

The band structure and the density of states (DOS) in an intermetallic semiconductor TiCoSb doped with a donor impurity by substituting Co atoms by Cu ones have been calculated. The dependence of the Fermi level position on the donor impurity concentration has been found. Possible mechanisms of conductivity at various concentrations of the donor impurity have been analyzed.

1. Introduction

Work [1] has started the cycle of researches concerning the electron structure and the structural, kinetic, and magnetic characteristics of intermetallic semiconductors of the MgAgAs structure type doped with a donor Cu impurity up to significant concentrations ($N_D \approx 10^{18} \div 10^{19} \text{ cm}^{-3}$). In this work, we study the influence of the donor impurity on the variation of the electronic structure in TiCoSb intermetallic semiconductor. The latter was doped by substituting Co atoms by Cu ones; the impurity concentration is changed from $N_D = 1.9 \times 10^{19} \text{ cm}^{-3}$ (at x = 0.001) to $N_D = 7.6 \times 10^{21} \text{ cm}^{-3}$ (at x = 0.4).

In works [2, 4–7], we studied how the heavy doping of intermetallic semiconductors with acceptor and/or donor impurities $(N_A, N_D \approx 10^{19} \div 10^{21} \text{ cm}^{-3})$ affects their electronic and crystalline structures, as well as the magnetic, electrokinetic, resonant, and optical characteristics. In the cited works, the acceptor impurity was introduced into *n*-ZrNiSn by substituting $Zr(4d^25s^2)$ atoms in the crystal structure by $Sc(3d^14s^2)$ ones [2,3], and Ni $(3d^84s^2)$ by Co $(3d^74s^2)$ [4]; the donor impurity was introduced into p-TiCoSb and n-ZrNiSn by substituting Co or Ni atoms by Ni and $Cu(3d^{10}4s^1)$ ones, respectively [1,6,7]. Those researches allowed us to elucidate the role of impurity bands in the mechanism of intermetallic semiconductor conductivity, to propose the models of band reorganization at varying the impurity concentration, and to formulate the conditions for the thermopower factor Z^* to achieve its maximal values [8]. The last result is also important from the practical point of view, because intermetallic semiconductors with a structure of the MgAgAs type belong to the most promising compounds with respect to their application as active elements in thermoelectric current generators [9]. In such a context, our researches seem logic and actual, especially if one takes into account possible practical implications of the results obtained.

The method of calculation of the electronic structure of $\text{TiCo}_{1-x}\text{Cu}_x\text{Sb}$, which was carried out in the framework of the coherent-potential approximation of the Korringa–Kohn–Rostoker self-consistent method (KKR-CPA-LDA), was described in works [2,4–7,10,11].

2. Calculation Results and their Discussion

The crystalline potential and the electron charge density were selected spherically symmetric inside the sphere and constant in the intermediate region (the "muffin-



Fig. 1. Density of states (DOS) in a $TiCo_{1-x}Cu_xSb$ compound with various contents x. Solid curves correspond to the total DOS; contributions from Ti, Co, and Sb atoms are marked by dashed, dotted, and dot-dashed curves, respectively

tin" method). In semiconductors of the MgAgAs structure type, only three of four possible atomic positions with $F\bar{4}3m$ symmetry are occupied. To raise the density of packing in a Wigner–Seitz cell, we introduced an extra empty sphere around the fourth, unoccupied position. The radii of non-overlapping spheres were chosen to achieve the maximal filling of the Wigner–Seitz cell. The calculations of the total density of states and the partial contributions from different atoms and electron shells with $l_{\rm max} = 2$ were fulfilled for all types of atoms. The iteration procedure for determining the self-consistent solution was continued until the difference between the following potential values had reached 10^{-4} Ry.

In Fig. 1, the result of calculations of the electron DOS for each component and the total DOS distribution for a solid solution $\text{TiCo}_{1-x}\text{Cu}_x\text{Sb}$ with various x values are depicted. From our calculations, it follows that undoped TiCoSb compound is semiconductor, where the energy gap E_g between the conduction and valence bands is formed owing to the strong hybridization between the *d*-states of transition elements (Ti and Co): the electron density in the conduction band is mainly determined by the *d*-states of Ti, while the valence band by the *d*-states of Co which overlap with *d*-states of Ti and *p*-states of Sb.

As follows from the analysis of dispersion dependences $E(\mathbf{k})$ (Fig. 2), the energy gap in the



Fig. 2. Position of the Fermi level in the band structure of $TiCo_{1-x}Cu_xSb$ for two contents

intermetallic semiconductor TiCoSb appears between points Γ and X of the Brillouin zone, and the amplitude of E_g is about 1 eV. The Fermi level E_F in TiCoSb semiconductor is located in the energy gap near the top of the valence band. The result obtained for TiCoSb coincides with those obtained earlier in the framework of calculations following the pseudo-potential [12] and CPA–LDA [6, 11] methods.

