume that, in this concentration range, the Coulomb gap disappears due to the filling of all the states of the impurity band, while the impurity band overlaps with the mobility edge of the conduction band, and the Fermi level E_C settles at the

minimum of the state density. Moreover, Fig. 3 yields that the contribution of the band carriers for the sample with $x = 0.01$ at $T \geq 270$ K increases, and we observe the metallization of the conductivity at $T \geq 300$ K, while the increase of $\rho(T)$ may be attributed to the band scattering mechanisms. Thus, already at $x = 0.01$ and high enough temperatures, there is a sufficient amount of free electrons with quite a high mobility which have an essential influence on the semiconductor conductivity. As a result, the conductivity in this concentration range increases by three orders.

It should be noted finally that, at $N_D > 9.5 \times 10^{20}$ cm^{-3} ($x > 0.06$), we observe stronger dependences $\chi(x)$ and $\sigma(x)$ and, at the same time, a decrease of the Seebeck coefficient with the change of the composition of the n-$TiCo_{1-x}Ni_xSb$ semiconductor solid solution. This is due to the appearance and the increase in the concentration of free electrons and the increase in the state density at the Fermi level in the conduction band (above E_C). Semiconductor n-$TiCo_{1-x}Ni_xSb$ has the metallic type of conductivity.

In analogy with the doping of semiconductors by acceptor impurities [12—14], we propose a model of the reconstruction of the impurity band of TiCoSb during the doping by donor impurities of various concentrations (Fig. 5).

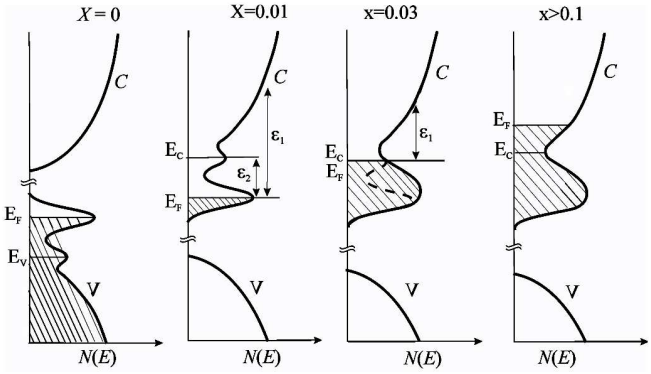

Fig. 5. Model of the impurity band reconstruction of TiCoSb under doping by donor impurities

5. Concluding Remarks

It is known that when the composition of the solid solution is changing in such a way that $E_C - E_F = \Delta E$ changes the sign, we observe the Anderson transition [16]. From the results presented above, it follows

a) p-$TiCo_{1-x}Ni_xSb$ solid solution at $x = 0$ is a compensated semiconductor. Its conductivity is of the activation type, the Fermi level E_F is fixed in the band gap by the acceptor band, and $E_C - E_F > 0$;

b) n-$TiCo_{1-x}Ni_xSb$ at $x > 0.06$ has the metallic conductivity which is determined by free electrons, the Fermi level is located in the conduction band, and $E_C - E_F < 0$.

Thus, the presented results show that the observed dielectric-metal transition in the conductivity in the $TiCo_{1-x}Ni_xSb$ semiconductor solid solution during a change in the composition is the Anderson transition. This transition is related to the reconstruction of the impurity band of the doped compensated semiconductor when the Fermi level moves through the impurity band as a result of the change of the impurity concentration and the compensation degree of the semiconductor. The agreement between the theoretical calculations and the experimental results, which indicate the conductivity transition from activated to metallic, shows the validity of the proposed model of the impurity band reconstruction during the doping of the TiCoSb semiconductor by donor impurities.

The research was supported by grants from the National Academy of Science of Ukraine (N 0106U000594) and the Ministry of Education and Science of Ukraine (N 0106U001299).

