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**PECULIARITIES OF STRUCTURAL,
ENERGY AND KINETIC CHARACTERISTICS
OF $VFe_{1-x}Ti_xSb$ THERMOELECTRIC MATERIAL**

The crystalline and electronic structures, the temperature and concentration dependences of the electric resistivity and the Seebeck coefficient of $VFe_{1-x}Ti_xSb$ thermoelectric material have been studied in the ranges of $T = 4.2 - 400$ K and $N_A^{Ti} \approx 9.5 \cdot 10^{19} \text{ cm}^{-3}$ ($x = 0.005$) – $3.9 \cdot 10^{21} \text{ cm}^{-3}$ ($x = 0.15$). The mechanism of simultaneous generation of defects of donor and acceptor nature was established. They change the compensation degree of semiconductor material and determine mechanism of conduction.

Key words: electronic structure, electric resistivity, Seebeck coefficient.

Introduction

As is known, parameter optimization of thermoelectric materials to obtain maximum values of thermoelectric figure of merit depends on a number of factors, in particular, carrier concentration (doping degree), scattering mechanisms, thermal conductivity, selection of crystallographic orientation, etc. [1]. The respective doping of intermetallic semiconductors, in particular, $n\text{-ZrNiSn}$, $n\text{-TiNiSn}$, $n\text{-HfNiSn}$ and $n\text{-VFeSb}$ ($MgAgAs$ structural type, $F\bar{4}3m$ space group), allows obtaining simultaneously high values of electric conductivity, the Seebeck coefficient and low values of thermal conductivity coefficient, assuring high efficiency of thermal into electric energy conversion and making them most studied new thermoelectric materials [2-6].

In this work, that contributes to further study of the effect of heavy doping ($N_A, N_D \sim 10^{19} \div 10^{21} \text{ cm}^{-3}$) of this class of semiconductors on their structural, energy, electrophysical and magnetic properties [2], we determine conditions for the origination of maximum thermoelectric power factor Z^* ($Z^* = \alpha^2 \cdot \sigma$, where α is the Seebeck coefficient, σ is the electric conductivity) on doping of $n\text{-VFeSb}$ with Ti atoms introduced into the compound by substitution for Fe atoms. The investigation also showed that obtaining a positive result, for instance, high Z^* values, without insight into deep processes in material structure and electric conductivity mechanisms, is, as a rule, of casual nature and will prevent from developing high-performance materials for thermal into electric energy conversion.

Investigation procedures

The object to be investigated included crystalline structure, electron density distribution (DOS), the kinetic and energy characteristics of $VFe_{1-x}Ti_xSb$. The samples were synthesized in the laboratory of Institute for Physical Chemistry, Vienna University. The X-ray structural analysis with employment of Fullprof program [7] was used to obtain the values of crystal lattice periods. The data arrays obtained by the powder method (diffractometer Guinier-Huber image plate system) 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) method in coherent potential approximation (CPA) and local density approximation (LDA) [8]. 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 [9]. 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 temperature and concentration dependences of the electrical resistivity (ρ) and the Seebeck coefficient (α) of $VFe_{1-x}Ti_xSb$ samples were measured with respect to copper in the ranges: $T = 4.2 - 400$ K, $N_A^{Ti} \approx 9.5 \cdot 10^{19} \text{ cm}^{-3}$ ($x = 0.005$) – $3.9 \cdot 10^{21} \text{ cm}^{-3}$ ($x = 0.15$).

Research on the electrokinetic and energy characteristics of $VFe_{1-x}Ti_xSb$

The initial testing of $VFe_{1-x}Ti_xSb$ samples for their homogeneity, the presence of uncontrolled phases and the fact of dissolution of impurity atoms in the matrix of $VFeSb$ compound performed with the aid of X-ray phase and structural analyses, revealed no traces of other phases, except for the basic one. In turn, the values of unit cell period increased, which is reasonable, since the atomic radius of Ti ($r_{Ti} = 0.145$ nm) is larger than that of Fe ($r_{Fe} = 0.127$ nm). The results of testing served the basis for further electrokinetic research.

