

Crystal Structure and Electrical Properties of $Gd_xMn_{1-x}S$ and $Ti_xMn_{1-x}Se$ Solid Solutions

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Abstract—Regions of the existence of sulfide $Gd_xMn_{1-x}S$ and selenide $Ti_xMn_{1-x}Se$ solid solutions have been identified. Their electrical and thermoelectric properties have been studied in the temperature range 80–900 K. It has been established that the substitution of Gd^{2+} and Ti^{2+} ions for Mn^{2+} cations initiates reversal of the type of charge carrier with respect to the starting compounds MnS and MnSe. The cation substitution in solid solutions brings about a change from the hole conduction ($\alpha > 0$) characteristic of the manganese monosulfide and monoselenide to the electronic conduction ($\alpha < 0$).

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1. INTRODUCTION

The MnS and MnSe compounds are known to be wide band-gap magnetic semiconductors with a NaCl-type face-centered cubic crystal structure in the stable α modification. The band gap E_g of these compounds exceeds 2.0 eV [1]. Below room temperature, the magnetic moments of Mn^{2+} ions in these compounds are antiferromagnetically aligned. Substitution of manganese cations by ions of transition metals favors the formation in the solid solutions of new physical properties not observed in the starting compounds. For instance, substitution of manganese by chromium ions to a level of more than 20 at % stimulates the appearance of ferromagnetic properties [2], with electronic conduction beginning to operate [3]. Reversal of the conduction type was observed to occur in $Co_xMn_{1-x}S$ solid solutions as well, when manganese ions are replaced by ions of Co to 40 at % [4].

The purpose of this work was to study the electrical conductivity and thermoelectric properties of the recently synthesized $Gd_xMn_{1-x}S$ solid solutions and polycrystalline samples of $Ti_xMn_{1-x}Se$ to identify possible causes of the phase transformation bringing about carrier sign reversal in manganese chalcogenides. The application potential underpinning such studies is based on the broadening of the class of wide-band-gap semiconducting compounds which find use in spintronics and optoelectronic devices.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Single crystals of samples of $Gd_xMn_{1-x}S$ solid solutions were melt-grown by the technique described at length in [5]. The temperature dependences of the electrical resistivity and of the Seebeck coefficient of single crystals of the solid solutions with gadolinium contents $x = 0.01, 0.05,$ and 0.10 were studied in the temperature range 80–900 K on parallelepiped-shaped samples measuring $3.00 \times 3.00 \times 5.00, 2.05 \times 3.80 \times 4.15,$ and $2.50 \times 3.90 \times 6.50$ mm, respectively.

The $Ti_xMn_{1-x}Se$ solid solutions were polycrystals synthesized in evacuated ampoules by the technology described in [6]. The samples were of cylindrical shape, 6.0 mm in diameter and up to 20.0 mm high. Rods of this size were prepared by pressing. After annealing at 1220 K for 48 h and exposure at 1400 K for 2 h, the samples were quenched. On polished end faces of the samples prepared in this way, copper contacts were evaporated.

The electrical conductivity $\sigma(T)$ and the Seebeck coefficient $\alpha(T)$ were studied by the two-point probe technique on a setup whose scheme and principle of operation are described in [4]. The setup provides a possibility of measuring simultaneously the electrical conductivity and thermopower of a sample at a preset temperature gradient.

