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The influence of heavy doping of TiCoSb intermetallic semiconductor with Cr atoms on structural, kinetic and energetic properties

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The structural, electrokinetic, and energetic properties of the $TiCo_{1-x}Cr_xSb$ semiconductor obtained by doping TiCoSb with Cr atoms introduced into the structure by substituting Co atoms in the crystallographic position 4*c* were studied. It was shown that in $TiCo_{1-x}Cr_xSb$ the structural defects of donor and acceptor nature are generated simultaneously in different ratios depending on the impurity concentration. At concentrations of $x \geq 0.02$, the conductivity of $TiCo_{1-x}Cr_xSb$ has a metallic character, and the contribution of current carrier scattering mechanisms to the value of electrical resistivity is of the same order as changes in the concentration of current carriers. It was established that at all temperatures in the range of concentrations $x = 0$–0.02, the rate of generation of donors exceeds the rate of generation of acceptors, and at concentrations $x > 0.02$, on the contrary, the rate of generation of acceptors is greater than that of donors. This is indicated by the positive values of thermopower coefficient $\alpha(x,T)$ of $TiCo_{1-x}Cr_xSb$ for $x > 0.03$.

Keywords: semiconductor, electrical conductivity, thermopower coefficient, Fermi level.

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Introduction

The interest in semiconductor solid solutions based on half-Heusler phases (MgAgAs-type, space group $F\bar{4}3m$ [1]) is caused by the possibility, through appropriate doping of basic semiconductors, to smoothly change their values of electrical conductivity σ, thermopower coefficient α and thermal conductivity κ and to obtain high values of thermoelectric factor Z ($Z=\alpha^2\cdot\sigma/\kappa$) [2, 3]. In this context, studies of the intermetallic semiconductor TiCoSb heavily doped with Cr impurity ($3d^54s^1$), introduced into the structure by replacement of Co atoms ($3d^74s^2$) in the crystallographic position 4*c*, are interesting. Since the Cr atom contains less 3*d*- electrons than the Co atom, the appearance of impurity acceptor states ε_A in the band gap ε_g was expected. In turn, by changing the concentration of such states, we can change the compensation degree of the semiconductor $TiCo_{1-x}Cr_xSb$ [2, 4] and the mechanism of electrical conductivity. This makes it possible to optimize the kinetic properties of the thermoelectric material to increase the efficiency of converting thermal energy into electrical one [2, 3].

By comparing the results of experimental studies and calculated electronic structure of the TiCoSb semiconductor, the authors [5] established the defectiveness of its crystal structure. A model of such structure and a mechanism of simultaneous "*a priori doping*" of TiCoSb with donor and acceptor impurities was proposed, which now becomes heavily doped and highly compensated [5]. The model provides the presence of about ~1% vacancies (Va) in the crystallographic position 4*a* of Ti atoms, and additional Co* atoms (~1%) are located in the tetrahedral voids of the structure. As a result, the formula of the compound TiCoSb should be written as $(Ti_{0.99}Va_{0.01})Co(Co^*_{0.01})Sb$. The transformation of the crystal structure of TiCoSb is accompanied by corresponding changes in the electronic structure of the semiconductor. In particular, the appearance of vacancies in position 4*a* gives rise to structural defects of an acceptor nature, and acceptor states will appear in the band gap ε_g (band ε_A^1). In turn, the presence of Co* atoms in tetrahedral voids leads to the appearance of structural defects of the donor nature and corresponding donor states (ε_D^1 band) [5].

Doping TiCoSb with Sc, V, Mo, Mn, Ni, and Cu atoms established for individual impurity atoms the simultaneous generation in the semiconductor in different ratios of donor and acceptor states, as well as individual donors or acceptors [2, 6, 7]. Thus, in $Ti_{1-x}V_xCoSb$ and $Ti_{1-x}Mo_xCoSb$ structural defects of an acceptor nature are simultaneously generated as vacancies in the positions of Ti and Co atoms, and the occupation of the 4*a* position of Ti atoms ($3d^24s^2$) by V ($3d^34s^2$) or Mo ($4d^55s^1$) atoms generates defects of a donor nature. Donor and acceptor states appear simultaneously in the band gap ε_g. In the case of doping TiCoSb with Sc atoms ($3d^14s^2$), only structural defects of an acceptor nature (Sc has less 3*d*- electrons than Ti) and impurity acceptor states appear in $Ti_{1-x}Sc_xCoSb$ [6]. When doping TiCoSb with Ni ($3d^84s^2$), Cu ($3d^{10}4s^1$), and Mn ($3d^64s^2$) atoms introduced into the structure by substitution of Co atoms in the 4*c* position, generation of only donor states in the case of Ni and Cu impurities was established. In the case of Mn impurity in $TiCo_{1-x}Mn_xSb$, donor and acceptor states are generated simultaneously in different ratios which determine the position of the Fermi level ε_F and the mechanisms of electrical conductivity [7].

The results of the study of the structural, kinetic, and energy properties of the $TiCo_{1-x}Cr_xSb$ semiconductor solid solution and their comparison with calculated electronic structure for the ordered variant, will allow to determine the mechanisms of electrical conductivity and the optimal conditions for the preparing of thermoelectric materials to effectively convert thermal energy into electrical one.

