
DEFECTS AND IMPURITY CENTERS, DISLOCATIONS, AND PHYSICS OF STRENGTH

Fast Ionic Transport in Ag_xTiS_2

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Abstract—The enthalpy of the subsystem of silver ions in the intercalation compounds Ag_xTiS_2 has been calculated from the electrochemically measured thermodynamic functions of the silver subsystem. The ionic conductivity and the coupled chemical diffusion coefficients for silver in the intercalation compound have been measured. The activation energy for diffusion of silver ions is determined and the obtained value is interpreted from analyzing the concentration dependence of the enthalpy of the ionic subsystem. The conclusion has been drawn that the high diffusion mobility is associated with the competition between the covalent and elastic interactions, which decreases the activation energy for diffusion of ions.

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1. INTRODUCTION

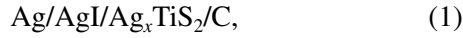
Superionic conductors have attracted the particular attention of researchers for a long time owing to their high atomic mobility, a property characteristic of liquids or even gases rather than solid materials. It is generally believed that conditions responsible for the manifestation of the superionic state are associated with the structural features of the material, namely, the presence of a large number of equivalent positions, which are accessible for mobile ions, and their connectivity [1]. However, the example of intercalation compounds of titanium dichalcogenides, many of which exhibit a high diffusion mobility of the intercalant and, consequently, have found a wide practical application in electronic devices, has clearly demonstrated that the aforementioned conditions are rather limited. Actually, the majority of the intercalated atoms occupy the same positions, which are octahedrally coordinated by the chalcogen [2]. Therefore, the number of such positions and their connectivity are identical for these materials, whereas the corresponding diffusion mobilities differ dramatically. Although the available experimental works on the determination of the diffusion coefficient have not embraced the majority of intercalation compounds, its value can be estimated from a comparison of the times necessary for the attainment of the homogeneous state upon homogenizing (repeated) annealing in the process of intercalation. During primary annealing, the significant role can be played by hindrances at the boundary between the intercalated metal and the titanium dichalcogenide. After homogenizing annealing, the intercalated component is uniformly distributed throughout the sample. The homogeneous state in the Ag-TiSe_2 system has been attained for 0.5 h at a tem-

perature of 200°C [3], whereas the analogous result, for example, in the Co-TiSe_2 system, requires a 100-h annealing at a temperature no lower than 800°C [4]. By assuming that the temperature dependence of the diffusion coefficient has an Arrhenius form and ignoring the difference in the preexponential factors and the scatter in the grain sizes, which are the parameters determining the diffusion length, we find that the diffusion mobilities of cobalt and silver ions differ by a factor of $\sim 10^6$, even though the structures of the host lattices and the types of occupied positions are completely identical.

It is obvious that the decisive role in the diffusion mobility of the intercalant is played by the nature of interaction between the mobile ion and the host lattice. Apparently, the determination of the character of this interaction and its relation to the diffusion parameters in intercalation compounds can shed light on the nature of the superionic state as a whole. The present study is devoted to the determination of the character of the interactions occurring in the sublattice of mobile ions in the Ag-TiS_2 system, which is here used as an example, in order to elucidate the role of different contributions to the diffusion mobility of silver ions. For this purpose, the ionic conductivity in the broadest single-phase region of the Ag_xTiS_2 system was measured as a function of the silver concentration and temperature. The character of interactions in the silver sublattice was determined from the analysis of the thermodynamic functions of the ionic subsystem, which, in turn, were found from the electrochemical experiment.

2. SAMPLES AND EXPERIMENTAL TECHNIQUE

The thermodynamic functions were determined by the electromotive force method with the use of electrochemical cells [5] containing AgI as a solid electrolyte. The measuring cell had the form



where AgI is the solid electrolyte with silver ionic conductivity and C is the graphite electrode. The electromotive force E of this electrochemical cell can be written in the following form [5]:

$$eE = -(\mu_{\text{Ag}} - \mu_{\text{Ag}}^{\text{Ag}}), \quad (2)$$

where E is the electromotive force of electrochemical cell (1); e is the elementary charge; and $\mu_{\text{Ag}}^{\text{Ag}}$ and μ_{Ag} are the chemical potentials of the silver atom in bulk metallic silver and in the Ag_xTiS_2 compound, respectively. Then, the entropy S and the enthalpy H , with allowance made for the relationship $\mu = H - TS$, can be represented by the following expressions:

