

# MECHANISM OF ACCEPTOR IMPURITY INITIATION IN THE TiCoSb INTERMETALLIC SEMICONDUCTOR HEAVILY DOPED WITH A V DONOR IMPURITY.

## 1. STUDIES OF THE CRYSTAL STRUCTURE AND THE DISTRIBUTION OF THE ELECTRON DENSITY OF STATES

V.A. ROMAKA<sup>1,2</sup>, YU.V. STADNYK<sup>3</sup>, P. ROGL<sup>4</sup>, L.G. AKSELRUD<sup>3</sup>,  
V.N. DAVYDOV<sup>3</sup>, V.V. ROMAKA<sup>3</sup>, YU.K. GORELENKO<sup>3</sup>, A.M. HORYN<sup>3</sup>

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<sup>1</sup>Ya. Pidstryhach Institute of Applied Problems of Mechanics and Mathematics,  
Nat. Acad. Sci. of Ukraine  
(3b, Naukova Str., Lviv 79060, Ukraine),

<sup>2</sup>National University "Lvivs'ka Politehnika"  
(12, S. Bandera Str., Lviv 79013, Ukraine; e-mail: vromaka@polynet.lviv.ua),

<sup>3</sup>Ivan Franko Lviv National University  
(6, Kyryl and Mefodii Str., Lviv 79005, Ukraine; e-mail: gorelenko\_yuriy@franko.lviv.ua),

<sup>4</sup>Institut für Physikalische Chemie, Universität Wien  
(Wien A-1090, Austria; e-mail: peter.franz.rogl@univie.ac.at)

Structural characteristics of the TiCoSb intermetallic semiconductor heavily doped with a donor V impurity (so that the electron concentration  $N_D^V$  varied from  $9.5 \times 10^{19}$  to  $1.9 \times 10^{21} \text{ cm}^{-3}$ ) have been studied, and the corresponding electron density of states (DOS) has been calculated. Different occupation numbers for the Co and (Ti,V) atomic positions in the  $\text{Ti}_{1-x}\text{V}_x\text{CoSb}$  crystal lattices have been revealed, which is equivalent to the introduction of acceptor impurities of two sorts into the semiconductor. The numerical simulation of the investigated physical phenomena has been demonstrated to describe them adequately, if the variable occupation numbers of the atomic lattice sites in the elementary cell of the compound are taken into account while constructing a Wigner-Seitz cell.

### 1. Introduction

In this work, we report the results of the first stage of our researches concerning the influence of significant concentrations of a donor V impurity on the modification of the crystalline and band structures, as well as on the distribution of the electron density of states (DOS), in the intermetallic TiCoSb semiconductor.

Studies of the influence of a heavy doping of the intermetallic TiCoSb semiconductor with donor Ni [1,2] and Cu [3] impurities allowed the dominant mechanisms of conductivity in wide temperature and concentration ranges to be determined and the conditions for reaching the maximal values of the thermoelectric power coefficient  $Z^* = \alpha^2 \sigma$ , where  $\alpha$  is the thermoelectric coefficient and  $\sigma$  is the electroconductivity of the

semiconductor, to be established [4]. The importance of the result obtained is emphasized by the fact that intermetallic semiconductors with a structure of the MgAgAs type are most studied now, being promising materials with respect to their use as working elements in thermoelectric current generators [5–9].

In work [10], it was pointed out that the intermetallic semiconductors TiNiSn, ZrNiSn, and HfNiSn, owing to reasons that were unknown at that time, are heavily doped and compensated semiconductors with the conductivity of the  $n$ -type at  $T \geq 1.7 \text{ K}$ , whereas TiCoSb is a semiconductor of the  $p$ -type at  $T \leq 95 \text{ K}$ . In other words, the authors of work [10] supposed that the electron type of conductivity, e.g., in ZrNiSn or the hole one in TiCoSb was connected with defects of the donor or acceptor nature, respectively. In this work, the origin of such defects in TiCoSb has been found.

While calculating the electron DOS distribution, the band spectrum, and the partial contribution of every component to the formation of continuous energy bands in intermetallic semiconductors, the KKR–CPA–LDA [11] and pseudo-potential [12] methods were used. In all relevant works, which we know of, the DOS calculations were carried out on the supposition that the occupation of atomic positions in an elementary cell of the compound was equal to unity, i.e. all atoms occupy positions in accordance with the MgAgAs structural type (see Fig. 1): 4 Co atoms in 4( $c$ )  $1/4 \ 1/4 \ 1/4$ , 4 Sb atoms in 4( $a$ )  $0 \ 0 \ 0$ , and 4 Ti atoms in 4( $b$ )  $1/2 \ 1/2 \ 1/2$ .

