

Structure and Properties of $\text{Ti}_{1-x}\text{Cr}_x\text{Se}_2$ Substitutional Solid Solutions

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Abstract—Titanium diselenide TiSe_2 is doped for the first time with an acceptor impurity through substitution of Cr^{3+} ions for Ti^{4+} ions in the host lattice. The structure and electrical resistivity of the TiSe_2 -based solid solutions are investigated in the vicinity of the compensation point, and the influence of the compensation point on the stability of the charge-density-wave state is analyzed. It is demonstrated that disorder in the guest sublattice does not lead to Anderson localization of charge carriers.

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1. INTRODUCTION

Intercalation of transition metals into titanium diselenide TiSe_2 brings about the localization of charge carriers [1], a reduction of the effective magnetic moment of intercalated atoms [2], and lattice contraction in the direction normal to the plane of the layer [3]. These phenomena have been interpreted in terms of the capture of free conduction electrons by $\text{Ti}-M-\text{Ti}$ covalent centers (where M is an intercalated metal) formed as a result of the hybridization of $\text{Ti } 3d_z^2$ orbitals in the host lattice and intercalant orbitals with similar symmetry [4].

The above interpretation is based on band structure calculations [5], which, in general, have been confirmed by spectral data [6]. According to the band structure calculations, the formation of covalent centers gives rise to an impurity band with localized states. The observed localization of charge carriers is associated with the fact that the Fermi level is shifted to the impurity band. The band structure calculations were performed under the assumption that the intercalant sublattice is ordered. However, all experimental studies [1–4, 6] were carried out with samples quenched from a high temperature to prevent an intercalant sublattice from being ordered. It is evident that this heat treatment can encourage Anderson localization of charge carriers due to the disorder arising in the intercalant sublattice and, hence, in the arrangement of $\text{Ti}-M-\text{Ti}$ centers.

It seems likely that the contribution from the disorder in the intercalant sublattice to the localization of charge carriers can be separated by comparing the titanium sublattices of the intercalation compounds and the corresponding substitutional solid solutions. In this

case, the titanium and substituting metal atoms are free of neighbors that are capable of participating in the formation of covalent centers and, furthermore, the degree of disorder can be retained.

The purpose of this work was to attempt to synthesize substitutional solid solutions of the general formula $\text{Ti}_{1-x}M_x\text{Se}_2$ ($M = \text{Cr}, \text{Fe}, \text{Co}$) and to investigate their structure and electrical conductivity in order to elucidate the influence of the location of impurity metal atoms in the crystal lattice of titanium diselenide and the degree of their disorder on the energy spectrum of charge carriers.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Samples of $\text{Ti}_{1-x}M_x\text{Se}_2$ ($M = \text{Cr}, \text{Fe}, \text{Co}$) substitutional solid solutions were prepared using the conventional tube synthesis from the following elements: titanium purified by iodine distillation (purity, 99.99; Aldrich 30.581-2), selenium (OSCh 19-5 grade; purity, 99.999), cobalt and chromium subjected to electrolytic cleaning (purity, 99.95), and carbonyl iron reduced in hydrogen (purity, 99.999). Heat treatment and homogenization of the samples were performed at a temperature of 900°C in evacuated (to a residual pressure of 10^{-5} Torr) silica glass tubes with intermediate grinding and pressing. According to the x-ray powder diffraction analysis, the synthesized samples in the case of $M = \text{Fe}$ and Co were homogeneous and consisted of the TiSe_2 diselenide intercalated with iron and cobalt, respectively. The x-ray diffraction patterns and the lattice