$$\begin{aligned} S_{\text{Ag}} - S_{\text{Ag}}^{\text{Ag}} &= e \left[\frac{\partial E}{\partial T} \right]_x, \\ H_{\text{Ag}} - H_{\text{Ag}}^{\text{Ag}} &= eT \left[\frac{\partial E}{\partial T} \right]_x - eE, \end{aligned} \quad (3)$$

where S_{Ag} and H_{Ag} are the entropy and the enthalpy of silver atoms in the compound, respectively; and $S_{\text{Ag}}^{\text{Ag}}$ and $H_{\text{Ag}}^{\text{Ag}}$ are the entropy and the enthalpy of silver atoms in bulk metallic silver, respectively. All these functions are calculated per silver atom. The subscript x indicates the constancy of the intercalant concentration. By determining the concentration and temperature dependences of the electromotive force of electrochemical cell (1), it is possible to obtain the thermodynamic functions of the subsystem of intercalated atoms. The posed problem of the determination of the character of the interaction occurring in the ionic subsystem requires the separation of the thermodynamic functions for silver ions rather than for atoms. In the pure ionic approximation, the chemical potential μ_{Ag} can be considered as the additive sum of the electronic and ionic contributions; that is,

$$eE = (\mu_{\text{Ag}}^{\text{Ag}} - \mu_{\text{Ag}}) = (\mu_{\text{Ag}}^e + \mu_{\text{Ag}}^i - \mu_e - \mu_i), \quad (4)$$

where μ_{Ag}^e and μ_{Ag}^i are the chemical potentials of electrons and ions in metallic silver, respectively; and μ_e and μ_i are the chemical potentials of electrons and ions in the compound, respectively.

It is obvious that, by using only the data on the electromotive force of electrochemical cell (1), it is impossible to separate unambiguously the thermodynamic functions of the ionic and electronic subsystems. For

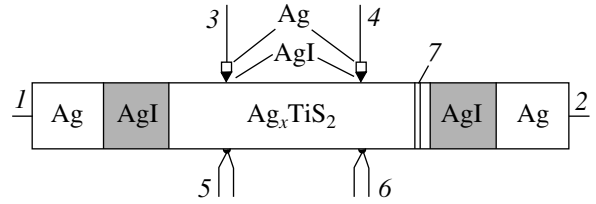


Fig. 1. A cell for the measurement of the ionic conductivity and the coupled chemical diffusion coefficients for the Ag_xTiS_2 compounds.

the Ag_xTiS_2 intercalation compounds, the situation is simplified because the chemical potential of the electronic subsystem as a function of the temperature and the electron concentration was calculated in our previous study [6]. In this case, the experimental dependences of the Seebeck coefficient, the magnetic susceptibility, and the plasma frequency were used as the initial data. Therefore, the thermodynamic functions of the subsystem of silver ions can be determined as the difference between the corresponding functions for the subsystem of silver atoms and the electronic subsystem. The results obtained in [6] have demonstrated that the concentration dependences of the electronic properties can be described by assuming that silver atoms are completely ionized upon intercalation, which exactly corresponds to the ionic approximation.

The preparation of Ag_xTiS_2 samples and the procedure used for measuring the electromotive force of electrochemical cell (1) were described in detail in [7]. The lattice constants of the material were determined using the X-ray diffraction analysis (DRON 4-13 X-ray diffractometer, $\text{CuK}\alpha$ radiation, Ni filter) at room temperature. The results obtained are in good agreement with the data available in the literature.

