Spin state of cations and magnetoelastic effect in the $Mn_{1-X}Yb_XS$

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ABSTRACT

Magnetic moment and magnetization curves of the $Mn_{1-X}Yb_XS$ ($0.05 \leq X \leq 0.2$) solid solutions have been experimentally studied at temperatures 4–700 K in magnetic fields up to 9 T. Spin states of manganese and ytterbium ions, the concentration region with the bi- and trivalent states of ytterbium ions are determined. The nonlinear field behavior of the magnetization at $X = 0.05$, the sharp Curie temperature drop and a decrease in the Neel temperature were found. The decrease in the coefficient of thermal expansion with increasing concentration of ytterbium in the magnetically ordered region and the interrelation between the magnetic and elastic subsystems of the $Mn_{1-X}Yb_XS$ solid solutions have been established.

1. Introduction

The materials that exhibit the correlation of the electrical and magnetic properties attract attention of researches as promising candidates for application in microelectronics and spintronics [1]. The compounds with variable valence undergo metal–insulators and magnetic phase transitions, when the magnetic characteristics of the materials can change without variation in magnetic symmetry [2]. According to the results of the previous studies [3–5], it is convenient to investigate these phenomena on the cation-substituted $Re_XMn_{1-X}S$ (Re=Gd, Sm) compounds based on the antiferromagnetic semiconductor manganese monosulfide. Study of phase diagrams of the homogeneous states of manganese sulfides showed the possibility of obtaining the single-phase compounds at a rare-earth element concentration up to 30%.

The sulfide YbS exhibits the anomalous magnetic [6] and kinetic properties [7]. The presence of the 4f and 5d orbitals relatively close by energy [8] causes a number of specific features of the compounds containing these elements. Under normal pressure, ytterbium sulfide is a semiconductor with a direct band gap of ~ 1.3 eV in the electron excitation spectrum and an indirect band gap of ~ 1.0 eV between the fully occupied 4f state and free sd states [9] located above the 3p valence band of sulfur ions by 4 eV [10]. As the pressure is increased, the band gap monotonically decreases, $dE_g/dp = (-6 \pm 1)$ eV/kbar [11]; at $P = 8$ GPa, the bands overlap with the formation of the metal state [12]. At $P = 10$ GPa, the quantum resonance is observed, i.e., the superposition of the $f^{13}c$ and f^{14} states with the change in valence from 2 to 3. The density of charge carriers reaches 0.4/Yb [12]. As was established from the IR spectra, the effective electron mass grows by an order of magnitude due to the strong f-electron correlations.

Ytterbium and manganese sulfides have the NaCl-type crystal lattice with the constants $a = 5.693$ Å (YbS) [13] and $a = 5.222$ Å (MnS) [14]. The lattice constants of the compounds with Yb exceed that of MnS by 10–13%. Under the critical pressure $P = 8$ GPa, the YbS lattice value compresses by 12% [9,12]. One can expect that upon substitute of ytterbium ions for manganese cations the pressure imposed by the nearest neighborhood will lead to the change in the valence of ytterbium ions and spin transition from singlet state to high spin state.

The aim of this study is to find the correlation of the magnetic and structural characteristics of the $Mn_{1-X}Yb_XS$ ($0.05 \leq X \leq 0.2$) upon isostructural cation substitution of ytterbium for manganese. Clarify the effects of the internal chemical pressure and hybridization of f–d orbitals on the spin state in the ytterbium ion with variable valence.

2. Experiment results and discussion

For the first time the synthesized $Mn_{1-X}Yb_XS$ crystals were grown in a quartz reactor as a result of a melting of polycrystalline powders of sulfides. The reactor with a charge in glass–carbon crucibles was pulled through a single-turn inductor of a high-frequency facility. At synthesis carrying out, high-purity argon was used [15].

