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Magnetic Properties of Single Crystals of the $Cr_xMn_{1-x}S$ Solid Solutions ($0 \le x < 0.3$)

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Abstract—The $Cr_xMn_{1-x}S$ single crystals have been synthesized based on manganese monosulfide as a result of cation substitution, and their magnetic properties have been studied. It has been established that the $Cr_xMn_{1-x}S$ solid solutions with a face-centered cubic NaCl structure are formed in the concentration region $0 \le x < 0.3$. The unit cell parameter of the solid solution decreases as the degree of substitution increases due to the variation in the ionic radius of cations. These substances are antiferromagnets. An increase in the degree of cation substitution in the $Cr_xMn_{1-x}S$ solid solutions is accompanied by a decrease in the number of 3*d* electrons in the *d* shell of manganese monosulfide and causes a decrease in the magnetic transition temperature from 149 K ($x = 0$) to 96 K ($x = 0.29$), which differs from previously known results.

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1. INTRODUCTION

Investigation of fundamental principles of the formation of new materials is an important direction in the development of the modern physics of condensed media and materials science. One method of controlling the physical properties of solids is the cation (anion) substitution. Selection of matrices to perform such investigations is determined by the possibility of varying their properties without a change in the crystal structure of the matrix. Conservation of the crystal structure of the matrix during the formation of a solid solution is the determining factor for elucidation of the mechanism of controlling its magnetic and electrical properties.

Manganese monosulfide with the Néel temperature of 150 K belongs to the Mott dielectrics [1]. Polycrystalline sulfides of the $Cr_xMn_{1-x}S$ system, which were synthesized on the basis of manganese monosulfide, were investigated in [2–5]. The results of the synthesis of solid solutions of this system were for the first time published in [2]. Magnetic properties of polycrystalline $Cr_xMn_{1-x}S$ samples are presented in [3, 4]. According to [3], these materials are antiferromagnets with the Néel temperature increasing to 240 K as the chromium concentration increases ($x = 0.67$). Investigation of the polycrystalline $Cr_xMn_{1-x}S$ sample with $x = 0.5$ showed the presence of the ferromagnetic transition at 66 K [4]. In the region of this transition, negative magnetoresistance (NMR) is found [5].

Discrepancies in the data presented in [3, 4] allowed us to pose the question on magnetic properties of the $Cr_xMn_{1-x}S$ sulfides again.

In this work, we present the results of the synthesis and investigation of the magnetic properties of single-crystalline chromium-substituted solid solutions of manganese monosulfide $Cr_xMn_{1-x}S$ ($0 \le x < 0.3$). It is known that the Cr^{2+} ion (d^4s^2, $S = 2$) differs from the manganese ion Mn^{2+} (d^5s^2, $S = 5/2$) by the number of electrons in the *d*-shell. After the cation substitution of divalent manganese ions in manganese monosulfide by divalent chromium ions, we could expect a decrease in the number of *d*-electrons, which in turn causes the change of interatomic electron correlation and exchange interactions. Investigations have been performed with the purpose to answer the question on the influence of the electron concentration on the magnetic properties of manganese monosulfide.

2. TECHNOLOGY OF THE SYNTHESIS AND EXPERIMENTAL TECHNIQUE

Polycrystalline sulfides $Cr_xMn_{1-x}S$ with the compositions $x = 0$, 0.10, 0.18, and 0.29 were synthesized from the batch consisting of mixed powders of manga-