parameters calculated from them coincided with those obtained earlier for the corresponding intercalation compounds [3]. No traces of substitutional solid solutions were found. The x-ray diffraction patterns of the $\text{Ti}_{1-x}\text{M}_x\text{Se}_2$ ($M = \text{Cr}$) samples with a chromium content in the range $x = 0-0.25$ were indexed in a trigonal crystal system with space group $P3m1$. The concentration dependences of the lattice parameters are plotted in Fig. 1. It can be seen from this figure that the lattice parameters of the samples with a chromium content of up to $x = 0.25$ virtually coincide with those of the TiSe_2 diselenide. The coincidence can be explained by the close radii of the titanium and chromium atoms. This situation differs radically from both the observed contraction of the host lattice along the c axis and the expansion of the lattice along the a axis due to intercalation. An abrupt increase in the parameter a_0 and a decrease in the parameter c_0 at a chromium content $x = 0.25$ can be attributed to the onset of intercalation of chromium atoms into the interlayer space. Thus, the $\text{Ti}_{1-x}\text{Cr}_x\text{Se}_2$ titanium diselenides at a chromium content $x < 0.25$ are of undeniable interest, especially from the standpoint of the posed problem of comparing intercalation compounds and substitutional solid solutions of the same composition. The concentration dependence of the lattice parameters at a chromium content $x > 0.25$ exhibits an intricate behavior. The $\text{Ti}_{0.5}\text{Cr}_{0.5}\text{Se}_2$ and $\text{Ti}_{0.25}\text{Cr}_{0.75}\text{Se}_2$ compounds crystallize in a monoclinic crystal system and have an $(a_0 \times a_0\sqrt{3} \times 2c_0)$ superstructure. The lattice parameters are as follows: $a_0 = 3.5593 \text{ \AA}$ and $c_0 = 6.10885 \text{ \AA}$ for the $\text{Ti}_{0.5}\text{Cr}_{0.5}\text{Se}_2$ compound and $a_0 = 3.3920 \text{ \AA}$ and $c_0 = 5.9920 \text{ \AA}$ for the $\text{Ti}_{0.25}\text{Cr}_{0.75}\text{Se}_2$ compound.

The electrical resistivity of the $\text{Ti}_{1-x}\text{Cr}_x\text{Se}_2$ substitutional solid solutions at a chromium content $x < 0.25$ was measured using single-crystal samples. Single crystals were grown by the gas-transport reaction method with an excess of selenium. During the reaction, the material was transferred to the cold end of the tube. The procedure resulted in the formation of single crystals $2 \times 3 \times 0.05 \text{ mm}$ in size. The chemical composition of the single crystals was determined using electron microprobe analysis with a JEOL-733 microscope. The error in the determination of the composition was equal to $\pm 1 \text{ mol } \%$. It turned out that the composition of the single crystals differed substantially from the composition of the initial material. The single crystals had the following compositions: TiSe_2 , $\text{Ti}_{1.006}\text{Cr}_{0.003}\text{Se}_2$, $\text{Ti}_{0.96}\text{Cr}_{0.03}\text{Se}_2$, $\text{Ti}_{0.95}\text{Cr}_{0.044}\text{Se}_2$, $\text{Ti}_{0.94}\text{Cr}_{0.08}\text{Se}_2$, $\text{Ti}_{0.86}\text{Cr}_{0.11}\text{Se}_2$, $\text{Ti}_{0.9}\text{Cr}_{0.1}\text{Se}_2$, $\text{Ti}_{0.87}\text{Cr}_{0.2}\text{Se}_2$, and $\text{Ti}_{0.26}\text{Cr}_{0.88}\text{Se}_2$. It can be seen that, in a number of cases, the sum of the stoichiometric coefficients of the titanium and chromium components is larger than unity. In principle, this can indicate the coexistence of substitution and intercalation. However, the constancy of the lattice parameters argues against the intercalation, at least, on a noticeable scale.

