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SEMICONDUCTORS AND DIELECTRICS

Electrical Conductivity and Thermopower in $Co_xMn_{1-x}S$ Sulfides

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Abstract—This paper reports on the results of investigations into the structural, electrical, and thermoelectrical properties of sulfides $Co_xMn_{1-x}S$ ($0 \le x \le 0.4$) in the temperature range 80–950 K. It is established that the thermopower coefficient α decreases significantly with an increase in the cobalt concentration in the lattice of the α-MnS compound. The $Co_xMn_{1-x}S$ compounds with cobalt concentrations in the range $0 \le x \le 0.3$ are semiconductors with hole conduction ($\alpha > 0$), whereas the compound with $x = 0.4$ exhibits metallic conduction ($\alpha < 0$). It is found that the band gap E_g of the compounds under investigation varies in the range from 1.46 eV for α-MnS ($x = 0$) to 0.26 eV for $Co_xMn_{1-x}S$ ($x = 0.4$).

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1. INTRODUCTION

Among 3*d* transition metal monochalcogenide compounds, which exhibit almost all types of magnetic ordering, sulfides are of special interest. This interest is associated primarily with the metal–insulator phase transitions revealed in manganese, nickel, and chromium sulfides. Moreover, it has been found that solid solutions of the general formula $Me_xMn_{1-x}S$ (*Me* = Fe, Cr) possess colossal negative magnetoresistance [1, 2]. The practical importance of colossal negative magnetoresistance effects and the prospect of their effective use have given impetus to intensive investigations of the aforementioned compounds and an active search for new materials that exhibit colossal magnetoresistance and undergo a metal–insulator phase transition (in particular, solid solutions based on manganese sulfide). Preliminary investigations into the transport properties of the solid solutions synthesized in the $Co_xMn_{1-x}S$ ($x = 0$–0.4) system have revealed that, in the temperature range from 80 to 150 K, the electrical resistance changes by 12 orders of magnitude with a change in the cobalt concentration [3]. All these findings have stimulated a continuation of the systematic investigations into the structural, electrical, and thermoelectrical properties of solid solutions in the system under consideration.

2. SAMPLES, THEIR CHARACTERIZATION, AND EXPERIMENTAL TECHNIQUE

Polycrystalline samples in the system $Co_xMn_{1-x}S$ ($0 < x < 0.4$) were synthesized from powders of cobalt, manganese, and sulfur (99.999%), which were taken in specified ratios. The synthesis was performed in evaluated (up to 10^{-4} Pa) quartz ampoules placed in a resistance furnace. The ampoules with weighed portions of powders were heated at a rate of 40 K/h to a temperature of 1260 K. Then, the ampoules were kept at this temperature during a week, after which they were cooled together with the furnace. The synthesis product were ground to powders, which were then pressed into samples used in measurements of the electrical resistance and thermopower. Samples $3 \times 5 \times 10$ mm in size were annealed under vacuum for 2 h.

The x-ray diffraction analysis of the powdered samples was performed at room temperature on an x-ray diffractometer (CuK_α radiation; scan step, 0.03°; exposure time per frame, 3 s). According to the x-ray powder diffraction data, the samples with a cobalt concentration in the range $0 < x \le 0.3$ have a face-centered cubic structure of the NaCl type, which is characteristic of the α-MnS phase. Apart from the reflections of the cubic phase, the x-ray powder diffraction pattern of the sample with $x = 0.4$ contain the (1 0 2) reflection, which can be assigned to a hexagonal structure of the NiAs type, as judged from the structure of cobalt sulfide. After the

additional heat treatment, the hexagonal structure in the sample of the composition $Co_{0.4}Mn_{0.6}S$ disappeared.