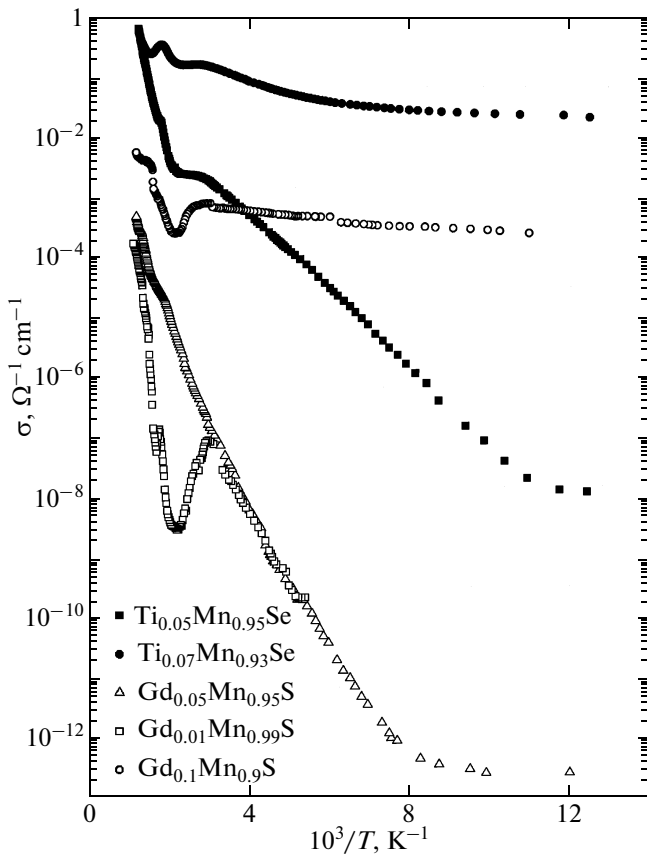


Fig. 1. Temperature dependences of the electrical conductivity of samples in the $Gd_xMn_{1-x}S$ and $Ti_xMn_{1-x}Se$ systems.

3. RESULTS OF THE MEASUREMENTS

X-ray structural analysis showed $Gd_xMn_{1-x}S$ samples to be solid solutions with a NaCl-type face-centered cubic structure characteristic of α -MnS. X-ray powder diffraction analysis revealed that the solubility in the $Gd_xMn_{1-x}S$ system reaches as high as 30 at % Gd. It was established that single-phase $Ti_xMn_{1-x}Se$ samples have also NaCl-type face-centered cubic structure of α -MnSe. The results obtained in the X-ray structural analysis of polycrystalline $Ti_xMn_{1-x}Se$ samples indicate that the single-phase state of the samples persists only up to the $x = 0.07$ composition. The unit

Unit cell parameters a and band gaps E_g for samples in the $Gd_xMn_{1-x}S$ and $Ti_xMn_{1-x}Se$ systems

Composition	a , nm	E_g , eV
$Gd_{0.01}Mn_{0.99}S$	0.5230	1.31
$Gd_{0.05}Mn_{0.95}S$	0.5274	1.24
$Gd_{0.1}Mn_{0.9}S$	0.5278	0.54
$Ti_{0.05}Mn_{0.95}Se$	0.5461	1.31
$Ti_{0.07}Mn_{0.93}Se$	0.5457	0.80

cell parameters of the solid solutions of both systems are listed in the table.

Figure 1 illustrates the results obtained in the study of the conducting properties performed on the samples of the solid solutions under investigation. The $\ln\sigma(10^3/T)$ behavior is characteristic of semiconducting compounds. In the $Gd_xMn_{1-x}S$ solid solutions, intrinsic conduction is observed above 700 K, and in the $Ti_xMn_{1-x}Se$ solid solutions, above 600 K. The table lists also the band gaps of the samples. The course of the $\sigma(T)$ graphs for $Gd_xMn_{1-x}S$ and $Ti_xMn_{1-x}Se$ suggests also that both systems feature a marked variation in the electrical conductivity with increasing temperature, starting from 80 K. Close to liquid nitrogen temperature, samples with a low content of Gd and Ti ions have electrical resistivities approaching that of insulators. Significantly, within a narrow temperature range around 80 K the electrical resistivity does not vary with increasing temperature (Fig. 1). Also, at low substitutions of manganese ions by transition metal ions the electrical resistivity increases compared with that of MnS and MnSe samples. As the substituting cation concentration x is increased still more, one observes a sharp drop of the electrical resistivity. A similar phenomenon was observed also in the cases of substitution of manganese in MnSe by ions of V, Cr, Fe, and Co [3], and in MnS—by cobalt ions [4].

Figure 2 plots the temperature dependences of the Seebeck coefficient of both solid solution systems. A common feature of the dependences $\alpha(T)$ of both systems is the transition from hole to electronic conduction occurring with increasing concentration of gadolinium and titanium ions. The dependence $\alpha(T)$ of the $Cd_{0.5}Mn_{0.95}S$ sample exhibits only electronic conduction throughout the temperature range covered. In the $Ti_xMn_{1-x}Se$ system, this phenomenon takes place at $x = 0.07$ (Fig. 2). In the $Gd_{0.01}Mn_{0.99}S$ and $Ti_{0.05}Mn_{0.95}Se$ solid solutions, carriers reverse sign at characteristic temperatures. In the $Gd_{0.01}Mn_{0.99}S$ sample, the sign changes from positive to negative at ~ 700 K. The dependences $\alpha(T)$ obtained for the $Ti_{0.05}Mn_{0.95}Se$ sample show the carrier sign to change from negative to positive at 200 K, with the temperature increasing from 80 K up. The dependences $\alpha(T)$ of both systems reveal anomalies whose appearance can be associated with the features observed in the dependences $\ln\sigma(10^3/T)$. The maxima (minima) can be accounted for, first, by the presence in the solid solutions of carriers of both signs; second, by their contents increasing or decreasing at different temperatures; and, third, by carrier mobility. For instance, the very strong growth of α in the $Gd_{0.01}Mn_{0.99}S$ solid solution observed to occur below the intrinsic conduction temperature (700 K) should be attributed to a decrease in the number of carriers, when injection of electrons into the conduction band involving impurity centers had stopped, while interband electron transfer has not yet started.

