===== **MAGNETISM** =====

Synthesis, Structure, and Magnetic Properties of Anion-Substituted Manganese Chalcogenides

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Abstract—The anion-substituted solid solutions of the $MnSe_{1-x}Te_x$ system have been synthesized. The crystal structure and magnetic properties of the synthesized solid solutions have been investigated. It has been shown that, in the concentration range $0 \le x \le 0.4$, the solid solutions have a face-centered cubic structure. It has been revealed that an increase in the concentration of the substituting element in the $MnSe_{1-x}Te_x$ system leads to an increase in the coefficient of thermal expansion of the sample. The investigation of the magnetic properties has been carried out at temperatures in the range $80\ K < T < 1000\ K$ in a magnetic field up to 8.6 kOe. It has been experimentally found that the type of antiferromagnetic order (the second type of ordering) remains unchanged over the entire concentration range up to $x = 0.4$ and that the paramagnetic Curie temperature and the Néel temperature decrease within the limits of 20%. Theoretical calculations have been performed using the Monte Carlo method, and the model of nanoclusters with an uncompensated antiferromagnetic moment has been proposed.

1. INTRODUCTION

In recent years, there has intensively developed a new scientific direction—spintronics which has used the advantages of nonvolatile magnetic memory and high-performance electrical information processing systems [1, 2]. In this regard, much attention has been paid to the search and design of new magnetic materials that exhibit unique combinations of magnetic, electrical, and optical properties associated with the specific features of their crystalline ordering and electronic band structure. Magnetic semiconductors that undergo metal−insulator phase transitions and magnetic phase transitions with variations in temperature and concentration are very promising materials. Among these materials are solid solutions of the $MnSe_{1-x}Te_x$ system, in which the end compounds MnSe and MnTe are antiferromagnets that have different types of structure and the semiconductor and metal types of conductivity at temperatures below room temperature [3−5]. Manganese selenide MnSe undergoes a structural phase transition from the cubic phase to the NiAs structure in the temperature range $248\ K < T < 266\ K$ [6]; at temperatures below 248 K, the phases coexist in the sample, which, in this case,

contains approximately 30% NiAs and 70% of the cubic phase [7]. The magnetic phase transition observed for MnSe in the cubic modification occurs at the Néel temperature $T_{Nc} = 135\ K$. For nickel arsenide NiAs, this temperature coincides with the temperature of the structural phase transition. Investigations of the magnetoelectrical properties of the MnSe compound have revealed the magnetoresistance effect in the magnetically ordered phase. As the Néel temperature is approached, the magnetoresistance increases [5].

The MnTe compound crystallizes in the hexagonal structure of the NiAs type [8] and exhibits unique properties under pressure. In particular, the Néel temperature increases and reaches $T_N = 520\ K$ at the pressure $P = 8\ GPa$, while the energy gap in the spectrum of electronic excitations decreases by a factor of 2. A decrease in the length of the metal−anion Mn−Te bond, according to theoretical calculations of the electronic band structure [9], induces a change in the crystal structure from hexagonal (H) to cubic (ZB) with the antiferromagnetic type of ordering. For the antiferromagnetic type of ordering, the difference between the binding energies per Mn−Te pair is $\Delta E_{ZB, H} = (-0.21) + (-0.10)$ eV/bond with the bond

length $R_{AF} = 2.70$ Å. For the ferromagnetic type of ordering, we have $\Delta E_{ZB, H} = (-0.40) + (-0.10)$ eV/bond with the bond length $R_F = 2.71$ Å. Moreover, the bond length in the NiAs structure is $R(Mn-Te) = 0.273$ Å [10]. The lattice constant $a = 5.44$ Å in the MnSe compound with the NaCl structure is somewhere between the values $2R_F$ and $2R_H$. Consequently, the substitution of tellurium for selenium at low concentrations can result in the formation of MnTe clusters with the ferromagnetic type of ordering and a distorted cubic structure. These quasi-degenerate states in the magnetic and crystal structures can be varied under external actions, i.e., by varying electric and magnetic fields, as well as the pressure.