The electrical resistivity σ and the thermopower coefficient α of the studied samples were measured at temperatures in the range from 80 to 950 K. The measurements were conducted using both the four-point and two-point probe techniques. The investigations were carried out in a continuous mode without reinstallation of the sample. Upon changing over from the low-temperature measurements to the high-temperature measurements, the cryogenic system was replaced with the heating element of the resistance furnace. The instrumentation of the experimental setup made it possible to measure changes in the electrical resistance with an accuracy of up to 0.001 Ω. The main instruments used in these measurements were as follows: an Shch-34 digital ohmmeter; an E6-12A teraohmmeter, which provided measurements of an electrical resistance of up to 10^{13} Ω; a V7-29 digital electrometric microvoltmeter; and a VK2-16 pointer-type electrometric microvoltmeter with an input resistance of 10^{16} Ω. Copper contacts were evaporated onto the samples. The thermopower coefficient was measured with respect to copper. The experimental setup used for measurements of the dependences $\alpha(T)$ was calibrated against the temperature dependences of the thermopower of iron and nickel with respect to copper. The obtained temperature dependences of the thermopower of the reference materials coincided with the dependences $\alpha(T)$ presented in *Handbook of Physical Quantities* [4]. The temperature gradient (10–15 K) across the sample was maintained over the entire temperature range of measurements of the thermopower coefficient. The measurement cell was shielded with a double metal screen. In order to exclude the effect of current-carrying elements on the quantity to be measured, the measurement cell was designed so that these elements could be short-circuited bypassing the sample. Moreover, the design of the measurement cell made it possible to take into account the changes in the electrical resistance of the current-carrying elements at all temperatures in the range of measurements, to record the values of these changes in a computer, and to subtract them from the measured values of the electrical resistance of the sample. The thermopower ΔE and the electrical resistance of the samples were measured by terminating leads from the measurement cell at different measuring instruments. The thermopower coefficient α was determined from the relationship $\alpha = \Delta E/(T_1 - T_2)$, where T_1 and T_2 are the temperatures of the upper and lower surfaces of the sample, respectively. The dependences $\sigma(T) = 1/\rho(T)$ were constructed for the average temperature of the sample, because it was impossible to completely exclude the temperature gradient along the length of the sample.

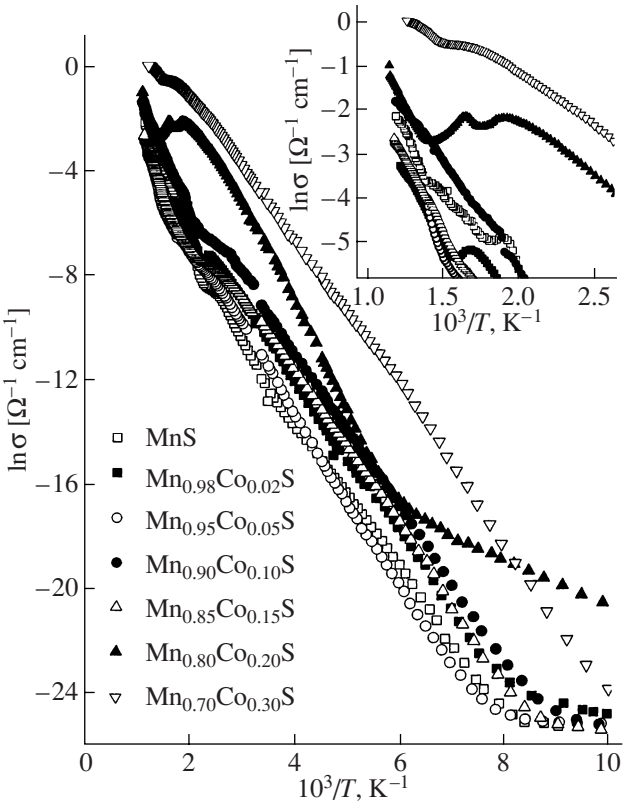

Fig. 1. Temperature dependences of the electrical conductivity measured for samples of the compounds $Co_xMn_{1-x}S$ ($0 \le x \le 0.3$).

3. RESULTS OF MEASUREMENTS

The x-ray diffraction data indicate that the parameter of the crystal chemical unit cell of the solid solutions in the $Co_xMn_{1-x}S$ system decreases linearly from 5.222 Å in manganese sulfide to 5.204 Å in the $Co_{0.3}Mn_{0.7}S$ compound. This suggests that MnS-based solid solutions with a structure of the rock salt type are formed in the system.