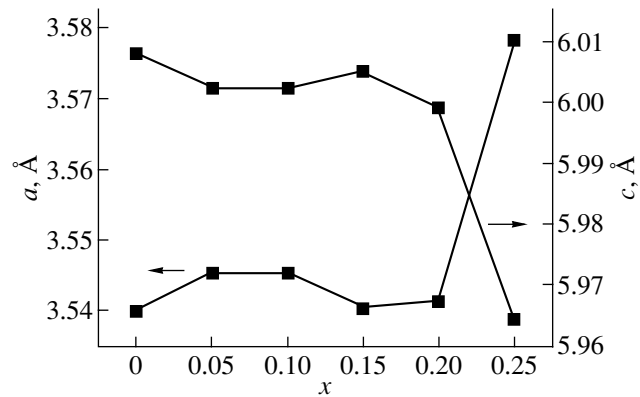


Fig. 1. Dependences of the lattice parameters of the TiSe_2 diselenide with a hexagonal structure on the concentration of substituting chromium.

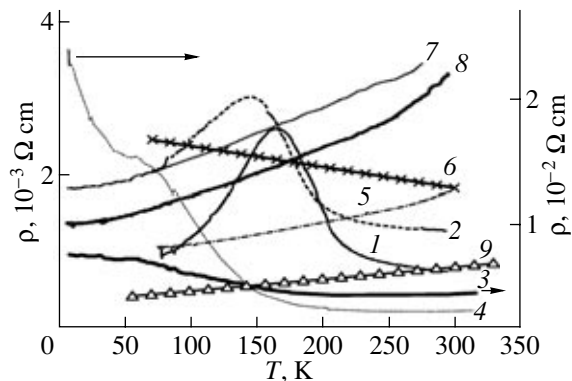


Fig. 2. Temperature dependences of the electrical resistivity measured along the basal plane of single crystals of the following compositions: (1) TiSe_2 , (2) $\text{Ti}_{1.006}\text{Cr}_{0.003}\text{Se}_2$, (3) $\text{Ti}_{0.96}\text{Cr}_{0.03}\text{Se}_2$, (4) $\text{Ti}_{0.95}\text{Cr}_{0.044}\text{Se}_2$, (5) $\text{Ti}_{0.94}\text{Cr}_{0.08}\text{Se}_2$, (6) $\text{Ti}_{0.9}\text{Cr}_{0.1}\text{Se}_2$, (7) $\text{Ti}_{0.86}\text{Cr}_{0.11}\text{Se}_2$, (8) $\text{Ti}_{0.87}\text{Cr}_{0.2}\text{Se}_2$, and (9) $\text{Ti}_{0.26}\text{Cr}_{0.88}\text{Se}_2$.

The ac resistivities of the aforementioned single crystals were measured by the four-point probe method in the temperature range 4.2–300 K. The temperature dependences of the electrical resistivity measured along the basal plane of the single crystals are shown in Fig. 2.

3. RESULTS AND DISCUSSION

The temperature dependence of the electrical resistivity of the TiSe_2 diselenide at temperatures below 202 K exhibits a characteristic resistive anomaly associated with the transition to a charge-density-wave state [7]. This provides a means for testing the measuring technique and, in particular, the quality of the contacts. In actual fact, our data for the TiSe_2 diselenide are in complete agreement with those reported by Vaterlaus [8], thus confirming the reliability of the results obtained for the other materials.