I. Methods of investigation

For our investigation, the $TiCo_{1-x}Cr_xSb$ samples were synthesized by a direct twofold arc melting of the constituent metals under high purity Ti-gettered argon atmosphere on a water-cooled copper bottom. For better homogenization, the alloys were re-melted twice. The pieces of the as-cast buttons were annealed for one month at a temperature of 1073 K in evacuated silica tubes. Then the ampoules were quenched in ice water. For the characterization of the annealed samples, *X*-ray powder diffractometry (diffractometer DRON-4.0, Fe *K*α radiation) was used. The chemical compositions of the prepared samples were examined by Scanning Electron Microscopy (SEM) using Tescan Vega 3 LMU electron microscope, Quantitative electron probe microanalysis (EPMA) of the samples was carried out by using an energy-dispersive X-ray analyzer with the pure elements as standards. The lattice parameters of $TiCo_{1-x}Cr_xSb$ samples were calculated using the Fullprof Suite program [8]. For the ordered variant of the $TiCo_{1-x}Cr_xSb$ crystal structure, the electronic structure was modeled by the KKR method (Korringa-Kohn-Rostocker method) in the approximation of the coherent potential of the CPA and the local density of the LDA [9] using the exchange-correlation potential Moruzzi-Janak-Williams (the licensed software AkaiKKR and SPR-KKR) [10]. To model the energy characteristics by calculating the DOS the Brillouin zone was divided into 1000 *k*-points. To capture all semi-core states of *p*-elements the width of the energy window was chosen of 22 eV. The calculation accuracy of the Fermi level position is ± 4 meV. Measurements of the temperature and concentration dependences of the electrical resistivity $\rho(T,x)$ and the thermopower coefficient $\alpha(T,x)$ (relative to the copper) of $TiCo_{1-x}Cr_xSb$ samples were performed in the ranges: $T = 80–400$ K, $x = 0.01–0.10$. To reduce an influence of a possible *p-n* junction at the contact points measurements of the voltage drop on the samples were carried out in different current directions [2].

II. Study of structural properties of $TiCo_{1-x}Cr_xSb$

According to the microprobe analysis data of the samples $TiCo_{1-x}Cr_xSb$, $x = 0–0.10$, the concentration of atoms on the surface of the studied samples is in accordance with the composition of the charge. In turn, the *X*-ray phase analysis of $TiCo_{1-x}Cr_xSb$ samples did not reveal traces of impurity phases, and the main phase is indexed in the MgAgAs structure type [1]. Given that the concentration of impurity Cr atoms is insignificant, it was impossible to detect the fact of the ordering of the $TiCo_{1-x}Cr_xSb$ crystal structure by *X*-ray methods.

The calculated lattice parameter $a(x)$ of $TiCo_{1-x}Cr_xSb$ samples, $x = 0–0.10$ revealed a complex nature of behavior with changes in chromium content (Fig. 1). Thus, in the concentration range $x = 0–0.02$, the lattice parameter values $a(x)$ predictably increase since the atomic radius of Cr (r_{Cr}= 0.128 nm) is slightly greater than the atomic radius of Co (r_{Co}= 0.125 nm). It is important to understand that the occupation of vacancies (Va) by Cr atoms in the 4*a* position of Ti atoms [5] can also cause an increase in the values of the unit cell parameter $a(x)$ of $TiCo_{1-x}Cr_xSb$. However, the maximum observed on the dependence $a(x)$ of $TiCo_{1-x}Cr_xSb$ at $x \approx 0.02$ and the subsequent decrease of $a(x)$ values at $x > 0.02$ is unexpected. It appears that in $TiCo_{1-x}Cr_xSb$ simultaneous partial replacement by Cr atoms in position 4*a* of larger Ti atoms (r_{Ti}= 0.146 nm) is also possible. In the semiconductor solid solution $TiCo_{1-x}Mn_xSb$, we observed a similar behavior of the unit cell parameter $a(x)$ with increasing concentration of Mn atoms (Fig. 1, inset) [7]. It was shown that doping of TiCoSb with Mn atoms simultaneously generates an acceptor band ε_A (substitution of Co atoms by Mn) and donor band ε_D of different nature.

Therefore, we can assume that alloying of TiCoSb with Cr atoms introduced into the structure by replacing Co atoms is accompanied by simultaneous changes in the crystallographic positions of Ti (4*a*) and Co (4*c*) atoms. This leads to the simultaneous appearance in the crystal structure of $TiCo_{1-x}Cr_xSb$ in different ratios of donor and acceptor structural defects. It is clear that changes in the crystal structure of $TiCo_{1-x}Cr_xSb$ will be reflected by changes in the electronic structure. Thus, in the case of substitution of Ti atoms ($3d^24s^2$) for Cr atoms ($3d^54s^1$) in position 4*a* or their occupation of vacancies (Va) in $TiCo_{1-x}Cr_xSb$, structural defects of the donor nature will be generated (Cr atom contains more *d*-electrons than Ti). At the same time, partial occupation of vacancies by Cr atoms will simultaneously lead to a decrease by the same number of acceptor states that existed in TiCoSb. As a result, two kinds of donor states will appear in the band gap ε_g of the $TiCo_{1-x}Cr_xSb$ semiconductor near the donor band ε_D^1: when Ti atoms are replaced by Cr atoms (donor band ε_D^2) and when vacancies are occupied (donor band ε_D^3).