2. SAMPLES, METHODS OF INVESTIGATION, AND EXPERIMENTAL DATA

The synthesis of samples in the $MnSe_{1-x}Te_x$ ($0 \leq x \leq 0.4$) system with a step in concentration $x = 0.1$ was performed by the solid-phase reaction method using a step mode. The charge of the samples was prepared from powders of electrolytic manganese, with special purification of lobes before their grinding, as well as selenium and tellurium of special-purity grade. The X-ray diffraction patterns of powders of the studied compositions were obtained at room temperature under CuK_α radiation in the point-by-point measurement mode: the time of collection of information at the point was $\tau = 3$ s, and the angular scan step was $\Delta 2\theta = 0.03°$. The X-ray diffraction investigations have demonstrated that the anion substitution in the $MnSe_{1-x}Te_x$ system with an increase in the tellurium concentration leads to a noticeable decrease in the intensity of the diffraction reflections. This is especially noticeable in the X-ray diffraction patterns (Fig. 1) for the reflections (111), (200), (220), and (311) in the range of small angles 2θ. There is a gradual shift of the angular positions of the reflections (422), (420), (331), and (400) in the range of large angles 2θ toward smaller values, which indicates an increase in the unit cell size of the samples. This change in the anion packing can be explained by the difference between the ionic radii of selenium and tellurium, which, in this case, are in the cubic closest packing in the divalent state [11]. In the divalent state, the ionic radius of selenium Se^{2-} lies in the range $r_{Se} = 0.198-0.200$ nm, whereas the ionic radius of tellurium Te^{2-} can vary in the range $r_{Te} = 0.221-0.224$ nm [11, 12]. The difference between the ionic radii by more than 11% for the substitutional anions in samples of the $MnSe_{1-x}Te_x$ system, apparently, leads to an increase in their unit cell sizes with an increase in the tellurium concentration. A decrease in the intensity of diffraction reflections in the X-ray diffraction patterns, most likely, is associated with the fact that the formation of solid solutions upon the substitution, especially in the anion sublattice, is accompanied by significant distor-
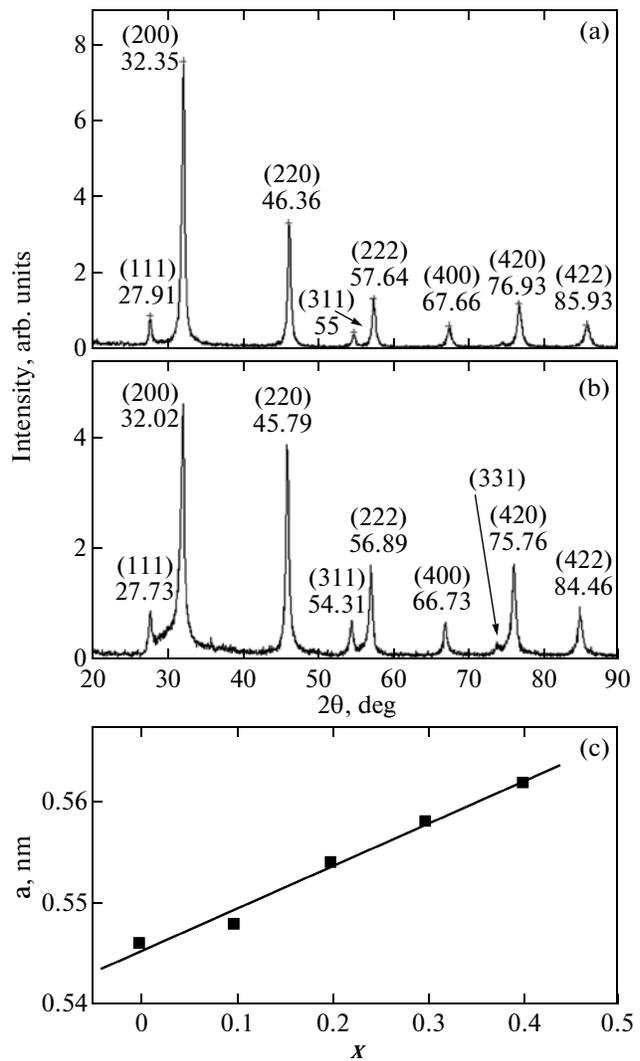

Fig. 1. (a, b) X-ray diffraction patterns of (a) $MnSe_{0.8}Te_{0.2}$ and (b) $MnSe_{0.6}Te_{0.4}$ samples measured at the temperature $T = 300$ K and (c) concentration dependence of the lattice constant.

tions of the crystal lattice, as well as by an increase in the disorder of the cubic structure with the space group $Fm\overline{3}m$ (225).

