

New Magnetic Materials $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ with a Metal–Insulator Transition

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Abstract—This paper reports on first results of the synthesis and study of the thermal, structural, electrical, resonance, and magnetic properties of new sulfide materials $\text{Me}_x\text{Mn}_{1-x}\text{S}$ ($\text{Me} = \text{Cu}$, $0 < x < 0.2$) synthesized based on manganese monosulfide. The materials have a NaCl cubic structure at 300 K and undergo a concentration metal–insulator transition with increasing degree of substitution and with varying temperature. The magnetic transition occurs in the region of the heat capacity anomaly. The Néel temperature is slightly dependent on the copper concentration. The samples with a high copper content exhibit metallic conduction at $T < 260$ K and semiconductor conduction at $T > 260$ K.

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1. INTRODUCTION

The design, synthesis, and study of new compounds are important problems in the physics of solid state and magnetism. One of methods of searching and designing materials with new physical properties is the method of cation (anion) substitution that is used for synthesizing solid solutions. The choice of the matrixes for such studies is determined, along with other conditions, by the solubility of a substitutional cation in the matrix. Manganese monosulfide is known [1] to crystallize in three structural modifications (cubic α and β phases and the hexagonal γ phase). The α -MnS phase has a face-centered cubic structure of the NaCl type. Monoxides of a number of 3d elements MnO (d^5), FeO (d^6), CoO (d^7), and NiO (d^8) have a similar structure [2]. Unlike the foregoing monoxides, copper monoxide CuO (d^9) [3] has a monoclinic structure that is a distorted variant of the NaCl cubic lattice. The Cu^{2+} copper ion is assumed to cause the distortion of the NaCl structure due to the Jahn–Teller effect.

This paper reports on the results of the synthesis and study of the physical properties of $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ sulfides. The studies were performed in order to elucidate possibilities of the formation of $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ solid solutions and the influence of the Jahn–Teller Cu^{2+}

ion on the physical properties and the Mott state in manganese monosulfide.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

The $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ samples were synthesized by two methods. Polycrystalline samples no. 1 with the compositions $x = 0.05, 0.15, 0.30$ were synthesized in evacuated quartz ampoules by annealing of a mixture of pure elements Cu, Mn, and S (taken in amounts corresponding to the charge composition) at a temperature of 960°C for a week. Powders no. 2 were synthesized from a mixture of oxides by sulfidization in a quartz reactor. From the powders, single crystals with compositions $x = 0.10, 0.15, 0.18$ were grown by crystallization from the melts. The crystal structure of the $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ materials synthesized was studied by X-ray diffraction on a DRON X-ray diffractometer with CuK_α radiation. The heat capacity of the single crystals was measured using a PPMS 9 (Quantum Design VSA) universal device in the temperature range 77–300 K. The magnetic susceptibility was measured on a high-sensitive MPMS®-XL SQUID magnetometer in the range 4.2–300 K in magnetic fields of 0.5 and 20.0 kOe. The resonance properties were measured on an SE/X-2544 X-band EPR spectrometer in

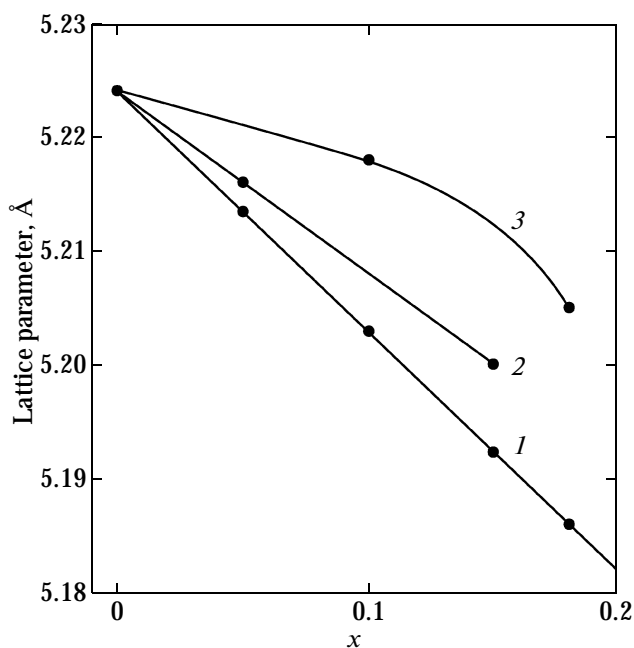


Fig. 1. Concentration dependences of the unit cell parameter of $\text{Cu}_x\text{Mn}_{1-x}\text{S}$: (1) the calculated dependence for the solid solution; (2) and (3) the experimental dependences for the polycrystal and the single crystals, respectively.

