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Magnetic properties of $Sm_xMn_{1-x}S$ solid solutions

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The structural and magnetic properties of $Sm_xMn_{1-x}S$ ($0.01 \leq x \leq 0.2$) solid solutions synthesized on the basis of an antiferromagnetic semiconductor α-MnS are experimentally studied in the temperature range 4.2–300 K in magnetic fields up to 9 T. The magnetic hysteresis in $Sm_{0.05}Mn_{0.95}S$ is observed in the magnetic fields $6\,T < H < 9\,T$ at low temperatures and linear magnetization dependence on field for compound with $x = 0.2$.

1 Introduction At present, much attention is focused on materials with strong correlation between magnetic and electrical properties [1–3]. In view of the practical applications, these compounds are promising for the creation of microelectronic elements; as far as the fundamental studies are concerned, the most intriguing are the materials containing variable-valence elements undergoing metal–insulator transitions and magnetic phase transformations including variations in magnetic properties at preservation of magnetic symmetry. Semiconductors EuS, SmS, and MnS [4–7] relate to these compounds. Rare-earth elements Eu and Sm have no electrons on 5d-orbitals and their electron configuration (without taking into account the 4f-orbitals) is similar to alkali-earth metals. The presence of 4f- and 5d-orbitals with relatively close energies causes a number of specific properties of the compounds containing these elements. A divalent samarium ion Sm^{2+} possesses the same isoelectronic configuration as that of Eu^{3+} and the transition energy $E_{fd} = 0.4\,eV$ from the $4f^6$–$4f^5(^6H)5d\ t_{2g}$ state [8]. The width of the gap (E_g) between the valence and conductivity bands in SmS is somewhat smaller compared to MnS. Under the external pressure $P \sim 6.5\,kbar$, the SmS lattice is abruptly compressed and the lattice parameter reaches the value $a_p = 0.569\,nm$; resistivity decreases by an order of magnitude; volume, by 13%; and magnetic susceptibility, by 60% [9–11]. The authors of Ref. [4] attributed this fact to the transition of a samarium ion from the trivalent to divalent state. Rare-earth ions, depending on valence type (Re^{3+} or Re^{2+}) can be located in the valence band or near the Fermi level, which determines the electronic properties affecting luminescence and conductivity of the compounds. The magnetic susceptibility of a divalent samarium ion Sm^{2+} is nearly temperature independent, which indicates Pauli paramagnetism. Magnetic susceptibility of a trivalent samarium ion Sm^{3+} is lower; it monotonically grows in the temperature range 280–800 K and sharply increases at $T < 200\,K$. One might expect that on cation substitution of manganese ions by samarium ions the pressure imposed by the nearest neighborhood may induce a set of phase transitions, such as magnetic and electrical.

The aim of this study is to investigate the effect of electron doping of $Sm_xMn_{1-x}S$ sulfide on the structural and magnetic properties of synthesized crystals at substitution of the manganese by samarium ions.

2 Synthesis and measurements For the first time the synthesized $Sm_xMn_{1-x}S$ crystals were grown in a quartz

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reactor as a result of a melting of polycrystalline powders of sulfides. The reactor with a charge in a glass-carbon crucible was pulled through a single-turn inductor of a high-frequency facility. During synthesis, high-purity argon was used [12].

The phase composition and the crystal structure of the $Sm_xMn_{1-x}S$ ($0.01 \leq x \leq 0.2$) samples were determined with a DRON-3 X-ray diffractometer using Cu Kα radiation at 300 K. The specific magnetization was measured in vacuum at 6 K in magnetic fields up to 9 T by PPMS device. Magnetization of the samples was measured using a SQUID magnetometer with a superconducting solenoid at 4.2–300 K in a field of $H = 0.05$ T.

3 Experimental results and discussion The monosulfide α-MnS is an antiferromagnet that crystallizes in a NaCl-type face-centered cubic (FCC) lattice. SmS has the same crystallographic structure with the lattice parameter $a_p = 0.569$ nm under pressure. Lattice parameters of intermediate compounds lie on the straight line a_{MnS}–a_{SmS}. The solubility limit of Sm in MnS achieve at $x = 0.3$ in $Sm_xMn_{1-x}S$. At this concentration additional phase Sm_2S_3 is observed by X-ray diffraction patterns. The X-ray diffraction analysis has shown that the $Sm_xMn_{1-x}S$ samples up to $x = 0.2$ (Fig. 1) are homogeneous and the lattice is similar to α-MnS. With an increase of Sm cation concentration x, the unit-cell parameter a is increased as a result of increasing of the ionic samarium radius.

