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Magnetic and Thermoelectric Properties of the $Mn_{1-X}Ni_XS$ Solid Solutions

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The new sulphide $Mn_{1-X}Ni_XS$ ($0 < X \leq 0.1$) solid solutions are synthesized. The structural, magnetic, electric and thermoelectric properties of the obtained materials have been studied. The X-ray diffraction analysis has shown that the synthesized $Mn_{1-X}Ni_XS$ samples have a NaCl-type FCC lattice. The $Mn_{1-X}Ni_XS$ samples are antiferromagnets with the Neel temperature ($T_N = 180$ K for $X = 0.05$ and $T_N = 200$ K for $X = 0.1$). The temperature dependence of magnetization is described by the Curie-Weiss law at $T > T_N$. The conductivity type change from the hole to the electronic at $X > 0.05$ is revealed on the basis of the thermoelectric power measurements. The resistivity and thermopower behaviors are explained in terms of the impurity subband formation into MnS electron excitation gap.

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I. INTRODUCTION

In connection with intensive development of a microelectronics and spintronics, interest of researchers to the magnetic semiconductor materials showing colossal magnetoresistivity effect (CMR) and metal - insulator transition (MIT) has increased. Cation-substituted $Mn_{1-X}Me_XS$ (Me - 3d-metal) sulfides synthesized on the basis of an α-MnS antiferromagnetic semiconductor are the promising materials for studying these effects [1–3]. It is known that α-MnS has a peculiar antiferromagnetic (AFM) order with a characteristic ferromagnetic orientation of the spins in alternating planes and a lattice distortion along one of the cube diagonals. In α-MnS the temperature T_S of a structural transition is comparable with the Neel temperature ($T_N \sim 150$ K). The α-MnS compound is semiconductor in the paramagnetic (PM) state. Single NiS crystals crystallize in the NiAs structure P6mmc space group. NiS is a semiconductor below T_N and metal above T_N with partially filled $3d(e_g)$ bands [4]. Giant magnetoresistance in NiS is due to a magnetic field induced transition from AFM anomalous metal phase to PM metal phase below 270K [5]. This fact suggests that it is possible to realize the CMR effect and MIT transition in $Mn_{1-X}Ni_XS$ compounds created on a α-MnS basis.

II. EXPERIMENTS AND DISCUSSION

The polycrystalline $Mn_{1-X}Ni_XS$ ($0 < X \leq 0.1$) samples were synthesized from pure elements of nickel, manganese and sulfur using the ampoule method. Phase composition and the crystal structure of the $Mn_{1-X}Ni_XS$ samples were determined with a X-ray diffractometer in CuK_α-radiation at 300 K. The specific magnetization and magnetic susceptibility were measured in vacuum by a ponderomotive method [6] in the temperature range 100 - 1000 K in magnetic field of 8.6 kOe. The resistivity and thermopower values were determined by a four-probe compensation method in dc current at 80-1000 K. The thermopower coefficient was measured relative to copper with the device described in [7].

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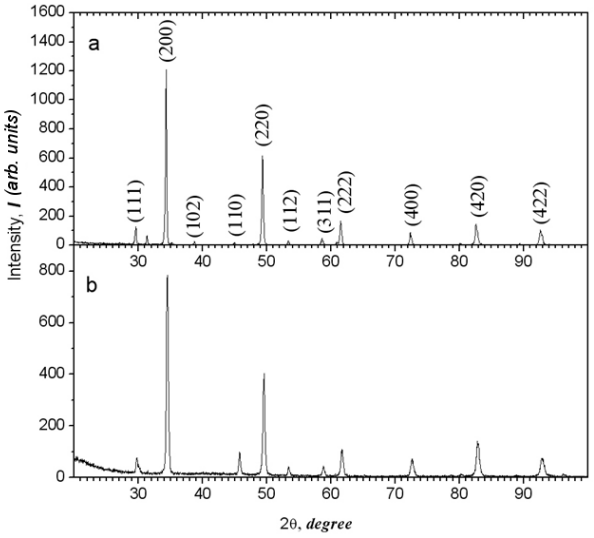

Fig. 1. X-ray diffraction patterns of $Mn_{0.95}Ni_{0.05}S$ (a) and $Mn_{0.9}Ni_{0.1}S$ (b) samples measured at $T = 300$ K before heat treatment.

