SEMICONDUCTORS
AND DIELECTRICS

Ordering of an Intercalated Impurity near the Temperature of Polaron Band Collapse in Ag$_x$TiTe$_2$

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Received June 6, 2000; in final form, September 15, 2000

Abstract—The phase diagram of an Ag$_x$TiTe$_2$ intercalation compound near the temperature of polaron band collapse is studied by x-ray structure analysis. The results obtained confirm the assumption made earlier that, at temperatures close to the polaron band collapse point, a homogeneous state cannot exist in the charge carrier concentration range in which the Fermi level lies between the bottom and the center of an impurity band. The reversible transition accompanied by ordering of intercalated silver is revealed upon heating to a temperature close to the polaron band collapse point. This transition is explained by the enhancement of Coulomb repulsion between impurity atoms due to the localization of charge carriers. © *2001 MAIK "Nauka/Interperiodica".*

1. INTRODUCTION

Intercalation of transition metals and silver into titanium diselenide and titanium ditelluride leads to localization of charge carriers in the form of polarons of a small radius [1]. This circumstance, as applied to the phase diagram, imposes certain limitations on the possibility of forming a single-phase state in the carrier concentration range in which the following condition is met: $E_L < E_F < E_d$, where E_L is the energy at the bottom of the polaron band, E_F is the Fermi energy, and E_d is the energy at the center of the polaron band [2]. This condition is important in the case when the polaron band lies above the Fermi level of the initial material and is fulfilled when silver serves as an intercalant [3]. The possibility of forming a single-phase state is restricted by the dominant contribution of the electronic subsystem to the thermodynamic functions of a material. However, the deviation from the temperature of polaron band collapse, for example, upon cooling, leads to a nearly exponential decrease in the density of states in the polaron band [4] and, hence, an equally rapid decrease in the contribution of the electronic subsystem to the total thermodynamic functions of a material. This suggests that, below the temperature of polaron band collapse, there is a certain temperature below which the criterion restricting the possibility of forming the single-phase state becomes invalid. Therefore, these materials should undergo a transition from a homogeneous (single-phase) state of the solid solution type (whose boundaries are determined by the interaction of intercalant ions) to an inhomogeneous (non-single-phase) state as the temperature of a maximum localization is approached. Moreover, it can be expected that the localization of electrons should provide an increase in the Coulomb repulsion between the

centers of charge localization and, as a consequence, an ordering of these centers in approximately the same temperature range. It is clear that the above phenomena can be observed only in materials in which the mobility of the ionic subsystem is high enough for relaxation processes in the intercalant lattice to take a reasonable time.

In order to verify these assumptions, we undertook an x-ray structure investigation of the Ag$_x$TiTe$_2$ system (which satisfies the above criteria) in the range from room temperature to a temperature well above the polaron band collapse point.

According to the phase diagram, which was obtained using an electrochemical method in our earlier work [5] (Fig. 1), the Ag$_x$TiTe$_2$ system has no single-
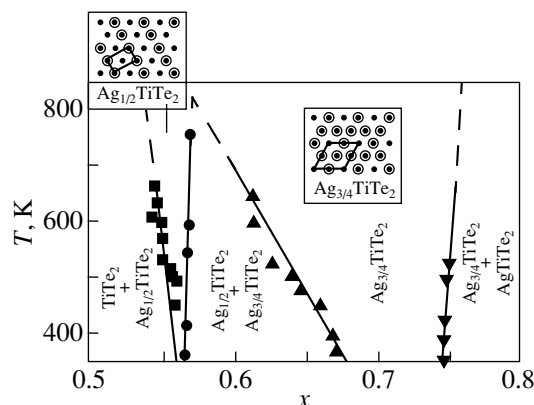