A linear increase of the parameter a of the crystal unit cell of the samples with an increase in the tellurium concentration allows us to draw the conclusion that, in the concentration range $0 \leq x \leq 0.4$, in the $MnSe_{1-x}Te_x$ system there exist solid solutions with a structure in the space group $Fm\overline{3}m$ (225) that is characteristic of manganese monoselenide [13]. The dependence of the lattice parameter a on the tellurium concentration x in samples of the $MnSe_{1-x}Te_x$ system is shown in Fig. 1c. We have also performed the investigations of the temperature dependence of the lattice constant for the $MnSe_{0.8}Te_{0.2}$ compound. The X-ray
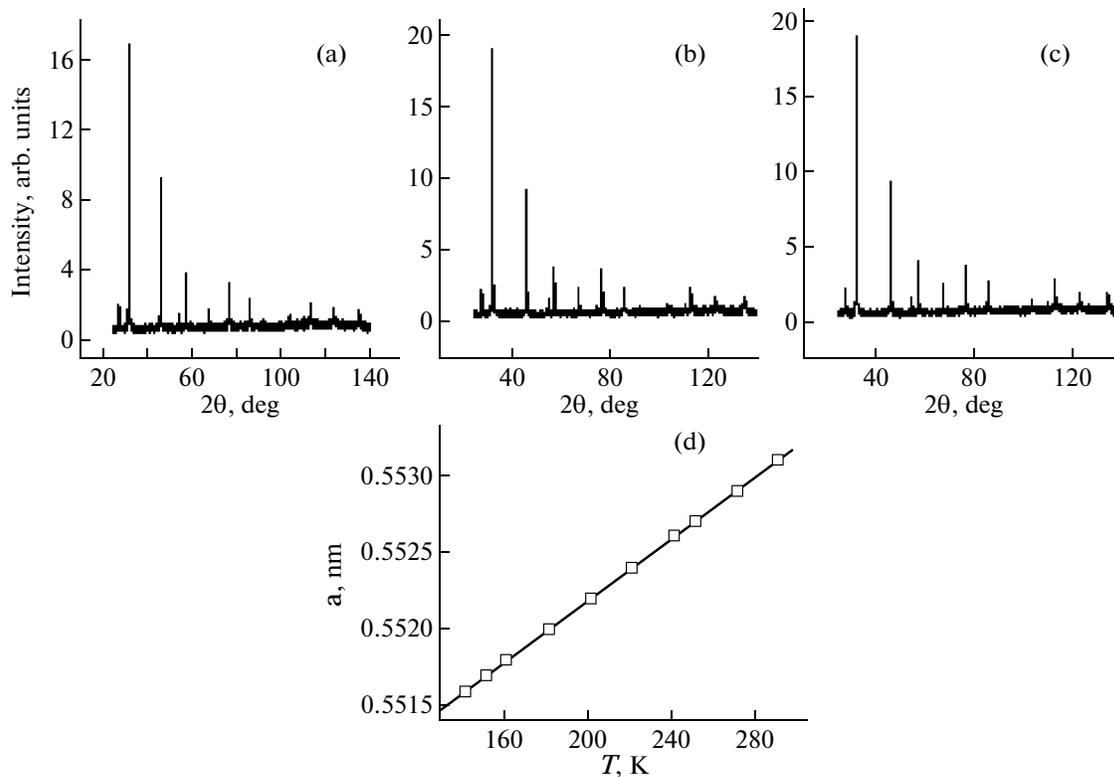
Fig. 2. (a–c) X-ray diffraction patterns of the $MnSe_{0.8}Te_{0.2}$ sample measured at temperatures T = (a) 273, (b) 200, and (c) 150 K and (d) temperature dependence of the lattice constant for this compound.

