Anderson transition in the cation-substituted compounds \(\text{Re}_x\text{Mn}_{1-x}\text{S}\)

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**Abstract.** The electrical properties of cation-substituted \(\text{Re}_x\text{Mn}_{1-x}\text{S}\) (Re = Gd, Sm, Ho) compounds are investigated in the temperature range of 77-1200 K. A change in the type of conductivity from semiconductor to "metal" in \(\text{Re}_x\text{Mn}_{1-x}\text{S}\) compounds at a critical concentration of \(X_c\) with an increase in the degree of cationic substitution is detected. The metal-dielectric concentration transition in the \(\text{Gd}_x\text{Mn}_{1-x}\text{S}\) system is accompanied by a decrease in the value of the specific electrical resistance by 12 orders of magnitude. For \(\text{Sm}_x\text{Mn}_{1-x}\text{S}\), a sharp maximum of resistance is detected at \(T = 100\) K, which can be caused by scattering of conduction electrons on spin fluctuations of localized electrons. The metal type of conductivity was established for \(\text{Sm}_{0.25}\text{Mn}_{0.75}\text{S}\). In the \(\text{Ho}_x\text{Mn}_{1-x}\text{S}\) system, the Anderson transition was detected for \(X_c = 0.3\) with a decrease in the value of the specific electrical resistance by 10 orders of magnitude.

1. **Introduction**

In disordered systems with changing composition, pressure, temperature, it is possible to form the Anderson-type metal-dielectric transition [1] as a result of changing the position of the Fermi level \(E_F\) and the mobility threshold \(E_C\) (\(E_C\) is the energy that separates localized states from delocalized ones). Promising materials for studying the metal-dielectric transition in magnetically ordered matter are 3d metal monosulfides and their solid solutions \(\text{Me}_x\text{Mn}_{1-x}\text{S}\) (Me = Cr, Fe, V, Co) [2, 3].

Substitution of manganese cations with rare-earth elements in MnS sulfides can induce a set of phase transitions: magnetic, electrical [4], as well as the metal-dielectric transition. From the point of view of fundamental research, special attention should be paid to compounds containing rare earth elements (Re = Gd, Sm, Ho) with metal-dielectric phase transitions, accompanied by a change in the type of conductivity from hole to electron type [5-10].

Substitution of manganese with a rare earth element in \(\text{Re}_x\text{Mn}_{1-x}\text{S}\) (Re = Gd, Sm, Ho) compounds will result in a shift in the f- level. Substitution of manganese with a trivalent ion will cause electronic doping and may induce orbital ordering [11-13], which will lead to splitting of the electron density of states. Depending on the location of the Fermi level relative to the split density of states, the electrical resistance may change several times [14].

The purpose of this work is to determine the metal-dielectric transition of the Anderson type, and the critical concentration at which the sign of charge carriers changes as a result of electronic doping during cationic substitution of manganese with gadolinium, samarium, holmium \(\text{Re}_x\text{Mn}_{1-x}\text{S}\) (Re = Gd, Sm, Ho).
The study of the relationship between the electrical, magnetic and structural subsystems of a crystal in the vicinity of the metal-dielectric transition opens up broad prospects for solving fundamental problems of solid state physics. The interaction between the magnetic and elastic subsystems leads to new magnetic states [15-20], which have a significant influence on transport properties. Non-stoichiometric substitution will lead to internal electrical polarization, which also affects the conductivity of semiconductors [21-27].

2. Experimental results and discussion

The Gd$_x$Mn$_{1-x}$S ($0.01 \leq X \leq 0.3$) samples are antiferromagnetic semiconductors. The electrical properties of solid solutions in the range of concentrations $X = 0.01-0.3$ and temperatures $80 \ \text{K} \leq T \leq 1200 \ \text{K}$ change dramatically. It was found that when Mn$^{2+}$ cations are replaced with Gd$^{3+}$ ions, metal-dielectric phase transitions are observed both in concentration ($X_c = 0.3$) and temperature ($T_c = 450 \ \text{K}$). The metal-dielectric concentration transition is accompanied by a decrease in the value of the specific electrical resistance by 12 orders of magnitude (Figure 1). At a temperature of 450 K on $\lg \rho (1/T)$ dependencies for $X = 0.01$; 0.1 maxima associated with the transition from semi-metallic to semiconductor conductivity are observed. In the temperature range of $\sim 670 \ \text{K}$, the $\lg \rho (1/T)$ dependencies of these compounds exhibit anomalies characteristic of transitions from impurity to intrinsic conductivity, similar to $\alpha$-MnS. (Figure 1, insert). The value of the $E_g$ band gap determined from the slope of the rectilinear part of the $\lg \rho (1/T)$ dependence decreases from 2.46 eV for $\alpha$-MnS ($X = 0$) to 0.64 eV for Gd$_x$Mn$_{1-x}$S ($X = 0.1$).