Fig. 1. High-temperature part of the phase diagram of the Ag$_x$TiTe$_2$ system. Insets show the ordering of silver in the corresponding phases.
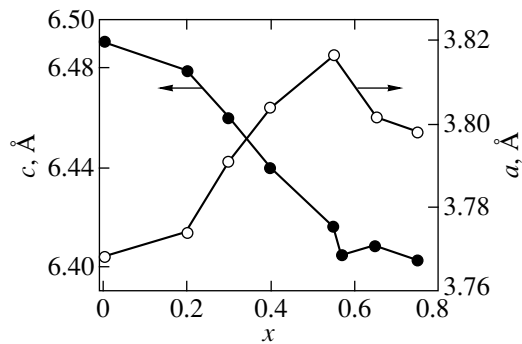
Fig. 2. Concentration dependences of the unit cell parameters of Ag_xTiTe_2 samples after slow cooling and prolonged storage at room temperature.

phase region at temperatures above 150°C at any silver concentrations as small as one likes. Upon intercalation, the conductivity decreases by almost a factor of 1000 and exhibits an activation character [5]. The host lattice layers approach each other due to intercalation [3], and a relative decrease in the conductivity as a function of the relative deformation is described by a relationship typical of other intercalation materials based on titanium dichalcogenides with a polar type of charge carrier localization [1]. The concentration dependence of the conductivity is well represented in the framework of the percolation theory by assuming the presence of Ti–Ag–Ti localized centers that form the sublattice in which polarons of a small radius can occur [6]. Taken together, these observations allow us to conclude that the intercalation of silver into titanium ditelluride brings about the formation of polarons. In this case, the polaron band lies somewhat higher than the Fermi level of the initial material and an increase in the intercalant concentration makes it possible to raise the Fermi level to energies above the top of the polaron band [3].

At the same time, as follows from the x-ray diffraction investigation of Ag_xTiTe_2 samples ($0 < x < 0.5$) which were slowly cooled and stored for a long time at room temperature and, according to [5], corresponded to a mixture of $TiTe_2$ and $Ag_{1/2}TiTe_2$ phases, their x-ray diffraction patterns at this temperature coincide with those of $TiTe_2$. Moreover, the unit cell parameters are found to be monotonic functions of the silver content at $x < 0.65$ (Fig. 2). These findings indicate that the material thus prepared involves only one phase and rule out the assumption made earlier that the second phase can exist in the form of inclusions undetectable by x-ray diffraction. Upon rapid cooling, the phases with ordered silver, which were found in [5] (see Fig. 1), are retained for a few days. Thus, it can be inferred that the polaron band collapse temperature near which the criterion restricting the possibility of forming a single-phase state becomes true [2] lies between room temperature and a temperature of 150°C above which the phase diagram was studied.

The aim of the present work was to elucidate the influence of the polaron band collapse on the possible ordering of polarons associated with impurity centers and on the phase diagram of Ag_xTiTe_2 at different positions of the Fermi level with respect to the polaron band. For this purpose, we investigated the structure of $Ag_{0.3}TiTe_2$, $Ag_{0.55}TiTe_2$, $Ag_{0.57}TiTe_2$, $Ag_{0.65}TiTe_2$, and $Ag_{0.75}TiTe_2$ samples in the temperature range 20–400°C. The location of the Fermi level with respect to the polaron band was evaluated from the following considerations. The $Ag_{0.3}TiTe_2$ composition at temperatures above 150°C falls in the two-phase region and, hence, should meet the condition $E_L < E_F < E_d$ [2]. Among single-phase compositions at temperatures above 150°C, the $Ag_{0.55}TiTe_2$ and $Ag_{0.57}TiTe_2$ samples are least enriched with silver and, as a consequence, should satisfy the condition $E_F \approx E_d$ [2]. For the $Ag_{0.75}TiTe_2$ sample at temperatures above the transition at 130–150°C, the conductivity remains metallic and the Seebeck coefficient retains the negative sign (*n*-type conductivity). In [3], these findings were interpreted by the filling of the impurity band and the shift of the Fermi level to the range of nonlocalized states. Therefore, the condition $E_F > E_h$ is satisfied for this sample. The $Ag_{0.65}TiTe_2$ composition is intermediate between $Ag_{0.57}TiTe_2$ and $Ag_{0.75}TiTe_2$, and, hence, should meet the condition $E_d < E_F < E_h$. Here, E_F is the Fermi level and E_L, E_h, and E_d are the energies at the bottom, top, and center of the polaron band, respectively.