The results of our studies of the dependences $\alpha(T)$ suggest that the Seebeck coefficient of samples in the $\text{Gd}_x\text{Mn}_{1-x}\text{S}$ system exceeds in absolute magnitude that of $\text{Ti}_x\text{Mn}_{1-x}\text{Se}$ samples throughout the temperature range covered.

4. DISCUSSION OF THE RESULTS

The most essential conclusion drawn from our studies of dependences $\sigma(T)$ and $\alpha(T)$ of the $\text{Gd}_x\text{Mn}_{1-x}\text{S}$ and $\text{Ti}_x\text{Mn}_{1-x}\text{Se}$ solid solutions consists in that substitution of Mn^{2+} cations by Gd^{2+} and Ti^{2+} ions brings about appearance in these compounds of charge carriers of two types, namely, of holes and electrons.

Earlier studies of MnSe and MnS showed convincingly that they are to a large extent ionic compounds. If the manganese and the anion atoms are coupled fully by ionic chemical bonds, the manganese atom transfers its two $4s$ electrons to the p shells of the selenium and sulfur atoms, which become filled. Nevertheless, experiments show the bonding in these compounds to be covalent to a certain extent. This was established, for instance, for MnSe from calculation of the covalence parameter drawing from neutron diffraction measurements [7]. Optical measurements performed in the IR range to derive the Shigetti charge [8] lead one to the same conclusion. X-ray absorption spectra showed that manganese donates two electrons, and selenium acquires one or two electrons in the course of formation of MnSe [9]. A similar situation was reported in a study of MnS . This accounts for observation of hole conduction in the MnSe and MnS semiconductors, because the lack of one electron in the p shell of Se^{2-} and S^{2-} may be considered as the presence of a vacancy (i.e., of a hole) in the valence band of these compounds.

The main result derived from studies of the dependences $\rho(T)$ of $\text{Gd}_x\text{Mn}_{1-x}\text{S}$ and $\text{Ti}_x\text{Mn}_{1-x}\text{Se}$, namely, the increase in electrical resistivity of their solid solutions at low concentrations of substituting ions compared with the electrical resistivity of MnS and MnSe can be attributed to partial charge balancing. This suggests a conclusion that the Gd^{2+} and Ti^{2+} cations, being donors, account for the electronic conduction in the solid solutions. Charge compensation in $\text{Gd}_x\text{Mn}_{1-x}\text{S}$ and $\text{Ti}_x\text{Mn}_{1-x}\text{Se}$ explains also the formation of the insulating state and the independence of the electrical resistivity ρ from the temperature near 80 K at low percentage of substitution of the manganese cations, because when the hole and the electron are bound, there are no carriers in these compounds. When the concentration of electrons increases markedly as a result of increasing concentration of transition metals inserted into the lattice, the compound transfers to the state of a heavily doped semiconductor, with the conduction in such compounds being fully mediated by