Substitution of the manganese by a samarium ion substantially influences the magnetic properties of the $Sm_xMn_{1-x}S$ solid solutions. The temperature dependences of the specific magnetization for $Sm_xMn_{1-x}S$ samples with $x = 0.01$ and 0.2 are shown in Fig. 2a and b. In the dependence $\sigma = f(T)$ of the compound with $x = 0.01$ (Fig. 2a), the temperature region exists where susceptibility is invariable and due to admixing of orbital moment.
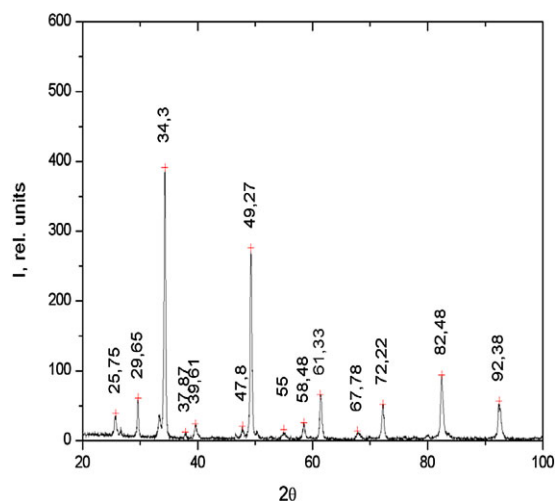
Figure 1 (online color at: www.pss-b.com) X-ray diffraction patterns of $Sm_{0.2}Mn_{0.8}S$ sample measured at $T = 300$ K.
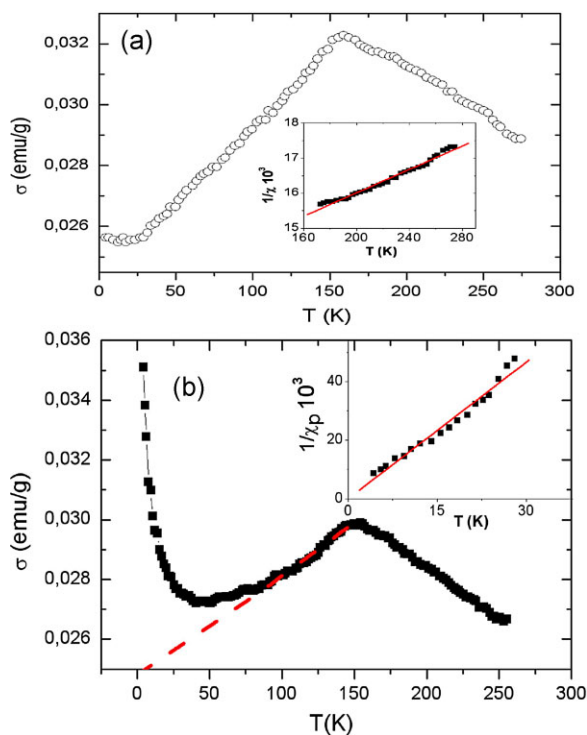
Figure 2 (online color at: www.pss-b.com) Temperature dependence of the specific magnetization of the $Sm_xMn_{1-x}S$ solid solutions measured in the field $H = 0.05$ T; $x = 0.01$ (a) and $x = 0.2$ (b). Inserts: inverse susceptibility minus the Van Vleck contribution (a) and the paramagnetic contribution to susceptibility (b).

The susceptibility value of a polycrystalline isotropic antiferromagnet is $\chi_{polyc}(T = 0) = 2/3 \chi_{max}(T_N)$ and $\chi_{max}(T_N) = 0.022$, whereas the Van Vleck contribution to a susceptibility is $\chi_{VV} = 0.004$. The inverse susceptibility without the Van Vleck contribution is presented in the insert in Fig. 2a. The experimental results are satisfactorily described by the linear dependence, on the basis of which the paramagnetic Curie temperature $\theta = -750$ K and the effective magnetic moment $\mu_{ef} = 5.5 \mu_B$ were determined in the $Sm_xMn_{1-x}S$ solid solution with $x = 0.01$.

In the $Sm_{0.2}Mn_{0.8}S$ solid solution, an additional paramagnetic contribution to susceptibility $\chi_{polyc} = \chi_{AF} + \chi_{VV} + \chi_{PM}$ is observed. The contribution caused by antiferromagnetic ordering is determined from an asymptotic continuation of the linear part of susceptibility to $T = 0$ K (dotted line in Fig. 2b). The results obtained from the expression $\chi = \chi_{ex} - \chi_{VV} - \chi_{AF}$ are given in the insert in Fig. 2b. In the temperature range of 4 K $< T < 20$ K, these data can be approximated by the Curie law $\chi_{PM} = C/T$ with the sufficiently high Curie constant and $\mu_{ef} = 11.2\mu_B$, which does not correspond to the moment of the samarium rare-earth ions. This contradiction may be eliminated taking into account the coexistence of ions with different valence (Sm^{2+} and Sm^{3+}) being in thermal equilibrium and assuming that the Boltzmann distribution law is valid. Then, the