1. *Buschow K.H.J., Mooij D.B., Palstra T.T.M. et al.*// Philips J. Res.— 1985.— **40**.— P.313—329.
2. *Terada M., Endo K., Fujita Y., Kimura R.*//J. Phys. Soc. Jap.— 1972.— **32**.— P.91—94.
3. *Pierre J., Skolozdra R.V., Tobola J. et al.*//J. Alloy. Comp.— 1997.— **262**. — P.101—107.
4. *Kaczmarska K., Pierre J., Beille J. et al.*// J. Magn. and Magn. Mater.— 1998.— **187**.— P.210—220.
5. *Tobola J., Pierre J., Kaprzyk S.*//J. Phys. B: Cond. Matter.— 1998.— **10**.— P.1013—1032.
6. *Kleinke H.*// Z. anorg. und allg. Chem.— 1998.— **624**.— P.1272—1278.
7. *Tobola J., Pierre J.*// J. Alloy. Comp.— 2000.— **296**.— P.243—252.
8. *Jung D., Koo H.-J., Whangbo M.-H.*// J. Mol. Struct.— 2000.— **527**.— P.113—119.
9. *Xia Y., Ponnambalam V., Pope A.L. et al.*//J. Appl. Phys.— 2000.— **88**, N4.— P.1952—1955.
10. *Stadnyk Yu., Gorelenko Yu., Tkachuk A. et al.*// J. Alloy. Comp.— 2001.— **329**.— P.37—41.
11. *Xia Y., Ponnambalam V., Pope A.L. et al.*// J. Phys: Cond. Matter.— 2001.— **13**.— P.77—89.
12. *Caruso A.N., Borca C.N., Ristoiu D. et al.*// Surf. Sci. Lett.— 2003.— **525**.— L109—L115.
13. *Romaka L., Stadnyk Yu., Shelyapina M.*// J. Alloy. Comp.— 2005. — **396**.— P.64—68.

14. *Stadnyk Yu.V., Romaka V.A., Gorelenko Yu.K. et al.*// Ibid.— 2005. — **400**.— P.29—32.

15. *Shklovskiy B.I., Efros A.L.* Electronic Properties of Doped Semiconductors. — Moscow: Nauka, 1979 (in Russian).

16. *Mott N.F., Davis E.A.* Electron Processes in Non-Crystalline Materials.— Oxford, Clarendon Press, 1979.

17. *Skolozdra R.V., Stadnyk U.V., Romaka L.P., Aliev F.G.*//J. Thermoelectr.— 1994.— **3**.— P.29—36.

18. *Skolozdra R.V.*// Ibid.— 1997.— **2**.— P.55—77.

19. *Patent of Ukraine, № 25472 A, 1998.* /Stadnyk Yu.V., Goryn A.M., Romaka L.P. et al.

20. *Aliev F.G., Brandt H.B., Kozyrkov V.V. et al.*// Pis'ma Zh. Eksp. Teor. Fiz.— 1987.— **45**, N 11.— P.535—537.

21. *Schroter M., Ebert P.H., Akai H. et al.*//Phys. Rev. B.— 1995.— **52**.— P.188—196.

22. *Akselrud L.G., Grin Yu. N., Zavalii P.Yu. et al.*// 12^{th}Europ. Crystallographic Meeting: Collected Abstr.— Moscow: Nauka, 1989.

23. *Durcewski K., Ausloos M.*// J. Magn. and Magn. Mater.— 1985.— **51**.— P.230—252.

24. *Romaka V. A., Stadnyk Yu. V., Sheljapina M. G. et al.*//Fiz. Tekhn. Polupr.— 2006. — **40**, iss.2. — P.136—141.

25. *Aliev F.G., Kozyrkov V.V., Moshchalkov V.V.* // J. Phys. B: — Condens. Matter.— 1990.— **80**.— P.353—357.

Received 14.06.05.
Translated from Ukrainian by M. Shendeleva

ПЕРЕХІД ДІЕЛЕКТРИК—МЕТАЛ ПРИ ЗМІНІ СКЛАДУ СИЛЬНОЛЕГОВАНОГО ТА КОМПЕНСОВАНОГО НАПІВПРОВІДНИКОВОГО ТВЕРДОГО РОЗЧИНУ $TiCo_{1-x}Ni_xSb$. ДОНОРНІ ДОМІШКИ

В.А. Ромака, Ю.В. Стадник, М.Г. Шеляпіна, Д. Фрушарт, В.Ф. Чекурін, Л.П. Ромака, А.В. Ткачук

Р е з ю м е

Визначено роль домішкової донорної зони в провідності сильнолегованого та компенсованиого напівпровідника TiCoSb. Здійснено розрахунок електронної структури напівпровідникового твердого розчину $TiCo_{1-x}Ni_xSb$. Запропоновано модель перебудови домішкової зони напівпровідника TiCoSb при легуванні донорними домішками. Теоретично передбачено та експериментально виявлено перехід провідності від активаційної до металічної при зміні складу твердого розчину $TiCo_{1-x}Ni_xSb$, який ми пов'язуємо з переходом Андерсона.