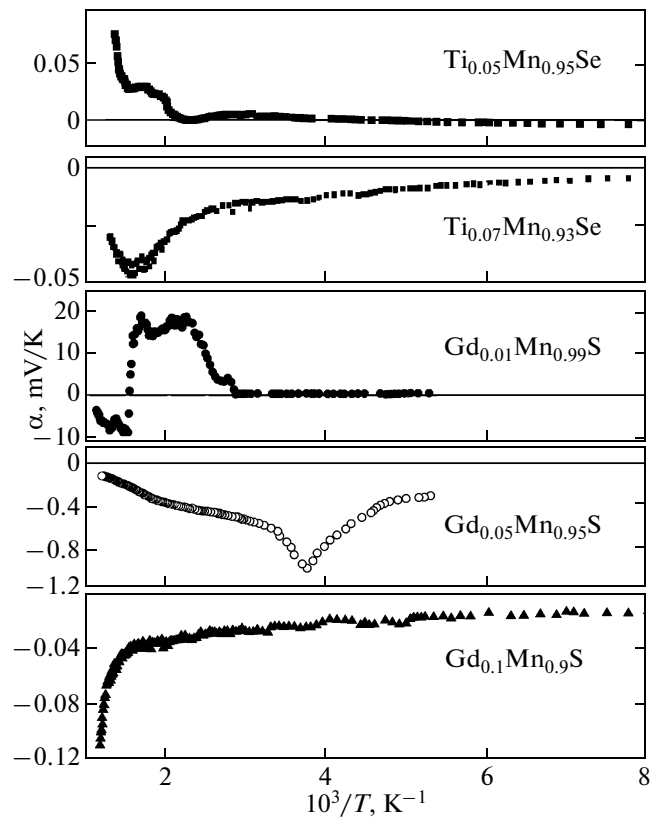


Fig. 2. Temperature dependences of the Seebeck coefficient of samples in the $\text{Gd}_x\text{Mn}_{1-x}\text{S}$ and $\text{Ti}_x\text{Mn}_{1-x}\text{Se}$ systems.

electrons. In this case, the Seebeck coefficient becomes negative.

This prompts immediately the question as to why the gadolinium and manganese cations become donors under such substitution? As a possible answer to this question, consider formation of the MnSe and MnS ionic compounds, in which after the transfer of the $4s$ electrons of manganese into the p shell of selenium and sulfur the $3d$ electrons in the unfilled d shell become outer electrons. Obviously enough, they can take part in charge transfer over the lattice, because their binding with the core of the Mn^{2+} ion in the unfilled d shell is weaker than that of the p electrons in the filled p shell of the Se^{2-} and S^{2-} ions. These electrons are nevertheless exchange coupled, and it is apparently this that accounts for their localization. Insertion into the lattice of Gd^{2+} cations, which have one $4d$ electron, and of Ti^{2+} cations, whose $3d$ shell contains two electrons only, should disrupt exchange interaction, because the numbers of d electrons in these ions and of d electrons in Mn^{2+} (which has five of them) differ considerably, and, besides, the distribution of the Gd^{2+} and Ti^{2+} ions over the lattice is disordered. It is known that exchange interaction mediates correlation of electron motion in neighboring ions

and, thus, minimizes the binding energy [10]. If, however, the numbers of d electrons on the neighboring selenium ions are different, this will interfere with correlation of their motion. In the particular case where the cations substituting for the manganese ion are distributed uniformly over the lattice, they may become bound by exchange coupling. The substituting cations would have formed their own sublattice. Because of the d electrons of Gd^{2+} and Ti^{2+} not being involved in exchange coupling, they are bound weaker to the cores of their ions. This may give rise to their collectivization, disruption of localization and formation of the itinerant state, thus making possible their free motion over the lattice under the action of an electric field. This is how d electrons of Gd^{2+} and Ti^{2+} provide electronic conduction in the $Gd_xMn_{1-x}S$ and $Ti_xMn_{1-x}Se$ solid solutions.

The assumption that it is the d electrons of ions substituting for the Mn^{2+} ion in MnS and $MnSe$ that are responsible for the onset of electronic conduction offers a convincing explanation also for the results of studies of the dependences $\rho(T)$ and $\alpha(T)$ which were conducted earlier on solid solutions of the $Mn_{1-x}M_xSe$ systems ($M—V, Cr, Fe, Co$) [3] and the $Co_xMn_{1-x}S$ system [4]. These solid solutions likewise reveal an increase in electrical resistivity under low cation substitution and a strong decrease in ρ of compounds with a noticeable substitution of manganese cations by d metals ($x \geq 0.2$). The $Mn_{1-x}Cr_xSe$ system for $x \geq 0.2$ and the $Co_{0.4}Mn_{0.6}S$ solid solution exhibit electronic conduction.

5. CONCLUSIONS

A comparison of the results of our study with earlier measurements performed on samples in the $Mn_{1-x}Cr_xSe$ and $Co_xMn_{1-x}S$ systems suggests a conclusion that the electronic conduction initiated by $3d$ electrons of the substituting ions becomes manifest the stronger, the larger is the difference in d shell filling. This indicates that the affinity of d electrons of substituting ions to the core of their ion is the stronger, the smaller is the difference in d shell filling between the substituting and the manganese ions. In the case of Gd^{2+} , the difference in d shell filling is the largest for the manganese ions. This may account for the weak binding of the d electrons with the core of their ions and for sharp reversal of hole to electronic conduction observed to occur with increasing concentration x , as well as for the noticeable difference in the Seebeck

coefficients between the $Gd_xMn_{1-x}S$ and $Ti_xMn_{1-x}Se$ systems.

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