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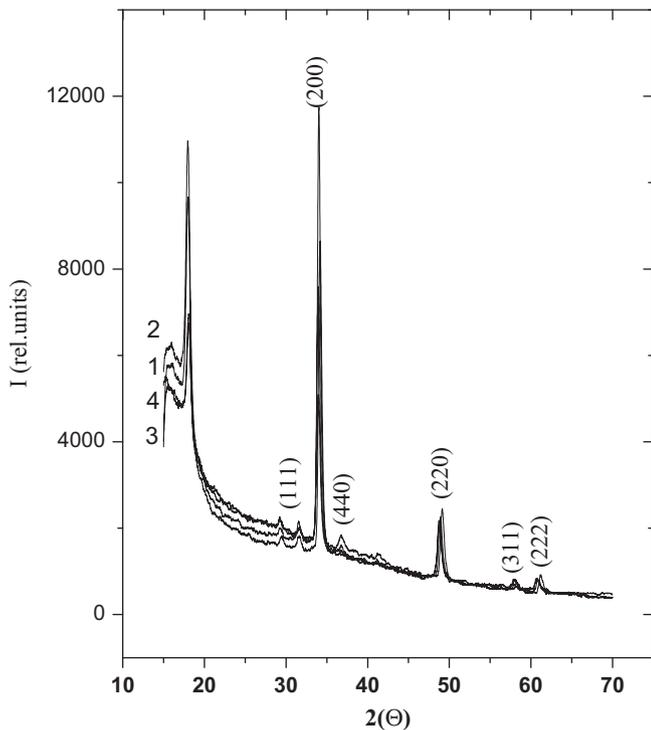E-mail address: apl@iph.krasn.ru (S.S. Aplesnin).

**Fig. 1.** X-ray diffraction patterns of the $Mn_{1-X}Yb_XS$ solid solutions for $X=$ (1) 0.05, (2) 0.1, (3) 0.15, and (4) 0.2.

Fig. 2. Temperature dependence of the inverse susceptibility in the magnetic field $H=0.86$ T for $Yb_{0.15}Mn_{0.85}S$. Inset: the inverse susceptibility in the vicinity of Neel temperature.

The X-ray diffraction analysis of the samples was made using a DRON-3 facility. The crystal structure of the $Mn_{1-X}Yb_XS$ ($0.05 \leq X \leq 0.2$) compounds were investigated on polished lateral surfaces of parallelepipeds at room temperature in the initial state and after the magnetic susceptibility measurements in the temperature range 80–700 K. X-ray diffraction patterns for several compositions are presented in Fig. 1. No reflections different from the fcc structure are observed. It was established that heating of the $Mn_{1-X}Yb_XS$ compounds to 700 K during the magnetic susceptibility measurements does not significantly affect the crystal structure: all the reflections characteristic of the NaCl-type structure remain. With an increase in concentration X of the cation substitute, parameter a of the unit cell linearly grows. Asymptotic continuation $a(x)$ of lattice constant to $X=1$ gives a value of $a(x=1)=0.559$ nm, which at 2.4% less than the lattice parameter for YbS. Is aware that the reduction of lattice on 4% under pressure [12] leads to a spin transition of ytterbium ion from singlet state $J=0$ to $J=7/2$, $S=1/2$. Therefore, chemical pressure imposed by manganese ions are not sufficient for electronic transition from Yb^{2+} to Yb^{3+}.

The magnetic properties of the samples were investigated on a PPMS XL facility (Quantum Design) in the temperature range $4\,K < T < 300\,K$ at a sample heating rate of $2°$/min. Specific magnetization and magnetic susceptibility of the samples in the temperature range $80\,K < T < 700\,K$ were determined by the Faraday method. Samples of the investigated compositions were placed into quartz ampoules whose size was no more than the space with the magnetic field gradient. The temperature dependence of the inverse magnetic susceptibility in the field $H=0.86$ T is presented in Fig. 2.

