
SEMICONDUCTORS
AND DIELECTRICS

Structural and Physical Properties of Cobalt-Intercalated Titanium Diselenide and Ditelluride Compounds

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Abstract—A complex investigation of the structural, electrical, and magnetic properties of cobalt-intercalated titanium diselenide and ditelluride compounds at different intercalant concentrations and temperatures is performed for the first time. The influence of the matrix on the physical characteristics of the intercalation materials is analyzed. © 2003 MAIK “Nauka/Interperiodica”.

1. INTRODUCTION

The considerable interest expressed by researchers in compounds prepared through intercalation of transition elements into titanium dichalcogenides is associated with the possibility of producing structures with alternating layers of magnetic and nonmagnetic atoms [1, 2]. These materials, unlike artificial two-dimensional magnetic structures, consist of layers whose thicknesses can be comparable to interatomic distances. In this case, the two-dimensional character of the structure manifests itself in the properties of the material to a maximum degree.

The initial matrices (TiS_2 , TiSe_2 , TiTe_2) used for intercalation have similar crystal structures and belong to the CdI_2 structure type [3]. As was shown earlier in [4, 5], the intercalation of $3d$ transition metals leads to hybridization of the $3d$ states of intercalated atoms with the band states of the TiSe_2 matrix. The contribution of intercalated atoms to the formation of new molecular orbitals depends on the nature of these atoms. The formation of the new states is accompanied by a distortion of the crystal lattice and a decrease in the electrical conductivity and the effective magnetic moment. Similar features have been observed for a number of intercalation materials based on titanium diselenide, especially for compounds in the Co_xTiSe_2 system [6].

To the best of our knowledge, intercalation compounds based on titanium ditelluride have not been studied. In this work, the experimental data on the structural, electrical, and magnetic characteristics of compounds in the Co_xTiTe_2 system were obtained for the first time. In order to gain detailed information on the mechanisms responsible for the physical properties of these compounds, it is necessary to elucidate the role played not only by intercalated unlike atoms that differ in the electronic structure of the d orbitals but also by the crystal matrix upon intercalation of like atoms. The

results of our investigation make possible a comparative analysis of the structure parameters and physical properties of Co_xTiSe_2 and Co_xTiTe_2 compounds.

2. SAMPLES AND EXPERIMENTAL TECHNIQUE

Samples of the compositions Co_xTiSe_2 and Co_xTiTe_2 were prepared according to the two-stage procedure described earlier in [5]. At the first stage, we synthesized TiSe_2 and TiTe_2 compounds. Then, we performed x-ray diffraction analysis of these compounds and examined their physical properties. The unit cell parameters of the synthesized compounds are in reasonable agreement with those available in the literature. For both systems, the concentrations of intercalated cobalt atoms fall in the range $0 < x \leq 0.5$. X-ray diffraction analysis and the determination of the structure parameters were carried out using a DRON-3M x-ray diffractometer. The errors in the determination of the lattice parameters a and c were equal to 1×10^{-4} and 4×10^{-4} nm, respectively.

The magnetic susceptibility was measured by the Faraday method in the temperature range 80–295 K. The electrical conductivity and the Seebeck coefficient were determined according to standard methods with the use of cylindrical sintered samples.

3. RESULTS AND DISCUSSION

In this work, we performed a combined analysis of the experimental results obtained for the above compounds and elucidated how the matrix used for intercalation affects the physical properties of the compounds under investigation. For this purpose, we compared the available data on the structural features of TiSe_2 and TiTe_2 . Table 1 presents the main structural and crystal chemical characteristics of these compounds [7, 8].

Table 1. Unit cell parameters, the distances d_{x-x} between TiX_2 layers, and the radii r_x of X^{2-} chalcogen ions

Compound	a_0 , nm	c_0 , nm	c_0/a_0	d_{x-x} , nm	r_x , nm
TiSe_2	0.3542	0.6004	1.69	0.2964	0.182
TiTe_2	0.3766	0.6491	1.72	0.3121	0.211

Table 2. Structural characteristics of samples in the Co_xTiSe_2 and Co_xTiTe_2 systems

Co_xTiSe_2				Co_xTiTe_2			
x	a , nm	c , nm	c/a	x	a , nm	c , nm	c/a
0	0.3540	0.6004	1.69	0	0.3766	0.6491	1.72
0.1	0.3542	0.5962	1.68	0.05	0.3771	0.6468	1.71
0.2	0.3548	0.5934	1.67	0.15	0.3804	0.6397	1.682
0.25	0.3548	0.5901	1.66	0.25	0.3822	0.6400	1.674
0.33	0.3554	0.5890	1.65	0.4	0.3836	0.6442	1.679
0.5	0.3565	0.5883	1.64	0.5	0.3838	0.6453	1.681