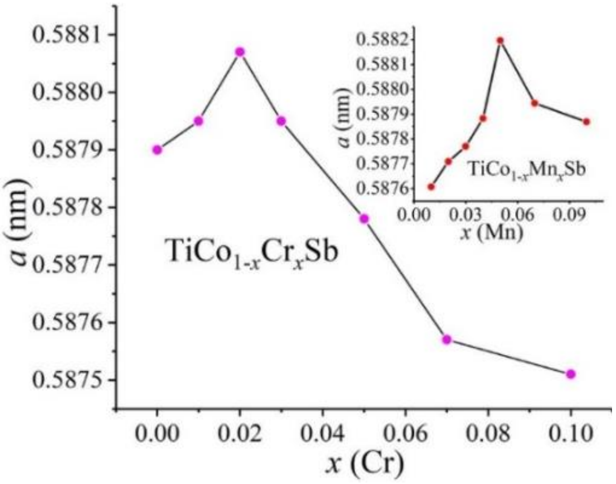


Fig. 1. Variation of the lattice parameter *a*(*x*) of $TiCo_{1-x}Cr_xSb$. Inset: change of *a*(*x*) of $TiCo_{1-x}Mn_xSb$ [7].

If Co atoms ($3d^74s^2$) are replaced by Cr atoms ($3d^54s^1$) in the crystallographic position 4*c*, structural defects of an acceptor nature will be generated in the $TiCo_{1-x}Cr_xSb$ semiconductor (Cr atom contains less *d*-electrons than Co), and in the band gap ε_g the acceptor band ε_A^2 will appear. As a result, the semiconductor $TiCo_{1-x}Cr_xSb$, $x = 0–0.10$, will simultaneously contain donor and acceptor states. The ratio of ionized in the $TiCo_{1-x}Cr_xSb$ donors and acceptors will determine the type of the semiconductor's main current carriers.

Considering the insignificant concentration of Cr atoms in $TiCo_{1-x}Cr_xSb$ and the accuracy of *X*-ray structural studies, we could not unambiguously identify the nature of structural transformations in the semiconductor. Therefore, the given considerations regarding possible changes in the structure of $TiCo_{1-x}Cr_xSb$ are of a qualitative nature. The modeling of the electronic structure of $TiCo_{1-x}Cr_xSb$ for its ordered variant and their comparison with the results of the study of the kinetic and energy properties of $TiCo_{1-x}Cr_xSb$ should clarify the conclusions regarding possible changes in the structure of the semiconductor. On this basis, it will be possible to model the crystal and electronic structure of the $TiCo_{1-x}Cr_xSb$ semiconductor in the future, which will be consistent with experimental data. And this will be the basis for optimizing the kinetic properties of the thermoelectric material by choosing alloying conditions [2].

III. Modeling of the properties of $TiCo_{1-x}Cr_xSb$ for an ordered version of the structure

To predict the behavior of the Fermi level ε_F, the band gap ε_g, and the kinetic properties of $TiCo_{1-x}Cr_xSb$, the DOS (density of electronic states) was calculated for the ordered version of the crystal structure of the semiconductor (Fig. 2). This involves only substitution of Co atoms with Ti atoms in the 4*c* position.

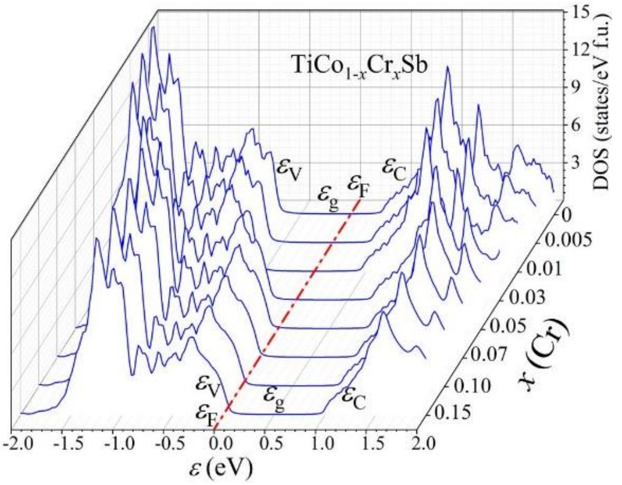


Fig. 2. DOS calculation for the ordered version of the $TiCo_{1-x}Cr_xSb$ structure.

Fig. 2 shows that in TiCoSb the Fermi level ε_F (dashed line) is located in the band gap ε_g near the edge of the conduction band ε_C, and electrons are the main current carriers. As mentioned above, the substitution of Co atoms for Cr atoms generates structural defects of an acceptor nature, then at the impurity concentration $x = 0.01$ in the $TiCo_{0,99}Cr_{0,01}Sb$ semiconductor, the Fermi level ε_F will move away from the conduction band ε_C and will be located near the middle of the band gap ε_g. An increase in the concentration of impurity Cr atoms will be accompanied by an increase in the concentration of acceptors. At the same time, the Fermi level ε_F will approach, and later enter the valence band ε_V $TiCo_{1-x}Cr_xSb$: a dielectric-metal conduction transition will occur, which is the Anderson transition [11]. In the experiment, such a movement of the Fermi level ε_F will lead to a change in the sign of the thermopower coefficient $\alpha(T,x)$, and the holes will become the main current carriers. At the same time, the type of conductivity of the $TiCo_{1-x}Cr_xSb$ semiconductor will also change from activation to metallic [2, 4], and the temperature dependences of the specific electrical resistivity will not contain activation areas. The electrical resistivity of $TiCo_{1-x}Cr_xSb$ will increase with increasing temperature. It is important that the band gap ε_g is preserved between the conduction band ε_C and the valence band ε_V of $TiCo_{1-x}Cr_xSb$.