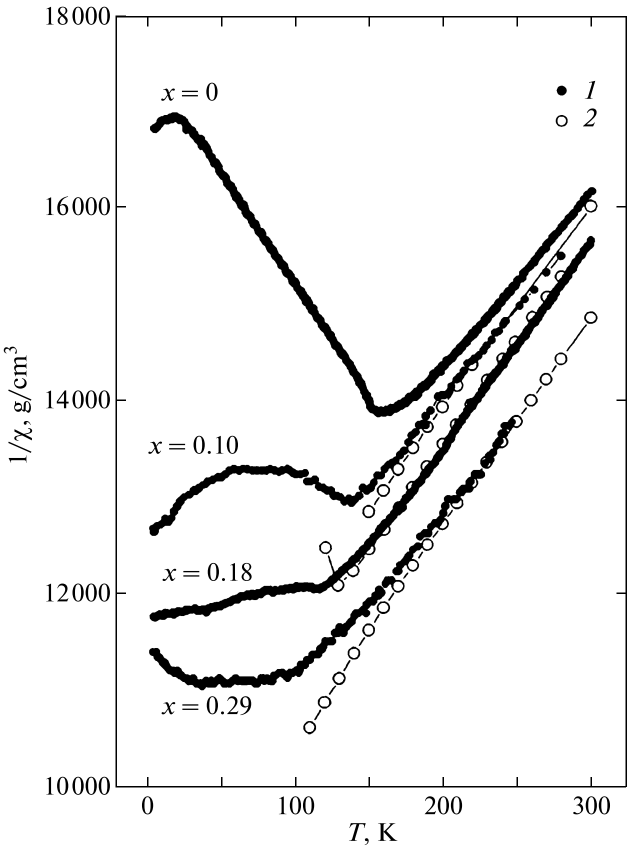

Fig. 1. Temperature dependences of the inverse magnetic susceptibility for the $Cr_xMn_{1-x}S$ single crystals ($0 \le x < 0.3$). (*1*) Results of measurements using a SQUID-magnetometer and (*2*) results found by the ESR method.

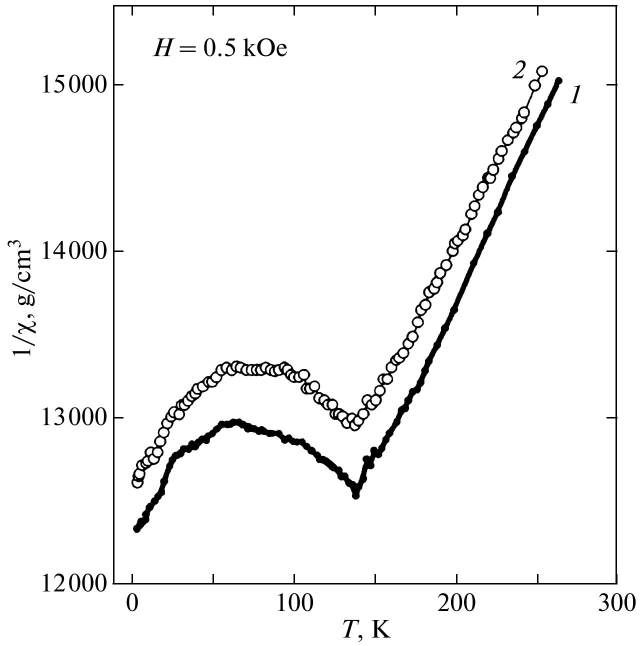

Fig. 2. Temperature dependences of the inverse magnetic susceptibility for the $Cr_xMn_{1-x}S$ single crystal at $x = 0.1$: (*1*) the direction of the magnetic field H lies in the (100) plane and (*2*) the direction of the magnetic field H is perpendicular to this plane.

nese monosulfide and chromium sulfide taken in weight amounts corresponding to values of x. Single crystals 0.5–2.0 cm^3 in size were grown from the synthesized $Cr_xMn_{1-x}S$ powders by spontaneous crystallization from the melt. Magnetic properties were measured using an MPMS®-XL SQUID-magnetometer in a temperature range of 4.2–300 K in magnetic fields of 0.5 and 20.0 kOe. Resonance properties were investigated using an SE/X-2544 ESR *X*-range spectrometer in a temperature range of 90–300 K. The chemical composition and stoichiometry of the samples were investigated at the Osaka University (Japan) by the X-ray fluorescence analysis.

3. RESULTS AND DISCUSSION

Results of investigation of the crystal structure of small-sized $Cr_xMn_{1-x}S$ single crystals are presented in [6]. The X-ray diffraction patterns of the samples are characteristic of the NaCl structure of manganese monosulfide with the *Fm*–3*m* cubic symmetry. As the degree of cationic substitution increases and the $Cr_xMn_{1-x}S$ solid solution is formed, compression of the lattice according to its expected behavior with the substitution of divalent manganese ions for divalent Cr^{2+} ions in octahedral sites is observed. In general, X-ray diffraction patterns of $Cr_xMn_{1-x}S$ are similar to X-ray diffraction patterns characteristic of single-crystal solid solutions of the $Fe_xMn_{1-x}S$ system [6]. Based on the analysis of the experimental data on investigation of structural properties presented in [6], we concluded that the $Cr_xMn_{1-x}S$ solid solutions are formed with $Mn^{2+} \longrightarrow Cr^{2+}$. Investigations with the use of an X-ray diffractometer for studying single crystals showed that the synthesized $Cr_xMn_{1-x}S$ crystals have a block structure. The results of investigations of the chemical composition and stoichiometry allowed us to conclude that the distribution of the Cr^{2+} impurities in the $Cr_xMn_{1-x}S$ crystal can be nonuniform, which leads to composition fluctuations for the samples with a high chromium content. Single crystals with the as-batched composition $x = 0.1$ were single-crystal blocks with the chemical compositions $x = 0.1$ and $x = 0.12$. The $Cr_xMn_{1-x}S$ single crystal with the composition $x = 0.29$ consisted of two blocks with different stoichiometry and lattice parameters. The chemical composition of one block corresponded to $x = 0.29$. It had the parameter of the fcc NaCl lattice $a = 5.17$ Å close to the expected value $a = 5.172$ Å for this composition of the solid solution. Other block of the single crystal, which is denoted as $x = 0.29^*$, had the lattice parameter $a = 5.14$ Å and magnetic properties corresponding to the composition $x = 0.35$.