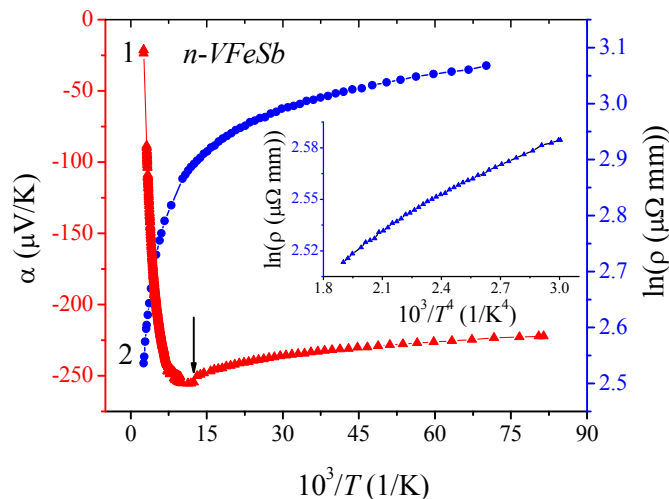


Fig. 1. Temperature dependences of the electric resistivity $\ln(\rho(1/T))$ (1) and the Seebeck coefficient $\alpha(1/T)$ (2) of n - $VFeSb$. Inset: dependence $\ln(\rho(1/T)^{1/4})$ in the range of $T = 12 - 80$ K.

Taking into account that the object of study is $VFe_{1-x}Ti_xSb$ solid solution, it is reasonable to start from the analysis of characteristics of basic n - $VFeSb$ semiconductor, and Fig. 1 shows the temperature dependences of the electric resistivity $\ln \rho(1/T)$ and the Seebeck coefficient $\alpha(1/T)$. It is seen that in

the range of $T = 4.2 - 80$ K we have hopping conduction of activation nature with a variable jump length ($\nu r \hbar$) ε_3^p [10], as indicated by the linear dependence $\ln(\rho(1/T)^{1/4})$ (inset in Fig. 1).

In turn, the negative values of the Seebeck coefficient speak for electrons as the majority charge carriers. With a rise in temperature ($T > 80$ K), the activation conduction changes into band (metallic) conduction determined by free electrons, and the Fermi level ε_F goes from the impurity donor band to conduction band. Under such conditions, the values of $\rho(T)$ increase with a rise in temperature due to scattering mechanisms (Fig. 2a, curve 1).

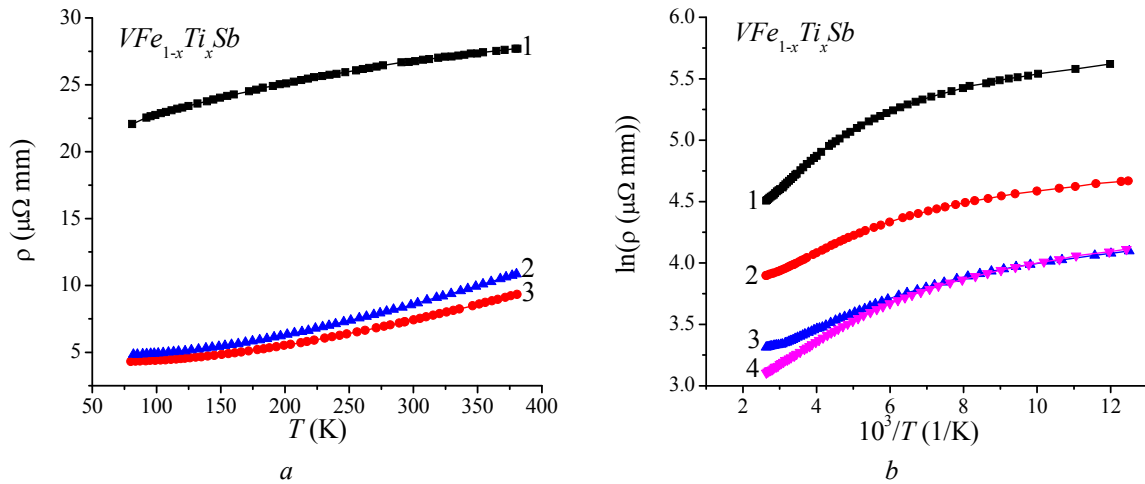


Fig. 2. Temperature dependences of the electric resistivity ρ of $VFe_{1-x}Ti_xSb$:
 a) $1 - x = 0$, $2 - x = 0.01$, $3 - x = 0.02$, b) $1 - x = 0.03$, $2 - x = 0.05$, $3 - x = 0.10$, $4 - x = 0.15$.

In transient region from the activation to band conduction (arrow in Fig. 1) we managed to determine the activation energy from the Fermi level ε_F to conduction band $\varepsilon_1^p = 1.6$ meV. On the other hand, the fact that hopping conduction is defining up to 80 K, and between the conduction band and impurity band there is a small energy gap, is indicative of considerable impurity band width (~ 7 meV).