It can be seen from Fig. 2 that, at a minimum chromium content ($x = 0.003$), the resistive anomaly revealed in the temperature dependence of the electrical resistivity and, accordingly, the transition to the charge-density-wave state are retained. The substitution at a higher chromium content ($x = 0.03$) leads to the suppression of this transition. The critical dopant concentration that is responsible for the suppression of the transition upon the substitution of chromium for titanium is considerably lower than the critical concentration observed upon the substitution of vanadium ($x_c = 0.10$) [8] or tantalum ($x_c = 0.07$) [9] for titanium. Quite possibly, the above difference can be associated with the presence of superstoichiometric titanium, whose concentration in the samples is uncontrollable and depends on the specific features of the procedure used for synthesizing the material. This assumption is also confirmed by the large difference in the threshold concentrations observed in the above substitutions and the substitution of niobium for titanium ($x_c = 0.2$) [9]. There are no physical arguments supporting the fact that the critical concentration x_c upon the substitution of niobium for titanium appears to be three times higher than that upon the substitution of tantalum for titanium. In this respect, it should be noted that all the data available in the literature concern the replacement of titanium by metals with a valence higher than the valence of titanium; therefore, the case in point is doping with donor impurities. However, the chromium ions involved in intercalation reactions resides in the Cr^{3+} state [2]. As is known, this state is the most stable of the other chromium states. Hence, we can assume that, in the case of substitution, chromium is also in the Cr^{3+} state. Therefore, the substitution of chromium for titanium is equivalent to doping with an acceptor impurity. It should be emphasized that transition metal dichalcogenides with a layered structure have never been doped previously with acceptor impurities. In the case of intercalation, this reaction is impossible because of the negatively charged nearest environment of the intercalated impurities [10]. According to our data, titanium atoms cannot be replaced by the majority of metal atoms with characteristic valences of 2 and 3. Most likely, this finding is explained by the large difference in the free energy of formation of titanium dichalcogenides and dichalcogenides of the substituting metal. In the case of the replacement by chromium, the corresponding difference is not so large [11]. Thus, the sole known example of doping of titanium dichalcogenides with acceptor impurities is provided by the substitution of chromium for titanium. It remains unclear whether the increased efficiency of suppression of the transition to the charge-density-wave state upon the substitution of chromium for titanium is a result of acceptor doping or stems from other factors, for example, from the scatter in the concentrations of superstoichiometric titanium.

The temperature dependence of the electrical resistivity for the solid solution at a chromium content $x = 0.1$ exhibits an activation behavior, and the electrical resistivity itself linearly increases with a decrease in the temperature. Similar temperature dependences of the electrical resistivity are observed for solid solutions at chromium contents $x = 0.044$ and 0.030 in the low-temperature range (Fig. 2). It is obvious that, in the case where the compounds possess conventional three-dimensional conduction, the electrical resistivity should increase exponentially as the temperature decreases. A linear behavior of the temperature dependence of the electrical resistivity can be observed for two-dimensional conduction [12]. As is known, the electrical conduction occurring through the activation mechanism is determined by the charge carrier concentration, which, in turn, is described by the Fermi integral

$$n = \int N(\varepsilon)f(\varepsilon)d\varepsilon, \quad (1)$$

where n is the charge carrier concentration, $N(\varepsilon)$ is the density of states, and $f(\varepsilon)$ is the Fermi–Dirac distribution function. In the two-dimensional case, the density of states at the Fermi level is independent of the energy. Consequently, the Fermi integral can be taken analytically and the electrical conductivity σ can be written in the form

$$\sigma \sim AT \ln \left(1 + e^{\frac{-E_a}{kT}} \right), \quad (2)$$

where A is a constant dependent on the effective mass of charge carriers and on the geometry of the sample, T is the temperature, E_a is the activation energy for electrical conduction, and k is the Boltzmann constant.

The temperature dependences of the electrical resistivity measured for the solid solutions doped with chromium at a higher concentration exhibits a metallic behavior during heating, most probably, due to the increase in the hole concentration. The total concentration dependence of the electrical resistivity $\rho(x)$ for $\text{Ti}_{1-x}\text{Cr}_x\text{Se}_2$ substitutional solid solutions at a temperature of 77 K is plotted in Fig. 3. This figure also shows the concentration dependence of the activation energy for electrical conduction according to the fitting of the experimental dependences with the use of relationship (2). It is clearly seen that the concentration dependence of the electrical resistivity at 77 K passes through a maximum at a chromium content $x = 0.044$. Since the increase in the chromium content should lead to a monotonic increase in the hole concentration, the presence of a maximum in the concentration dependence of the electrical resistivity can only be explained by the compensation of intrinsic electrons in the conduction band of the TiSe_2 diselenide. The band structure of this compound has been extensively investigated over the past thirty years. These investigations have established that the TiSe_2 diselenide is an intrinsic semiconductor [13],