The dc ionic conductivity σ_i was measured by the Wagner method in the cell depicted in Fig. 1. The ion current was passed between contacts 1 and 2. In the steady state, the silver ion current is described by the Wagner formula

$$j_i = -\frac{\sigma_i}{e_i} (\nabla \mu_i + e_i \nabla \varphi), \quad (5)$$

where $\nabla \varphi$ and $\nabla \mu_i$ are the gradients of the electrical and chemical potentials of silver ions, respectively. The electrical potential difference measured by electrochemical probes 3 and 4 (Fig. 1) is determined by the difference between the electrochemical potentials of silver ions:

$$e\Delta U_i = \eta_4^i - \eta_3^i, \quad (6)$$

where η_i is the electrochemical potential of silver ions ($\eta_i = \mu_i + e\varphi$). After the electric current is switched off, the residual difference between the electrochemical potentials of ions is provided by the residual gradient of

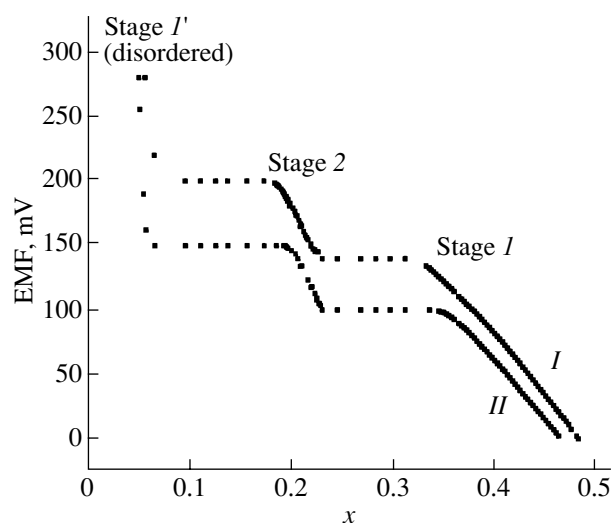


Fig. 2. Concentration dependences of the electromotive force (EMF) of the Ag/AgI/Ag_xTiS₂/Pt cell at temperatures of (I) 300 and (II) 200°C. The inclined portions of the curves correspond to single-phase regions (designated near the corresponding portions), and the “plateau” portions correspond to regions with a mixture of phases (the first-order phase transition).

their concentration. The process of equalization of the concentration is described by the second Fick’s law. The solution to the corresponding equation under the aforementioned initial and boundary conditions in the long-time limit can be represented in the form [8]

$$\ln(\Delta n(t)) = -\frac{\pi^2 \tilde{D}t}{L^2}, \quad (7)$$

where Δn is the difference in the concentrations between the observation points, L is the diffusion length, \tilde{D} is the coupled chemical diffusion coefficient, and t is the time (in seconds). In the case where the electronic conductivity considerably exceeds the ionic conductivity, the electrochemical potentials in relationship (6) can be replaced by the chemical potentials [8]. These chemical potentials and the potential measured by electrochemical probes 3 and 4 (Fig. 1) are related by expression (2). The dependence of the electromotive force of the ionic probes on the concentration of silver atoms is determined from the experiment [7]. After the sample attained a steady state, the voltage drop was measured by electrochemical probes 3 and 4, which made it possible to control the composition of the sample in two cross sections. Moreover, these probes were used for controlling the temperature in the cross sections of measurements. The coupled chemical diffusion coefficients were also calculated from the Nernst–Einstein formula with the use of the experimental values of the ionic conductivity σ_i under the assumption that all silver ions are equally involved in the transport processes.

The electrical measurements were performed under isothermal conditions where the temperature gradient between probes 3 and 4 did not exceed 1 K. In order to prevent the degradation of the samples, all measurements were carried out in the nitrogen atmosphere preliminarily dried and purified from oxygen. The residual oxygen pressure was determined from the temperature of the reduction of copper oxide to metallic copper and did not exceed 10^{-15} Torr. The ion current amounted to 10–100 μ A and was stabilized with an accuracy of no worse than 5%. The electromotive force of the ionic probes was measured accurate to within ± 1 mV. The temperature was recorded with an accuracy of ± 0.1 K and maintained constant to within ± 1 K.

For the diffusion measurements, the samples were prepared in the form of polycrystalline cold-pressed TiS₂ parallelepipeds $30 \times 5 \times 2$ mm in size. After pressing, the samples were annealed in order to remove the possible pressing texture and to improve contacts between grains. Silver was electrochemically introduced into the samples by passing electric current through contacts 1 and 7. The composition of the sample was also varied by passing a current pulse of required width and polarity through contacts 1 and 7 without a recharging of the measuring cell.

