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**METALS  
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## Structure and Properties of the Intercalation Compound $\text{Cu}_x\text{TiSe}_2$

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**Abstract**—Compounds in the pseudobinary Cu–TiSe<sub>2</sub> intercalation system are directly synthesized from elements. The phase diagram of the system is investigated, the solubility limit of copper is measured, and the structure of the material is determined. In the copper concentration range up to 60 mol %, single crystals are grown and the temperature dependence of the electrical resistance is measured. It is demonstrated that, in the concentration range under investigation, the intercalation of the system with copper gives rise to a set of phenomena observed upon intercalation of alkali metals.

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### 1. INTRODUCTION

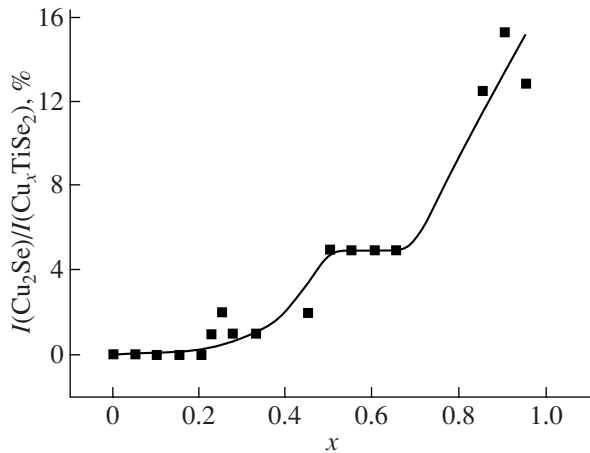
The recently discovered phenomenon of the coexistence of the state with charge density waves and superconductivity in the  $\text{Cu}_x\text{TiSe}_2$  system has aroused considerable interest in this material. Following the pioneering work by Morosan et al. [1], in all the subsequent studies performed in this field (see, for example, [2, 3]), it has been noted that the solubility of copper in the  $\text{Cu}_x\text{TiSe}_2$  system is restricted by the limited composition  $\text{Cu}_{0.11}\text{TiSe}_2$ . Such a low value of the limited solubility has no analogs among intercalation compounds of titanium dichalcogenides and should probably be caused by significant physical factors. In order to verify this result, we synthesized compounds in the Cu–TiSe<sub>2</sub> system and performed their structural investigation.

### 2. SAMPLES, EXPERIMENTAL TECHNIQUE, RESULTS, AND DISCUSSION

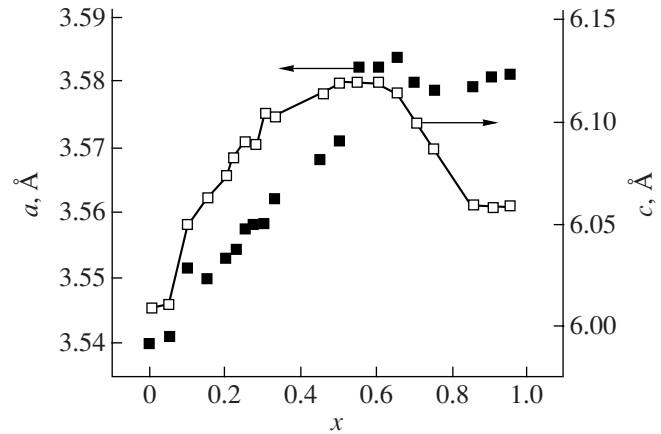
In contrast to the gas-transport reaction method employed in all the other works, we used the conventional tube synthesis as the main technique with ceramic samples prepared through the diffusion solid-phase intercalation of metallic copper into the preliminarily synthesized titanium diselenide  $\text{TiSe}_2$ . For intercalation of titanium diselenide, we used copper of the OSCh 11-4 grade with a purity of 99.99%. The intercalation reaction was carried out at temperatures of 450 and 950°C in evacuated (to a residual pressure of  $10^{-5}$  Torr) silica glass tubes. The copper granules used in the synthesis had a characteristic size of  $\sim 5 \times 2 \times 2$  mm. Apparently, it is because of such a large size of

copper granules that a homogeneous material could not be synthesized in one experiment despite the obviously high diffusion mobility of copper. For this reason, the samples were subjected to homogenization by means of grinding, mixing, pressing, and subsequent annealing at the same temperature. For the samples synthesized at a temperature of 950°C, this procedure was sufficient to obtain a visually homogeneous material. The material synthesized at a temperature of 450°C proved to be inhomogeneous and contaminated with  $\text{Cu}_2\text{Se}$ . The homogenization repeated many times led to a decrease in the content of the  $\text{Cu}_2\text{Se}$  phase. However, the complete removal of this phase was achieved only after performing at least three homogenization cycles. This effect has never been observed in materials intercalated by metals with a diffusion mobility substantially different from superionic values. Since the saturated vapor pressure of selenium over titanium diselenide is sufficiently high, the large coefficient of copper diffusion in both phases  $\text{TiSe}_2$  and  $\text{Cu}_2\text{Se}$  leads to the formation of a considerable amount of the foreign phase.