DOS calculation for the ordered version of the $TiCo_{1-x}Cr_xSb$ structure allows modeling the behavior of the kinetic properties of the semiconductor, in particular, $\rho(x,T)$ and $\alpha(x,T)$ (Fig. 3). Modeling the behavior of the thermopower coefficient $\alpha(x,T)$, as expected, shows positive values at all temperatures for concentrations of

$TiCo_{1-x}Cr_xSb$, $x > 0.01$, and the maximum values of $\alpha(x,T)$ are reached at $x \approx 0.08$. Since the value of the specific electrical resistivity is inversely proportional to the density of states at the Fermi level, the 1/DOS(ε_F) dependence allows us to predict the behavior of the electrical resistivity of the $TiCo_{1-x}Cr_xSb$ semiconductor (Fig. 3*b*).

We can see that the dependence 1/DOS(ε_F) passes through a maximum at the concentration of Cr atoms, $x \approx 0.01$, and then rapidly decreases and reaches quasi-saturation at $x > 0.07$. This behavior of 1/DOS(ε_F) is understandable, because the growth of the dependence in the section $x = 0$–0.01 is associated with the crossing of the Fermi level ε_F of the middle of the band gap ε_g, which will cause the smallest values of DOS(ε_F) and the maximum values of $\rho(x,T)$ $TiCo_{1-x}Cr_xSb$. When the concentration of the Cr impurity increases, $x > 0.01$, the Fermi level ε_F will move in the direction of the valence band ε_V. This will lead to an increase in both the concentration of holes and the density of states at the Fermi level of $TiCo_{1-x}Cr_xSb$. Experimental studies of the properties of $TiCo_{1-x}Cr_xSb$ will show the degree of correctness of the modeling results.

IV. Study of kinetic and energetic properties of $TiCo_{1-x}Cr_xSb$

The change in values with temperature of the specific electrical resistivity ρ and the the thermopower coefficient α of $TiCo_{1-x}Cr_xSb$, $x = 0$–0.10, is shown in Fig. 4. For $TiCo_{1-x}Cr_xSb$ samples at compositions $x = 0$ and $x = 0.01$, we can see activation parts at high temperatures on the dependences ln($\rho(1/T,x)$) and $\alpha(1/T,x)$. This is evidence of the location of the Fermi level ε_F in the band gap ε_g. Since at all temperatures the sign of the thermopower coefficient of $TiCo_{1-x}Cr_xSb$ samples at $x = 0$ and $x = 0.01$ is negative, the main carriers of electric current are electrons. At the same time, the Fermi level ε_F is close to the conduction band ε_C. Therefore, $TiCo_{1-x}Cr_xSb$ samples with compositions $x = 0$ and $x = 0.01$ are doped and compensated semiconductors of the electronic conductivity type [4]. Their temperature dependence of the resistivity ln($\rho(1/T,x)$) (Fig. 4) can be described by the well-known expression (1) [4]:

$$\rho^{-1}(T) = \rho_1^{-1} exp\left(-\frac{\varepsilon_1^{\rho}}{k_B T}\right) + \rho_3^{-1} exp\left(-\frac{\varepsilon_3^{\rho}}{k_B T}\right), \qquad (1)$$

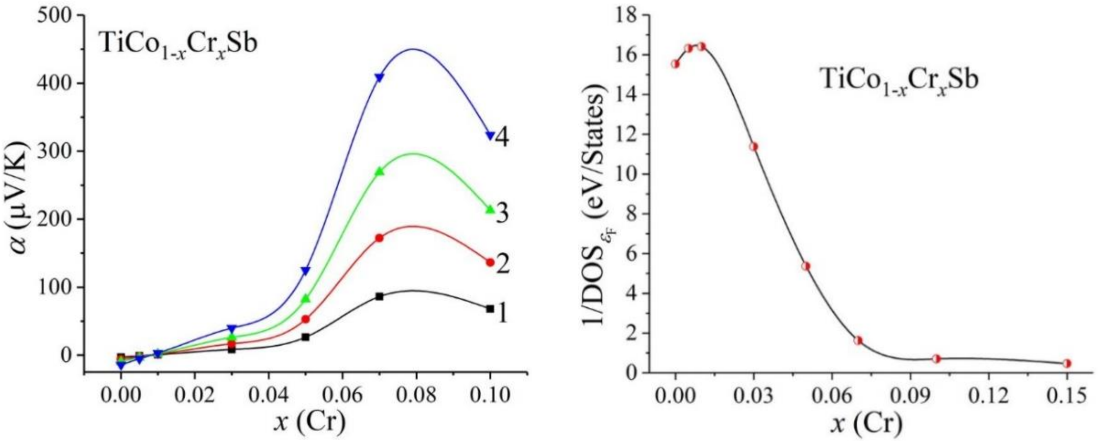
where the first term describes the activation of current carriers $\varepsilon_1^{\rho}(x)$ from the Fermi level ε_F into the conduction band ε_C, and the second term describes the jump conduction $\varepsilon_3^{\rho}(x)$ with energies close to the Fermi level ε_F. For semiconductors $TiCo_{1-x}Cr_xSb$ with compositions $x = 0$ and $x = 0.01$, the thermopower coefficient $\alpha(1/T,x)$ (Fig. 4) changes with temperature according to expression (2) [11]:

$$\alpha = \frac{k_B}{e}\left(\frac{\varepsilon_i^{\alpha}}{k_B T} - \gamma + 1\right), \qquad (2)$$

where γ depends on the scattering mechanisms. Based on formula (2), the values of the activation energies $\varepsilon_1^{\alpha}(x)$ and $\varepsilon_3^{\alpha}(x)$ were calculated. The authors of [2] showed that in heavily doped and compensated semiconductors, the values of the activation energies $\varepsilon_1^{\alpha}(x)$ are proportional to the amplitude of the large-scale fluctuation of the continuous energy bands. The amplitude of the band modulation is proportional to the compensation degree of the semiconductor [4].