Introduction of Ti atoms into $VFeSb$ compound by substitution for Fe atoms must generate in a crystal structural defects of acceptor nature, since Ti ($3d^2 4s^2$) has four $3d$ -electrons less than Fe ($3d^6 4s^2$). Figs. 2-4 show the temperature and concentration dependences of the electric resistivity and the Seebeck coefficient of $VFe_{1-x}Ti_xSb$. As long as in n - $VFeSb$ the Fermi level ε_F is in conduction band, doping of semiconductor with the lowest concentrations of Ti acceptor impurity must lead to a reduction of free electrons concentration, and the Fermi level ε_F must drift to the band bottom. As is seen from Fig. 2a, in the concentration range of $VFe_{1-x}Ti_xSb$, $0 \leq x \leq 0.02$, the semiconductor has still nonactivation, metallic type of conduction, indicating to location of the Fermi level in conduction band. However, surprising is the fact that at fixed temperature in the same concentration range the values of $\rho(x)$ are reduced (Fig. 3a).

For instance, at $T = 160$ K the values of $\rho(x = 0) = 24.28 \mu\Omega \cdot m$ are reduced to $\rho(x = 0.005) = 5.11 \mu\Omega \cdot m$ and $\rho(x = 0.01) = 4.96 \mu\Omega \cdot m$. That is, by introducing into n - $VFeSb$ a huge number of acceptors ($N_A^{Ti} \approx 3.8 \cdot 10^{20} \text{ cm}^{-3}$) we not only managed to “draw” the Fermi level ε_F to the energy gap, but, on the contrary, conduction seems to have increased, which in a semiconductor is possible only with increase in the number of free electrons. This result suggests that in $VFe_{1-x}Ti_xSb$

crystal, simultaneously with acceptors, donors are generated by the mechanism which is unknown so far. Another variant of such $\rho(x)$ behaviour is assumption on the liquidation of semiconductor material state.

At the concentrations $N_A^{Ti} \approx 5.7 \cdot 10^{20} - 1.9 \cdot 10^{21} \text{ cm}^{-3}$ ($x = 0.03 - 0.15$) the temperature dependences of electric resistivity of $VFe_{1-x}Ti_xSb$ expectedly acquire semiconductor nature (Fig. 2b) indicating that the Fermi level ε_F has left conduction band for the energy gap. This result confirms the acceptor nature of structural defects that originate in $VFe_{1-x}Ti_xSb$ crystal, which accounts for a drastic increase in $\rho(x)$ values (Fig. 3a). At the same time, the nature of change in the values of the Seebeck coefficient $\alpha(x)$ (Figs. 3b, 4) testifies that the Fermi level is now located near the valence band, since the Seebeck coefficient values are now positive.

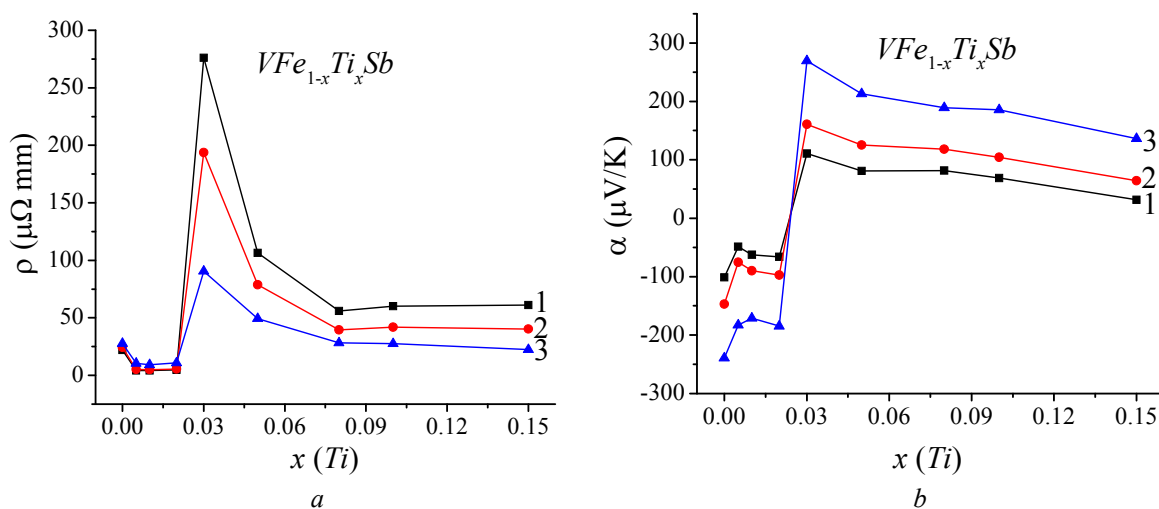


Fig. 3. Change in the values of the electric resistivity $\rho(x)$ (a) and the Seebeck coefficient $\alpha(x)$ (b) of $VFe_{1-x}Ti_xSb$ at different temperatures: 1 – $T = 80 \text{ K}$, 2 – $T = 160 \text{ K}$, 3 – $T = 380 \text{ K}$.