The characterization of the visually homogeneous samples was performed using the X-ray structural analysis (DRON-6 X-ray diffractometer,  $\text{CuK}_\alpha$  radiation, Fe filter). It should be noted that, despite the visual homogeneity of the synthesized material, the X-ray diffraction patterns of these samples do contain weak lines of the  $\text{Cu}_2\text{Se}$  phase. Figure 1 illustrates the variation in the content of this phase in the samples according to the estimates obtained from the intensity ratio of the most intense lines of the  $\text{Cu}_2\text{Se}(111)$  phase and the  $\text{Cu}_x\text{TiSe}_2(101)$  phase, which is isostructural with  $\text{TiSe}_2$ . Therefore, the actual copper content  $x$  in the  $\text{Cu}_x\text{TiSe}_2$



**Fig. 1.** Intensity ratio of the  $\text{Cu}_2\text{Se}(111)$  and  $\text{Cu}_x\text{TiSe}_2(101)$  lines as a function of the copper content  $x$  in the sample.



**Fig. 2.** Lattice constants of the  $\text{Cu}_x\text{TiSe}_2$  compound as a function of the copper content  $x$ .

compound is less than the nominal content by a value corresponding to the data presented in Fig. 1, because a part of the copper amount went to form the  $\text{Cu}_2\text{Se}$  phase.

For all the studied compounds, it has been established that the main phase is isostructural with titanium diselenide and has the lattice parameters dependent on the copper content in the sample. Therefore, this phase can be identified as  $\text{Cu}_x\text{TiSe}_2$ . The dependences of the lattice parameters  $a$  and  $c$  for the  $\text{Cu}_x\text{TiSe}_2$  compound on the copper content  $x$  specified in the weighed portions of the material under investigation are presented in Fig. 2. It can be clearly seen from this figure that, at a copper content  $x > 0.8$ , the lattice parameters become constant, which, obviously, indicates the copper solubility limit. This inference is well consistent with the observed drastic increase in the  $\text{Cu}_2\text{Se}$  content in the given range of copper concentrations (Fig. 1). It is clear that the  $\text{Cu}_2\text{Se}$  phase is formed from the undissolved copper which interacts with selenium of the vapor over the surface of the  $\text{Cu}_x\text{TiSe}_2$  phase.

Since the error introduced upon the formation of the  $\text{Cu}_2\text{Se}$  phase in the copper concentration range  $x < 0.8$  is considerably smaller than the change in the copper content specified in the synthesis (Fig. 1), the solubility of copper in  $\text{TiSe}_2$  substantially exceeds the copper concentration  $x = 0.11$  reported in [1]. It seems likely that this difference is associated with the different procedures used for the preparation of the samples. In [1], the intercalation of copper into the  $\text{TiSe}_2$  compound was performed using the gas-transport reaction method simultaneously with the growth of the crystals. In this case, copper chloride  $\text{CuCl}$  was used as a source of copper and a carrier gas (chlorine). It is evident that an increase in the copper content requires that the  $\text{CuCl}$  concentration be increased in the effective volume of the reactor. However, this increase leads to an increase in the chlorine partial pressure and, consequently, to a

shift in the equilibrium of the reaction  $\text{CuCl} + \text{TiSe}_2 = \text{Cu}_x\text{TiSe}_2 + \text{Cl}$  toward the left. Therefore, the solubility limit  $x = 0.11$  obtained using the gas-transport reaction method for synthesizing the titanium diselenide samples should be considered not as the equilibrium between metallic copper and  $\text{Cu}_x\text{TiSe}_2$  but as the equilibrium between the  $\text{CuCl}$  and  $\text{Cu}_x\text{TiSe}_2$  phases. The solubility limit obtained in our case corresponds to the equilibrium between the  $\text{Cu}_x\text{TiSe}_2$  phase and metallic copper.

It has been established that, over the entire range of copper solubility in  $\text{TiSe}_2$  (including the solubility limit at  $x = 0.8$ ) under investigation, the X-ray powder diffraction patterns of the titanium diselenide samples do not contain lines that can be attributed to ordering of copper in the lattice of the  $\text{Cu}_x\text{TiSe}_2$  compound. The concentration dependence of the lattice parameters of the  $\text{Cu}_x\text{TiSe}_2$  compound is characterized by an increase in the lattice parameter  $c_0$  at copper concentrations in the range  $x < 0.6$ . This behavior is characteristic of alkali metals that do not form covalent bonds with the host lattice. In this case, the intercalation is accompanied by transfer of valence electrons to the conduction band of  $\text{TiSe}_2$ , as a rule, without a noticeable distortion of the density of states in it. Evidently, this process should lead to an increase in the concentration of free charge carriers and, consequently, to an increase in the metallic conductivity. In order to verify this statement, we measured the temperature dependences of the electrical conductivity and the Hall constant for the  $\text{Cu}_x\text{TiSe}_2$  single crystals. The measurements were carried out for single-crystal samples along the basal plane of the crystals.