2. EXPERIMENTAL TECHNIQUE

Samples used in this work were prepared by the standard pulse synthesis. The techniques of preparation and characterization were described in detail in [5]. The sample compositions lying in the single-phase region at temperatures above 150°C were electrochemically checked using the calibration curves obtained earlier in [3, 5]. X-ray powder diffraction analysis of the $Ag_{0.57}TiTe_2$ sample was performed on a STOE diffractometer ($CuK_{\alpha1}$ radiation, Ge monochromator, transmission mode, 5°-linear-response position-sensitive detector, $2\theta = 2°–80°$). The sample was placed in an evacuated capillary 1 mm in diameter, and the measurements were carried out in a high-temperature chamber. The $Ag_{0.30}TiTe_2$ and $Ag_{0.55}TiTe_2$ samples were investigated with a DRON-3.0 x-ray instrument (CuK_{α} radiation, Ni filter, $2\theta = 22°–60°$) in a GPVT-1500 high-temperature chamber under vacuum (10^{-4} Torr). The high-temperature x-ray diffraction study of the $Ag_{0.65}TiTe_2$ and $Ag_{0.75}TiTe_2$ samples was performed using synchrotron radiation (position-sensitive detector, monochromator selecting a synchrotron radiation wavelength $\lambda = 1.9373$ Å, interplanar distances $d = 1.6–3.6$ Å) in a GPVT-1500 high-temperature chamber (VÉPP-3, Bud-

ker Institute of Nuclear Physics, Siberian Division, Russian Academy of Sciences). Prior to measurements, samples were allowed to stand at a specified temperature for 30 min. The data obtained for all the samples with the use of different instruments and radiation wavelengths demonstrate similar characteristic features in the temperature evolution, which suggests the comparability of these results.

3. RESULTS AND DISCUSSION

The x-ray diffraction patterns of the aforementioned samples at different temperatures and the temperature dependences of the unit cell volume are shown in Figs. 3 and 4, respectively.

For the $Ag_{0.3}TiTe_2$ sample, it is seen that heating leads to the appearance of additional lines which correspond to the superstructure $2a_0 \times 2a_0 \times c_0$ (the phase with a structure of the $Ag_{3/4}TiTe_2$ type [5]), are observed in the temperature range 50–130°C, and disappear upon further heating. The repetition of heating–cooling cycles demonstrated that the order–disorder transition is reversible but requires a prolonged holding (about a week) of the sample at room temperature. The temperature dependence of the unit cell parameters shows a wide scatter in the data in the range of ordering due to a drastic increase in the linewidths in this temperature range. As a consequence, because of the low accuracy of x-ray diffraction data, we could not answer the question as to whether the additional reflections correspond to the precipitation of another phase and the ordering of silver throughout the sample. However, the last assumption seems more probable, because the formation of the $2a_0 \times 2a_0$ superstructure in the case when intercalant atoms occupy an octahedral set of sites in the van der Walls gap becomes possible at a silver content $x = 0.25$, which is close to the silver content in the given sample. On the other hand, according to the electrochemical data, the material under investigation is two-phase when heated above 150°C. The localization of conduction electrons upon heating leads not only to an increase in the contribution of the electronic subsystem to the total thermodynamic functions but also to the enhancement of the Coulomb repulsion between the localization centers associated with intercalated silver. Therefore, it can be assumed that there is a temperature range in which the localization has already been sufficient for the ordering of these centers but insufficient for the phase decomposition through the mechanism proposed in [2].