diffraction patterns were measured in the temperature range 110 K < T < 300 K with a temperature step of 10 K. Figures 2a–2c show the X-ray diffraction patterns for three temperatures (273, 200, and 150 K). The performed analysis of the X-ray diffraction patterns has not revealed the formation of additional phases with a decrease in the temperature. In addition to the inclusion of the thermal vibrations of the atoms in the analysis, it is necessary to take into account the role of disorder in the distribution of the anions over the crystal lattice. In particular, the temperature dependence of the intensity ratio $I(T)/I(T = 110$ K) is not described by the Debye−Waller factor, $\ln(I/I_0) = -A(T/\Theta)^2$, where Θ is the Debye temperature and A is the temperature-independent constant determined by the material. Figure 2d shows the temperature dependence of the lattice parameter a for the tellurium concentration $x = 0.2$ in the $MnSe_{1-x}Te_x$ system, which was determined from the shift of the (200) reflection. A monotonic linear increase in the lattice parameter of the sample with an increase in the temperature indicates a weak interaction of electrons with acoustic phonons.

The thermal expansion of the material was measured on a NETZSCH DIL-402C dilatometer at temperatures in the range from 120 to 700 K in the dynamic mode at a heating rate of 5 K/min. The results obtained from the investigations of the defor-

mation $\Delta L/L$ and the coefficient of thermal expansion $\alpha(T)$ for two samples of the $MnSe_{1-x}Te_x$ ($x = 0.2, 0.4$) system are presented in Fig. 3. An increase in the concentration of the substituting element in the MnSe system leads to an increase in the coefficient of thermal expansion of the material. The disordered arrangement of the anions in the crystal lattice contributes to the asymmetry of the mutual repulsion of the atoms and corresponds to an enhancement of anharmonic vibrations. After changing over to the magnetically ordered region, the negative change in the deformation indicates a compression of the crystal lattice. The temperature dependence of the thermal expansion coefficient $\alpha(T)$ exhibits a clear anomaly observed at the Néel temperature $T_N = 120$ K. A good agreement between the coefficients of thermal expansion determined by different methods from the elongation per unit length of the sample and from the lattice constant, i.e., $\alpha(T) = (1/a)(da/dT) = 1.8 \times 10^{-5}$ K^{-1}, indicates the absence of structural dislocation or inhomogeneities within a few percent.

The magnetic properties were investigated using the ponderomotive method in a magnetic field of 8.6 kOe at temperatures in the range from 80 to 1000 K for the samples placed in evacuated quartz ampoules. The inset to Fig. 4 show the temperature dependences of the specific magnetization measured
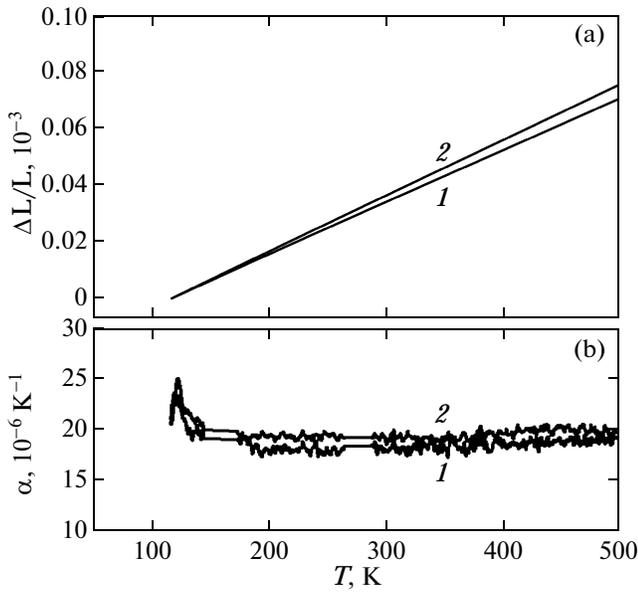
Fig. 3. Temperature dependences of (a) the elongation per unit length of the sample $\Delta L/L(T)$ and (b) the coefficient of thermal expansion $\alpha(T)$ for the $MnSe_{1-x}Te_x$ samples with tellurium concentrations $x =$ (1) 0.2 and (2) 0.4.