From the activation areas of $\ln \rho(1/T)$ dependences (Fig. 2b) we calculated the values of activation energies from the Fermi level ε_F to percolation level of conduction band (valence band) ε_1^p and electron jumps ε_3^p along the states with the energies close to the Fermi level, and from the activation areas of $\alpha(1/T)$ dependences (Fig. 4) – the values of activation energies ε_1^α and ε_3^α that yield, respectively, the values of modulation amplitude of intermittent energy bands and small-scale fluctuation of heavily doped and strongly compensated semiconductor (Fig. 5) [2, 10]. It is clear that the higher is compensation degree, the larger is modulation amplitude [10].

Recall that compensation degree shows the ratio between the number of ionized donors and acceptors: the closer are their values, the higher is compensation degree, and with full compensation the number of acceptors and donors is equal. In the case of $n-VFeSb$ the amplitude value of large-scale fluctuation is $\varepsilon_1^\alpha = 41.5 \text{ meV}$, and the depth of potential well $\varepsilon_3^\alpha = 0.2 \text{ meV}$.

Substitution in $VFeSb$ compound of the smallest in the experiment number of Fe atoms for Ti ($x = 0.005$) atoms is expectedly accompanied by a drastic increase in semiconductor degree of compensation, which points to growth of dependence $\varepsilon_1^\alpha(x)$ on the area $VFe_{1-x}Ti_xSb$, $x = 0 - 0.005$ (Fig. 5a). However, further introduction of acceptor impurity into a semiconductor which is still n -type ($\alpha(x) < 0$), when the Fermi level ε_F is still in conduction band, is unexpectedly attended by the same drastic decrease in the values of modulation amplitude of continuous energy bands $\varepsilon_1^\alpha(x)$.

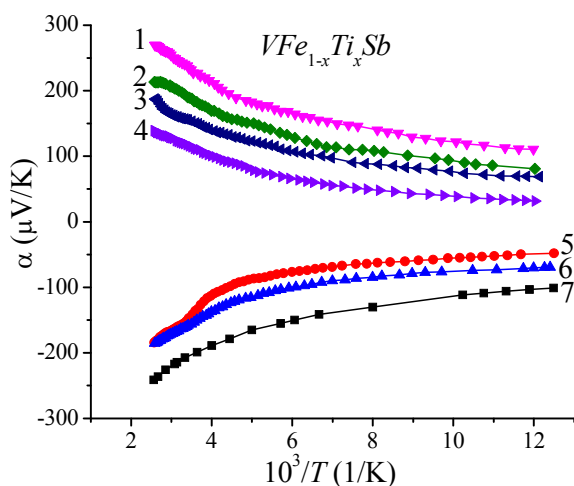


Fig. 4. Temperature dependences of the Seebeck coefficient $\alpha(1/T)$ of $VFe_{1-x}Ti_xSb$:
 $1-x = 0.03$, $2-x = 0.05$, $3-x = 0.10$, $4-x = 0.15$, $5-x = 0.005$, $6-x = 0.02$, $7-x = 0$.

Such a decrease in the values $\varepsilon_1^\alpha(x)$ on the area of concentrations $0.005 < x < 0.03$ is possible only when, simultaneously with acceptors, donors are generated in a crystal by the mechanism which is so far unknown. In so doing, in the concentration area $0.005 < x < 0.03$ the rate of generation of donors in $VFe_{1-x}Ti_xSb$ seems to be higher compared to acceptors. A similar conclusion was also made on the basis of $\rho(x)$ behaviour in the same concentration area, when on introducing into n-type semiconductor of acceptor impurity the values of $\rho(x)$ were not increased, as expected, but reduced (Fig. 3a). The concentration limits of uncontrolled donors can be estimated as $N_D: 3.6 \cdot 10^{20} \text{ cm}^{-3}$ ($x = 0.02$) $< N_D < 5.7 \cdot 10^{20} \text{ cm}^{-3}$ ($x = 0.03$). Another variant of such behaviour $\varepsilon_1^\alpha(x)$ in the concentration area $0.005 < x < 0.03$ is the assumption of liquidation of semiconductor material state.