The crystals were grown using the gas-transport reaction method in the two main variants. First of all, the  $\text{Cu}_x\text{TiSe}_2$  single crystals were grown with the use of bromine as a carrier gas. For this purpose, copper bromide and the required amount of metallic copper were

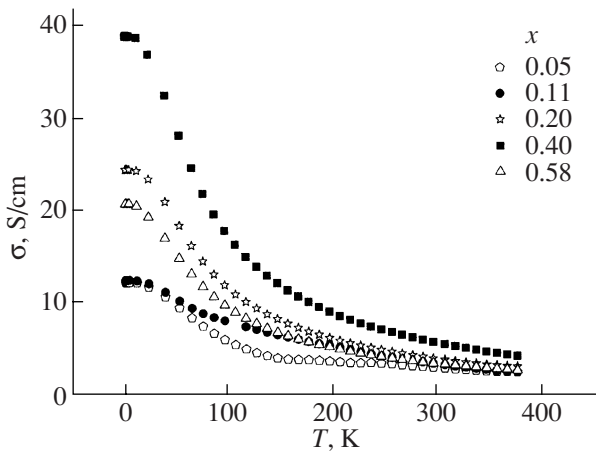


Fig. 3. Temperature dependences of the electrical conductivity of the  $\text{Cu}_x\text{TiSe}_2$  single crystals.

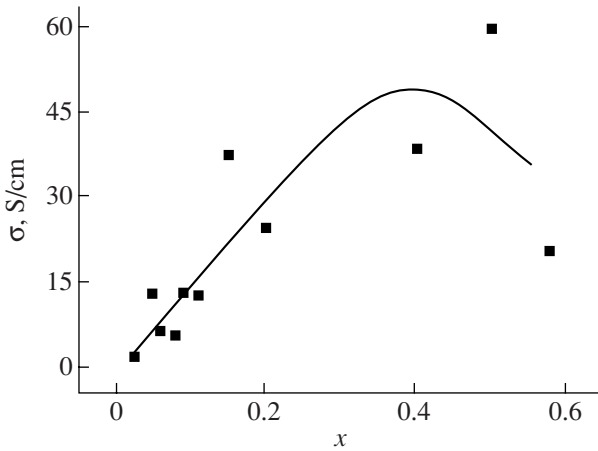


Fig. 4. Concentration dependence of the electrical conductivity of the  $\text{Cu}_x\text{TiSe}_2$  single crystals at a temperature of 1.6 K.

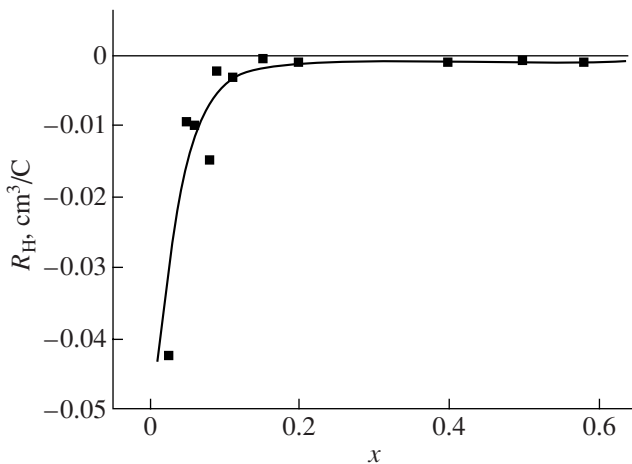
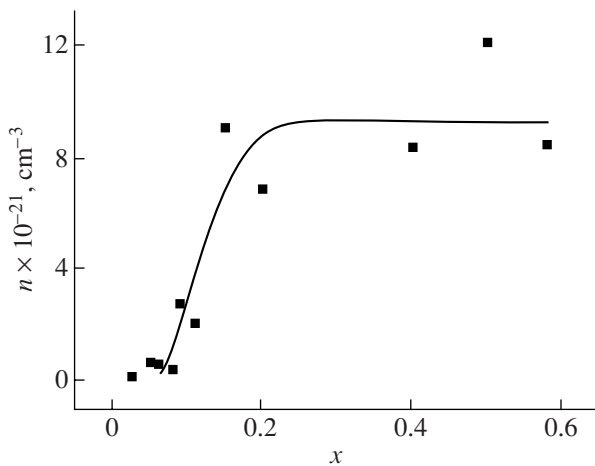