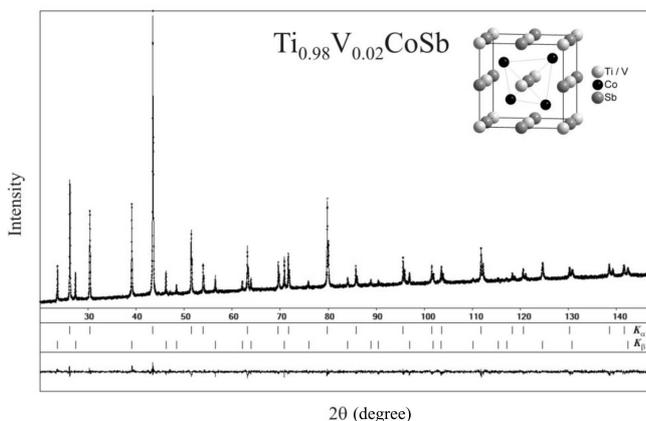


Fig. 1. Model of the crystalline structure of the TiCoSb compound and the experimental, calculated, and differential x-ray diffraction patterns of  $Ti_{1-x}V_xCoSb$  at  $x = 0.02$

As a result, the conclusions drawn on the basis of such calculations often contradicted the experimental results. We will demonstrate that numerical methods would adequately describe physical processes in semiconductors concerned, if – while constructing the corresponding Wigner–Seitz cell – one should take into account the actual occupation numbers of atomic positions in a unit cell of the crystalline compound.

An approach that was proposed in works [13, 14] for the description of heavily doped and strongly compensated semiconductors supposes the availability of large potential fluctuations in the crystal bulk. The origin of such fluctuations consists in randomly distributed positively and negatively charged centers. A question concerning the reasons and the mechanisms of emergence of such centers arises, especially if the latter appear, for instance, in the course of technological processes of fabrication of a semiconducting material, under thermal annealing conditions, and so on, rather than they are formed by the controllable introduction of an impurity. Such issues are urgent for the fabrication of intermetallic semiconductors, when they are synthesized by fusing the blend of initial components, and this process is followed by uncontrollable cooling. In this work, we will demonstrate one of the mechanisms giving rise to the emergence of charged centers, which is valid both for the undoped TiCoSb semiconductor and for the case of its heavy doping with a donor impurity, in particular, by substituting V ( $3d^34s^2$ ) atoms for Ti ( $3d^24s^2$ ) ones.

The structural characteristics in TiCoSb at doping the latter with a donor V impurity and the formation of a solid  $Ti_{1-x}V_xCoSb$  solution (with  $N_D^V$  varying from

about  $9.5 \times 10^{19} \text{ cm}^{-3}$  at  $x = 0.005$  to  $1.9 \times 10^{21} \text{ cm}^{-3}$  at  $x = 0.01$ ) have been studied, and the corresponding distributions of the electron DOS have been calculated.

The techniques used for the fabrication of specimens, the regimes of homogenizing annealing and X-ray diffraction researches, and the procedure of DOS calculations in the framework of the self-consistent Korringa–Kohn–Rostoker method, using the coherent potential approximation (KKR–CPA–LDA), were described in work [1].

## 2. Structural Researches of $Ti_{1-x}V_xCoSb$

The x-ray phase, structural, and microprobe analyses confirmed that the  $Ti_{1-x}V_xCoSb$  specimens under investigation were single-phase (Fig. 1). Making use of an HZG-4a automatic X-ray diffractometer and the WinCSD software [15], the method of combined X-ray diffraction [16] was applied to every specimen in order to measure the corresponding period of an elementary cell  $a$ , to specify its crystalline structure, and to calculate the Bragg factor  $R_{Br}$  of correspondence between the model representation of the  $Ti_{1-x}V_xCoSb$  crystalline structure and the X-ray diffraction experimental results. The results of structural researches of  $Ti_{1-x}V_xCoSb$  are listed in the Table. Using the method of combined x-ray diffraction allowed us to obtain the value for the period of an elementary cell  $a$  which is comparable with that obtained from neutron diffraction measurements (see the Table). The essence of structural researches consisted in finding such a variant of the arrangement of atoms (or their absence) in the  $Ti_{1-x}V_xCoSb$  elementary cell, at which the Bragg factor is minimal.