As can be seen from the Table 1, the d_{x-x} distance (specifying the van der Waals gap) between chalcogen atoms located in the adjacent layers in TiTe_2 is larger than that in TiSe_2 . The relative increase in the d_{x-x} distance is determined to be $\Delta d_{x-x}/d = 0.054$. This can indicate, at first glance, an increase in the degree of two-dimensionality of the crystal structure and, hence, a weakening of the interaction between TiX_2 layers and an increase in the compressibility in the order $\text{TiSe}_2 \rightarrow \text{TiTe}_2$. However, the d_{x-x} distances given in Table 1 can serve only as a measure of the geometric width of the van der Waals gap. The final conclusion regarding the change in the degree of two-dimensionality of the crystal structure can be drawn with due regard for the fact that the radius of Te^{2-} ions exceeds the radius of Se^{2-} ions due to a larger size of the Te $4p$ orbitals. Indeed, when changing over from Se^{2-} to Te^{2-} ions, the relative increase in the ionic radius $\Delta r_x/r_{\text{Se}} = 0.093$ appears to be nearly twice as large as that in the interlayer distance. This estimate demonstrates that the “physical” width of the van der Waals gap in TiTe_2 is smaller than that in TiSe_2 . Consequently, the interaction between layers in the former compound should be stronger than the interlayer interaction in the latter compound. The above inference is confirmed by the compressibilities determined from the pressure dependences of the unit cell parameters of these compounds. According to the data obtained in our previous work [9], the compressibility dc/c_0dp in the direction perpendicular to the layers is equal to $0.73 \times 10^{-11} \text{ Pa}^{-1}$ for titanium ditelluride and $1.53 \times 10^{-11} \text{ Pa}^{-1}$ for titanium diselenide. The larger size of the Te $4p$ orbitals should also affect their interaction with $3d$ electrons of intercalant atoms. Therefore, it can be expected that, under the

same conditions, the behavior of the structural characteristics for compounds in the Co_xTiTe_2 system should differ from that in the Co_xTiSe_2 system.

The structural data obtained for Co_xTiTe_2 and Co_xTiSe_2 intercalation compounds are presented in Table 2.

Analysis of the structural data shows that, as the cobalt content increases, the lattice parameter a increases monotonically in both systems, whereas the behavior of the lattice parameter c and the ratio c/a for compounds in these systems differs significantly. From the structural data presented in Table 2, we calculated the relative changes in the unit cell parameters a and c for the compounds under investigation (Fig. 1). It can be seen from Fig. 1 that the parameter a characterizing the distance between cobalt atoms in a layer increases monotonically in both systems; however, its variation is more pronounced for Co_xTiTe_2 compounds. The degree of contraction of the unit cell along the c axis for the Co_xTiTe_2 crystals is larger than that for the Co_xTiSe_2 crystals at the initial stage of cobalt intercalation but turns out to be noticeably smaller as the cobalt concentration increases. This difference in the behavior of the unit cell parameter c can be associated with the following two factors. (1) The Te–Co–Te covalent bonds become stronger due to an increase in the overlap of orbitals. (2) As the TiTe_2 layers approach each other, the electron–electron repulsion increases and hinders further distortion of the unit cell in the Co_xTiTe_2 crystals. In the Co_xTiSe_2 crystals, which, as was noted above, are characterized by a larger physical width of the van der Waals gap, the degree of contraction of TiSe_2 layers continues to increase at higher cobalt concentrations.

Our data on the magnetic susceptibility χ for Co_xTiSe_2 [6] and Co_xTiTe_2 (Fig. 2) compounds indicate that the magnitudes of χ and its temperature dependences correspond to a paramagnetic state. As the cobalt content increases, the magnetic susceptibility χ increases in both systems but remains substantially smaller for compounds based on titanium ditelluride at the same intercalant content. These findings should be interpreted with due regard for the change in the electronic structure of the matrix and the possible transformation of the electronic configuration of intercalant atoms.

The effective magnetic moments of cobalt atoms in the studied compounds (Fig. 3) were determined from the experimental magnetic susceptibilities after elimination of the temperature-independent contributions caused by paramagnetism of the free charge carriers and diamagnetism of the filled electron shells of the atoms involved.