Based on formulas (1) and (2), the depth of the Fermi level ε_F was calculated and the change in the degree of compensation of the semiconductor $TiCo_{1-x}Cr_xSb$ was estimated by calculating the values of $\varepsilon_1^{\alpha}(x)$. In the semiconductor TiCoSb, the depth of the Fermi level ε_F relative to the conduction band ε_C (negative values of the thermopower coefficient) is ε_1^{ρ}=100.6 meV, and the amplitude of the bands reaches ε_1^{α}=214.1 meV. The obtained results of activation energy values for TiCoSb coincide with literature data [2, 5].

Doping TiCoSb with the smallest concentration of Cr atoms in the experiment, $x = 0.01$, rapidly brought the Fermi level ε_F closer to the conduction band ε_C by a distance of ε_1^{ρ}= 7.3 meV. This behavior of the Fermi level in $TiCo_{0,99}Cr_{0,01}Sb$ is possible either under the condition of a rapid increase in the concentration of donor states or a rapid decrease in the band gap ε_g due to the redistribution of electronic states. We can assume that in $TiCo_{0,99}Cr_{0,01}Sb$ these phenomena occur simultaneously.



a *b*

Fig. 3. Calculation of the behavior of the thermopower coefficient $\alpha(x,T)$ (*a*) and 1/DOS(ε_F) (*b*) for the ordered variant of the $TiCo_{1-x}Cr_xSb$ structure: 1 – T=80 K; 2 – T=160; 3 – T=250 K; 4 – T=380 K.