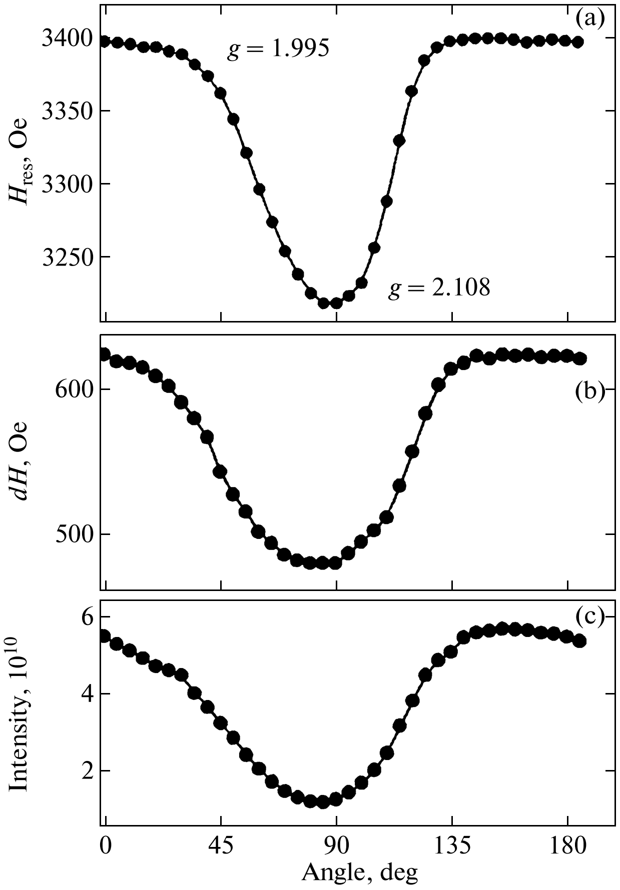

Fig. 3. Angular dependences of (a) resonant field, (b) width, and (c) intensity of the ESR line for the $Cr_xMn_{1-x}S$ single crystal at $x = 0.1$: 0° and 180° correspond to the direction of the magnetic field H lying in the (100) plane, and 90° corresponds to the direction of the magnetic field H perpendicular to the (100) plane.

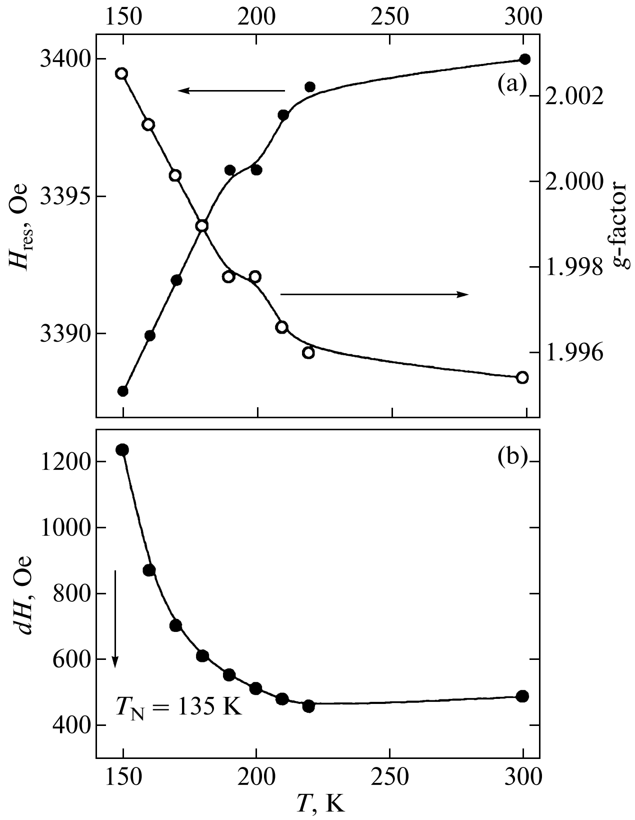

Fig. 4. Temperature dependences of (a) resonant field and g-factor and (b) ESR line for the $Cr_xMn_{1-x}S$ single crystal at $x = 0.1$.