3. RESULTS AND DISCUSSION

3.1. Thermodynamics of the Subsystem of Mobile Ions

The dependences of the electromotive force of electrochemical cell (1) on the silver content x in the Ag_xTiS₂ compounds at temperatures of 200 and 300°C are plotted in Fig. 2. According to relationship (2) and the Gibbs phase rule, the inclined portions of the curves correspond to single-phase regions (designated near the corresponding portions) and the “plateau” portions between them correspond to regions with a mixture of phases. The behavior of the dependence $E(x)$ is in agreement with the data available in the literature [9]. The single-phase regions correspond to intercalation stages 1', 2, and 1.

The temperature dependences of the electromotive force of electrochemical cell (1) for stages 1 and 2 allow us to construct the boundaries of single-phase regions in the T – x plane with a high accuracy. The form of the boundaries of single-phase regions was discussed in our previous paper [7], where we made the inference that the main factor responsible for their positions is the elastic interaction of the intercalant with the host lattice.

From the viewpoint of the posed problem, among the thermodynamic functions, the enthalpy of the ionic subsystem is of primary interest. This enthalpy is determined by the interactions with the participation of mobile ions. The temperature dependences of the electromotive force of electrochemical cell (1) allow us to calculate the entropy of the intercalant subsystem. By using the entropy obtained for the electronic subsystem

in [6], it is easy to calculate the concentration dependence of the entropy of the ionic subsystem. These data are of independent interest and will not discuss in the present paper. However, they were used for calculating the enthalpy of the ionic subsystem according to formulas (2)–(4).

The character of the interactions occurring in the sublattice of mobile ions is conveniently interpreted within the framework of the lattice gas model [10]. In this approximation, the specific enthalpy has the following form:

$$H_{\text{Ag}} = H_0 - \frac{\lambda n}{2}, \quad (8)$$

where H_0 is the enthalpy upon the interaction of the ion with the lattice (which is the rigid framework in the case of superionic materials or the host lattice in the case of intercalants), the term $\lambda n/2$ describes the interaction in the sublattice of mobile ions, n is the concentration of the mobile ions, and λ is the ion–ion interaction constant. It is evident that, in order to correctly apply relationship (8) to our calculations, it is necessary to determine the nature of the interaction in the sublattice of mobile ions. It is customary to take into account two contributions, i.e., the Coulomb repulsion of likely charged ions and their interaction with each other through fields of elastic lattice distortions. To date, a large number of works have been published in which the above interactions are differently taken into account. The review of these publications can be found, for example, in [1].

As can be easily seen, the lattice gas model suggests that the quantity H_0 does not depend on the concentration of intercalated ions. It is clear that this assumption can be valid only in the case where the lattice distortions induced upon intercalation are relatively weak. Since the dependence of the lattice constants on the intercalant concentration is observed for almost all compounds, the above approximation seems to be highly artificial. As was shown in [11], it is common practice to attempt to take into account this factor by using rather complex expressions for the ion–ion interaction constant λ , which cannot be directly verified in the experiment for the case of conventional three-dimensional materials. For intercalation compounds, the problem regarding the dependence of the energy of elastic distortions induced by intercalated ions on their concentration was solved by Dahn et al. [12], who took into account the concentration dependence of the elastic energy at the intercalation stage. According to the model proposed in [12], the incorporation of an intercalant ion generates a quasi-elastic distortion (referred to by those authors as the “quasi-elastic dipole”), which decays away from the intercalated ion. These dipoles repel from each other in the direction normal to the plane and are attracted within one gap at large distances. The interlayer bonds and elastic properties of the intercalated ion are simulated by springs with the