The main result of structural researches is the establishment of the fact that the atomic positions are characterized by different occupation numbers (in essence, it is the imperfection of the crystalline structure) which depend on the  $Ti_{1-x}V_xCoSb$  composition (Fig. 2). It is worth noting that the method of researches used by us does not allow a distinction to be made between Ti

**Concentration and structural characteristics of  $Ti_{1-x}V_xCoSb$**

$x$	$a$ , Å	$R_{Br}$ , %	$N_D^V$ , $\text{cm}^{-3}$
0	5.88233(6)	4.16	0
0.005	5.88190(6)	5.77	$9.5 \times 10^{19}$
0.01	5.88190(6)	5.98	$1.9 \times 10^{20}$
0.02	5.88170(6)	8.24	$3.8 \times 10^{20}$
0.03	5.88129(7)	7.80	$5.7 \times 10^{20}$
0.04	5.88123(7)	6.79	$7.6 \times 10^{20}$
0.06	5.88113(6)	6.86	$1.1 \times 10^{21}$
0.08	5.88072(7)	5.81	$1.5 \times 10^{21}$
0.1	5.88042(7)	5.91	$1.9 \times 10^{21}$

and V atoms, and that is why we quote the occupation number for the (Ti,V) position. From Fig. 2, it follows that even the crystalline structure of the initial TiCoSb compound is imperfect; in particular, only 95.8% of Co and 93.3% of Ti atomic positions are occupied. Unoccupied positions of Co and Ti atoms are vacancies, which is equivalent to the introduction of acceptor impurities of two sorts into the semiconductor, with the impurity concentration being comparable with that of vacancies. The experimental result obtained gives an answer to the question put in work [10] and concerning the mechanism of an “a priori doping” of TiCoSb with an acceptor impurity.

Doping TiCoSb with a donor V impurity substantially influences the occupation degree of Co and (Ti,V) atomic positions in the semiconductor’s elementary cell. The results exposed in Fig. 2 allow us to draw a conclusion concerning the variation dynamics of acceptor and donor impurity concentrations. A reduction of the atomic position occupation number at growing  $x$  means that the rate of acceptor impurity generation is higher than the rate of donor impurity introduction. In its turn, minor changes of the atomic position occupation numbers – in the content ranges  $x \approx 0.04 \div 0.06$  for Co atoms and  $x \approx 0.03 \div 0.06$  for (Ti,V) ones – evidence for the approximately identical rates of acceptor and donor impurity emergence. At last, the increase of the atomic position occupancy (at  $x > 0.06$ ) testifies that the rate of donor impurity generation exceeds the acceptor one.

Hence, a controllable introduction of a donor V impurity into TiCoSb is accompanied by a simultaneous generation of acceptor impurities of several kinds. In so doing, the acceptor impurity concentration changes following another law, which is different from that for a donor impurity and is close to dependences 1 and 2 in Fig. 2. As a result, we obtain a heavily doped and strongly compensated crystalline semiconductor with partial structural disordering – local amorphization. The relationship between the acceptor and donor impurity concentrations (the compensation degree) will govern the electrokinetic and magnetic properties of the semiconductor under investigation.

### 3. Calculations of $\text{Ti}_{1-x}\text{V}_x\text{CoSb}$ Electronic Structure

The calculations of the electron DOS distribution in  $\text{Ti}_{1-x}\text{V}_x\text{CoSb}$  were carried out for the case of an ordered crystalline structure, i.e. all atoms occupy their positions in accordance with the MgAgAs structural type (Fig. 1),

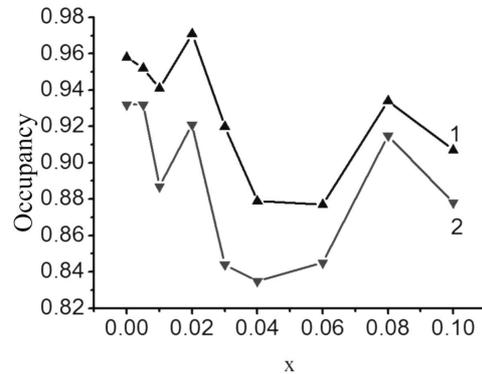


Fig. 2. Dependences of the occupation numbers of Co (1) and (Ti,V) (2) atomic positions on the  $\text{Ti}_{1-x}\text{V}_x\text{CoSb}$  composition

as well as if local amorphization – a disordered structure – was taken into account. In the latter case, the Wigner–Seitz cell was constructed making allowance for varying the occupation numbers of the Co and (Ti,V) atomic positions. The crystal potential and the electron charge density were selected spherically symmetric inside the sphere and constant in the intermediate region (the “muffin-tin” method). The radii of nonoverlapping spheres were chosen following the criterion of maximal cell filling. The total density of states and partial contributions from different sorts of atoms and electron shells with  $l_{\max} = 2$  for all types of atoms were calculated. The procedure of finding the self-consistent solution was continued until the difference between the consequent values of potential reached  $10^{-4}$  Ry.