![Figure 1. Temperature dependences of the resistivity of Gd$_x$Mn$_{1-x}$S samples with X = 0.01 (1); X = 0.1 (2); X = 0.3 (3). Insert: temperature dependence of the resistivity for X = 0.1 in the temperature range of 500-900 K.](image)

The metal-dielectric concentration transition is observed in antiferromagnetic cation-substituted sulfides doped with rare earth elements with variable valence Sm$_x$Mn$_{1-x}$S ($0.01 \leq X \leq 0.25$). The energy of the localized f-state relative to bottom of conduction band determines the gap structure in the electronic excitation spectrum and the electrical properties of Sm$_x$Mn$_{1-x}$S compounds. An increase in the concentration of samarium causes a shift in the Fermi level and a change in the electron density of states at Fermi level. The temperature dependence of the resistance in solid solutions of Sm$_x$Mn$_{1-x}$S changes qualitatively with increasing concentration (Figure 2).

![Figure 2.](image)

Figure 2 shows the temperature dependences of the resistance of Sm$_x$Mn$_{1-x}$S solid solutions. With increasing concentration, the change in temperature resistance is 20 % for X = 0.15 with a minimum at $T = 220 \ \text{K}$. The temperature dependence of the resistance in Sm$_x$Mn$_{1-x}$S, has a sharp maximum at $T = 100 \ \text{K}$ for the substitution concentration $X = 0.2$ and the metallic type of conductivity for the composition with $X = 0.25$. Anomalies in the electrical resistance can be explained by an electronic jump between Sm$^{2+}$ and Sm$^{3+}$ from the occupied to the empty 5d- level with the activation energy $E_a$. The minimum electrical resistance can be explained using the Anderson model.
The maximum observed on the temperature dependence of the electrical resistance for the composition $X = 0.2$ (Figure 2b), may be caused by scattering of conduction electrons on spin fluctuations of localized electrons.

Figure 2. Temperature dependences of the resistivity of samples of the Sm$_X$Mn$_{1-X}$S system with $X = 0.15$ (a); $X = 0.2$ (b); $X = 0.25$ (c) – for the sample Sm$_{0.25}$Mn$_{0.75}$S (1) and the dependence of the resistance on the temperature $\rho(T) / \rho(\Theta) = (T/\Theta)$ (2) taking into account the electron-phonon interaction.

For Sm$_{0.25}$Mn$_{0.75}$S (Figure 2c) the metal type of conductivity is established and the electrical resistance mechanism is associated with electron scattering on acoustic phonons and magnetic scattering on uncompensated antiferromagnetic manganese clusters at $T < 180$ K. As a result of substitution of manganese with samarium in a solid solution of Sm$_X$Mn$_{1-X}$S, the electronic structure is reconstructed, and the resistance cannot be explained on the basis of the phase of samarium sulfide since the behavior of the SmS conductivity differs qualitatively compared to $X = 0.25$.

The change in the specific electrical resistance depending on the temperature is observed in antiferromagnetic compounds Ho$_X$Mn$_{1-X}$S. Figure 3 shows $\rho(T)$ for three concentrations $X = 0.01; 0.2; 0.3$. Temperature dependences $\text{lg} \rho(10^3/T)$ for solid solutions with $X \leq 0.1$ indicate the semiconductor type of conductivity. For small replacement concentrations of Ho$_{0.01}$Mn$_{0.99}$S, the activation energy is determined by the tangent of the angle of inclination of the linear part $\text{lg} \rho (1/T)$, which changes with an increase in temperature from $\Delta E = 0.25$ eV to $\Delta E = 1.4$ eV.