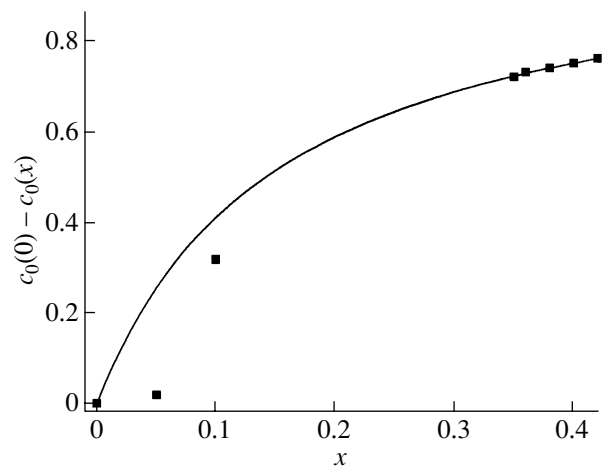


Fig. 3. Approximation of the experimental dependence of the increase in the lattice constant c_0 on the silver content x in the Ag_xTiS_2 compounds at the first stage upon intercalation according to the model proposed in [12]. The solid line corresponds to the results of the calculations, and points are the experimental data. The significant discrepancy in the range of low silver contents x is probably associated with the presence of disordered stages, which makes it impossible to uniquely calculate the lattice constant c_0 .

equilibrium length equal to the initial interlayer distance c_0 and the stiffness K and by springs with the length c_L (the equilibrium interlayer distance at the maximum intercalant concentration) and the stiffness k . Then, the resulting energy per ion can be determined from the expressions [12]

$$\frac{E}{N} = J \frac{x}{\alpha + x}, \quad \text{where } J = \frac{K}{2}(c_L - c_0)^2, \quad \alpha = \frac{K}{k}.$$

Here, x is the dimensionless concentration. An increase in the intercalant concentration leads to an increase in the gap width and, hence, a decrease in the energy expended for intercalating new ions into the same gap. The experimental phase diagram of the Ag_xTiS_2 system [7, 13] confirms the validity of the proposed model for at least this material. Consequently, with allowance made for the elastic interaction, relationship (8) takes the form

$$H_{\text{Ag}} = H_0 - \frac{\lambda n}{2} - J \frac{x}{\alpha + x}. \quad (9)$$

The situation can be simplified if we obtain the numerical value of the constant α from the concentration dependence of the lattice parameter c_0 , which describes the change in the interlayer distance upon intercalation. The result of the approximation of the experimental dependence $c_0(x)$ is presented in Fig. 3. It can be seen from this figure that the dependence $c_0(x)$ is satisfactorily described by the model proposed in [12] for the parameters $\alpha = 0.15174$ and $c_L = 6.74568 \text{ \AA}$. Within the framework of the model proposed in [12], the value of the parameter J can be determined from the

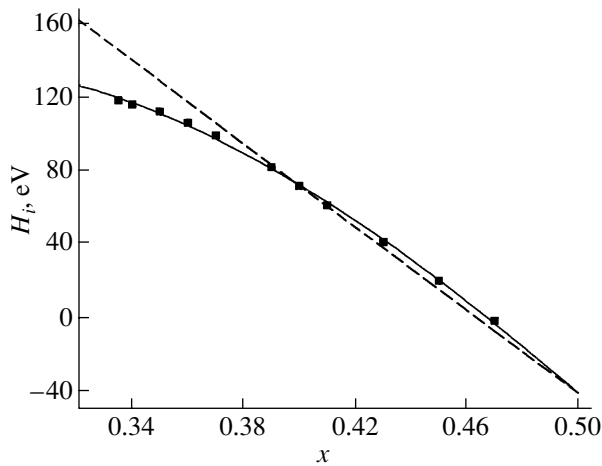


Fig. 4. Approximation of the experimental concentration dependence of the enthalpy H_i for the silver subsystem in the Ag_xTiS_2 compounds at the first stage. The solid line indicates the approximation according to model (9), and the dashed line represents the approximation with the use of relationship (8), i.e., without regard for elastic distortions introduced by the intercalant into the host lattice. Points are the experimental data.

temperature of the triple point in the phase diagram determined in [7, 13]. The obtained value is $J = 0.435$ eV.

The concentration dependence of the enthalpy of the ionic subsystem was approximated by expression (9) with the above parameters of the elastic ion–lattice interaction. The result of this approximation is presented in Fig. 4. For comparison, Fig. 4 also shows the approximation within the framework of the conventional lattice gas model, which disregards the elastic lattice distortions that accompany a change in the concentration of mobile ions. It can be seen from Fig. 4 that, although both approximations over the larger part of the homogeneity region of stage 1 lead to good results, the accuracy of the approximation with the use