in a magnetic field of 8.6 kOe for samples of the $MnSe_{1-x}Te_x$ system with tellurium concentrations $x = 0.2$ and 0.4. The performed analysis of the inverse magnetic susceptibility $10^{-2}/\chi = f(T)$ has demonstrated that, at temperatures in the vicinity of 325 K, there is a deviation from the Curie–Weiss law. At the same time, the main parameters of the temperature dependences of the inverse magnetic susceptibility $10^{-2}/\chi = f(T)$ and the specific magnetization $\sigma = f(T)$ for samples in the $MnSe_{1-x}Te_x$ system monotonically vary with an increase in the tellurium concentration in the sample. This indirectly confirms the existence of solid solutions in the $MnSe_{1-x}Te_x$ system in the concentration range $0 \leq x \leq 0.4$. The temperature dependences of the magnetization exhibit maxima that indicate the occurrence of an antiferromagnetic phase transition in the investigated compounds at temperatures in the range from 110 to 130 K. The Néel temperature of the samples under investigation smoothly decreases from 132 K for $MnSe_{0.9}Te_{0.1}$ to 118 K for $MnSe_{0.6}Te_{0.4}$. With an increase in the concentration of the substituting element, the paramagnetic Curie temperature decreases in the absolute value from $\Theta_P = -350$ K for $x = 0.1$ to $\Theta_P = -270$ K for $x = 0.4$. Similarly changes are observed for the magnitude of the magnetic moment determined from the slope of the high-temperature part of the dependence $10^{-2}/\chi = f(T)$ within the limits of the error of the calculation: $\mu \sim 5.50$ μ_B for $MnSe_{0.9}Te_{0.1}$ and $\mu \sim 5.13$ μ_B for $MnSe_{0.6}Te_{0.4}$. The hysteresis of the magnetic susceptibility at temperatures in the range from 80 to 350 K is observed in the dependences $1/\chi = f(T)$ for all the
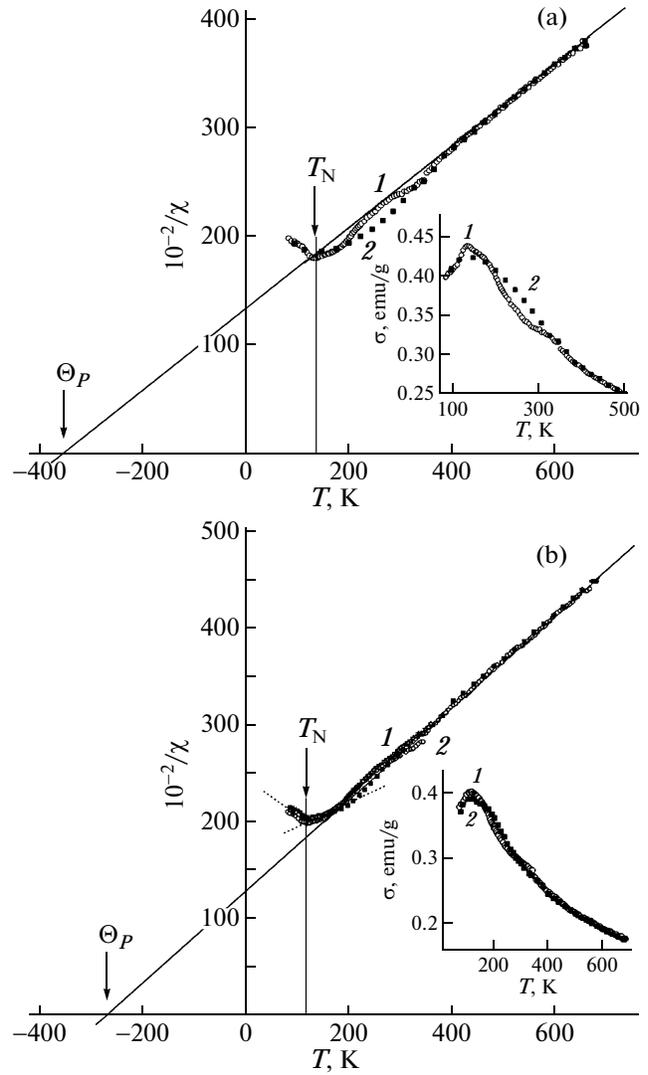

Fig. 4. Temperature dependences of the magnetic susceptibility and magnetization (shown in insets) measured during (1) heating and (2) cooling of the $MnSe_{1-x}Te_x$ solid solution samples with tellurium concentrations $x =$ (a) 0.2 and (b) 0.4.

samples under investigation, but it is most pronounced for the $MnSe_{0.8}Te_{0.2}$ compound (Fig. 4a).