The analysis of the temperature dependences of the electrical resistivity measured for samples of the $Co_xMn_{1-x}S$ solid solutions with a cobalt concentration in the range $0 \le x \le 0.3$ (Fig. 1) has demonstrated that the electrical conductivity of these materials exhibit a semiconductor behavior. At temperatures above 500–600 K, the temperature dependences of the electrical conductivity exhibit anomalies that are characteristic of the crossover from impurity conduction to intrinsic conduction [5]. The band gap E_g, which was determined from the slope of the straight-line portion in the dependence $\ln\sigma(10^3/T)$, decreases from 1.46 eV in α-MnS to 0.42 eV in the sample with a cobalt concentration $x = 0.3$. The electrical resistivity of the samples with a cobalt concentration in the range $x = 0.05$–0.40 decreases by ten orders of magnitude. At temperatures in the range from 80 to 950 K, the samples with a cobalt

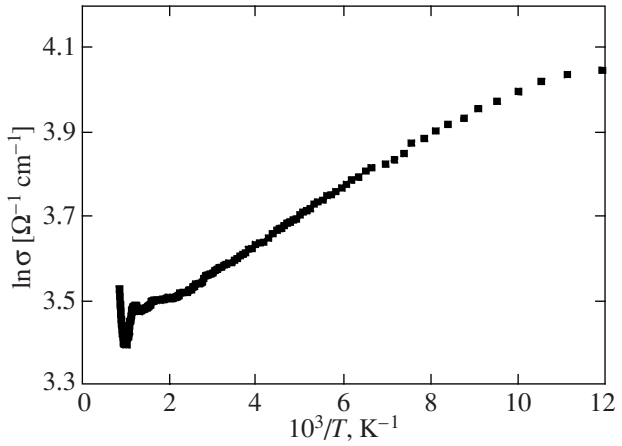

Fig. 2. Temperature dependence of the electrical conductivity measured for the sample of the $Co_{0.4}Mn_{0.6}S$ compound.

concentration $x = 0.4$ possess metallic conduction. As the temperature increases above 950 K, the metallic conduction of these samples gives way to conduction of the semiconductor type. The band gap determined from the slope of the straight-line portion in the dependence $\ln\sigma(10^3/T)$ (Fig. 2) is $E_g \sim 0.26$ eV.

Figure 3 shows the temperature dependences of the thermopower coefficient measured for different solid solutions in the $Co_xMn_{1-x}S$ system. The dependence $\alpha(10^3/T)$ for pure manganese sulfide is similar to that obtained in [6]. The positive sign of the Seebeck coefficient confirms the hole type of conduction in solid solutions with a cobalt concentration $x \le 0.3$. The thermopower coefficient α decreases in magnitude with an increase in the cobalt content in solid solutions and does not exceed 100 μV/K for the $Co_{0.3}Mn_{0.7}S$ compound. For the $Co_{0.4}Mn_{0.6}S$ solid solution, the Seebeck coefficient does not exceed 20 μV/K in magnitude and has a negative sign. As the temperature increases above 870 K, the Seebeck coefficient of this compound changes sign and becomes positive.

Thus, we can state that the $Co_xMn_{1-x}S$ solid solutions studied in this work undergo metal–insulator phase transitions with variations in both the temperature and the cobalt concentration.

4. DISCUSSION OF THE RESULTS

The observed large value of the thermopower coefficient α and its decrease with an increase in the temperature from 150 to 200 K for the $Co_xMn_{1-x}S$ solid solutions with a cobalt concentration $x \le 0.15$ can be explained by a drastic decrease in the number of charge carriers at temperatures below 200 K because of the compensation of charge carriers in the α-MnS compound and in solid solutions based on this sulfide phase. This is indicated by the fact that the electrical resistivity $\rho(T)$ remains unchanged at temperatures below 120 K.