It can be seen from Fig. 3 that the effective magnetic moments of cobalt atoms in the Co_xTiTe_2 compounds are smaller than those in the Co_xTiSe_2 compounds. This difference accounts for the lower magnetic susceptibility of the former compounds as compared to that of the latter compounds. Analysis of the results obtained in previous studies of titanium diselenides intercalated with transition elements demonstrates that the effective magnetic moments determined in this work are close to those of cobalt atoms in the $3d^7$ configuration. As was shown earlier in [5], the filling of the cobalt d orbitals in the titanium diselenide corresponds, to a greater extent, to a high-spin state and the decrease in the effective magnetic moment, as compared to μ_{eff} for a free ion, is associated with the delocalization of the $3d$ electrons involved in the formation of covalent bonds. This can also be responsible in part for the smaller values of μ_{eff} for the Co_xTiTe_2 compounds. However, the decrease in the physical width of the van der Waals gap and the increase in the electron–electron repulsion should enhance the effect of the crystal field of ligands surrounding the intercalant atom. Consequently, the electronic configuration of cobalt atoms can transform into a low-spin state. In this case, the theoretical spin moment of the Co^{2+} ion is equal to $1.73\mu_{\text{B}}$, which is in better agreement with the effective magnetic moment determined for the Co_xTiTe_2 compounds.

The experimental investigation of the kinetic properties revealed that all the Co_xTiTe_2 compounds, like the Co_xTiSe_2 compounds [6], possess metallic conductivity in the temperature range covered (Fig. 4). However, the concentration dependences of the electrical conductivity of the former compounds exhibit a qualitatively different behavior as compared to that of the latter compounds (Fig. 5). Upon intercalation of small amounts of cobalt into TiSe_2 , the electrical conductivity of the Co_xTiSe_2 intercalation compounds, unlike the conductivity of the matrix [6] (for TiSe_2 , $\sigma \approx 10^5$ S/m

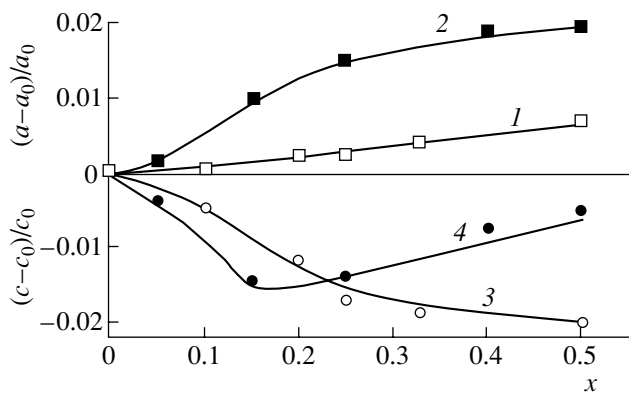


Fig. 1. Relative changes in the unit cell parameters (1, 2) a and (3, 4) c as functions of the cobalt content in (1, 3) Co_xTiSe_2 and (2, 4) Co_xTiTe_2 compounds.

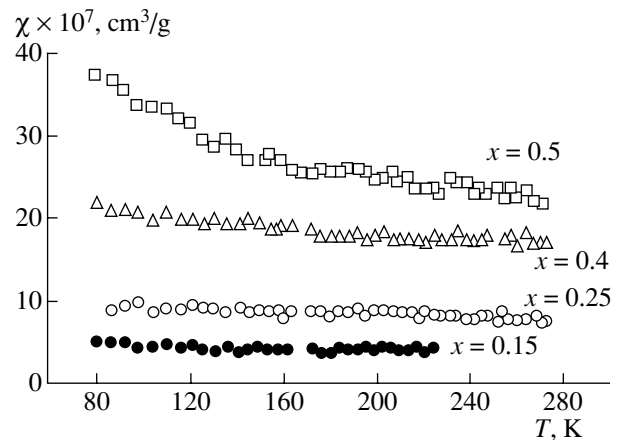


Fig. 2. Temperature dependences of the magnetic susceptibility for Co_xTiTe_2 compounds at different cobalt contents.

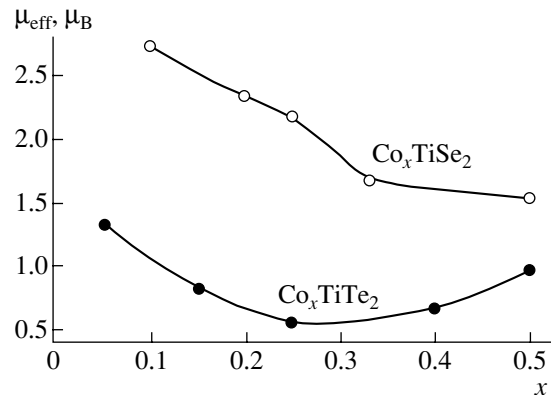


Fig. 3. Concentration dependences of the effective magnetic moment of cobalt for Co_xTiSe_2 and Co_xTiTe_2 compounds.