It should be noted that in a small temperature range of 300 K < $T$ < 600 K, the resistivity does not depend on the temperature. This behavior $\rho(T)$ is typical for impurity semiconductors with depletion of the current carrier concentration at impurity levels. With increasing substitution concentration, the activation energy increases and is $\Delta E = 0.3$ eV in the temperature range of 150 K < $T$ < 300 K for $X = 0.1$. With a further increase in the concentration of substitution cations (X), a sharp decrease in electrical resistance is observed. For compounds with $X = 0.3$, "metallic conductivity" was found. With an increase in the concentration of holmium ions, the value of the specific electrical resistance decreases for a composition with $X = 0.3$ by 10 orders of magnitude. The relative change in the resistivity of $1/R$ dR/dT reveals two maxima at $T = 270$ K and $T = 448$ K for $X=0.1$. The maximum of resistance in the high temperature range 720 K < $T$ < 900 K for $x = 0.1$ and 590 K < $T$ < 780 K for $x = 0.3$ appeared as a result of substitution of manganese ions with holmium ions.
Figure 3. Temperature dependences of the resistivity of samples of the Ho$_X$Mn$_{1-X}$S system with $X = 0.01$ (1); $X = 0.2$ (2); $X = 0.3$ (3).

For large concentrations of holmium with $X = 0.3$, solid solutions of the Ho$_X$Mn$_{1-X}$S can already be attributed to degenerate semiconductors, in which the specific electrical resistance does not depend on temperature and the resistance value is intermediate between the semiconductor and the metal.

The intercalation of a small concentration of holmium ions qualitatively changes the temperature dependence of the thermopower (Figure 4a), in comparison with MnS. In the temperature range of 640 K $< T < 875$ K, the thermopower drops sharply, as well as the electrical resistance, for $X = 0.01$. In a solid solution of Ho$_X$Mn$_{1-X}$S with $X = 0.1$, the sign of the thermopower changes from negative to positive and observed the jump in resistance at $T = 450$ K. As the temperature increases, there are two broad maxima and a minimum in the thermopower at $T = 700$ K (Figure 4b). For $X = 0.3$ (Figure 4c), the temperature dependence of the thermopower has the form typical for semiconductors with a non-activation type of conductivity $\alpha = A + BT$. Parameters A and B differ by an order of magnitude in the region of low $80$ K $< T < 350$ K with $A = 0.004$ mV/K, $B = 2.8 \times 10^{-5}$ and high $350$ K $< T < 600$ K temperatures with $A = 0.05$ mV/K, $B = 1.9 \times 10^{-4}$.

Kinetic properties in solid solutions of Ho$_X$Mn$_{1-X}$S can be explained by the action of chemical pressure and hybridization of electron wave functions on t$_{2g}$ and e$_g$ orbitals. The pressure exerted by holmium ions on the nearest manganese cations leads to a decrease in the local crystal symmetry, orthorhombic or rhombohedral, and, respectively, to the removal of two - and three-fold degeneration of t$_{2g}$ and e$_g$ levels of manganese ions and to the formation of orbital charge ordering. The critical temperature at which the orbital order disappears is determined by the competition of Coulomb, exchange, and electron-phonon interactions [28-29]. In vanadates with t$_{2g}$ ordering of orbitals, the transition temperatures are in the range 240 K – 350 K, and in manganites 700 K – 850 K. The electron structure changes at the Mn-Ho interface, and the corresponding energy levels are located near the top of the valence band and the bottom of the conduction band in the electronic zone diagram. When the orbital order disappears, the energy levels shift down in energy, resulting in an increase in the elastic energy of the lattice. The maxima in the thermopower $\alpha(T)$ are caused by the intersection of the Fermi level with the impurity level [30].
The next feature is that at small concentrations of substitution of manganese ions with rare earth metal ions, an increase in electrical resistance is observed in comparison with the electrical resistance of the initial sample of manganese monosulfide. With a further increase in the concentration of substitution cations (X), a sharp decrease in electrical resistance is observed. A similar phenomenon was observed when replacing manganese in MnS with cobalt ions.

3. Conclusion
Cationic substitution in solid solutions of Re_xMn_{1-X}S with rare earth elements of gadolinium, samarium, and holmium leads to an electronic metal-dielectric transition, both in concentration and temperature.

In this case, the Gd_xMn_{1-x}S (0.01 ≤ X ≤ 0.3) system changes the hole-type conductivity to electronic, so the conductivity in such substances is completely determined by electrons. A solid solution of Sm_xMn_{1-x}S containing samarium ions with variable valence reveals a sharp maximum of resistance at T = 100 K for X = 0.2 and a metallic type of conductivity for concentration X_{C} = 0.25.

For the Ho_xMn_{1-x}S system, a critical concentration of X_{C} = 0.3 was found, at which the metal-dielectric transition is realized. The solid solutions of Ho_{0.3}Mn_{0.7}S can be attributed to degenerate semiconductors.

Based on the studies of Re_xMn_{1-X}S (Re = Gd, Sm, Ho) compounds it is possible to predict and create new materials with specified physical and technical parameters for the development of spin electronics semiconductor devices.

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