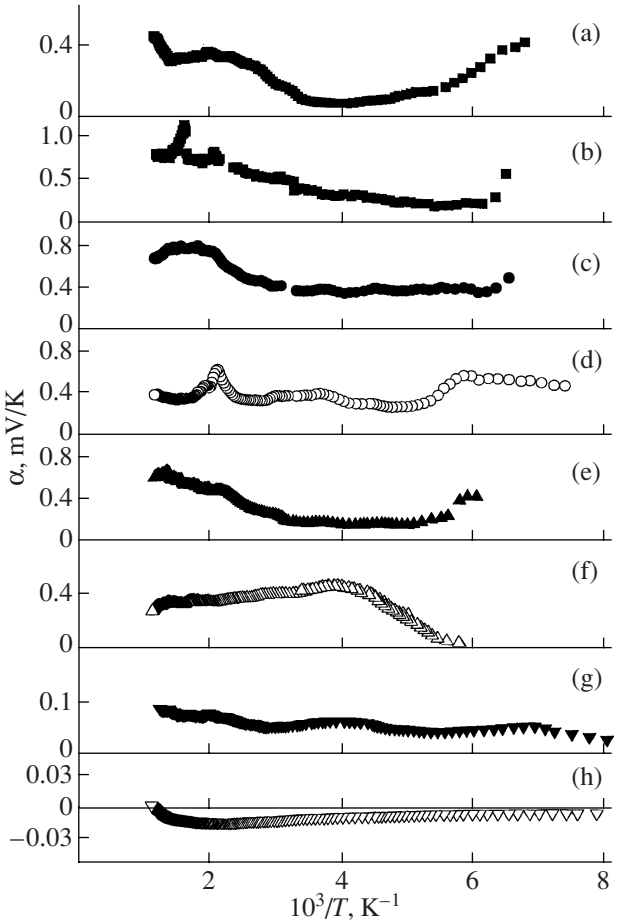

Fig. 3. Temperature dependences of the Seebeck coefficient measured for different samples: (a) MnS, (b) $Co_{0.02}Mn_{0.98}S$, (c) $Co_{0.05}Mn_{0.95}S$, (d) $Co_{0.1}Mn_{0.9}S$, (e) $Co_{0.15}Mn_{0.85}S$, (f) $Co_{0.2}Mn_{0.8}S$, (g) $Co_{0.3}Mn_{0.7}S$, and (h) $Co_{0.4}Mn_{0.6}S$.

The constant value of the electrical resistivity $\rho(T)$ suggests that electrons of the donor impurity reside in the bound state below a specific temperature at which the materials become insulators. It seems likely that, during heating above 150 K, when bound electrons of the donor impurity gradually become unbound, the electrical conductivity begins to rapidly increase according to the semiconductor law, whereas the thermopower voltage is determined by the corresponding decrease in the electrical resistance. This circumstance manifests itself in a drastic decrease in the thermopower coefficient α at temperatures in the range from 150 to 200 K.

A decrease in the thermopower coefficient α with an increase in the cobalt content in the lattice of the α-MnS compound suggests that cobalt acts as a donor impurity, because the magnitude of the thermopower is determined by the combined effect of two types of charge carriers that compensate for each other. In the $Co_{0.4}Mn_{0.6}S$ solid solution, the charge carriers generated by cobalt become predominant. Therefore, the

magnitude and sign of the thermopower can be governed only by the cobalt concentration. The appearance of donor states in α-MnS upon substitution of cobalt for manganese is most likely associated with the fact that the *d* shell of the cobalt cation has two more electrons than the corresponding shell of the manganese cation.

The metallic conduction observed in the $Co_{0.4}Mn_{0.6}S$ solid solution at temperatures in the range from 80 to 950 K can be explained by the fact that this material is a heavily doped semiconductor with the observed compensation of charges generated by donor and acceptor impurities. Hence, the temperature dependence of the electrical conductivity $\sigma(T)$ does not contain a portion corresponding to impurity conduction (owing to the absence of transfer of new charge carriers to the conduction band); in this case, the dependence $\sigma(T)$ exhibits metallic behavior. However, at high temperatures (above 950 K), when there occurs transfer of new charge carriers from the valence band to the conduction band, the dependence $\sigma(T)$ assumes the shape characteristic of semiconductors. The change in the sign of the thermopower coefficient $\alpha(T)$ for the $Co_{0.4}Mn_{0.6}S$ solid solution at temperatures above 870 K (Fig. 3) also counts in favor of the hypothesis that, at high temperatures, the $Co_{0.4}Mn_{0.6}S$ solid solution is a semiconductor.

5. CONCLUSIONS

Thus, the above investigations into the structural, electrical, and thermoelectrical properties of sulfides in the system $Co_xMn_{1-x}S$ ($0 \le x \le 0.4$) have demonstrated that the compounds with a cobalt concentration in the range $0 \le x \le 0.3$ are semiconductors with hole conduction ($\alpha > 0$), whereas the compound with $x = 0.4$ exhibits metallic conduction ($\alpha < 0$). It has been revealed that, in the compounds with a cobalt concentration $x < 0.3$, the crossover from impurity conduction to intrinsic conduction is observed at a temperature $T \sim 600$ K and that the compound with $x = 0.4$ undergoes a crossover from metallic conduction to intrinsic conduction at $T > 950$ K.

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