The results of DOS calculations (Fig. 3) obtained in both cases showed that the undoped TiCoSb specimen is a semiconductor, in which the energy gap between the conduction and valence bands is formed as a result of the strong hybridization of  $d$ -states of Ti and Co transition metals. The electron DOS in the conduction band is mainly determined by the  $d$ -states of Ti, and that in the valence one by the  $d$ -states of Co which overlap the  $d$ -states of Ti and  $p$ -states of Sb. The Fermi level  $\varepsilon_F$  is located near the top of the valence band, which has to provide the positive sign of the thermoelectric coefficient in experiment.

The calculations of DOS in  $\text{Ti}_{1-x}\text{V}_x\text{CoSb}$  in the case of an ordered structure revealed a drift of  $\varepsilon_F$  toward the conduction band even at minimal concentrations of the donor impurity; at  $x \approx 0.02$ , the Fermi level becomes fixed by the mobility edge of the conduction band. A further increase of the donor impurity concentration is accompanied by entering the Fermi level into the conduction band and its drift over the latter.

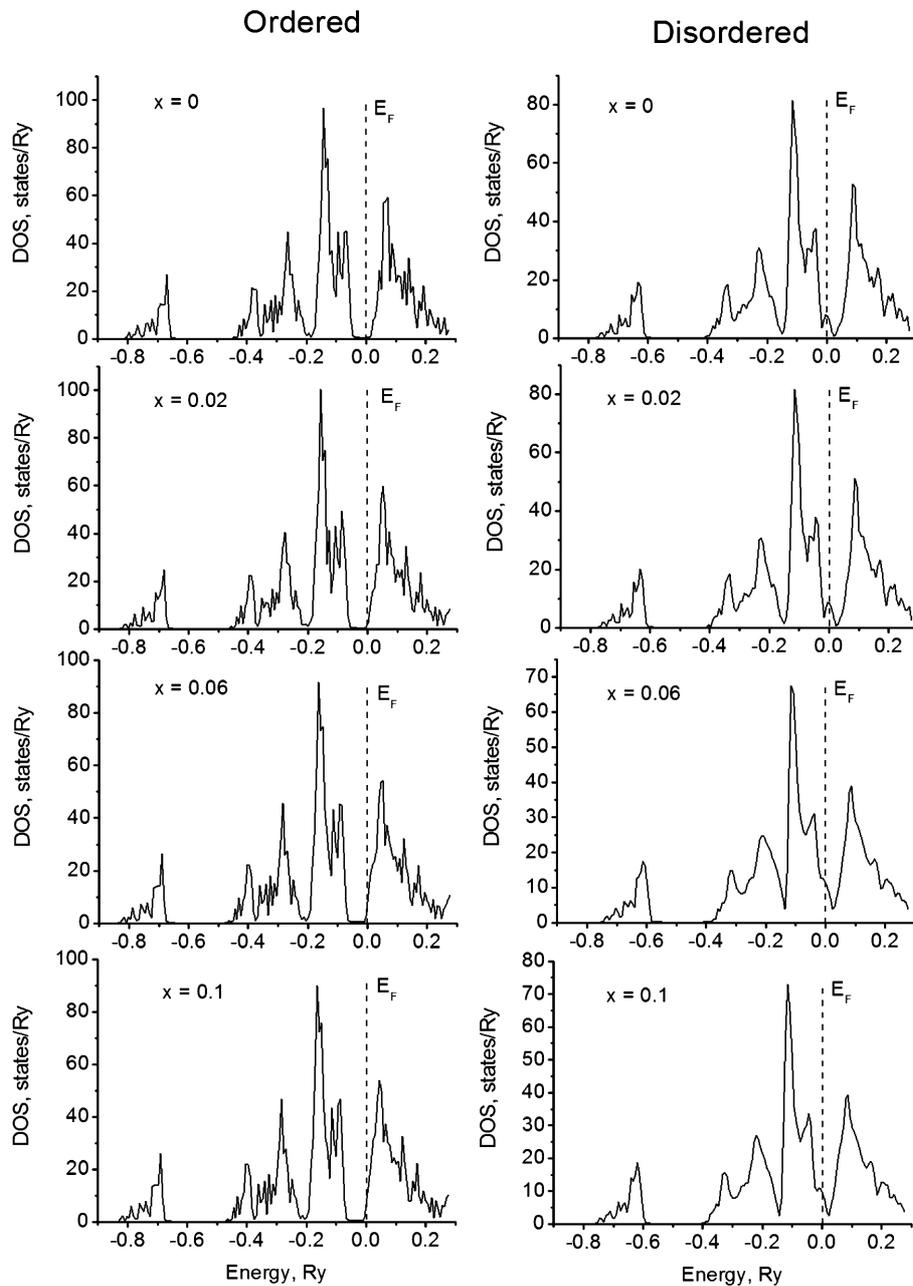


Fig. 3. Distributions of the total electron DOS for the ordered and partially disordered arrangements of atoms in the  $\text{Ti}_{1-x}\text{V}_x\text{CoSb}$  elementary cell

Proceeding from the fact that, in  $\text{Ti}_{1-x}\text{V}_x\text{CoSb}$  with  $x < 0.02$ , the Fermi level is located beyond the continuous energy bands, the conductivity of this semiconductor may possess an activation character, i.e. actual may be the hopping mechanism of charge transfer [17] and the activation of current carriers from the Fermi level onto the percolation one [13, 14]. At  $x \geq 0.02$ ,

when those two levels intersect, no activation sections were observed in the temperature dependences of the  $\text{Ti}_{1-x}\text{V}_x\text{CoSb}$  conductivity.

Making allowance for the local amorphization in the  $\text{Ti}_{1-x}\text{V}_x\text{CoSb}$  crystal structure gives rise to the essentially different results of calculations of the electron DOS distribution. It follows from Fig. 3 that a new