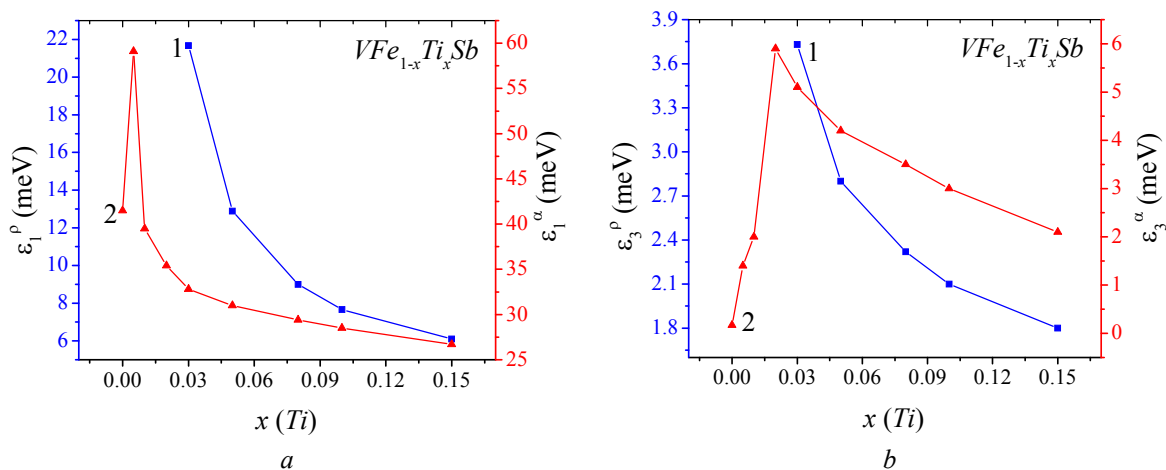


Fig. 5. Change in the values of activation energies (1) and (2) (a) and (1) and (2) (b) of $VFe_{1-x}Ti_xSb$.

The conductivity of $VFe_{1-x}Ti_xSb$, $0.03 \leq x \leq 0.15$ is of semiconductor nature, and the value of $\alpha(x) > 0$, pointing to a change in the type of majority carriers from electrons to holes. Thus, the rate and concentration of generated acceptors exceeds the rate and concentration of donors. As a result, the compensation degree is reduced, as indicated by the decay of dependence $\varepsilon_1^\alpha(x)$ (Fig. 5a).

At the concentrations of Ti impurity, when material shows semiconductor properties, the fact of drift of the Fermi level ε_F to valence band shows the nature of change in the values of activation

energy $\varepsilon_1^p(x)$ from the Fermi level ε_F to valence band edge (Fig. 5a). It is seen that the energy gap between the Fermi level and valence band edge is reduced from $\varepsilon_1^p(x=0.03) = 21.7$ meV to $\varepsilon_1^p(x=0.15) = 6.1$ meV, and the concentration of *Ti* impurity proved to be insufficient for valence band to be crossed by the Fermi level.

Predicted is behaviour of hopping conduction activation energy $\varepsilon_3^p(x)$ in $VFe_{1-x}Ti_xSb$, $0.03 \leq x \leq 0.15$. The fact that the values of energy $\varepsilon_3^p(x)$ are drastically reduced is related to increased overlapping of acceptor wave functions due to their large concentration ($N_A^{Ti} \approx 3.9 \cdot 10^{21} \text{ cm}^{-3}$ ($x = 0.15$)). On the contrary, the depth of potential well of small-scale fluctuation which is proportional to ε_3^α , starts to be reduced only after crossing by the Fermi level of the mid band gap, which agrees with the pattern of change in the values of continuous energy modulation amplitude $\varepsilon_1^\alpha(x)$.

Thermoelectric power factor of $VFe_{1-x}Ti_xSb$

Fig. 6 represents a change in the values of thermoelectric power factor $Z^*(x)$ from which it is seen that in the concentration range $0 < x < 0.03$ the values of $Z^*(x)$ in $VFe_{1-x}Ti_xSb$ are greater than in the undoped semiconductor $VFeSb$. From Fig. 6 it also follows that when crossing the Fermi level and conduction band percolation level, when the values of the Seebeck coefficient are still high, and the values of the electric conductivity of $VFe_{1-x}Ti_xSb$ are already high, on the dependences $Z^*(x)$ there are extremes at all investigated temperatures, which corresponds to criterion of achievement of maximum values of thermoelectric power factor Z^* [2].