For most of the compositions, the temperature dependence of magnetic susceptibility has the maximum associated with the Neel temperature. In the paramagnetic region, there are two features in the temperature behavior of magnetization that are related to the local minimum dM/dT at temperatures T_1 and T_2 lying within the ranges $224\,K < T_1 < 234\,K$ and $300\,K < T_2 < 309\,K$. Above T_2,
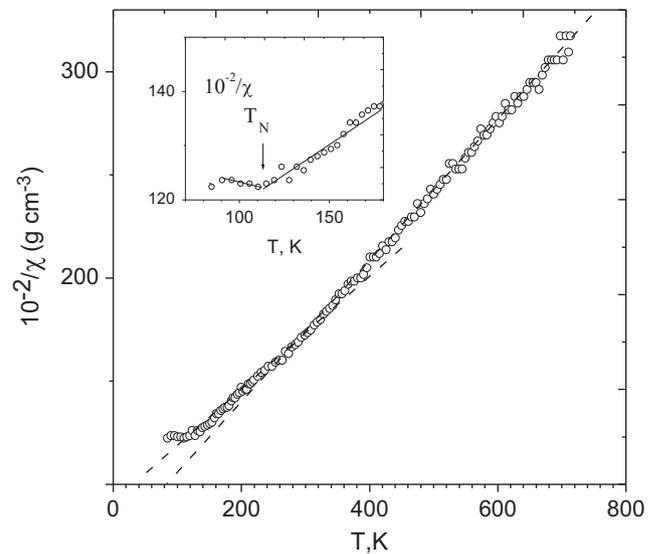
the magnetic susceptibility is described by the Curie–Weiss law $1/\chi(T)=(T+\theta)/C$ with negative paramagnetic Curie temperature θ for all compositions (Fig. 2). Concentration dependences of the paramagnetic Curie and Neel temperatures are shown in Fig. 3. Paramagnetic temperature θ determined in the high-temperature region sharply drops upon substitute of ytterbium ions for manganese.

This can be explained by the formation of superparamagnetic clusters with the strong ferromagnetic interaction between manganese ions (A_{MnMn}) that are the nearest neighbors of the ytterbium ion. The bivalent ytterbium ion has a larger volume as compared with the trivalent ion and one Yb ion is surrounded by $z=12$ Mn ions in the 1st coordination sphere. The concentration of such manganese ions is $c_g=zx(1-x)^{z-1}$. The dependence $\theta(X)$ can be described in the molecular field approximation as $\theta(X)/\theta_{MnS}=(1-x-\lambda_{MnMn}c_g)$ for $X \leq 0.1$, where $\theta_{MnS}=550$ K and $\lambda_{MnMn}=A_{MnMn}/K_{MnMn}$. At $X > 0.1$, ytterbium ions have the magnetic moment and interact with manganese and ytterbium spins, which should be taken into account in the calculation of the exchange field and the paramagnetic Curie temperature. The experimental data on $\theta(x)$ are fitted by the theoretical function with the parameter $\lambda_{MnMn}=1.6$ (solid line in Fig. 3a).

If the substitute of a bivalent ytterbium ion for Mn^{2+} retains the exchange interactions between the manganese spins, then the Neel temperature decreases linearly with increasing concentration, $T_N(x)/T_N(x=0)=1-1.13(1)x$. The sharper Neel temperature decreasing $T_N(X)/T_N(x=0)=1-1.76(7)X$ in the solid solutions also indicates the variation in the value of the Mn–Mn exchange interaction, possibly even with the change in the exchange sign.