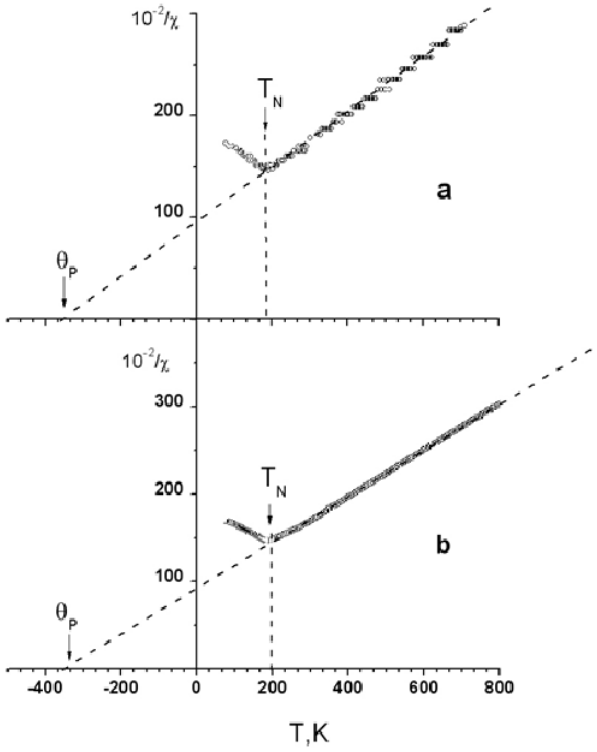

Fig. 2. Temperature dependences of the magnetic susceptibility for $Mn_{0.95}Ni_{0.05}S$ (a) and $Mn_{0.9}Ni_{0.1}S$ (b) samples measured in the magnetic field 8,6 kOe.

The X-ray diffraction analysis has shown that the synthesized $Mn_{1-X}Ni_XS$ samples have a NaCl-type FCC lattice but before heat treatment there were observed four reflexes (002), (102), (110), (112) of a weak intensity, associated with γ-modifications of MnS (Fig. 1). With the increase X of the cation substitution concentration, the parameter a of the unit cell decreases from 5.24 Å for MnS up to 5.21 Å for $Mn_{0.95}Ni_{0.05}S$ as the ionic radius of the substituent reduction.

The specific magnetization investigations results of $Mn_{1-X}Ni_XS$ ($0 < X \leq 0.1$) solid solutions are presented on Fig. 2. Samples $Mn_{1-X}Ni_XS$ are antiferromagnets. The Neel temperatures are increasing ($T_N = 180$ K for $X = 0.05$ and $T_N = 200$ K for $X = 0.1$) as the Ni concentration grows. The specific magnetization temperature dependence is described by the Curie-Weiss law at $T > T_N$ similar to the dependence for α-MnS monosulfide [2]. The asymptotic paramagnetic temperature (Θ_P) and Curie-Weiss constant (C), determined from the magnetic susceptibility temperature dependences are $\Theta_P =$ –340 K; $= 2.31$ for $X = 0.05$; $\Theta_P =$ –350 K and $= 2.46$ for $X = 0.1$. The negative value of a paramagnetic temperature shows the prevalence of antiferromagnetic bonds. The effective magnetic moment values μ_{eff} for manganese cation in solid solutions calculated from tangent of inclination for hight-temperature part of $10^{-2}/\chi = f(T)$ dependence, within a calculation errors, is concluded $\mu_{eff} = 5.04 \pm 0.01\mu$ for $X = 0.05$ and $\mu_{eff} = 5.16 \pm 0.01\mu$ for $X = 0.1$. The probable decrease in unit cell volume of $Mn_{1-X}Ni_XS$ solid solutions compared to the manganese monosulphide could lead to the increased exchange interactions. Apparently, this is the reason for the increase in temperature of magnetic phase transition "magnetic order - magnetic disorder" in the solid solutions. It is necessary to note stability of the magnetic characteristics of new solid solutions in the 77 $\sim$ 800 K temperature range because dependences $1/\chi(T)$ are identical at heating and cooling.

The specific resistivity temperature dependence of the ($X = 0.05$) sample shows to semiconductor character of its conductivity with energy activation 0.1 eV (Fig. 3(a)). In this case, a sharp decrease in resistivity (by $\sim$ 10 orders of magnitude) is observed with increasing of temperature in the magnetically ordered region (Fig. 3(a), insert). A similar behavior of the electrical resistivity is characteristic for compounds with the metal-insulator transition, for example, V_2O_3 [8]. In the paramagnetic phase ($>$ 180 K) it is a constant value $\rho(T)$ indicating the degenerate state of the conduction electrons (Fig. 3(a) insert).

The Seebeck coefficient α for this ($X = 0.05$) sample in the whole temperatures range is positive, which confirms the p-type conductivity in $Mn_{1-X}Ni_XS$ solid solutions with $X = 0.05$ (Fig. 4(a)), similar to α-MnS. With increasing of nickel concentration in the lattice of α-MnS coefficient α decreases and for $X = 0.1$ value α becomes negative in the temperature range 80 - 750 K (Fig. 4(b)). The coefficient α in this temperature range has a value of $\alpha < 0.05$ mV / K and weakly dependent on temperature. The α decreasing with increasing of Ni concentration in the lattice of α-MnS indicates that nickel acts as a donor impurity. Nickel ions inhibit the