In the case of $Ag_{0.55}TiTe_2$, the superstructure lines that correspond to the ordering of the $a_0 \times a_0\sqrt{3} \times c_0$ superstructure are observed even at room temperature. On the other hand, the data on the unit cell parameters of this sample fit well in the concentration dependence. This implies that the ordering stems most likely from an insufficient treatment of the sample at room temperature rather than from the stability of this superstruc-

ture. For this sample, as for $Ag_{0.3}TiTe_2$, the heating to temperatures in the range 100–110°C leads to a sudden appearance of the lines which are indexed in the $2a_0 \times 2a_0 \times c_0$ superstructure and disappear with further heating. Upon heating above 120°C, we can see only the lines of the $a_0 \times a_0\sqrt{3} \times c_0$ superstructure (the $Ag_{1/2}TiTe_2$ phase in Fig. 1) in complete agreement with the high-temperature part of the phase diagram.

For the $Ag_{0.57}TiTe_2$ sample, no lines differing from the lines of $TiTe_2$ are observed at room temperature. This agrees well with the data for $Ag_{0.3}TiTe_2$ and suggests that the presence of the superstructure in $Ag_{0.57}TiTe_2$ is, most likely, an artifact and that the ordering of silver at room temperature can be achieved only through the ion–ion interaction.

The superstructure lines attributed to $Ag_{0.57}TiTe_2$ appear upon heating to approximately the same temperature as for the other samples; however, the further structural evolution is much more complex. Upon heating to 150°C, we observe the lines of the $a_0 \times a_0\sqrt{3} \times c_0$ superstructure (the $Ag_{1/2}TiTe_2$ phase in Fig. 1) in complete agreement with the high-temperature part of the phase diagram. With further heating to temperatures above 300°C, apart from these lines, we can see the lines corresponding to the $2a_0 \times 2a_0 \times c_0$ superstructure (the $Ag_{3/4}TiTe_2$ phase in Fig. 1). In the phase diagram, this corresponds to the region of a mixture of the $Ag_{1/2}TiTe_2$ and $Ag_{3/4}TiTe_2$ phases. Then, upon heating to 400°C, the lines of the $Ag_{1/2}TiTe_2$ phase disappear, which is associated with the transition to the $Ag_{3/4}TiTe_2$ phase in the single-phase region. The lines of this phase remain stable up to the highest temperatures and exhibit only a gradual thermal broadening.

For the $Ag_{0.65}TiTe_2$ sample, the superstructure lines indexed under the assumption of the $2a_0 \times 2a_0 \times c_0$ superstructure are observed even at room temperature. However, the heating to 130°C leads to a structural transformation responsible for a weakening of the (002) reflection, which completely disappears at 200°C. This can indicate that the $2a_0 \times 2a_0 \times c_0$ ordering gives way to the $2a_0 \times 2a_0 \times 2c_0$ ordering with the same initial space group $P\bar{3}m1$. Apparently, this transition is associated with the orientational ordering of $2a_0 \times 2a_0 \times c_0$ planar networks in the sequence $ABABAB$, where A and B are one of the four possible sets of vacant octahedral sites ordered according to the $2a_0 \times 2a_0$ motif. The same tendency is observed for $Ag_{0.57}TiTe_2$ samples above 400°C and for the $Ag_{0.75}TiTe_2$ sample in a limited temperature range near 100°C (Fig. 3).