The variation in the exchange interaction is related to the rearrangement of the electronic structure at the Mn–Yb interface due to the lowering of the local crystal structure and splitting of the t_{2g} levels. The pressure imposed by the nearest Yb ions increases the splitting of the crystal field (Δ_{te}) between the t_{2g} and e_g levels. In the high-spin state, five states with the same spin direction are occupied. The loss $2\Delta_{tg}$ in the energy caused by the occupation of the high-energy e_g level by two electrons is compensated by the gain $-10J$ in the exchange energy (J is the Hund exchange interaction between electrons). A decrease in the spin in manganese ion, when four electrons are located at the t_{2g} level and one electron, at the e_g level, is related to the loss in the Hund exchange energy up to $-6J$ and the gain in the energy of the crystal field. The competition of the crystal and exchange fields
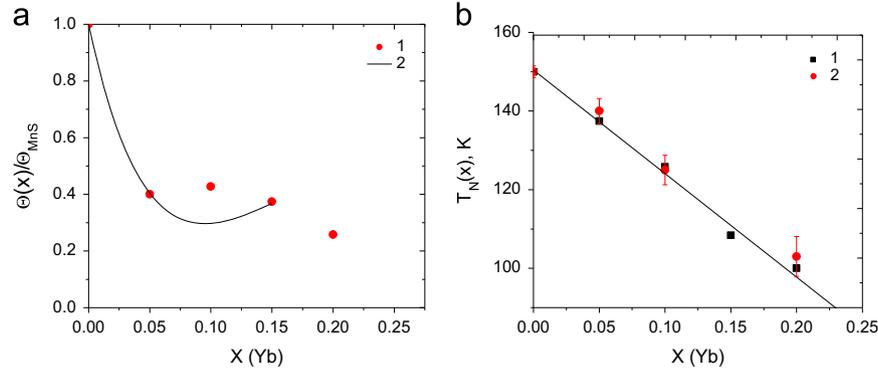
Fig. 3. Concentration dependence of the paramagnetic Curie temperature normalized by the temperature $\theta_{MnS}=550$ K (a): experimental (1) and calculated (2) in the molecular field approximation $\theta(x)/\theta_{MnS}=(1-x-\lambda_{MnMn}c_g)$, where $c_g=zx(1-x)^{z-1}$ with the parameters $\lambda_{MnMn}=1.6$. Neel temperatures of the $Mn_{1-X}Yb_XS$ solid solutions determined from the magnetic susceptibility (1) and from the coefficient of thermal expansion $\alpha(T)$ (2) (b).
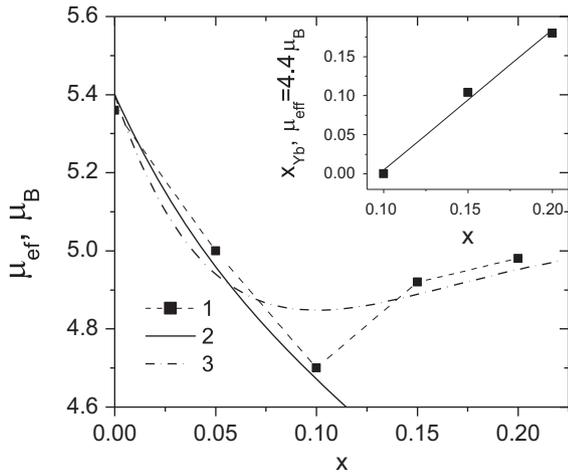

Fig. 4. The effective magnetic moment $\mu_{eff}=(3kC/N\mu_B^2)^{1/2}$ of the $Mn_{1-X}Yb_XS$ solid solutions (1) and the sum of the magnetic moments of manganese and ytterbium ions $\mu_{eff}=\mu_{Mn}(1-x-c_g)+\mu_{Mn(Yb)}\,c_g+\mu_{Yb}x$ with $\mu_{Yb}=0$ (2) and $\mu_{Yb}=4.4\mu_B$ (3). Inset: concentration of the trivalent ytterbium ion is shown and approximated by the linear function $x_{Yb}=-0.18+1.8x$.

results in additional kinetic exchange and broadening of the conduction band.

The ferromagnetic exchange between the Mn-Mn spins located on the interface Mn–Yb is implemented via conduction electrons: $I\sim t^2/J$ when the condition $t\ll J$ is performed (t is the hopping integral). The change in the Mn–S–Mn exchange angle caused by the distortion and rotation of the octahedron at $T=T_2$ decreases the antiferromagnetic indirect exchange interaction K_{MnMn} and changes the sign of the resulting exchange: $K=-K_{MnMn}+I$.