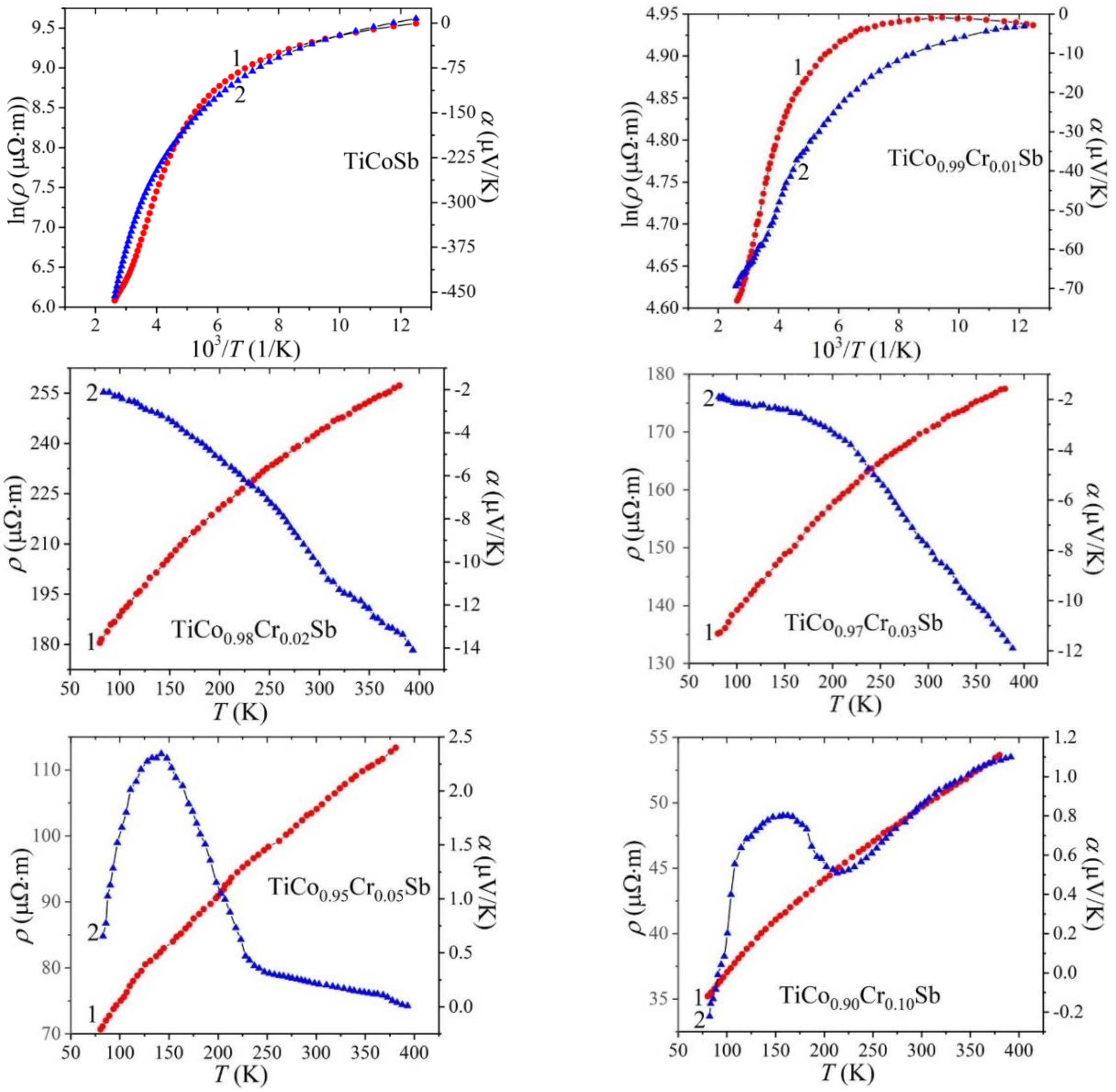


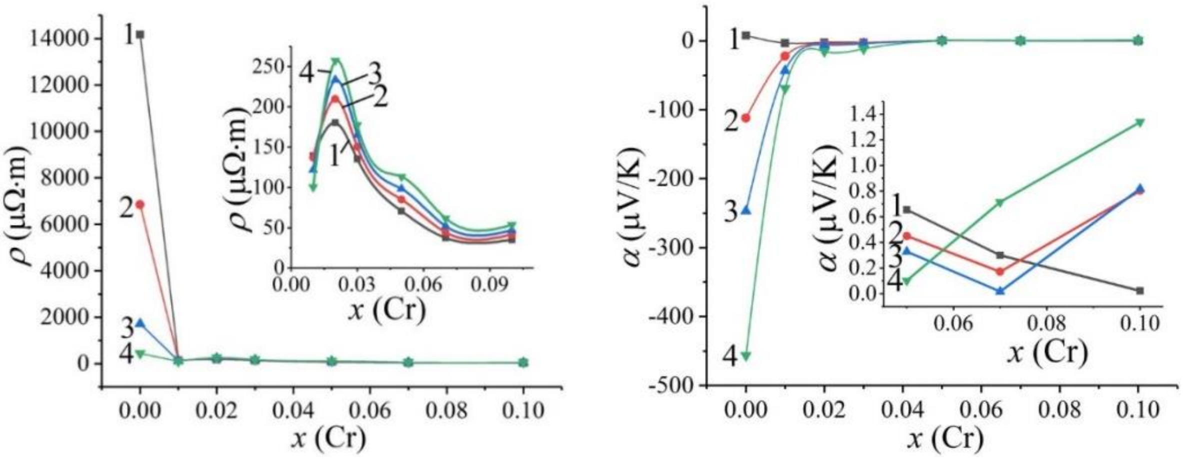
Fig. 4. Temperature dependences of the electrical resistivity ρ (1) and the thermopower coefficient α (2) of $TiCo_{1-x}Cr_xSb$.

Likewise, the amplitude of the fluctuation of the continuous energy bands of $TiCo_{0,99}Cr_{0,01}Sb$ decreased rapidly to the value $\varepsilon_1^{\alpha} = 14.1$ meV, indicating a decrease in the compensation degree, and the semiconductor becomes weakly compensated when the concentration of donor states far exceeds that of acceptor states.

As mentioned above, in $TiCo_{1-x}Cr_xSb$ this is possible in cases of partial replacement of Ti atoms ($3d^24s^2$) by Cr atoms ($3d^54s^1$) in position 4*a* or occupation of vacancies (Va) by Cr atoms. Considering that at concentrations of $TiCo_{1-x}Cr_xSb$, $x = 0$–0.01, the lattice parameter $a(x)$ increases (Fig. 1), we can assume that vacancies (Va) in position 4*a* are occupied by Cr atoms, which simultaneously generates donor states and decreases by the same number of acceptor states ($\varepsilon_A{}^1$ band) that existed in TiCoSb [5]. Let us recall that in the case of substitution of Ti atoms with Cr atoms in position 4*a* in the semiconductor $TiCo_{1-x}Cr_xSb$, donor states will also be generated, but in this case, the lattice parameter $a(x)$ should decrease ($r_{Cr} = 0.128$ nm and $r_{Ti} = 0.146$ nm). Therefore, the option of Cr atoms occupying vacancies (Va) in position 4*a* at concentrations $x = 0$–0.01 looks more convincing.

At concentrations $x \geq 0.02$ at all investigated temperatures, the activation parts disappear on the dependences $\ln(\rho(1/T,x))$ of $TiCo_{1-x}Cr_xSb$, and the resistivity values $\rho(T,x)$ tend to increase, which is characteristic of the metallic type of conductivity (Fig. 4). This can happen either if the Fermi level ε_F leaves the band gap ε_g and is located in the continuous energy bands, or the band gap itself ε_g disappears when the continuous energy bands are overlapped due to the redistribution of electronic states. When TiCoSb is alloyed with Mn atoms by replacing Co atoms on the dependences $\ln(\rho(1/T,x))$ $TiCo_{1-x}Mn_xSb$, $x = 0$–0.10, activation areas occurred at high temperatures and all concentrations. This experimental result indicated the location of the Fermi level ε_F in the band gap ε_g of the semiconductor $TiCo_{1-x}Mn_xSb$ [7].

The answer to the question about the location of the Fermi level ε_F in $TiCo_{1-x}Cr_xSb$ for $x \geq 0.02$ is given by the analysis of the behavior of the thermopower coefficient $\alpha(T,x)$, which rapidly decreases, for example, at $T = 300$ K from $\alpha_{x=0.02} = -10$ μV/ K to $\alpha_{x=0.05} = 0.04$ μV/K and $\alpha_{x=0.1} = 1.1$ μV/K (Fig. 4). Thus, in the concentration range $0.02 \leq x < 0.05$, the values of the thermopower coefficient



a *b*

Fig. 5. Change in electrical resistivity $\rho(x,T)$ (*a*) and thermopower coefficient $\alpha(x,T)$ (*b*) of $TiCo_{1-x}Cr_xSb$: 1 – T=80 K; 2 – T=160 K; 3 – T=250 K; 4 – T=380 K.