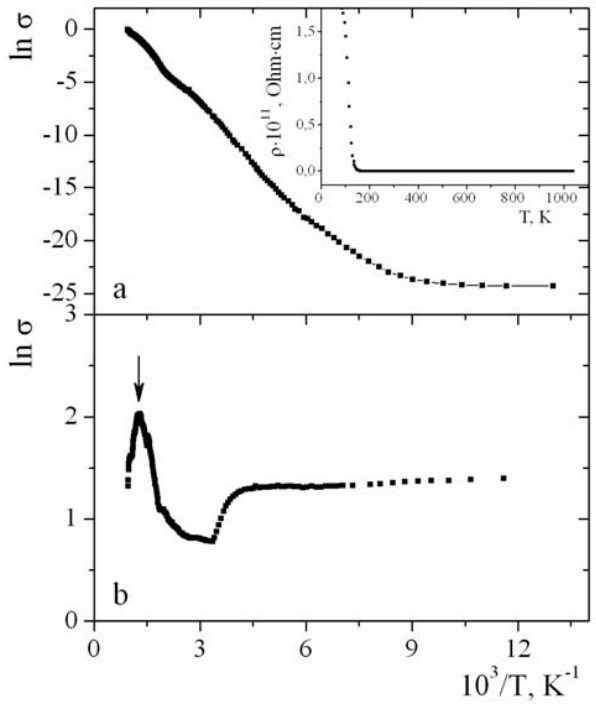

Fig. 3. Temperature dependences of conductivity for the $Mn_{1-X}Ni_XS$ samples with $X = 0.05$ (a) and $X = 0.1$ (b).

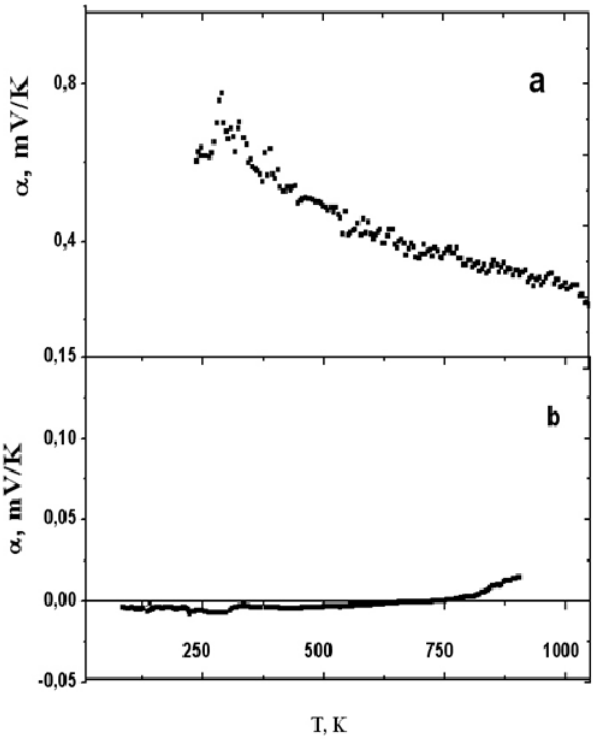

Fig. 4. Temperature dependences of thermopower coefficient for $Mn_{1-X}Ni_XS$ samples with $X = 0.05$ (a) and $X = 0.1$ (b).

hole conductivity (p-type) of α-MnS and create donor (electron) conductivity (n-type). The weak dependence of versus the temperature of the sample with $X = 0.1$ can be explained by the fact that this sample is heavily doped semiconductor, in which it is the phenomenon of compensation of the charges created by the donor and acceptor impurities, as the value of thermoelectric power is determined by the total contribution of two types of charge carriers (holes and electrons).

The conductivity dependence $\sigma(T)$ for this sample in the temperature range 80-300 K is similar to the metal (Fig. 3(b)). However, at temperatures above 300 K the dependence $\sigma(T)$ is characteristic of a semiconductor that can be explained with the transition of new charge carriers from the valence band to the conduction band. At temperatures $\sim$ 750 K in the conductivity dependence Lnσ $(10^3/T)$ a sharp peak (Fig. 3(b), see a mark by arrow) is observed connected with a transition from semiconducting to metallic type of conductivity. In the same temperature range ($T > 750$K) the sign of the Seebeck coefficient α changes on the positive value. This is typical for (n-p)-transition [9].

III. CONCLUSION

There are synthesized the new antiferromagnetic $Mn_{1-X}Ni_XS$ sulphide solid solutions with FCC α-MnS. According to the data on resistivity and thermopower, in the system of the $Mn_{1-X}Ni_XS$ solid solutions ($0 < X \leq 0.1$) both concentration and temperature metal-insulator transitions occur accompanied by the change in conductivity from p-type to n-type. The changes in the Seebeck coefficient are correlated with changes in electrical conductivity. This transition is an electronic phase transition from nonmetal to metal phase without changes of a structure. The transition has been explained in terms of the impurity subband formation in the chemical potential neighbourhood. Changes in the electron density of state and mobility of electron and hole as results of shift of chemical potential versus temperature are described the temperature dependences of resistivity and thermopower.

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