The temperature dependence of the unit cell volume for samples with silver contents $x = 0.65$ and 0.75 exhibits a small minimum at a temperature of ~120°C, which corresponds to the ordering with twice the c period. The unit cell volume of the sample with $x = 0.57$
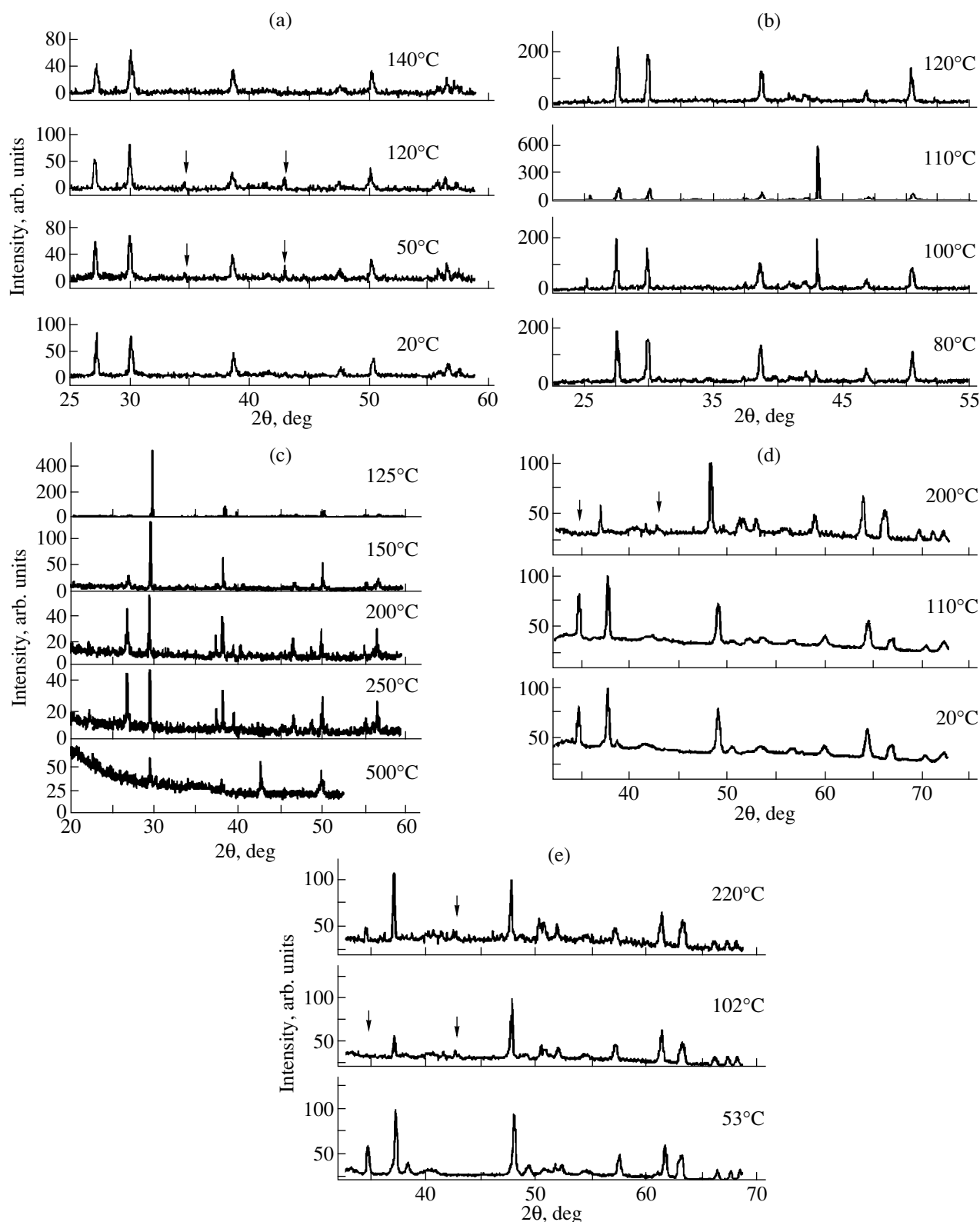
Fig. 3. Fragments of experimental x-ray diffraction patterns obtained at characteristic temperatures for (a) $Ag_{0.3}TiTe_2$, (b) $Ag_{0.55}TiTe_2$, (c) $Ag_{0.57}TiTe_2$, (d) $Ag_{0.65}TiTe_2$, and (e) $Ag_{0.75}TiTe_2$ samples. Arrows indicate the positions of