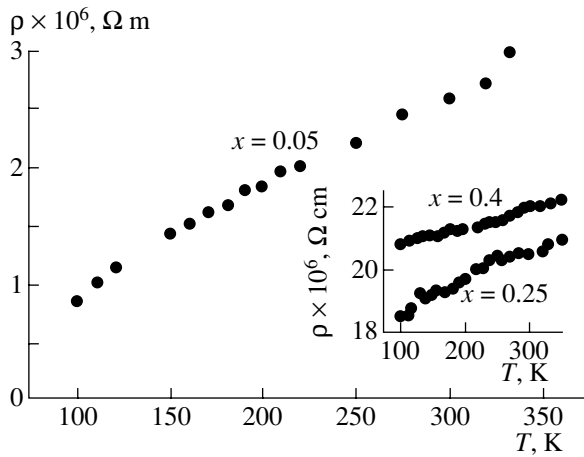


Fig. 4. Temperature dependences of the electrical resistivity of Co_xTiTe_2 compounds at different cobalt contents.

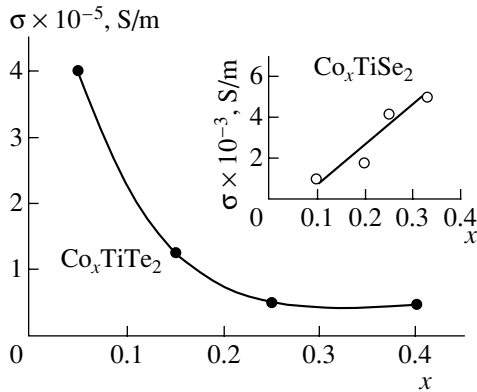


Fig. 5. Dependences of the electrical conductivity for Co_xTiSe_2 (inset) and Co_xTiTe_2 compounds on the cobalt content ($T = 295$ K).

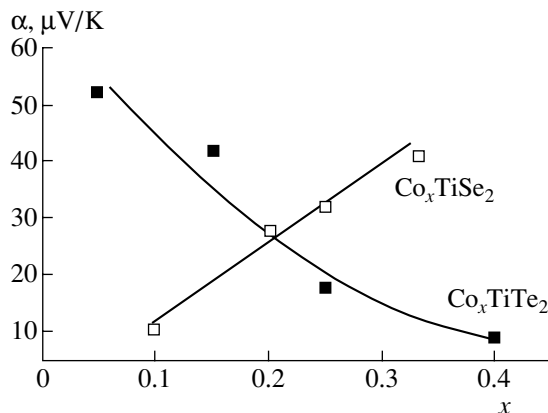


Fig. 6. Dependences of the Seebeck coefficient for Co_xTiSe_2 and Co_xTiTe_2 compounds on the cobalt content ($T = 295$ K).

[10]), first rapidly decreases and then begins to increase. In contrast, the electrical conductivity of the Co_xTiTe_2 compounds appreciably decreases with an increase in the intercalant content. For compounds in both systems, the concentration dependences of the Seebeck coefficient (Fig. 6) are qualitatively similar to those of the electrical conductivity. This suggests that the intercalation of cobalt into titanium diselenides and ditellurides is attended primarily by a change in the mobility of charge carriers. An increase in the mobility of charge carriers in the Co_xTiSe_2 compounds can be associated both with the overlap of the wave functions of electronic states of cobalt atoms due to the distances between them being shorter and with the formation of a partly filled impurity band. For the Co_xTiTe_2 compounds, the temperature and concentration dependences of the electrical conductivity and the Seebeck coefficient indicate that the mobility of charge carriers decreases. Note that, in this case, the mobility is governed by lattice-vibration scattering and scattering by intercalated atoms, which play the role of scattering centers. The wave functions of the electronic states of cobalt atoms within one layer overlap to a smaller extent owing to the larger cobalt–cobalt distance determined by the unit cell parameter a , which, in the Co_xTiTe_2 compounds, more substantially increases upon intercalation.

4. CONCLUSIONS

Thus, the results obtained in the above investigation demonstrated that, although different titanium dichalcogenides have similar crystal structures, more rigorous analysis of the mechanisms responsible for the physical properties of intercalation compounds should include not only the differences in the electronic structure of intercalated $3d$ transition metal atoms but also the specific features of the matrices used for intercalation.

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