3. DISCUSSION OF THE RESULTS

A possible explanation for the anomalous behavior of the temperature dependences of the magnetic susceptibility and magnetization of solid solutions in the $MnSe_{1-x}Te_x$ system at temperatures in the vicinity of 330 K is based on the assumption that nanoclusters of the MnTe compound are formed in the matrix of the $MnSe_{1-x}Te_x$ solid solution. The magnetic structure of the manganese monotelluride consists of ferromagnetic planes that are antiferromagnetically coupled with each other. The MnTe nanoclusters can contain
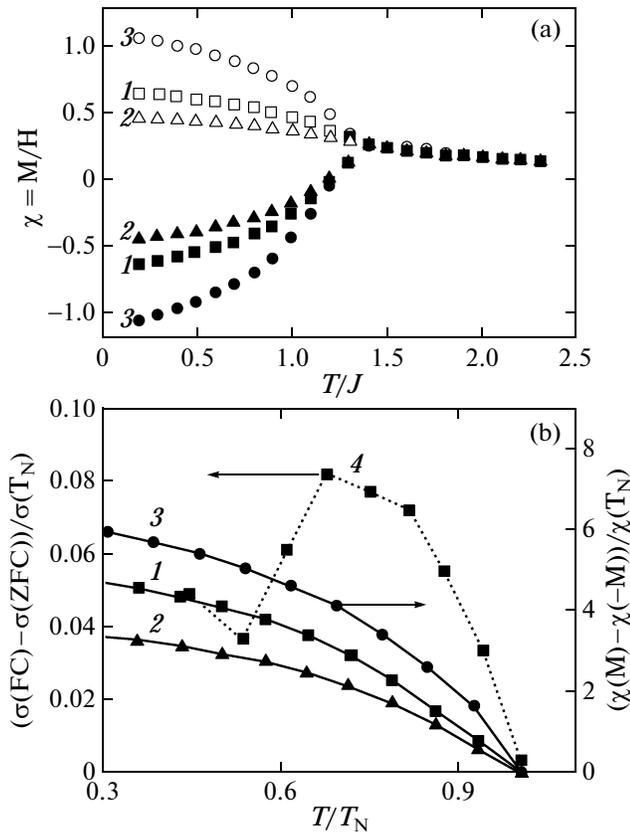
Fig. 5. (a) Temperature dependences of the magnetic susceptibility calculated by the Monte Carlo method in the normalized magnetic field $H/J = 0.05$ for a number of samples with sizes $N = $ (*1*) $15 \times 16 \times 16$, (*2*) $23 \times 24 \times 24$, and (*3*) $9 \times 12 \times 12$ particles in the cases where the net magnetic moment is directed parallel to the magnetic field (open symbols) and the net magnetic moment is directed antiparallel to the magnetic field (closed symbols). (b) Theoretical values of (*1–3*) the relative change in the magnetic susceptibility $(\chi(M) - \chi(-M))/\chi(T_N)$ for the same samples and (*4*) the magnetization calculated from the ratio $(\sigma(FC) - \sigma(ZFC))/\sigma(T_N)$ for the $MnSe_{0.8}Te_{0.2}$ sample.

both even and odd numbers of ferromagnetic planes. This can result in the formation of a superparamagnetic antiferromagnetic cluster with an uncompensated magnetic moment, which is blocked in the anisotropy field below the Néel temperature T_N.