The effective magnetic moment $\mu_{eff}=(3k_B\,C/N\mu_B^2)^{1/2}$ was calculated from the inverse susceptibility measured in the high-temperature region and for set compounds is presented in Fig. 4. In limit case for $x=0$ and $x=1$ it is equal to $\mu_{eff}=5.5\mu_B$ for MnS [14] and $\mu_{eff}=4.4\mu_B$ [8] for YbS under pressure. The magnetic moment is decreased and has minimum at $X=0.1$. At the boundary of Mn–Yb ions the sulfur octahedron is shrink up and crystal field may give rise the rearrangement of the electron density between t_{2g} and e_g states in the manganese ion. That leads to electron transition with a change in the spin state for Mn^{2+}.

Let us the $\mu_{eff}(x)$ of solid solution presents in the form of superposition of manganese ions $\mu_{Mn}=5.5\,\mu_B$ with $S=5/2$ with concentration $(1-x-c_g)$, μ_{effMn} of Mn ions at the interface Mn–Yb ions with concentration $c_g=zx(1-x)^{z-1}$ and magnetic moment of ytterbium ion μ_{Yb} with concentration x. As a results $\mu_{eff}(x)$ may be presented as $\mu_{eff}=\mu_{Mn}(1-x-c_g)+\mu_{effMn}\,c_g+x\,\mu_{Yb}$, where the

parameter μ_{effMn} is found from the fitting $\mu_{eff}(x)$ to experimental data. The obtained value of the magnetic moment $\mu_{effMn}=4.14\mu_B$ corresponds to the $S=3/2$ spin with $\mu=3.9\mu_B$. Model using with fixed the magnetic moment of ytterbium ion bad describe the experimental results.

Let us assume that ytterbium ion has been in the singlet state at the small concentrations and it can be present as the superposition of the magnetic moments $\mu_{Yb}=0$ (Yb^{2+}) and $\mu_{Yb}=4.4\mu_B$ (Yb^{3+}) in the vicinity of ytterbium ion percolation through the lattice. In the concentration range $0<X\leq0.1$, the magnetic moment of the $Mn_{1-X}Yb_XS$ solid solutions decreases with increasing ytterbium concentration: $\mu_{eff}=\mu_{Mn}(1-x-c_g)+\mu_{Mn(Yb)}c_g$, where $\mu_{Mn(Yb)}$ is magnetic moment of manganese ions that surround a single ytterbium ion. The experimental data on $\mu_{eff}(x)$ are fitted by this function with the parameter $\mu_{Mn(Yb)}=4.9\mu_B$, that corresponds to spin $S=2$. Therefore, ytterbium ions do not contribute to the magnetic moment and the latter is caused by the spins of manganese ions. As the value of X is increased ($X>0.1$), the contribution of ytterbium ions to the magnetic moment is observed: $\mu_{eff}=\mu_{Mn}(1-x-c_g)+\mu_{Mn(Yb)}c_g+\mu_{Yb}X_{Yb}$. The concentration of the trivalent ytterbium ions (see the inset in Fig. 4) is approximated by the linear function $X_{Yb}=-0.18+1.8x$, $0.1<X<0.3$.

The magnetic moment was measured in the field range $-9\,T<H<9\,T$ in the magnetically ordered and paramagnetic states (Fig. 5). In the $Mn_{1-X}Yb_XS$ solid solution, the hysteresis is observed in the field range $4\,T<H<6\,T$ (see the inset in Fig. 5) and vanishes upon heating at $T\geq50$ K. The magnetization curve M(H) has the inflection point in this field range and is not described by the linear function at $T=100$ K (Fig. 5a). As the concentration is increased to $X=0.2$, the field dependence of magnetization becomes linear at all temperatures. There is no residual magnetization and the magnetization curves are symmetrical relative to the change in the magnetic field sign.

This behavior of M(H) can be explained by the formation of the uniaxial anisotropy on manganese ions at the Mn–Yb interface and the decrease in the local exchange field due to the local deformation of sulfur octahedron. The competition of the anisotropy (H_A) and exchange (H_E) fields can either increase or decrease the spin-flop field $H_c=\sqrt{2H_AH_E}$. Possibly, with increasing concentration the spin-flop field grows and appears beyond the field range $0\,T<H<9\,T$.