the temperature range 90–300 K. The electrical properties were measured by the dc four-probe method using a PPMS 6000 setup and a specially equipped setup with a program control.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The results of studying the phase composition and crystal structure of $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ show that the homogeneous $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ solid solutions with the cubic structure of the MnS matrix are formed in a fairly narrow concentration range (to $x = 0.15$). The substantial change of the physical properties of $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ is demonstrated by a change in the color of the material formed. If manganese monosulfide powder has a green color, $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ compounds take a yellow color, which indicates on a change in the optical properties and a shift of the absorption band toward red side of the spectrum. Fig. 1 shows the concentration dependences of the cubic lattice parameter (NaCl, $FM-3m$). Curve 1 corresponds to the dependence calculated for the $\text{Cu}_x^{2+}\text{Mn}_{1-x}^{2+}\text{S}^{2-}$ solid solution with 3d ions in the octahedral sites; curves 2 and 3 corresponds to the experimental dependence for samples nos. 1 and 2, respectively. Taking into account that the ionic radius of the divalent Cu^{2+} copper ions (0.78 Å) is smaller than that of Mn^{2+} manganese ions (0.91 Å), we

can expect a fairly substantial decrease in the cubic lattice parameter when the solid solution forms. The experimental concentration dependences of the lattice parameter are slightly dependent on the composition, e.g., as compared to the known data for the $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ and $\text{Cr}_x\text{Mn}_{1-x}\text{S}$ systems [4]. The studies of the stoichiometry show that the real composition of $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ samples with $x = 0.1$ corresponds to the composition with $x = 0.10$, and the chemical composition of the samples with $x = 0.15$ corresponds to the real compositions $x = 0.15$ and $x = 0.25$. The X-ray diffraction patterns of the samples with the composition in charge $x = 0.18$ have additional structural reflections (with intensity less than 5%), along with the structural reflections typical of NaCl. A comparison of the experimental data with the ACTM card-index data shows that additional structural reflections are not described by an impurity of the hexagonal CuS phase (dark blue color) or the monoclinic phase CuO. The calculations performed using the “Diamond” program allowed the conclusion that the additional lines in the X-ray diffraction patterns of the samples can be described by the monoclinic structure of $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ with the lattice parameters $a = 5.5$ Å, $b = 3.5$ Å, $c = 4$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 95^\circ$, and space group $C12/c1$ (15). A set of the results of analyzing the structural properties of $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ allows the assumption that the difference in the concentration dependences of the NaCl unit cell parameter of the solid solution from the expected dependence is due to local distortions of the lattice in the vicinity of copper ions and succeeding formation (at high concentrations) of an attendant solution with the monoclinic structure.

Figure 2 depicts most typical temperature dependences of the electrical resistivity of $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ measured in the range 77–300 K. As the degree of cation substitution increases to $x = 0.18$ (in charge, here and in what follows) the resistivity decreases very significantly (by five orders of magnitude) with respect to the value characteristic of manganese monosulfide. For the samples with compositions $0.15 < x < 0.18$, there is a scatter in the data measured in the samples with the same compositions that is explained by the fluctuation of the real chemical composition of the material. In the range 200–300 K, the conductivity of the samples with compositions $0 < x < 0.15$ can be described by the standard exponential dependence with the activation energy that decreases from 0.25 eV ($x = 0.05$) to 0.07 eV ($x = 0.1$). The substantial decrease in the thermal energy gap observed in $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ at low copper concentrations agrees with the results of visual change in the sample color. In the polycrystalline materials, the behavior of the resistivity depends on the rate of varying temperature during the experiment, and the temperature dependence of the resistivity has, as a