$\alpha(T,x)$ of $TiCo_{1-x}Cr_xSb$ are negative, and at concentrations $0.05 \leq x$ – positive. This behavior $\alpha(T,x)$ is fundamentally consistent with the results of modeling the electronic structure for the ordered structure (Fig. 2). On the other hand, a slight increase in impurity concentration is sufficient for the transition of the Fermi level ε_F from the conduction band ε_C to the valence band ε_V. This could indicate a rapid decrease in the band gap ε_g of the $TiCo_{1-x}Cr_xSb$ semiconductor.

The behavior $\rho(x,T)$ and $\alpha(x,T)$ of $TiCo_{1-x}Cr_xSb$ at different temperatures is interesting (Fig. 5). The analysis of the concentration dependences $\rho(x,T)$ and $\alpha(x,T)$ of $TiCo_{1-x}Cr_xSb$ complements the obtained results and conclusions. Doping by the smallest concentration of the Cr impurity in the experiment leads to a rapid decrease in the electrical resistivity, for example, at T = 80 K from the value $\rho_{x=0}$= 14170 μΩ·m to $\rho_{x=0.01}$= 139.3 μΩ·m. A decrease in the electrical resistivity $\rho(x,T)$ at concentrations x = 0–0.01 indicates a rapid increase in the electron concentration. This result correlates with the nature of the change in the Fermi level ε_F position which in $TiCo_{0.99}Cr_{0.01}Sb$ approached the conduction band level ε_C. We can also assume a rapid decrease in the width of the band gap ε_g of the semiconductor. The obtained experimental results of the change in specific electrical resistance $\rho(x,T)$ correspond to the results of calculations for an ordered version of the crystal structure of the semiconductor (Fig. 2).

At concentrations $x > 0.01$, when the Fermi level ε_F is located in the continuous energy band and the conductivity has a metallic character, we do not, however, observe a monotonous change of the $\rho(x,T)$ and $\alpha(x,T)$ values. Thus, at concentrations $x = 0.01$–0.02, the electrical resistivity $\rho(x,T)$ increases. If the Fermi level ε_F is in the band gap ε_g of $TiCo_{0.98}Cr_{0.02}Sb$, then the change in the values of the resistivity would be associated exclusively with a decrease in the concentration of electrons (negative values of $\alpha(x,T)$). The reason for such a decrease would be the generation of acceptors that capture electrons. However, the insert in Fig. 5a shows that in the semiconductor $TiCo_{0.98}Cr_{0.02}Sb$, the values of resistivity $\rho(x,T)$ are higher, the higher the temperature. It is in this order that the dependences of electrical resistivity $\rho(x,T)$ are located for $x > 0.02$. This behavior of the electrical resistivity $\rho(x,T)$ is characteristic of metals when the increase in resistivity is caused by the action of current carrier scattering mechanisms. Therefore, we cannot attribute the growth of the electrical resistivity of $TiCo_{1-x}Cr_xSb$ at concentrations $x = 0.01$–0.02 only to a decrease in the concentration of electrons, and the changes due to the scattering of current carriers in $TiCo_{1-x}Cr_xSb$ are of the same order as the changes which are associated with a change in the concentration of current carriers.

At concentration $x = 0.02$ at all investigated temperatures, an extremum appears in the $\rho(x,T)$ dependence of $TiCo_{1-x}Cr_xSb$. The appearance of an extremum on the $\rho(x,T)$ dependence in a semiconductor of the electronic conductivity type is the result of a change in the ratio of ionized donor and acceptor states in favor of acceptors. Indeed, at concentrations of Cr impurity atoms, $x > 0.03$, the sign of $\alpha(x,T)$ for $TiCo_{1-x}Cr_xSb$ becomes positive (Fig. 5*b*, inset). This is possible, as mentioned above, only when Cr atoms occupy the 4*c* position of Co atoms. However, this should lead to an increase in the lattice parameter $a(x)$ of $TiCo_{1-x}Cr_xSb$. In the experiment, we observe a monotonous decrease.

We can assume that in the $TiCo_{1-x}Cr_xSb$ semiconductor, both the substitution of Co atoms for Cr atoms in position 4*c*, which generates acceptor states, and the occupation of crystallographic position 4*a* by Cr atoms, which generates donor states, occur simultaneously at different rates. The given experimental results do not allow us to obtain numerical values of the rate of generation of acceptor and donor states, which can be done only by comparing the results of experimental measurements of structural and kinetic properties with modeling of these properties for different cases of arrangement of atoms in the unit cell. However, these results are beyond the scope of this paper.

Conclusions

According to the performed study of the structural, electrokinetic, and energy properties of the $TiCo_{1-x}Cr_xSb$ semiconductor obtained by doping TiCoSb with Cr atoms introduced into the structure by replacing Co atoms in the 4c crystallographic position, it was shown that in

$TiCo_{1-x}Cr_xSb$ the structural defects of donor and acceptor nature are generated simultaneously. At concentrations $x \geq 0.02$, the conductivity of $TiCo_{1-x}Cr_xSb$ has a metallic character, and the contribution of current carrier scattering mechanisms to the value of electrical resistivity is of the same order as changes in the concentration of current carriers. It was established that at all temperatures in the concentration range $x = 0$–0.02, the rate of generation of donors exceeds the rate of generation of acceptors, and at concentrations $x > 0.02$, on the contrary, the rate of generation of acceptors is greater than that of donors. This is indicated by the positive values of thermopower coefficient $\alpha(x,T)$ of $TiCo_{1-x}Cr_xSb$ at $x > 0.03$. To understand the mechanism of structural and energy transformations in $TiCo_{1-x}Cr_xSb$, it is necessary to simulate these properties for different cases of atom arrangement in the unit cell.