which, however, exhibits a tendency to involve excess titanium [14]. This excess titanium can serve as a source of electrons that can be compensated upon the substitution of chromium for titanium. The presence of only one maximum in the dependence $\rho(x)$ suggests that the concentrations of superstoichiometric titanium in all the samples under investigation are equal or close to each other. Taking into account that intercalated titanium is in the Ti^{4+} state and, hence, introduces four electrons into the conduction band and that the substitution of the Cr^{3+} ion for the Ti^{4+} ion of the host lattice leads to the appearance of one hole, the concentration of excess titanium can be estimated at 1.1 mol %. As a result, the refined formula of the solid solutions can be written as $\text{Ti}_{1.01-x}\text{Cr}_x\text{Se}_2$.

The band diagram illustrating the observed concentration dependence of the electrical resistivity is shown in Fig. 4. The substitution of chromium for titanium leads to the formation of an impurity level in the band gap between the valence band (predominantly formed by the Se p orbitals) and the conduction band bottom (formed by the Ti $3d_z^2$ orbitals). In solid solutions at a chromium content $x < 0.1$, electrons are transferred from the conduction band to the acceptor level. At high chromium contents, the conduction band is depleted and electrical conduction occurs through the valence band; i.e., electrons are transferred from the valence band to the acceptor level and holes generated in the valence band contribute to the electrical conduction. This brings about the metallization of the material at a chromium content $x \geq 0.11$. The activation energy for electrical conduction of solid solutions at a chromium content $x < 0.044$ is associated with the excitation of electrons from the acceptor level to the conduction band. At $x > 0.1$, the activation energy is determined by the excitation of electrons from the valence band to the acceptor level. An increase in the activation energy with an increase in the chromium content indicates that the acceptor level is located closer to the bottom of the conduction band rather than to the top of the valence band. The activation energies in both ranges are in good agreement with the experimentally determined band gap between the valence and conduction bands of the TiSe_2 diselenide [13], because the sum of the activation energies at chromium contents $x = 0.03$ and 0.10 should be close to the total band gap. In actual fact, the sum of the activation energies amounts to $8 + 20 = 28$ meV, whereas the band gap determined at room temperature is approximately equal to 40 meV [13]. The difference between the above values can be associated with the following three factors: the accuracy in the determination of the band gap at such a high temperature, the finite width of the impurity level, and the influence of substitution on the band gap.

It should be noted that no transition to a charge-density-wave state is observed at a chromium content $x = 0.044$ corresponding to the compensation of intrinsic electrons by impurity holes. Although this transition in

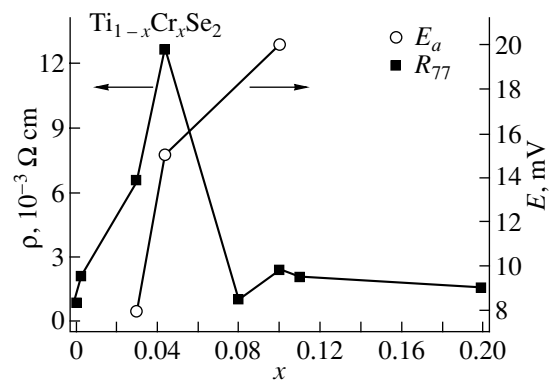


Fig. 3. Total concentration dependence of the electrical resistivity $\rho(x)$ measured at a temperature of 77 K (closed squares) and the concentration dependence of the activation energy for electrical conduction (open circles) of $\text{Ti}_{1-x}\text{Cr}_x\text{Se}_2$ substitutional solid solutions.