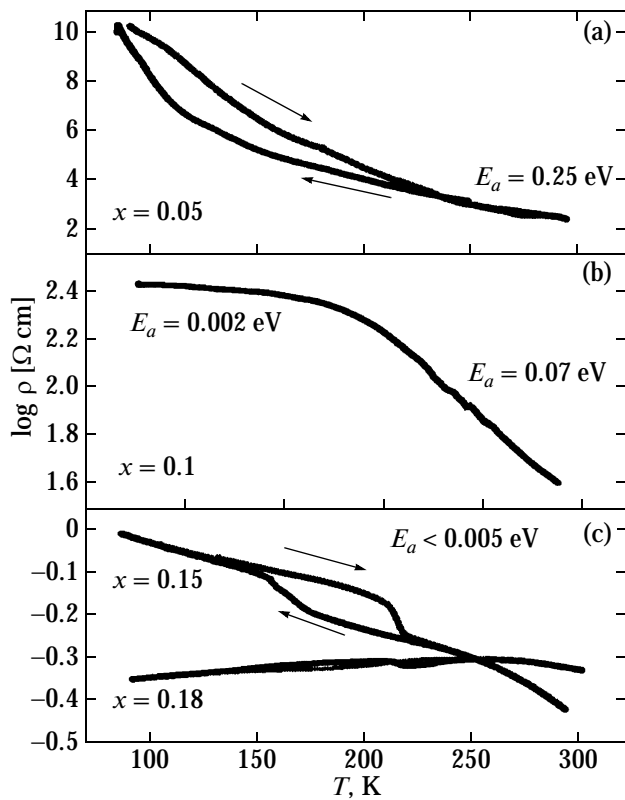


Fig. 2. Temperature dependences of the resistivity of $\text{Cu}_x\text{Mn}_{1-x}\text{S}$.

rule, a hysteresis (Fig. 2a). The resistivity of the single crystals with a low degree of substituting almost has no thermal hysteresis as temperature varies uniformly during the experiment (Fig. 2b). In the sample ($x = 0.1$), the activation energy of conductivity decreases as temperature decreases to $T < 200$ K. The activation energy of the sample with $x = 0.15$ does not exceed 0.003 eV, and the temperature dependence of the resistivity demonstrates a reversible anomaly with the thermal hysteresis in the range 160–220 K. At 300 K, the resistivity of the sample with $x = 0.18$ is $0.36 \Omega \text{ cm}$ at the current of 1.5 mA. This sample has the metallic type of conductivity at temperatures below 260 K.

To elucidate the existence of phase transitions and their critical temperatures, we measured the heat capacity of the $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ samples with $x = 0.15$ and 0.18. The results are depicted in Fig. 3. The heat capacity anomaly exists near ~ 150 K, which is close to known data for manganese monosulfide [5]. The increase in the degree of substitution in our $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ samples synthesized by the same method shifts the phase transition temperature from 144 ± 5 K at $x = 0$ to 153 ± 1 K at $x = 0.18$ (the inset to Fig. 3). It should be underlined that there are no thermal anom-

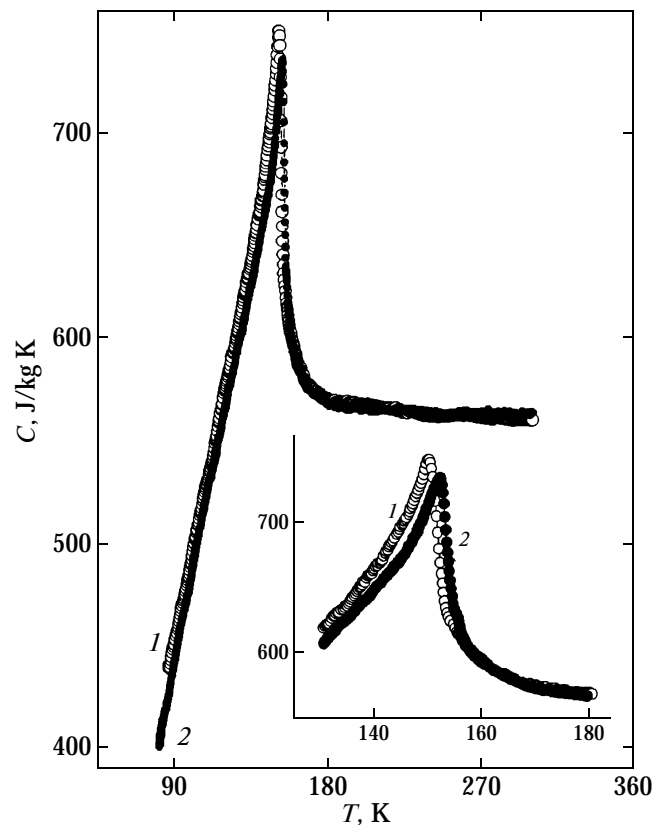


Fig. 3. Temperature dependences of the heat capacity of the $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ single crystals with $x = (1)$ 0.15 and (2) 0.18.

alies indicating on phase transitions in the temperature range 200–300 K.