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[1] R. Marazza, R. Ferro, G. Rambaldi, *Some phases in ternary alloys of titanium, zirconium, and hafnium, with a MgAgAs or $AlCu_2Mn$ type structure*, J. Less-Common Met. 39, 341 (1975); https://doi.org/10.1016/0022-5088(75)90207-6.

[2] V.A. Romaka, Yu.V. Stadnyk, V.Ya. Krayovskyy, L.P. Romaka, O.P. Guk, V.V. Romaka, M.M. Mykyychuk, A.M. Horyn, *The latest heat-sensitive materials and temperature transducers*, Lviv Polytechnic Publishing House, Lviv (2020); https://opac.lpnu.ua/bib/1131184. [in Ukrainian].

[3] L.I. Anatychuk, Thermoelements and thermoelectric devices. Reference book, Naukova dumka, Kyiv (1979). [in Russian].

[4] B.I. Shklovskii and A.L. Efros, *Electronic properties of doped semiconductors*, Springer-Verlag, Berlin, Heidelberg (1984); https://doi.org/10.1007/978-3-662-02403-4.

[5] V.A.Romaka, Yu.V. Stadnyk, L.G. Akselrud, V.V. Romaka, D. Frushart, P. Rogl, V.N. Davydov, Yu.K. Gorelenko, *Mechanism of local amorphization of a heavily doped $Ti_{1-x}V_xCoSb$ intermetallic semiconductor*, Semiconductors, 42(№7), 753 (2008); https://doi.org/10.1134/S1063782608070014.

[6] Yu Stadnyk, V.V. Romaka, L. Romaka, L. Orovchik, A. Horyn, *Synthesis, electrical transport, magnetic properties and electronic structure of $Ti_{1-x}Sc_xCoSb$ semiconducting solid solution*, J. Alloys Compd., 805, 840 (2019); https://doi.org/10.1016/j.jallcom.2019.07.088.

[7] V.A. Romaka, Yu.V. Stadnyk, L.P. Romaka, A.M. Horyn, I.M. Romaniv, V.Z. Pashkevych, A.Ya. Horpeniuk, *Features of structural, energetic, electrokinetic investigation of energy and electrokinetic characteristics of thermoelectric material $TiCo_{1-x}Mn_xSb$*, J. Thermoelectricity, 3, 5 (2020); http://jt.inst.cv.ua/jt/jt_2020_03_en.pdf.

[8] T. Roisnel, J. Rodriguez-Carvajal, *WinPLOTR: a windows tool for powder diffraction patterns analysis*, Mater. Sci. Forum, Proc. EPDIC7 378, 118 (2001); https://doi.org/10.4028/www.scientific.net/MSF.378-381.118.

[9] M. Schruter, H. Ebert, H. Akai, P. Entel, E. Hoffmann, G.G. Reddy, *First-principles investigations of atomic disorder effects on magnetic and structural instabilities in transition-metal alloys*, Phys. Rev. B, 52, 188 (1995); https://doi.org/10.1103/PhysRevB.52.188.

[10] V. Moruzzi, J. Janak, A. Williams, *Calculated Electronic Properties of Metals*, Pergamon Press, NY (1978); https://doi.org/10.1016/B978-0-08-022705-4.50002-8.

[11] *N.F. Mott and E.A. Davis*, Electronic processes in non-crystalline materials, Clarendon Press, Oxford (1979); https://doi.org/10.1002/crat.19720070420.

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Вплив сильного легування інтерметалічного напівпровідника TiCoSb атомами Cr на структурні, кінетичні та енергетичні властивості

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Досліджено структурні, електрокінетичні та енергетичні властивості напівпровідника $TiCo_{1-x}Cr_xSb$, отриманого легуванням TiCoSb атомами Cr, уведеними у структуру шляхом заміщення у кристалографічній позиції 4*c* атомів Co. Показано, що у $TiCo_{1-x}Cr_xSb$ одночасно у різних співвідношеннях залежно від концентрації домішки генеруються структурні дефекти донорної та акцепторної природи. За концентрацій $x \geq 0.02$ провідність $TiCo_{1-x}Cr_xSb$ носить металічний характер, а внесок від дії механізмів розсіювання носіїв струму у значення електроопору є одного порядку зі змінами концентрації носіїв струму. Встановлено, що за всіх температур на ділянці концентрацій $x = 0$–0.02 швидкість генерування донорів переважає швидкість генерування акцепторів, а за концентрацій $x > 0.02$ навпаки, швидкість генерування акцепторів є більшою, ніж донорів. На це вказують додатні значення термо-ерс $\alpha(x,T)$ $TiCo_{1-x}Cr_xSb$ за $x > 0.03$. Для розуміння механізму структурних та енергетичних перетворень у $TiCo_{1-x}Cr_xSb$ необхідно провести моделюванням цих властивостей за різних варіантів просторового розміщення атомів у вузлах комірки.

Ключові слова: напівпровідник, електропровідність, коефіцієнт термо-ерс, рівень Фермі.