additional reflections associated with the ordering of silver near the polaron band collapse temperature. Conditions: (a, b) $Cu\,K_{\alpha}$ radiation, (c) $Cu\,K_{\alpha_1}$ radiation, and (d, e) synchrotron radiation at the wavelength $\lambda = 1.9373$ Å.
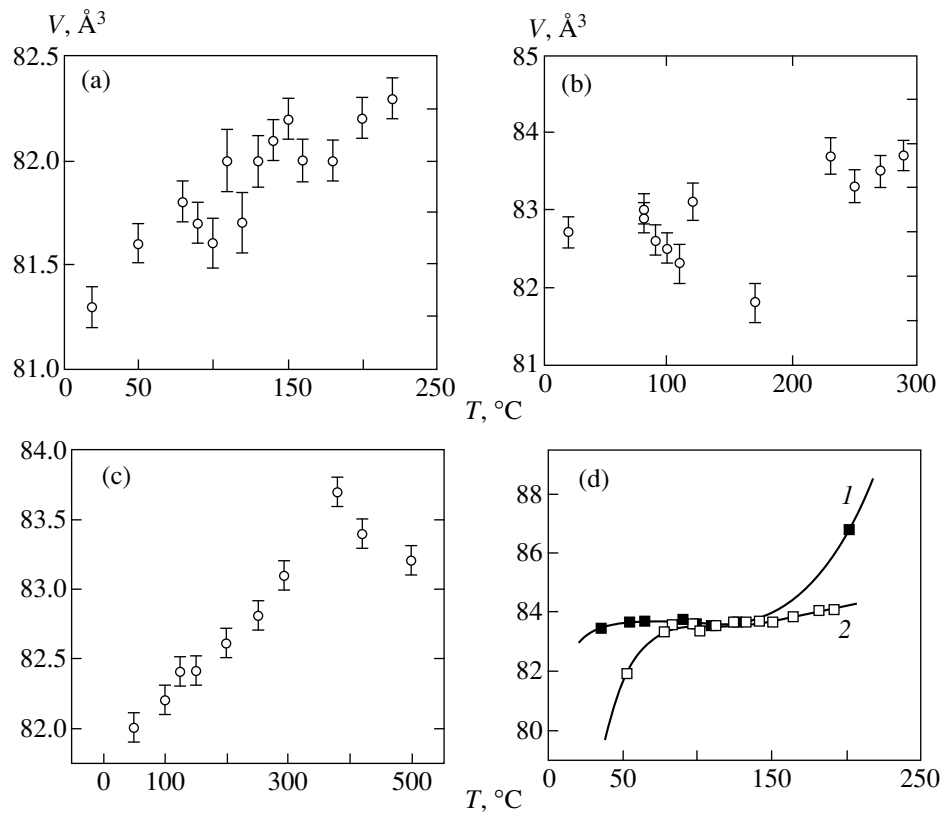
Fig. 4. Temperature dependences of the unit cell volume for Ag_xTiTe_2 without regard for a multiple increase in the parameters due to silver ordering: (a) $Ag_{0.3}TiTe_2$, (b) $Ag_{0.55}TiTe_2$, (c) $Ag_{0.57}TiTe_2$, and (d) (1) $Ag_{0.65}TiTe_2$ and (2) $Ag_{0.75}5TiTe_2$.