DOS maximum appears near the valence band. This maximum is associated with the generation of vacancies at Co and (Ti,V) atomic positions, and it fixes the location of  $\varepsilon_F$ . Doping TiCoSb with a donor V impurity and a simultaneous generation of the compensating acceptor impurity do not result in a monotonous drift of the Fermi level toward the conduction band, as it took place in the case of the ordered structure. Since the concentrations of both the donor and acceptor impurities increase simultaneously up to  $x \approx 0.06$ , the conductivity of the heavily doped  $\text{Ti}_{1-x}\text{V}_x\text{CoSb}$  semiconductor and the current carrier type in it are determined by the compensation degree.

Our calculations also testify that a drastic change of the DOS at the Fermi level  $n(\varepsilon_F)$  is to be observed at  $x \geq 0.01$ . For lower  $x$ -values (lower impurity concentrations),  $n(\varepsilon_F)$  is determined by  $d$ -electrons of Ti with a substantial contribution of  $d$ -states of V. For  $x > 0.01$ , the contribution made by V's  $d$ -electrons dominates.

Thus, doping of the intermetallic TiCoSb semiconductor with a donor V impurity is accompanied by the generation of defects possessing an acceptor origin, as well as by the simultaneous variation of the semiconductor compensation degree, which modifies, in its turn, the relative position of the Fermi level with respect to the percolation level in the conduction band and changes the mechanisms of conductivity.

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МЕХАНІЗМ ГЕНЕРАЦІЇ АКЦЕПТОРНОЇ ДОМІШКИ  
В ІНТЕРМЕТАЛІЧНОМУ НАПІВПРОВІДНИКУ  
TiCoSb ПРИ СИЛЬНОМУ ЛЕГУВАННІ  
ДОНОРНОЮ ДОМІШКОЮ V.  
1. ДОСЛІДЖЕННЯ СТРУКТУРИ  
ТА РОЗПОДІЛУ ЩІЛЬНОСТІ  
ЕЛЕКТРОННИХ СТАНІВ

В.А. Ромака, Ю.В. Стадник, П. Рогл, Л.Г. Аксельруд,  
В.М. Давидов, В.В. Ромака, Ю. К. Гореленко, А.М. Горинь

Резюме

Досліджено структурні характеристики та виконано розрахунок розподілу щільності електронних станів інтерметалічного напівпровідника TiCoSb, сильнолегованого донорною домішкою V ( $N_D^V \approx 9,5 \cdot 10^{19} \div 1,9 \cdot 10^{21} \text{ см}^{-3}$ ). Виявлено різний ступінь зайнятості позицій атомів Co та (Ti, V) в елементарній комірці  $\text{Ti}_{1-x}\text{V}_x\text{CoSb}$ , що еквівалентно введенню у напівпровідник двох сортів акцепторної домішки. Показано, що чисельні методи розрахунку адекватно описують фізичні процеси у напівпровіднику, якщо при побудові комірки Вігнера–Зейтца враховувати ступінь зайнятості позицій атомів в елементарній комірці кристалічної сполуки.