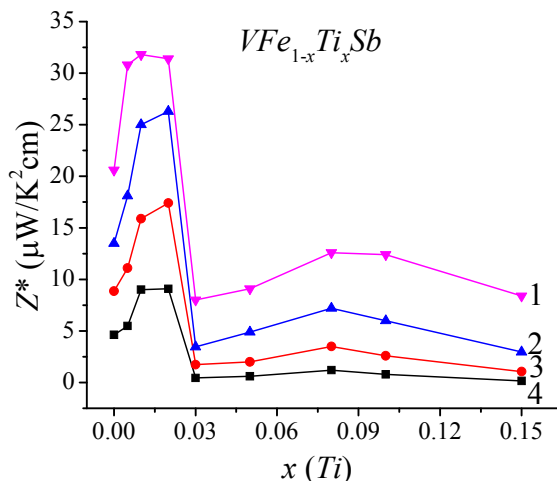


Fig. 6. Change in the values of thermoelectric power factor Z^* of $VFe_{1-x}Ti_xSb$:
 1 – $T = 380$ K; 2 – $T = 250$ K; 3 – $T = 160$ K; 4 – $T = 80$ K.

Thus, on the basis of the results of electrokinetic studies presented here it can be asserted that the obtained solid solution $VFe_{1-x}Ti_xSb$ is a promising thermoelectric material. However, the level of investigations performed did not allow clear identification of electric conductivity mechanisms, which makes it impossible to predict the kinetic characteristics of $VFe_{1-x}Ti_xSb$ and to develop the technology of thermoelectric material production with high efficiency of thermal into electric energy conversion. This gave an impetus to in-depth study of spatial arrangement of atoms in $VFe_{1-x}Ti_xSb$ and of semiconductor electron structure.

Refinement of crystalline and electronic structures of $VFe_{1-x}Ti_xSb$

First and foremost, it is necessary to understand what determines the electron type of conduction of $VFeSb$ compound. A microprobe analysis of the surface of $VFeSb$ samples revealed 1% deficit of Sb atoms. A similar result was obtained in [11], which is attributable to the presence of structural defects in the form of vacancies in position $4b$ of Sb atoms. The refinement of $VFeSb$ crystalline structure by virtue of low concentration of structural defects prevented from the identification of vacancies: the models of crystalline structure were in the limits of error both for the variant of 100% occupation by atoms of their positions, and for the variant of existence of $\sim 1\%$ vacancies of Sb atoms. Based on the ordered model of structure $VFeSb$, where all the atoms occupy positions in conformity with $MgAgAs$ structural type, and the occupation degree is 100%, the value of crystal lattice period $a(x)$ was calculated (Fig. 7a).

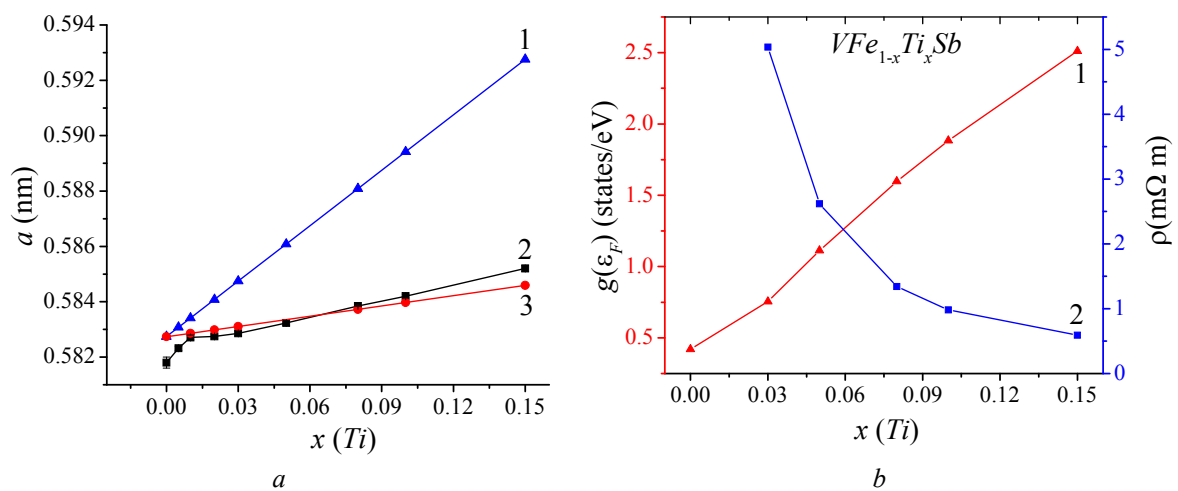


Fig. 7. Change in the values of crystal lattice period $a(x)$ (a) and calculated DOS values on the Fermi level $g(\varepsilon_F)$ and the electric resistivity $\rho(x)$ (b) of $VFe_{1-x}Ti_xSb$: a) 1 – calculation with Ti atoms substituted for Fe ; 2 – experimental results, 3 – calculation with Ti atoms substituted for V ; b) 1 – $g(\varepsilon_F)$, 2 – $\rho(x)$.