Activation energies for coupled chemical diffusion $E_a(\ln \tilde{D})$ and ionic conduction $E_a(\ln \sigma_i T)$ in the Ag_xTiS_2 compounds at the first stage as a function of the silver content x and coupled chemical diffusion coefficients calculated from the Nernst–Einstein equation $\tilde{D}(\sigma_i)$ and determined from the time dependence of the polarization decay \tilde{D}_{exp} at a temperature of 250°C

| x | $E_a(\ln \tilde{D}),$ eV | $E_a(\ln \sigma_i T),$ eV | $\tilde{D}(\sigma_i) \times 10^{-5},$ cm ² /s | $\tilde{D}_{\text{exp}} \times 10^{-5},$ cm ² /s |
|-------|-----------------------------|------------------------------|---|--|
| 0.355 | 0.231 | 0.228 | 1.10 | 1.04 |
| 0.373 | 0.228 | 0.232 | 1.28 | 1.27 |
| 0.405 | 0.246 | 0.234 | 1.71 | 1.73 |
| 0.425 | 0.251 | 0.236 | 1.99 | 2.01 |

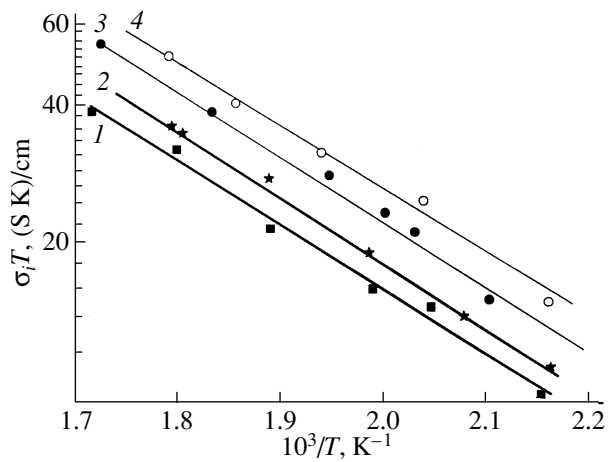


Fig. 5. Temperature dependences of the ionic conductivity for the Ag_xTiS_2 compounds at silver contents $x = (1)$ 0.355, (2) 0.373, (3) 0.405, and (4) 0.425.

of expression (9) is significantly higher, especially in the range of $x \approx 0.33$, where the discrepancy between the experimental data and the results of the lattice gas model many times exceeds the experimental error. The parameters of the approximation with the use of expression (9) are as follows: $H_0 = 1.80$ eV and $\lambda/2 = 2.34$ eV (which differ from the parameters $H_0 = 0.86$ eV and $\lambda/2 = 1.06$ eV in the lattice gas approximation).

3.2. Diffusion of Silver Ions in Ag_xTiS_2

The temperature dependences of the ionic conductivity σ_i for the Ag_xTiS_2 compounds in the Arrhenius coordinates are plotted in Fig. 5. The concentration dependences of the activation energies E_a for chemical diffusion and ionic conduction are summarized in the table together with the coupled chemical diffusion coefficients calculated from the ionic conductivities and measured experimentally. A good agreement observed in the coupled chemical diffusion coefficients and the activation energies determined by different methods indicates the correctness of the chosen model, according to which all silver ions are assumed to be equally involved in the transport process. This is also confirmed by the linear behavior of the concentration dependences of these quantities (Fig. 6).

Since the temperature dependences of the ionic conductivity σ_i and the coupled chemical diffusion coefficient have a typical behavior, the activation energy E_a , according to the conventional interpretation, can be treated as the height of the barrier that should be overcome by the ion in a diffusion jump. In this case, we can use the expression for the enthalpy of the ionic subsystem for the interpretation of the concentration dependence of the activation energy E_a ; that is,

$$E_a = H_{\text{Ag}}^{\text{ex}} - H_{\text{Ag}}^{\text{oct}}, \quad (10)$$

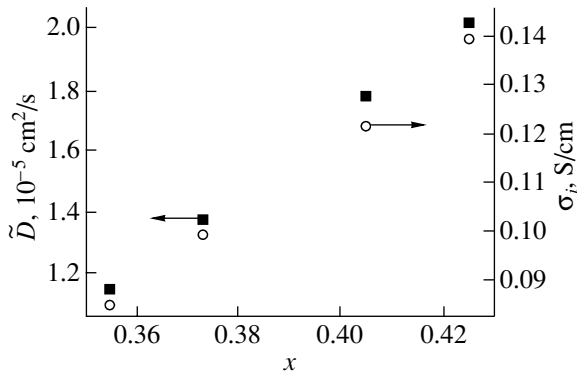


Fig. 6. Dependences of the coupled chemical diffusion coefficient D and the ionic conductivity σ_i on the silver content x in the Ag_xTiS_2 compounds at the first stage.