decreases with an increase in temperature above the ordering temperature. The temperature dependence of the unit cell volume for the sample with $x = 0.55$ has a minimum at $T \sim 170°C$. Since the formation of polarons in intercalation materials based on titanium dichalcogenides is usually accompanied by the lattice contraction, the coincidence of temperatures that correspond to the minimum volume and the onset of the ordering confirms the assumption made earlier about the polaron nature of the ordering. The absence of these anomalies in similar dependences for samples with a smaller silver content ($x = 0.33$) can be explained by the separation into phases with different silver contents, which results in a large width of x-ray lines and considerably decreases the accuracy in the determination of lattice parameters.

Therefore, the experimental data on the temperature evolution of the Ag_xTiTe_2 structure are in good agreement with the results of electrochemical investigations into the high-temperature part of the phase diagram for this material [5].

Note that the ordering temperature and the temperature of a minimum in the temperature dependence of the unit cell volume are close to the temperature of the metal–semiconductor transition found in [3] at which the material acquires semiconductor properties upon heating. This allows us to assume that these transitions

have the same origin. The coincidence of the high-temperature parts of the phase diagrams obtained by electrochemical and x-ray diffraction methods with substantial differences in the low-temperature parts makes it possible to attribute this transition to the polaron band collapse. Then, the ordering can be ascribed to the localization of electrons on Ti–Ag–Ti centers and its attendant increase in the Coulomb repulsion between these centers. This assumption is in good agreement with the occurrence of an ordered state in a relatively narrow temperature range at low silver concentrations ($Ag_{0.3}TiTe_2$), because the deviation from the polaron band collapse point toward both the high-temperature and low-temperature ranges leads to a broadening of the polaron band and a decrease in the degree of localization of charge carriers. It should be noted that, for materials with $E_d < E_F$, the electronic contribution to the total entropy of the material upon polaron band collapse becomes positive and stabilizes the ordered state [2]. Thus, an increase in the stability of the ordered state with an increase in the silver concentration can be explained by the change in the contribution of the electronic subsystem to the total thermodynamic functions of the material and an increase in the strength of the conventional ion–ion interaction. For $Ag_{0.55}TiTe_2$ and $Ag_{0.57}TiTe_2$ ($E_F \approx E_d$), the contribution of the electronic subsystem to the total thermodynamic functions is

close to zero [2]. Therefore, the onset of the ordering upon heating can be explained only by the enhancement of Coulomb repulsion between Ti–Ag–Ti centers due to the localization of electrons, whereas the other structural transitions occur in accordance with the high-temperature phase diagram and can be interpreted in the framework of the purely ionic model. For samples with compositions lying in the homogeneity region of the $Ag_{3/4}TiTe_2$ phase, the ordering at room temperature can be associated with the usual interaction between intercalated silver ions. This explains its stability over the entire temperature range covered. However, an anomaly of the unit cell volume in the form of a minimum in its temperature dependence and an additional ordering toward the normal to the basal plane are observed in the range of the metal–semiconductor transition which is attributed to the polaron band collapse. It seems likely that this effect should be caused by the enhancement of the Coulomb repulsion between the Ti–Ag–Ti centers (polarons) of electron localization.

It is worth noting that the lattice contraction toward the normal to the basal plane, which is observed already at room temperature (Fig. 2), suggests that the phase diagram of Ag_xTiTe_2 even in its lowest-temperature part is determined not only by pure ionic interactions but is also due to a weak localization of conduction electrons.

4. CONCLUSION

Thus, the enhancement of the Coulomb repulsion at temperatures near the polaron band collapse point can impose certain limitations on the possibility of forming a single-phase state through the condition $E_d < E_F$ and leads to the ordering of polarons formed in this case and, hence, to the appearance of an additional gap in the density of states. In the case of Ag_xTiTe_2, the crossover to the activation conductivity is observed at the ordering temperature with a simultaneous increase in the magnitude of the Seebeck coefficient and the change in its sign [3], which can indicate the gap formation at the Fermi level. On the other hand, the difference between the relaxation time of the electronic properties and the decay time of the ordered state upon cooling to room temperature is very large: the conductivity and the thermopower reach their equilibrium values after holding at room temperature for several hours, whereas the time it takes for the ordering to break down completely is as much as several days. Thus, the problem of the band nature remains unresolved and calls for further investigation.

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Translated by O. Borovik-Romanova