Spin of manganese ion at the interface Mn-Yb is located in the local exchange field $H_{Mn(Yb)}=z_1A_{MnMn}S_{Mn(Yb)}+z_2K_{MnMn}S_{Mn}$ and spin of Mn^{2+} in the bulk has the local exchange field $H_{Mn}=zK_{MnMn}S_{Mn}$. Distribution function of local fields exhibits two maximum at $H_{Mn(Yb)}$ and H_{Mn} and gives rise to the additional small maxim in the susceptibility presented in inset to Fig. 6 at $T^*<T_N$ for $X=0.1$. Peculiarity in the temperature dependence of spin–spin correlation function may be manifested in a structural
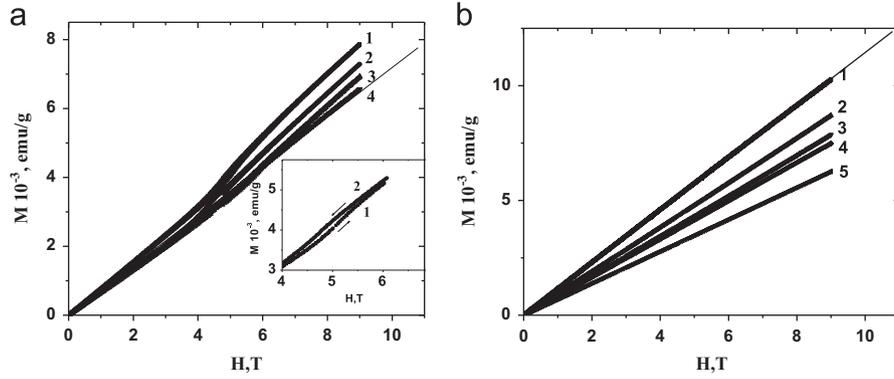
Fig. 5. Field dependences of magnetization measured at the temperatures $T=5(1)$, 25(2), 50(3), 100(4), and 200 K (5) (numbered top-down) for the $Mn_{1-X}Yb_XS$ solid solutions with $X=0.05$ (a) and 0.2 (b). The insert presents field dependences of magnetization measured with increasing (1) and decreasing (2) magnetic field for $X=0.05$.
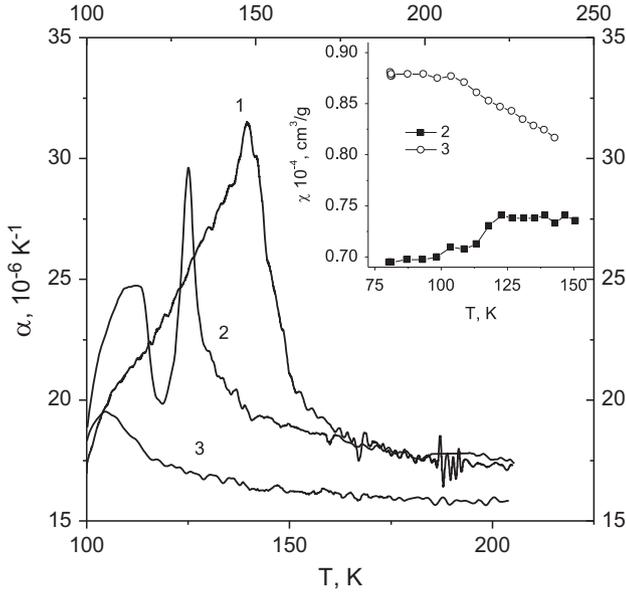

Fig. 6. Temperature dependence of coefficient of thermal expansion $\alpha(T)$ for the $Mn_{1-X}Yb_XS$ samples with $X=0.05(1)$, 0.1(2), 0.2(3). The inset: the susceptibility versus temperature in the magnetic field $H=0.86$ T for $X=0.1(2)$, 0.2(3).

characteristics. To verify this fact, we measured the coefficient of thermal expansion of the solid solutions.