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susceptibility due to SmS can be determined as:

$$\chi = \frac{N\mu_B^2}{3k}\frac{A_1 + A_2\exp\left(-\frac{\Delta E}{kT}\right)}{B_1 + B_2\exp\left(-\frac{\Delta E}{kT}\right)}, \tag{1}$$

$$B_i = \sum_j (2J+1)\exp\left(-\frac{E_j}{kT}\right),$$

$$A_i = \sum_j \left[\frac{g_J^2(J+1)J\mu_B^2}{T} + 3k\alpha_j\right](2J+1)\exp\left(-\frac{E_j}{kT}\right),$$

$$\alpha_J = \frac{\mu_B^2}{6(2J+1)}\left[\frac{F(J-1)}{E_{J+1}-E_J} - \frac{F(J)}{E_j-E_{j-1}}\right],$$

$$F(J) = \frac{1}{J}[(S+L+1)^2 - J^2][J^2 - (S-L)^2],$$

Here, index i takes two values: $i = 1$ (summation over multiplet Sm^{2+} levels) and $i = 2$ (summation over Sm^{3+} multiplet levels), $\Delta E = 0.18\,eV$ is the activation energy, N the number of multiplet levels, E the multiplet energy, g the g-factor, $J = L + S$, k the Boltzmann constant, and S and L are the spin and orbital moments, respectively. Using this formula, the Sm^{3+} ion concentration may be estimated in the $Sm_{0.2}Mn_{0.8}S$ solid solution. It was established that for this composition a samarium ion exists in the divalent state and is characterized by the $4f^6$ configuration.

Substitution of the manganese cations by nonmagnetic ions will lead to the reduction of the effective magnetic moment $\mu_{ef}^{ex} = 4.8\mu_B$ and to the decrease the Curie temperature $\theta = -500\,K$, found from fitting $1/\chi$ by linear dependence on temperature in the range of $180\,K < T < 280\,K$. The magnetic moment of Sm^{+2} ion reveals a nonlinear dependence on temperature [4] and the average value of magnetic moment is approximately equal to $3\mu_B$ in the range of $150\,K < T < 300\,K$ temperatures. The effective magnetic moment $\mu_{ef}^{th} = (1-x)\mu_B^{Mn} + x\mu_B^{Sm} = 5\mu_B$ is determined on the assumption that electrons are located only in Mn^{+2} and Sm^{+2} ions in the $Sm_{0.2}Mn_{0.8}S$ solid solution. The difference between $\mu_{ef}^{th} - \mu_{ef}^{ex} = 0.2\mu_B$ may arise from formation of impurity subband near the Fermi level, where a fraction of the electrons delocalize, which causes the reduction of magnetic moment.

Another interesting fact is that the Neel temperature is not practically changed and the paramagnetic Curie temperature decreased by 33%. This can be explained in terms the following model. The magnetic structure of $Sm_{0.2}Mn_{0.8}S$ solid solution is nonuniform and consists of Van Vleck paramagnetism from SmS clusters, antiferromagnetic MnS and ferromagnetic exchange between Sm and Mn ions. This exchange arises from the electron hopping from the 3d level Mn^{+2} to Sm^{+2} ions in the parallel arrangement of magnetic moments in 3d and 4f shells. The concentration of the exchanges K (Mn–Sm) is proportional to the samarium-ion concentration according to Monte Carlo simulations for A_xB_{1-x} binary alloy. Using the normalization requirement $x_{J(MnMn)} + x_{K(MnSm)} + x_{I(SmSm)} = 1$ concentration of antiferromagnetic interactions is

$x_{J(MnMn)} = 0.6$, $x_{K(MnSm)} = 0.2$. The Neel temperature of MnS having second ordering type is equal to $T_N = \rho zJ$, $\rho = 2/3S(S+1)$, $z = 6$ and for $Sm_{0.2}Mn_{0.8}S$ solid solution $T_N = \rho z\ (Jx_{J(MnMn)} + Kx_{K(MnSm)})$. For $K/J = 2$ Néel temperatures $T_N(x = 0.01) = T_N(x = 0.2)$ are equal and the ratio of paramagnetic Curie temperature $\theta(x = 0.2)/\theta(x = 0.01) = 0.66$ is in good agreement with experimental data.