Figure 1 represents the temperature dependences of the inverse magnetic susceptibility for single crystals of the $Cr_xMn_{1-x}S$ solid solutions measured in magnetic field $H = 0.5$ kOe. Measurements were performed for two samples of the same composition prepared from single crystals with the as-batched compositions $x = 0.10$, 0.18, and 0.29. It is established that the temperature corresponding to the peak of magnetic susceptibility, which indicates the presence of the magnetic transition in the $Cr_xMn_{1-x}S$ single crystals, decreases monotonically from 149 K ($x = 0$) to 96 K for $x = 0.29$, which substantially differs from results [3]. As the degree of substitution increases, the additional anomaly in the region ~40 K appears in the temperature dependence of magnetic susceptibility for $x = 0.18$ and $x = 0.29$. For the sample with the composition $x = 0.29$* (stoichiometry $x = 0.35$), the temperature behavior of magnetic susceptibility was similar to the behavior observed in spin glasses. One clearly expressed peak was observed in the temperature dependence of magnetic susceptibility for this sample in the region ~60 K.

Figure 2 represents the temperature dependences of the inverse magnetic susceptibility of the sample with $x = 0.1$ measured for two directions of the magnetic field, namely, perpendicular to the sample plane ((100) plane) and parallel to this plane. The experiment showed that weak anisotropy of magnetic susceptibility is observed over the whole measured temperature range. The presence of magnetic anisotropy at 300 K was confirmed by the results of investigation of the sample with $x = 0.1$ by the electron spin resonance method (Fig. 3). Here, the resonant field measured for the orientation of the magnetic field perpendicular to the (100) sample plane is lower than the field measured for the orientation of the magnetic field parallel to the sample plane. The line width of the dH for $x = 0.1$ is 0.4–0.6 kOe at room temperature and reaches more than 3 kOe in the region of the magnetic transition; in the magnetically ordered state, the line is unobservable (Fig. 4). For the sample with $x = 0.29$, which corresponds to the stoichiometric state, no anisotropy of magnetic properties is found. In general, the ESR results indicate the paramagnetic state of the $Cr_xMn_{1-x}S$ samples in the range T_N – 300 K. Temperature dependences of the inverse magnetic susceptibil-

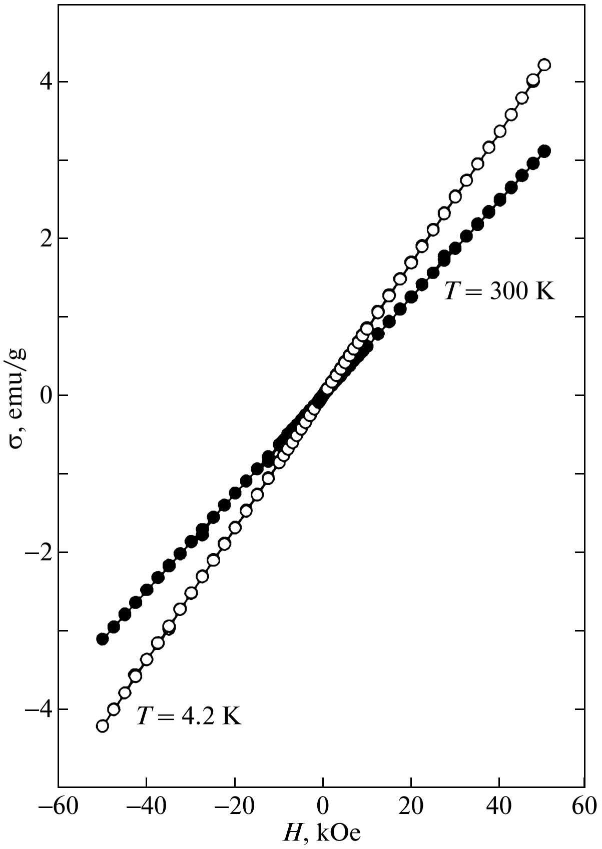

Fig. 5. Field dependences of magnetization at 4.2 and 300 K for the $Cr_xMn_{1-x}S$ single crystal at $x = 0.18$.