The magnetic susceptibility in the normalized magnetic field $H/J = 0.05$ was calculated using the Monte Carlo method for a number of samples with sizes (expressed in terms of the concentration of particles in the cluster) $N = 9 \times 12 \times 12$, $15 \times 16 \times 16$, and $23 \times 24 \times 24$ in the uniaxial anisotropy field normalized on the exchange field ($H_a/H_E = 0.005$) for two cases: (i) the net magnetic moment is directed parallel to the magnetic field and (ii) the net magnetic moment is directed antiparallel to the magnetic field. Figure 5a presents the calculated values of the magnetic susceptibility. At temperatures above the Néel temperature

$T_N/J = 1.3$, the magnetic moments are directed parallel to the magnetic field, and below this temperature, the net magnetic moment is blocked in the anisotropy field. In the sample with macroscopic dimensions, the magnetic moment induced by spins in the plane is rotated in the direction of the magnetic field due to the excitation of spin waves. Owing to the restriction of the linear dimensions of the sample, there arises an energy gap in the spin-wave spectrum of the order of $\Delta \approx 2zJS\pi/L$, which is equal to the activation energy for the spin flip in the magnetic field. For comparison with the experimental data for the same samples, the relative change of the magnetic susceptibility is calculated as the difference between the magnetic susceptibilities for the magnetic moment directed parallel and antiparallel to the magnetic field, which is normalized to the magnetic susceptibility at the temperature T_N, i.e., $(\chi(M) - \chi(-M)/\chi(T_N))$ (Fig. 5b, right axis). Figure 5b also presents the values of the magnetization at the Néel temperature for the $MnSe_{0.8}Te_{0.2}$ compound (left axis), which were calculated from the experimental values according to the ratio $(\sigma(FC) - \sigma(ZFC))/\sigma(T_N)$. The performed calculations indicate that there is a tendency toward the formation of nanoclusters ~5 nm in size, which account for approximately 1% of the weight of the $MnSe_{0.8}Te_{0.2}$ solid solution. As judged from the height of the additional maximum of the magnetic susceptibility at $T = 350$ K, the maximum density of isolated MnTe clusters is reached at a tellurium concentration of 0.2 and corresponds to a random distribution of clusters in the vicinity of the percolation through the anion sites.

According to the Monte Carlo calculations, the second type of ordering takes place in the antiferromagnet with a face-centered cubic structure under the condition $\Theta_P/T_N > 2$. In the molecular field approximation, we can estimate the exchange parameters in the first (J_1) and second (J_2) coordination spheres with spin $S = 5/2$:

$$-6J_2 = 3/2S(S+1)T_N,$$

$$12J_1 + 6J_2 = -3/2S(S+1)\Theta_P.$$

The solution of the system gives the following exchange parameters: $J_1 \approx 4$ K and $J_2 \approx 3$ K. These parameters decrease by 20% upon the substitution of tellurium for selenium, whereas the second type of ordering is retained. The dependence of the magnetic susceptibility on the prehistory of the sample indicates a possible dependence of the magnetic susceptibility on the magnetic field. In our recent work [14], we revealed the peak of the magnetization at the temperature $T = 260$ K in the magnetic field $H = 0.05$ T for the MnSe compound, which is probably attributed to the formation of a hexagonal structure and the coexistence of two crystalline structures. This maximum disappears upon the anion substitution, and only a sin-

gle broad maximum is observed in the temperature range $T = 100-180$ K.

4. CONCLUSIONS

Thus, the structural and magnetic investigations of the properties of the anion-substituted solid solutions in the $MnSe_{1-x}Te_x$ system have made it possible to determine their crystal structure, which corresponds to the space group $Fm\bar{3}m$ (225). It has been established that the substitution of tellurium for selenium induces a chemical pressure and leads to the formation of a single-phase cubic structure. The investigation of the magnetic properties has revealed that, with an increase in the degree of substitution in the anion sublattice, the paramagnetic Curie temperature and the Néel temperature decrease by no more than 20%. It has been found that the magnitude of the magnetic moment changes in a similar manner. The hysteresis of the magnetic susceptibility in the temperature range $80-350$ K has been observed for all the studied samples; however, it is most pronounced for the $MnSe_{0.8}Te_{0.2}$ compound. The experimental results have been interpreted using the theoretical calculations performed by the Monte Carlo method. A model has been proposed for nanoclusters ~5 nm in size, which have an uncompensated antiferromagnetic moment and account for approximately 1% of the weight of the $MnSe_{1-x}Te_x$ solid solution.

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