The field dependence of magnetization measured in the $Sm_{0.05}Mn_{0.95}S$ sample is qualitatively different from $\sigma(H)$ for MnS [13]. Figure 3a shows the $\sigma(H)$ curve measured at the temperature $T = 6\,K$ for the $Sm_xMn_{1-x}S$ solid solution with $x = 0.05$. The maxima of $d\sigma(H)/dH$ a derivative curve in the field dependence of magnetization were found with increasing and decreasing magnetic fields, respectively, at $H = 8.1\,T$ and at $H = 6.9\,T$. The hysteresis is illustrated in the insert in Fig. 3a with the maximum change in the specific magnetization $\Delta\sigma = 0.2\,emu/g$ calculated as $\Delta\sigma = \sigma_{inc}(H) - \sigma_{decr}(H)$. The susceptibility variation determined from $\sigma(H)$ by the linear dependence $\sigma = -0.066 + 0.72\ H$ in the fields $H > 10\,T$ and $\sigma = -0.05 + 0.65\ H$ in the fields $0 < H < 6\,T$ is $\Delta\chi = 0.07$. The linear $\sigma(H)$ dependence versus magnetic field is observed for the $Sm_{0.2}Mn_{0.8}S$ sample in the range of $-9\,T < H < 9\,T$ fields (Fig. 3b).

This effect may be explained on the assumption of the existence of the anisotropy field $H_A = 0.2\,K$ and rise of
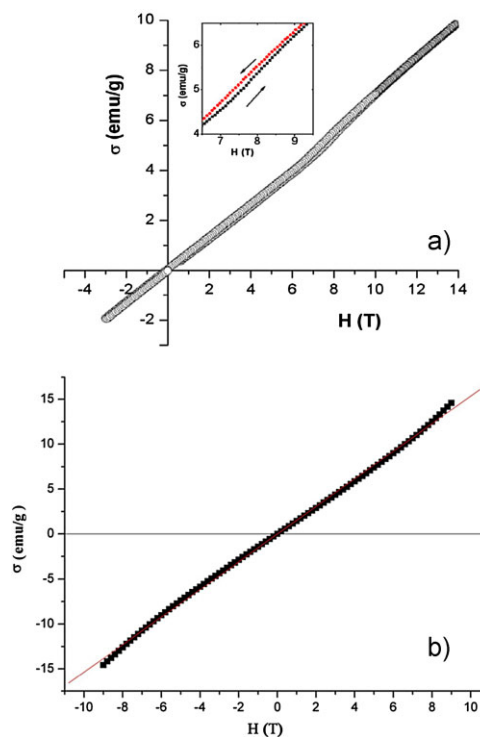
Figure 3 (online color at: www.pss-b.com) Field dependences of magnetization for the $Sm_xMn_{1-x}S$ sample: (a) $x = 0.05$; (b) $x = 0.2$ at $T = 6\,K$. The field region with the maximum of $d\sigma(H)/dH$ derivative is emphasized in the insert.

external magnetic field leads to $90°$ rotation of the antiferromagnetic vector for compound with $x = 0.05$ and to a magnetization jump at $H > H_c$, where H_c is the spin-flip field and determine as $H_c = \sqrt{2}\, H_E H_A$, H_E is the exchange field that may be estimated from the paramagnetic Curie temperature $\theta = SH_E$, $H_E \approx 300$ K, critical field $H_c \approx 8$ T. The measurements $M(H)$ are carried out for the polycrystal sample. The magnetization jump is due to small crystalline particles that in the easy axis of the magnetization are disposed in the angle interval $-3° < \varphi < 3°$, where φ is the angle between external magnetic field and uniaxial anisotropy field. For the single crystal sample is $\Delta\sigma = \chi\, H_c \approx 5$ emu/g and for polycrystal sample is $\Delta\sigma = \chi\, H_c\, \Delta\varphi/180° \approx 0.2$ emu/g. The anisotropy field and exchange field decrease in the Sm$_x$Mn$_{1-x}$S compounds with increasing samarium-ion concentration. Magnetic structure becomes nonuniform and the spin-flip field disappears. As a result $\sigma(H)$ is a linear function.

The paramagnetic Curie temperatures, Neel temperatures, and effective magnetic moments of the Sm$_x$Mn$_{1-x}$S system with $x = 0.01$ and 0.2 have been determined. Variations in these quantities are explained by the Van Vleck and paramagnetic contributions of a divalent samarium ion. The magnetic hysteresis in Sm$_x$Mn$_{1-x}$S ($x = 0.05$) system has been discovered in the field region 6 T $< H < 9$ T and the change in susceptibility within 5% has been found to be related to the existence of the spin-flip field. A linear dependence $\sigma(H)$ is revealed for $x = 0.2$. The results obtained show that in a sufficiently wide temperature range of Sm$_x$Mn$_{1-x}$S compositions $(0.01 \leq x \leq 0.2)$ the substitution of manganese ions by samarium ions retains a divalent state of samarium ion and action of the pressure imposed by the nearest neighborhood is compensated by exchange and electrostatic interaction with manganese ions.

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