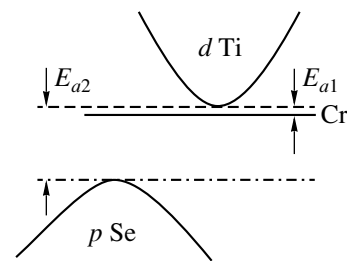


Fig. 4. Energy band diagram illustrating the observed concentration dependence of the electrical resistivity of $\text{Ti}_{1-x}\text{Cr}_x\text{Se}_2$ substitutional solid solutions.

the TiSe_2 diselenide has been studied for nearly thirty years, its nature is still not clearly understood. Initially, the transition to a charge-density-wave state was treated as a Peierls transition [8]. However, the concentration of intrinsic charge carriers is too low for the observed splitting of the bands. Furthermore, the observed effect is enhanced with decreasing concentration as the stoichiometric composition is approached. More recently, it was suggested that the transition under consideration occurs through the mechanism of electron-hole pairing with the formation of an excitonic insulator state [15]. According to this model, the electron and hole concentrations should be equal or close to each other. In this respect, the suppression of the transition to a charge-density-wave state upon doping with donor impurities was naturally explained as resulting from the disturbance of the electron-hole balance. However, it can be seen from the above data that acceptor doping gives rise to exactly the same effect even at the point of complete compensation. Moreover, the temperature of the transition to the charge-density-wave state in a lightly doped solid solution ($x = 0.003$) is lower than that in the TiSe_2 initial compound (Fig. 2), as is the case with doping by donor impurities [7, 8]. This can indicate that the electron-hole balance is not a governing factor responsible

for the stability of the charge-density-wave state. In our previous work [16], we revealed from the experiment that the charge-density-wave state is retained upon the intercalation of the TiSe_2 diselenide with silver. The observed stability of the charge-density-wave state was explained under the following assumptions: (i) electrons introduced during the intercalation are captured by Ti–Ag–Ti covalent centers (so that doping does not disturb an electron–hole balance of free charge carriers) and (ii) lattice distortions are absent. However, it can be seen that, in the case of $\text{Ti}_{1-x}\text{Cr}_x\text{Se}_2$ substitutional solid solutions, these conditions are not sufficient to ensure the stability of the charge-density-wave state. The only difference between the TiAg_xSe_2 and $\text{Ti}_{1-x}\text{Cr}_x\text{Se}_2$ systems is that the silver atoms in the former compound are ordered in a superstructure identical to the superstructure formed as a result of the generation of the charge-density-wave state, whereas the chromium sublattice in the latter compound is completely disordered. Quite probably, it is this order or disorder in the guest sublattice that can be responsible for the stability of the charge-density-wave state. It should also be noted that similar superstructures were observed in compounds formed upon the intercalation of transition metals (such as iron, cobalt, and nickel) into the TiSe_2 diselenide [17]. However, to the best of our knowledge, data on the electrical properties that can be used to reveal the existence of a charge-density-wave state in these compounds are not available in the literature.

4. CONCLUSIONS

Thus, the temperature dependence of the electrical resistivity of $\text{Ti}_{1-x}\text{Cr}_x\text{Se}_2$ substitutional solid solutions can be completely described under the assumption that the localization of charge carriers has a semiconductor nature. No indication of the Anderson localization is revealed, even though the guest sublattice is disordered in the concentration range under investigation. It should be emphasized that the disturbing effect of impurities introduced into the titanium diselenide through substitution is stronger than the effect observed upon intercalation, because, in the former case, the impurities are embedded directly in a structural fragment responsible for the charge transfer in the material [18]. Upon intercalation, the impurities are embedded in the space between structural fragments and should produce a substantially weaker effect, all other factors being equal. Since the Anderson localization is not observed even in the case of a stronger disturbing effect, its role in the intercalation apparently cannot be significant. Therefore, the results obtained from band structure calculations based on regular structural models can be useful in interpreting the properties of materials even in the absence of a hypothetical order in the intercalant sublattice.

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