The electron paramagnetic resonance (EPR) studies of the resonance properties of $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ were carried out on the sample with $x = 0.15$. The EPR spectrum of $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ has one resonance line. Figure 4 shows the temperature dependences of (a) the line width, (b) the resonance field, and (c) the line intensity for $x = 0.15$. The temperature dependence of the EPR parameters is typical of the paramagnetic state. The broadening of the magnetic resonance line and its disappearance near the heat capacity anomaly near 150 K indicate the existence of a transition to a magnetically ordered state. Unlike manganese monosulfide, the resonance field in the copper-containing samples depends on temperature. At $x = 0.15$, the g factor is 1.986 at room temperature, and it decreases with temperature to $g = 1.966$. This result indicates a strengthening of the binding of the magnetic subsystem with the lattice and a stronger influence of the increase in local fields with decreasing temperature.

Figure 5 shows the results of studying the magnetic susceptibility of $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ sulfides: curve (1) presents the data for the MnS single crystal, and curves 3,

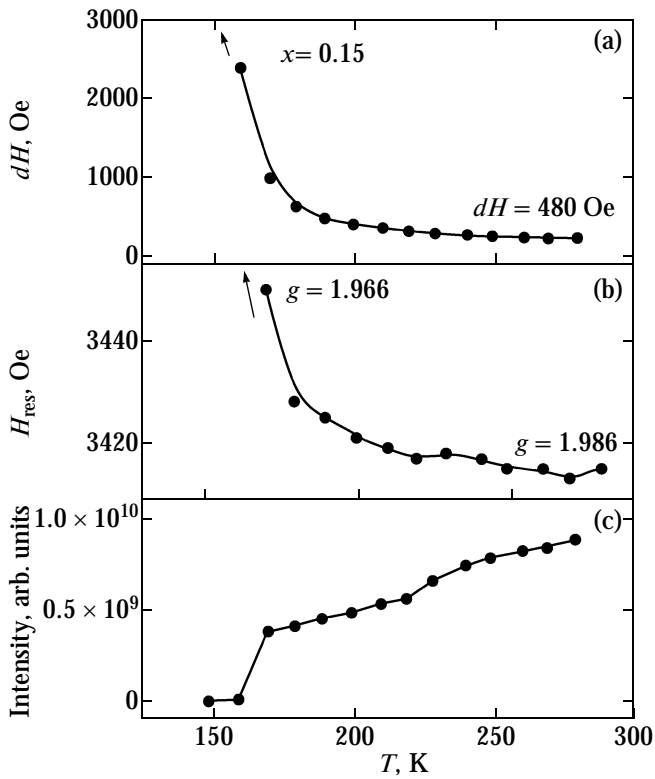


Fig. 4. Temperature dependences of (a) width, (b) resonance field, and (c) intensity of the electron paramagnetic resonance line for the $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ single crystals with $x = 0.15$.

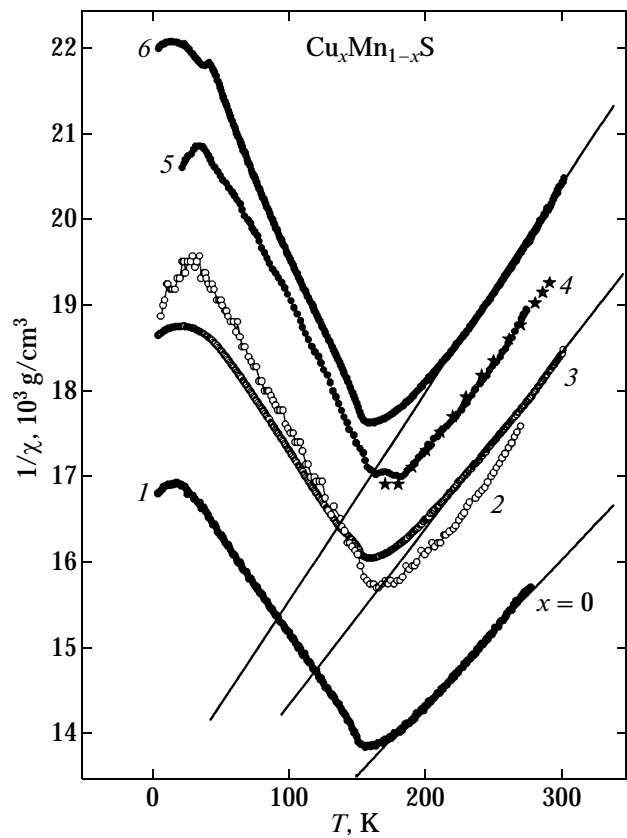


Fig. 5. Temperature dependences of the reverse magnetic susceptibility $\chi^{-1}(T)$ of polycrystalline $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ with $x = (2) 0.05$ and $(5) 0.15$ and single-crystal $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ with $x = (1) 0$, $(3) 0.10$, $(4) 0.15$, and $(6) 0.18$.