Fig. 5. Concentration dependence of the Hall constant of the  $\text{Cu}_x\text{TiSe}_2$  single crystals at a temperature of 1.6 K.

added to the silica glass tube with  $\text{TiSe}_2$ . The process occurs rather intensively even at low temperatures, such as  $400^\circ\text{C}$ , and makes it possible to obtain crystals  $5 \times 5 \times 0.01$  mm in size. At higher copper concentrations ( $x \sim 0.3$  and more), the growth of crystals is substantially retarded. Quite probably, this circumstance is associated with the fact that the high content of metallic copper leads to a decrease in the pressure of the carrier gas as a result of the binding of bromine. Consequently, we had to use the conventional growth method with iodine as a carrier gas for crystals with a high copper content. This method has been applied at temperatures of no lower than  $600^\circ\text{C}$  and has also made it possible to obtain sufficiently large crystals of high quality. The chemical composition of the crystals, as a rule, slightly differed from the composition of the batch and was determined using the electron microprobe analysis with a JEOL-733 microscope. The analysis has demonstrated that the content of the carrier gas in the grown crystals does not exceed 0.1 at % for the low-temperature method and lies outside the detection limits in the case of the crystal growth performed with the use of iodine at temperatures above  $600^\circ\text{C}$ . It should be noted that, during the low-temperature growth of the crystals, the material was transferred to the hot end of the tube, whereas the high-temperature variant of the crystal growth was accompanied by the transfer of the material to the cold end of the tube. This circumstance, together with different degrees of contamination of the crystals grown by these two methods, suggests that the crystal growth, quite possibly, can occur through different mechanisms. With these two methods, we succeeded in growing crystals at copper concentrations in the range  $0 < x < 0.58$ ; i.e., it is this range that almost completely coincides with the range of an increase in the lattice parameter  $c_0$  with increasing  $x$ .

The electrical conductivity was measured by the four-point probe method in the Montgomery geometry [5]. The results of the electrical conductivity measurements are presented in Figs. 3 and 4. It can be clearly seen from these figures that the electrical conductivity of the  $\text{Cu}_x\text{TiSe}_2$  single crystals exhibits a metallic behavior and increases with an increase in the copper content. These data are in good agreement with the conclusions regarding the donor character of copper in the  $\text{Cu}_x\text{TiSe}_2$  single crystals in the concentration range  $x \cong 0-0.6$ . The donor character of copper is also confirmed by the negative value of the Hall constant (Fig. 5). The direct evidence for the charge transfer from copper to the  $\text{TiSe}_2$  lattice is the dependence of the charge carrier concentration calculated from the Hall constant on the copper content  $x$  in the  $\text{Cu}_x\text{TiSe}_2$  single crystals (Fig. 6).

In the copper concentration range from 0.6 to 0.8, the lattice parameters are characterized by an unusual behavior; more specifically, the lattice undergoes compression in the direction of the normal to the basal plane of the crystal with an increase in the copper content. Such behavior is characteristic of materials in which



**Fig. 6.** Dependence of the charge carrier concentration calculated from the Hall constant at a temperature of 1.6 K on the copper content  $x$  in the  $\text{Cu}_x\text{TiSe}_2$  single crystals.

the intercalation leads to the formation of covalent centers that capture conduction electrons. As was shown earlier in [6], this situation can arise in the case where the hybrid  $4s$  Cu/ $3d$  Ti states of the Ti–Cu–Ti centers, which can act as traps of free charge carriers, on the one hand, and as centers of deformation of the lattice, on the other hand, are located slightly above the Fermi level in  $\text{TiSe}_2$ . Consequently, the occupation of these states begins to occur when the Fermi level reaches the bottom of the band of the impurity states. The Fermi level by itself increases as a result of transfer of copper electrons to the conduction band of  $\text{TiSe}_2$ , which has been indicated by direct measurements using angular resolution photoemission spectroscopy (ARPES) [7]. This inference could be verified by direct measurements of the electrical resistance of the samples; however, we have so far failed to grow single crystals of the required composition ( $x = 0.6$ – $0.8$ ). It should be noted that the concentration dependences of both the electrical conductivity and the charge carrier concentration in the vicinity of the composition with  $x = 0.6$  exhibit a tendency toward saturation or even toward decrease. This

confirms our assumptions, although the observed effect is very weak for convincing statements.

### 3. CONCLUSIONS

Thus, it has been established that the solubility of copper in titanium diselenide  $\text{TiSe}_2$  reaches 80 mol % and that, in the copper concentration range  $x < 0.6$ , the intercalation of the system with copper results in charge transfer to the conduction band of  $\text{TiSe}_2$ .

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