Doping the intermetallic semiconductor TiCoSb with a donor Cu impurity causes $E_{\rm F}$ to drift toward the conduction band (Figs. 1 and 2). The calculations testify that the Fermi level becomes located at the mobility edge of the conduction band already at $x \approx 0.01$. The further increase of the donor impurity concentration is accompanied by the entry of $E_{\rm F}$ into the conduction band and its drift in the continuous energy band. For the impurity concentration that corresponds to the content $TiCo_{0.7}Cu_{0.3}Sb$, the Fermi level is located (see Figs. 1 and 2) deeply in the conduction band. The calculation of the $E_{\rm F}$ position and the electron density distribution in a hypothetical compound TiCuSb obtained by substituting all Co atoms in the TiCoSb compound by Cu ones demonstrates that, owing to the overlapping of the conduction and valence bands, the energy gap disappears, and there emerges a metal with a characteristic location of the Fermi level (Fig. 1).

As is evident from Fig. 3, the contributions of different components of $\text{TiCo}_{1-x}\text{Cu}_x\text{Sb}$ to the total electron density at the Fermi level $n(E_{\rm F})$ are different. Inserting the donor Cu impurity even in insignificant



Fig. 3. Contributions of different components of semiconductor solid solution $\text{TiCo}_{1-x}\text{Cu}_x\text{Sb}$ to the total value of electron DOS at the Fermi level

concentrations into TiCoSb gives rise to a drastic increase of $n(E_{\rm F})$, mainly owing to the contribution of *d*-states of Cu. At the Cu impurity concentrations corresponding to the contents x > 0.1 of TiCo_{1-x}Cu_xSb, the contributions of the *d*-states of Ti and Co atoms into $n(E_{\rm F})$ increase, while the contribution of the *d*-states of Cu atoms does not change. The calculations testify that if intermetallic semiconductor TiCoSb is doped with a Cu impurity, the maximal variation of the DOS at the Fermi level occurs at the impurity concentrations which correspond to the contents x < 0.1 of TiCo_{1-x}Cu_xSb (Fig. 4). This result agrees with those presented in Fig. 3.

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Fig. 4. Dependence of the quantity $1/n(E_{\rm F})$ on the donor Cu impurity concentration in TiCoSb

We also calculated the dependence of the thermopower for a semiconductor solid solution $\text{TiCo}_{1-x}\text{Cu}_x\text{Sb}$ on its content at T = 300 (Fig. 5). The calculations were carried out making use of the Mott relationship for the thermopower in the case where the conductivity of the semiconductor is governed by the motion of electrons on the Fermi level [12]:

$$\alpha = \frac{\pi^2}{3} \frac{k_{\rm B}T}{e} \frac{\partial}{\partial E} \ln \sigma(E) | E = E_{\rm F}.$$

The Mott dependence suggests that the conductivity of the semiconductor $\sigma(E)$ is proportional to the DOS at the Fermi level and is very close to experimental data ($\sigma(E) \sim n(E)\mu(E)$, where it is supposed that the mobility of charge carriers $\mu(E)$ weakly depends on energy). In this case, the slope of the curve that describes the dependence of the thermopower is determined by the relation given above $(\alpha/T \sim [\partial \ln \sigma(E)/\partial E]_{E=E_{\rm F}})$. From the above-said, the similarity between the behavior of the dependences $1/n(E_{\rm F}) = f(x)$ (Fig. 4) and $\alpha = f(x)$ (Fig. 5) becomes clear.

The analysis of the results of experimental studies presented in Figs. 1–4 for TiCoSb compound allowed us to suggest that, since the Fermi level $E_{\rm F}$ is located near the valence band in this case, we are concerned with an analog of a semiconductor with the hole type of conductivity, for which the Fermi level is fixed by the Coulombic gap of the acceptor impurity band. Therefore, we must obtain $\alpha > 0$ for the thermopower. Furthermore, since the Fermi level in TiCo_{1-x}Cu_xSb with x < 0.01 is located outside the continuous energy bands, the conductivity of the semiconductor should have activation character at low temperatures. In this



Fig. 5. Dependence of the thermal emf factor on the donor Cu impurity concentration in TiCoSb; dotted curve corresponds to theoretical calculations, squares – to experimental data

case, the hopping mechanism of conductivity over the impurity band is engaged (till the conductivity over the impurity band becomes metallic [12]), and the current carriers are activated into the continuous energy band. At x > 0.01, when $E_{\rm F}$ is fixed by the mobility edge of the conduction band or enters into the continuous energy band and drifts in it, the conductivity of TiCo_{1-x}Cu_xSb will be governed by free electrons.

Therefore, doping the intermetallic semiconductor TiCoSb with a donor Cu impurity brings about the change of the mechanism of conductivity – from activation to metallic one (the Anderson transition is realized [12]) – which occurs owing to the reconstruction of the energy spectrum of the semiconductor and the drift of the Fermi level first from the top of the conduction band through the energy gap of the semiconductor and, after its entry into the conduction band, across the latter.

The adequacy of the theoretical results obtained to the results of experimental researches will be the subject of the next work.

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ОСОБЛИВОСТІ ЛЕГУВАННЯ ІНТЕРМЕТАЛІЧНОГО НАПІВПРОВІДНИКА *p*-ТіСоSb ДОНОРНОЮ ДОМІШКОЮ Сu. 1. РОЗРАХУНОК ЕЛЕКТРОННОЇ СТРУКТУРИ

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Резюме

Проведено розрахунок зонної структури та розподілу електронної густини інтерметалічного напівпровідника TiCoSb, легованого донорною домішкою шляхом заміщення атомів Со на Сu. Встановлено залежність розташування рівня Фермі від концентрації донорної домішки, проаналізовано можливі механізми електропровідності для різних концентрацій домішки.