It turned out that the values of period obtained from the experiment are lower than calculated ones, namely $a_{exp} = 0.5818$ nm and $a_{calc} = 0.5827$ nm. The question arises: what is the reason for this difference? If it is remembered that microprobe analysis revealed Sb deficit of $\sim 1\%$ [11], as well as the assumption that this can be manifestation of vacancies in position $4b$ of Sb atoms, then the difference in the values of $VFeSb$ lattice period can serve a weighty argument for this assumption.

On the other hand, the assumption as to the presence in $VFeSb$ structure of vacancies in $4b$ position which is equivalent to generation of donors looks logical, being consistent with the above results of kinetic research of $n-VFeSb$ that pointed to the existence in semiconductor of donors of unknown origin. Thus, the negative values of the Seebeck coefficient of $VFeSb$ and the presence of hopping mechanism of charge transport along the impurity donor band formed by defects is another argument for the assumption of the presence of vacancies in position ($4b$) of Sb atoms.

Taking into account that the atomic radius of Ti ($r_{Ti} = 0.145$ nm) is larger than that of Fe ($r_{Fe} = 0.127$ nm), it is reasonable to increase the values of crystal lattice period $a(x)$ of $VFe_{1-x}Ti_xSb$ with increasing the content of Ti (Fig. 7a, curve 2). Based on the assumption that doping of $n-VFeSb$ with Ti atoms is accompanied by ordering of crystalline structure, and impurity atoms of Ti displace Fe atoms from crystallographic position $4c$, a change in $a(x)$ values was calculated (Fig. 7a, curve 1). In the calculations we assumed that the initial structure $VFeSb$ is ordered.

Comparison of two dependences, i.e. a change in the values of unit cell period $a(x)$ obtained experimentally and calculated for the case of substitution of Fe atoms by Ti , shows that the rate of change in the values $a(x)$, obtained experimentally, in the concentration area $0 \leq x \leq 0.01$ coincides with the rate of change in $a(x)$, obtained by calculation (similar slope of dependences 1 and 2 in Fig. 7a). Such consistency of $a(x)$ behaviour indicates that in $VFeSb$ compound in this area Fe atoms are mainly displaced by Ti atoms.

At the same time, the nature of change in the calculated values of $a(x)$ in case of substitution of Fe atoms by Ti atoms in the concentration range $x > 0.01$ is basically different from the experimental results (Fig. 7a, curve 1). As long as the atomic radius of Sb ($r_{Sb} = 0.159$ nm) is the largest in $VFeSb$ compound, increase in the values of $a(x)$ is only possible with replacement by Ti atoms of smaller atoms, namely either Fe , or V atoms ($r_V = 0.135$ nm), or these atoms simultaneously in different ratios. The result of calculation of a change in $a(x)$ values in concentration area $x > 0.01$ for the case when Ti atoms would replace only V atoms (Fig. 7a, curve 3), is close to the experimental results, however, does not coincide with it.

Thus, structural investigations allow asserting that in different concentration ranges Ti atoms simultaneously in different ratios occupy crystallographic positions of Fe and V atoms: in the concentration range $0 \leq x \leq 0.01$ Ti atoms to a larger extent occupy position of Fe atoms, and in the range $x > 0.01$ – position of V atoms.