where $H_{\text{Ag}}^{\text{oct}}$ and $H_{\text{Ag}}^{\text{ex}}$ are the enthalpies of the silver ions in the main position and in the position over the barrier, respectively. In the interlayer gap, there are only two sets of positions accessible for intercalant atoms [2], namely, the positions octahedrally and tetrahedrally coordinated by the chalcogen atoms. Since the main positions occupied by silver ions are octahedral positions, the tetrahedral positions correspond to the excited state. By definition, the ion–ion interaction is the interaction of each ion with each ion when the interaction constant is independent of the ion concentration. From this definition, it is clear that transfer of the silver ion from the octahedral position to the tetrahedral position does not affect the quantity $\frac{\lambda}{2}n$. It has been reliably established that the intercalation of ions into the tetrahedral positions leads to weaker elastic distortions as compared to their intercalation into the octahedral positions [2]. Consequently, the excitation of the silver ion should be accompanied by a decrease in the elastic strain energy. However, the fact that the octahedral position is the main position means that the ion–lattice interaction H_0 is stronger and determines the equilibrium position of the ion in the lattice. Therefore, by ignoring the elastic distortion induced by the mobile ion in the excited state, the expression of the activation energy for ionic conduction takes the form

$$E_a = \Delta H_0 - \frac{J}{\alpha + x}, \quad (11)$$

where ΔH_0 is the difference between the enthalpies of the ion–lattice interaction in the ground and excited states. By optimizing this expression with respect to the experimental values of the activation energy for ionic conduction (Fig. 7), we determine the quantity $\Delta H_0 = H_{\text{Ag}}^{\text{ex}} - H_{\text{Ag}}^{\text{okt}} = 0.88$ eV. It can be easily seen that, if it were not for the influence of the elastic interaction decreasing the diffusion barrier, the activation energy

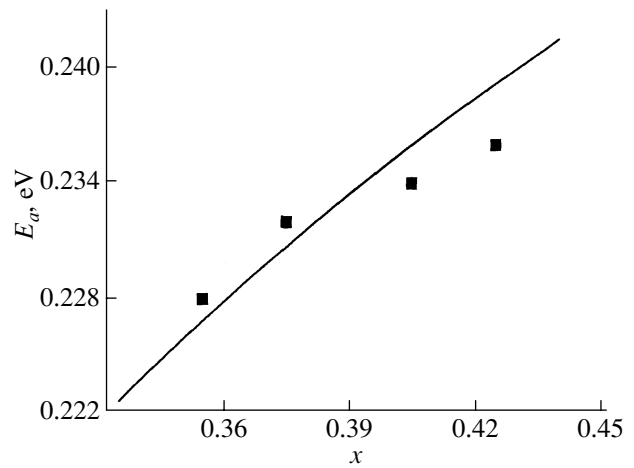


Fig. 7. Concentration dependence of the activation energy for ionic conduction of the Ag_xTiS_2 compound at the first stage. Points are the experimental data, and the solid line corresponds to the results of the optimization according to expression (11) with the use of the parameters J and α determined in the text.

would be approximately equal to 1 eV, as is the case with classical solids.

4. CONCLUSIONS

Thus, the results obtained from the above investigation have demonstrated that the high diffusion mobility in intercalation compounds can be associated with the competition between the energy of interaction of an atom with the nearest environment, which apparently has a covalent nature, and the energy of elastic lattice distortion induced by the intercalated atom in the host lattice. This approach can be extended to all solid materials in which chemical bonding has ionic and/or covalent nature. Consequently, the diffusion mobility can be controlled either by enhancing the competing interaction with the aim of increasing the diffusion mobility or by weakening this interaction in order to retard the diffusion process. Thus, superionic materials are distinguished by that they provide a nearly complete compensation of these interactions.

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