The results of investigations of coefficient of thermal expansion α for the $Mn_{1-X}Yb_XS$ samples are presented in Fig. 6. The anomalies of $\alpha(T)$ are observed at Neel temperature. As the concentration of the substitute in the $Mn_{1-X}Yb_XS$ system is increased, the coefficient of thermal expansion in the magnetically ordered region decreases; in the paramagnetic phase, the values of $\alpha(T)$ are nearly invariable. At the transition to the magnetically ordered region, the lattice is compressed due to the magnetoelastic interaction, which can be presented in the form $\beta u \langle S_i S_{i+h} \rangle$, where β is the parameter of the magnetoelastic interaction and u is the relative displacement of ions. Minimization of the intrinsic energy dE/du in the molecular field approximation

$$E = -Jz \langle S_i S_{i+h} \rangle - \beta u \langle S_i S_{i+h} \rangle + 1/2 k u^2 \quad (1)$$

where J is the exchange interaction, k is the elastic constant, and z is the number of interacting ion spins yields the displacement value $u = \beta \langle S_i S_{i+h} \rangle / k$. Compressibility of the lattice in the magnetically ordered range can be caused by two factors: variation in the elastic parameters β/k and the spin correlation function $\langle S_i S_{i+h} \rangle$. The variation in the parameter of the magnetoelastic interaction can be estimated knowing the behavior of the effective exchange and the

lattice parameter in the solid solution with the change in the concentration of ytterbium ions. Since the parameter $\beta = dJ/du$ characterizes the variation in the exchange value with the lattice parameter, the variation in the exchange is proportional to the Neel temperature: $dJ/dX \sim (2/3\, S(S+1)z)^{-1} dT_N/dX = 0.01$. The lattice parameter grows with the concentration: $da(X)/dX = 0.35$. As a result, the parameter of the magnetoelastic interaction decreases by 0.3% ($d\beta/dx = 0.0032$). At the same time, the elasticity modulus for ytterbium sulfide exceeds that for manganese monosulfide about 10%. The coefficient of thermal expansion is

$$\alpha(T) = du(T)/dT = \langle S_i S_{i+h} \rangle d(\beta/k)/dT + \beta/k\, d\langle S_i S_{i+h} \rangle/dT \approx \beta/k\, d\langle S_i S_{i+h} \rangle/dT. \quad (2)$$

The temperature dependence of $\alpha(T)$ is due to change in spin-spin correlation function versus temperature and two maximum in $\alpha(T)$ are attributed to inflection points of function $\langle S_i S_{i+h} \rangle$ at $T = 105$ K and at $T_N = 126$ K. At concentration $X > X_c$ (X_c is percolation concentration) dispersion in the distribution function of local exchange fields is increased, spin–spin correlation function is decreased as a result of the coefficient of thermal expansion reveal the smeared maxim in $\alpha(T)$ in the vicinity of Neel temperature.

3. Conclusions

Upon substitute of the rare-earth element Yb with variable valence for manganese ions in the $Mn_{1-X}Yb_XS$ solid solutions, the antiferromagnetic state remains in the concentration range $0.05 \leq X \leq 0.2$. Paramagnetic Curie temperature sharply drops upon substitute of ytterbium ions for manganese as a result of the competition of the exchange interactions in the solid solution and to the reduction of the effective magnetic moment in the concentration range $0 < x \leq 0.1$. The microscopic mechanism of the reduction of the magnetic moment is related to the change in the electron structure of manganese ions interacting with ytterbium ions. For the compositions with $X \leq 0.1$, ytterbium ions do not contribute to the magnetic moment of $Mn_{1-X}Yb_XS$. For the compositions with $X > 0.1$, the bi- and trivalent states of ytterbium ions in the solid solutions were found. In the $Mn_{1-X}Yb_XS$ solid solution, the hysteresis is observed in the field range 4 T $< H <$ 6 T and vanishes upon heating at $T \geq 50$ K.

It has been established that the coefficient of thermal expansion of the samples decreases with increasing concentration of ytterbium in the antiferromagnetic region. The relative variation in the sample size has been attributed to weakening of the spin correlations in the solid solution. Two peak appearing in the coefficient of thermal expansion arise from nonuniform distribution function of local exchange fields.

Acknowledgments

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