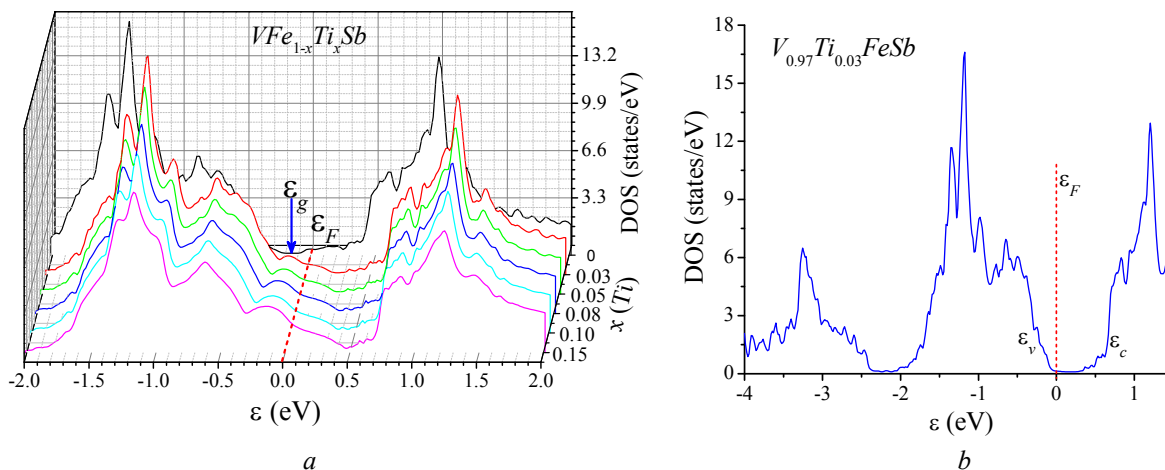


Fig. 8. Calculation of the electron density of states DOS for variants of ordered structure $VFe_{1-x}Ti_xSb$ (a) and $V_{0.97}Ti_{0.03}FeSb$ (b).

For a deeper insight into physical processes in a realized solid solution, the electron structure was calculated for both extreme cases, namely substitution in $VFeSb$ compound of Fe and V atoms by Ti (Fig. 8). Thus, calculation of electron state density on the Fermi level $g(\epsilon_F)$ for the case of substitution in $VFeSb$ compound of Fe atoms by Ti shows that the values of $g(\epsilon_F)$ increase only in the concentration range of $VFe_{1-x}Ti_xSb$, $0 \leq x \leq 0.15$, and the values of resistivity $\rho(x)$ calculated on this basis are reduced, which is typical of metal (Fig. 7b). This result, as is shown by the calculation of density of electron states DOS (Fig. 8a), is due to energy gap disappearance in the case of introduction into $VFeSb$ compound of already the lowest concentration of Ti impurity ($x = 0.005$) by substitution of Fe atoms.

It is worth mentioning that the temperature and concentration dependence of electrical resistivity is studied in the range $0 \leq x \leq 0.02$, when conductivity has metallic type, and adding supposedly acceptor Ti impurity into n -type semiconductor $n-VFeSb$ was unexpectedly accompanied

by a reduction of resistivity values. Exactly this result, namely increase in DOS on the Fermi level $g(\varepsilon_F)$ and, as a consequence, electric resistivity reduction, is provided by electron structure calculations for the case of substitution in $VFeSb$ compound of Fe atoms by Ti . Hence, the analysis performed allows asserting that on introducing into $VFeSb$ compound of Ti atoms in concentration area $0 \leq x \leq 0.02$ the latter to a larger extent displace Fe atoms, which is accompanied by energy gap disappearance, and the resulting material $VFe_{1-x}Ti_xSb$ is metal.

On the other hand, calculation of the electron density of states DOS for another extreme case has shown that substitution in $VFeSb$ compound of V atoms by Ti atoms for atomic concentration an order higher ($x = 0.03$) does not destruct the semiconductor state of $V_{0.97}Ti_{0.03}FeSb$, and the Fermi level ε_F is in a forbidden gap near valence band ceiling (Fig. 8b). Exactly this result was revealed by the experimental studies of electric resistivity and the Seebeck coefficient at $x \geq 0.03$, when a change in resistivity values with temperature was of activation nature, and the Seebeck coefficient values were positive.

Thus, the analysis performed makes it possible to assert that on introducing into $VFeSb$ compound of Ti atoms in concentration area $x \geq 0.03$, the latter to a larger extent displace V atoms, which is attended by the appearance of forbidden gap and generation in a crystal of acceptor-nature structural defects and the resulting material is a semiconductor. As long as studies of $VFe_{1-x}Ti_xSb$ have shown a simultaneous occupation by Ti atoms of positions of V and Fe atoms in different ratios depending on impurity concentration, to establish the exact proportion of such substitution is so far problematic.

Conclusions

Investigation of the process of introducing into $VFeSb$ compound of Ti atoms has revealed a complex mechanism of a simultaneous substitution in different ratios depending on the concentration of impurity atoms of crystallographic position of Fe atoms, as well as V atoms. The result obtained makes it possible to predict behaviour of the kinetic characteristics of $VFe_{1-x}Ti_xSb$ and to obtain a material with high efficiency of thermal into electric energy conversion.

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