4, and 6 present the data for the $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ single crystals with the compositions $x = 0.10$, 0.15 , and 0.18 , respectively. Curves 2 and 5 show the data for the polycrystalline $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ samples with $x = 0.05$ and 0.15 , respectively. The results are fairly close for the single crystal and the polycrystal with $x = 0.15$ (in charge). For comparison, curve 4 corresponds to the temperature dependence of the reverse magnetic susceptibility measured by the EPR method. The magnetic properties were measured in the ZFC (cooling in a zero magnetic field) conditions in magnetic field $H = 0.5$ kOe. In the magnetic field 0.5 kOe (curve 1), MnS demonstrates one phase transition with the magnetic susceptibility maximum at 149 K, which is close to the known results [5, 6]. As the degree of substitution in the $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ solid solution increases, the magnetic susceptibility decreases over entire temperature range, which correlates to the concentration dependence of the resistivity. The materials are antiferromagnets as demonstrated by the minimum in the temperature dependence of the reverse susceptibility and the negative values of the paramagnetic Curie temperature (Fig. 5). The temperature corresponding

to the Néel temperature (T_N) at which the magnetic susceptibility maximum takes place is close to the temperature at which there is the heat capacity anomaly. The total shift of the Néel temperature in the $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ solid solution with changing the degree of substitution does not exceed 5° . At low temperatures, there is additional anomaly of the magnetic susceptibility that is not described by a paramagnetic contribution. The field dependences of the magnetization $\sigma(H)$ of $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ were measured in the magnetic field range to ± 50 kOe at temperatures of 4.2, 77, and 300 K. At room temperature, the $\sigma(H)$ dependence is linear and typical of the paramagnetic states. In the antiferromagnetic state of $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ solid solutions, unlike manganese monosulfide, we revealed the dependence of the magnetic susceptibility on applied field. Figure 6 depicts the field dependences of the magnetization for $x = 0.10$ (curve 1) and 0.15 (curve 2) measured at 4.2 K. The magnetization varies nonlinearly with magnetic field; however, there is no magnetic hysteresis. Similar dependence of the magnetic susceptibility in the magnetically ordered state was found in antiferromagnetic MnO [7]. Moreover, we

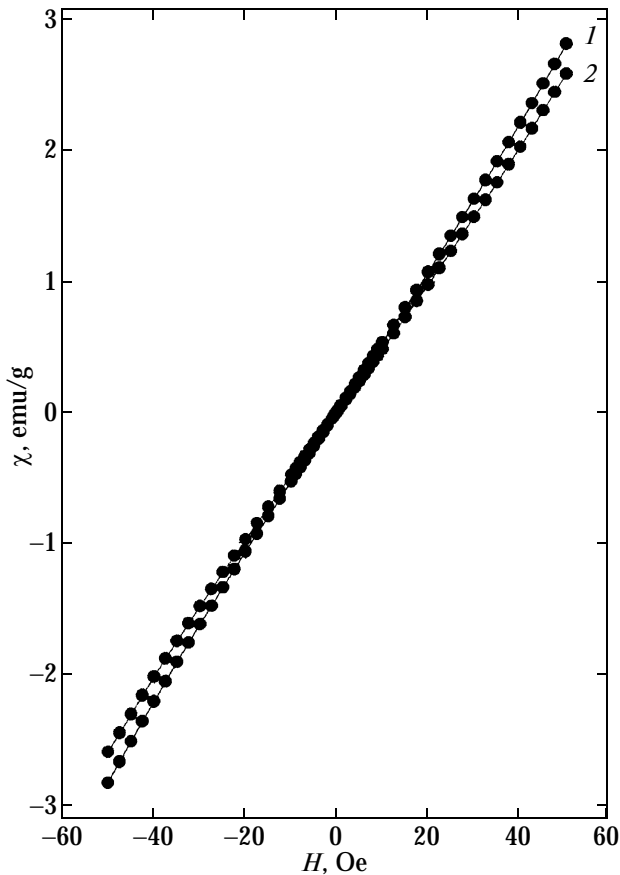


Fig. 6. Magnetic-field dependences of the magnetization of the $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ single crystals with $x = (1) 0.10$ and $(2) 0.15$ at a temperature of 4.2 K.

assume, as in [7], that the dependence of the magnetic susceptibility on the magnetic field in the antiferromagnetic state can be due to reorganization of the domain structure.