ity calculated based on the results of resonant investigations are presented in Fig. 1 (symbols *2*). We observe rather good agreement with the results of direct measurements of magnetic susceptibility by the SQUID magnetometry (Fig. 1, symbols *1*). The temperature behavior of magnetic susceptibility of the $Cr_xMn_{1-x}S$ single crystals ($0 \le x < 0.3$) at $T > T_N$ can be described by the Curie–Weiss law with the explicit spin effective magnetic moment. At temperatures in the vicinity of the Néel temperature, the deviation from the Curie–Weiss law is observed, which can be explained by the formation of the short-range magnetic order.

Field dependences of magnetization of the $Cr_xMn_{1-x}S$ samples were measured at temperatures of 4.2, 77, and 300 K in magnetic fields up to 20 kOe. It is established that for the composition $x = 0.18$, the linear law of the field dependence of magnetization is observed for all temperatures (Fig. 5). Such a situation is typical of both the paramagnetic and antiferromagnetic states in magnetic fields lower than the field corresponding to the spin-flop transition. For the composition $x = 0.29$* at 4.2 K, the field dependence of magnetization is nonlinear with a narrow hysteresis in the fields up to 3 kOe, which indicates the possibility of both the appearance of the ferromagnetic component of the magnetization and the formation of the domain structure.

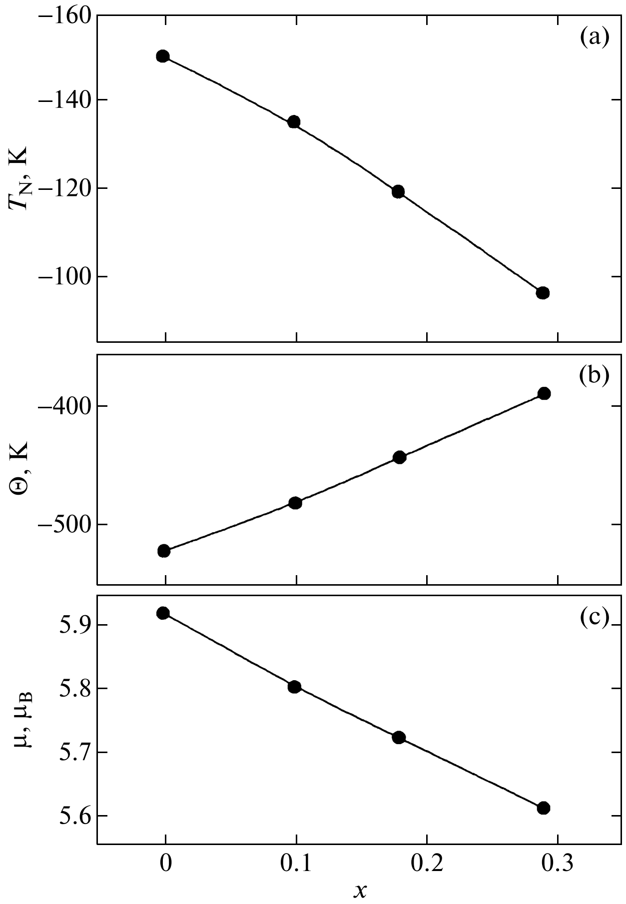

Fig. 6. Concentration dependences of (a) the Néel temperature, (b) paramagnetic Curie temperature, and (c) effective magnetic moment for single crystals of the $Cr_xMn_{1-x}S$ solid solutions.

It is known that the temperature of the antiferromagnetic transition of manganese monosulfide linearly increases during the compression of the cubic NaCl lattice under the pressure [7]. This fact indicates that the absolute value of the antiferromagnetic exchange integral increases as the interatomic distance decreases. The chemical pressure caused by the cation substitution of the manganese ions by the chromium ions is also accompanied by a decrease in the unit cell parameter of manganese monosulfide similarly to that it is observed in MnS under the pressure. Figure 6 represents the concentration dependences of the Néel temperature, paramagnetic Curie temperature, and effective magnetic moment in the paramagnetic region for $Cr_xMn_{1-x}S$. The synthesized substances are antiferromagnets. The substitution of the manganese ions by chromium ions in the $Cr_xMn_{1-x}S$ solid solutions causes a decrease in the magnetic transition temperature despite the lattice compression. Taking into account that the substitution by chromium