Figure 7 shows the concentration dependences of (a) the Néel temperature, (b) the paramagnetic Curie temperature, and (c) the effective magnetic moment measured in the paramagnetic region of the $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ samples. The behavior of the magnetic susceptibility in the paramagnetic state can be described by the Curie–Weiss law with increasing magnitude of the paramagnetic Curie temperature and decreasing effective magnetic moment μ_{eff} (curve 1) close to the pure spin state $\text{Cu}_x^{2+}\text{Mn}_{1-x}^{2+}\text{S}^{2-}$ ($S(\text{Mn}^{2+}) = 5/2$, $S(\text{Cu}^{2+}) = 1/2$) (curve 2). The deviations from the Curie–Weiss law in the behavior of the magnetic susceptibility can be explained by the formation of a short-range magnetic order that is observed at $T < 200$ K, where the activation energy of the conductivity of the samples is changed. Taking this fact, the hysteresis and anomaly of the resistivity for the com-

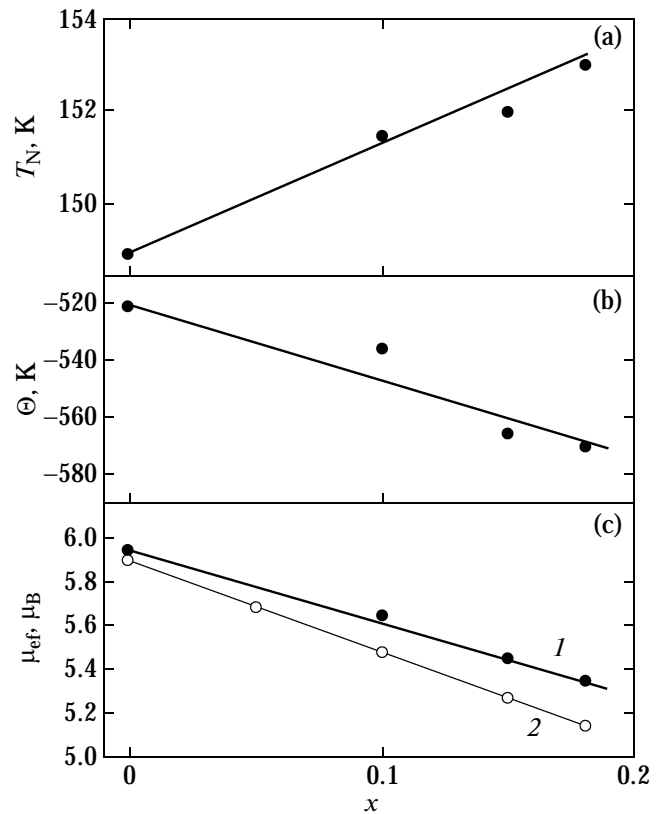


Fig. 7. Concentration dependences of (a) the Néel temperature, (b) the paramagnetic Curie temperature, and (c) the effective magnetic moment according to (1) experimental results and (2) calculated values for $\text{Cu}_x\text{Mn}_{1-x}\text{S}$.

position $x = 0.15$ can be related to a magnetic transition. However, to make more correct inferences, the crystal structure of the samples should be studied in this temperature range.

The found scatter in the values of the resistivity for the single-crystal $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ samples of the same composition can be explained as follows. The $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ single crystals were grown from even finished synthesized materials. The single crystal growth technology is related to heating of the powders to the melting temperature followed by slow cooling with a thermal gradient. This process occurs in the temperature range 1000–1600°C. At high temperatures $T > 700^\circ\text{C}$, diffusion processes occur in manganese monosulfide [8]. We suggest that, owing to high-temperature diffusion, the impurity distribution in the matrix becomes nonuniform, and the formation of cluster is possible. As a result, the single crystals grown with high degree of substitution have fluctuations of the composition and corresponding scatter in the experimental parameters.

4. CONCLUSIONS

Thus, new manganese monosulfide-based $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ materials have been synthesized. It was established that, in the range 4.2–300 K, the cation substitution of copper ions for manganese ions in manganese monosulfide decreases the resistivity and the magnetic susceptibility, which is accompanied by the change in the conductivity type. These materials are antiferromagnets with the Néel temperature that is slightly dependent on the degree of substitution.

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