Nonuniform Magnetic States and Electrical Properties of $Sm_XMn_{1-X}S$ Solid Solutions

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The real and imaginary parts of magnetic permeability at the three frequencies 100 Hz, 1 kHz and 10 kHz and magnetic moment in magnetic field $H = 0.05$ T in the $Sm_XMn_{1-X}S(0.1 \leq \times \leq 0.25)$ solid solutions at the temperatures 5 K–300 K were measured. Magnetization curves were measured in the range of fields -9 T $< H < 9$ T at the temperatures $T = 5$ K, 50 K. Non-linear behavior of the magnetization versus field, residual magnetic moment, logarithmic dependence of imaginary parts of the magnetic permeability maximum on frequency and sharp drop of $Im(\mu)$ at $T < 40$ K for compound $Sm_{0,25}Mn_{0.75}S$ were found. The electrical resistivity of the $Sm_xMn_{1-x}S(0.15 < x < 0.25)$ solid solution in the range of temperatures 80 K–300 K were measured. Minimum and maximum in the temperature dependence of the resistivity were found respectively at $T = 220$ K for $X = 0.15$ and at $T = 100$ K for $X = 0.2$ compounds. This behavior is explained a result of the mobility edge movement and the disorder of the deformation and spin density fluctuations with short-range order.

Index Terms—**Conductivity, magnetic semiconductors, magnetization processes.**

I. Introduction

At present, much attention is focused on the materials with the strong correlation between magnetic and electrical properties [1]. In view of 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. Among these compounds are EuS [2] and SmS [3]. Rare-earth elements Eu and Sm have no electrons on 5d-orbitals and their electron configuration (without taken into account of 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 isoelectron configuration as that of Eu^{3+} and the transition energy $E_{fd} = 0.4$ eV from the $4f^6 - 4f^5(^6H)5dt_{2g}$ state [4]. Width of the gap (E_g) between the valence and conductivity bands in SmS is somewhat smaller as compared to MnS [5]. Under the external pressure $P \sim 6.5$ kBar, the SmS lattice is abruptly compressed and the lattice parameter reaches the value $a_p = 5.69$ Å; resistivity decreases by an order of magnitude; volume, by 13%; and magnetic susceptibility, by 60% [6]. The authors [6] attributed this fact to the transition of a samarium ion from the divalent to trivalent state. Magnetic susceptibility of a divalent samarium ion Sm^{2+} is nearly temperature-independent, which indicates Van-Fleck 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.

MnS and SmS sulfides possess a crystal structure of NaCl-type face-centered cubic lattice with constant lattice $a = 5.222$ Å (MnS) [7] and $a = 5.965$ Å (SmS) [8] that is fall drop under pressure. One might expect that upon cation substitution of manganese ions by samarium ions the pressure imposed by the nearest neighborhood may induce an electrons in d-band, that causes the ferromagnetic exchange between manganese ions located near boundary of samarium cluster. A competition between ferro- and antiferromagnetic interactions can give rise to a new magnetic structure.

The aim of this study is to investigate the effect of electron doping of $Sm_XMn_{1-X}S$ sulphide on the structural, magnetic, and electrical properties of synthesized crystals upon substitution of manganese by samarium ions having mixed valence.

II. Magnetic Properties $Sm_XMn_{1-X}S$

Phase composition and the crystal structure of the $Sm_XMn_{1-X}S$ samples were determined with a DRON-3 X-ray diffractometer in CuK_α-radiation at 300 K. According to the data of the X-ray diffraction analysis, the $Sm_XMn_{1-X}S$ samples have a NaCl-type face-centered cubic (FCC) lattice similar to α-MnS. Specific magnetization was measured in vacuum at 5 K and 50 K temperatures in magnetic fields up to 9 T. Magnetization of the samples in the field $H = 0.05$ T, the real and imaginary parts of magnetic permeability at the three frequencies 100 Hz, 1 kHz and 10 kHz were measured using a PPMS in the temperature range of $5\ K < T < 300\ K$.

Temperature dependence of the inverse susceptibility measured in $H = 0.05$ T differs from typical antiferromagnet having minimum of the susceptibility at Neel temperature. The

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paramagnetic Neel temperature and magnetic phase transition temperature is very difficulty determined from the data on the temperature dependence χ (T) and μ (T) that are integral characteristics. Susceptibility of $Sm_XMn_{1-X}S$ solid solution consists of three main parts: χ_{AFM} antiferromagnetic susceptibility of the magnetic moments of the manganese ions, that link indirect exchange via sulfur, and χ_{FM} ferromagnetic contribution due to manganese spins on the surface samarium cluster Mn-Sm, and Van-Fleck contribution to χ_{VV} from samarium ions. High value of the susceptibility at $T > 100$ K arises from adding of orbital magnetic moments of terms having near value of energies. The energy difference between multiplet levels is $\Delta E\,(J, J+1) \approx 300\ cm^{-1}$ for Sm^{2+} ion and heating gives rise to change in the Van-Fleck magnetic susceptibility at $T > 150$ K. Similar behavior $\chi_{VV}(T)$ is observed for Sm^{3+} ion in SmS sulfide. The increasing of samarium concentration in $Sm_XMn_{1-X}S$ leads to rise of Van-Fleck contribution to susceptibility and decreasing of the averaging value of antiferromagnetic exchange.

The complex $\mu = Re(\mu) + Im(\mu)$ magnetic permeability study allows to determine the dynamical magnetization process and the relaxation of magnetic moment.

Real part of the magnetic permeability at the frequency 1 kHz and magnetic moment in field $H = 0.05$ T divided to magnitudes $Re(\mu(T = 290\ K))$ $M(T = 290\ K)$ measured at $T = 290$ K show various temperature dependencies of $Re(\mu)/Re(\mu(T = 290\ K)$ permeability and $M(T)/M(T = 290\ K)$ magnetization of $Sm_XMn_{1-X}S$ for compound with $X = 0.25$ at $T < 40$ K.

Detailed analysis of the frequency dependence real part of magnetic permeability of this sample, presented in a Fig. 1, have found out reduction of value $Re(\mu)$ with buildup of frequency below some critical temperature T_g which depends on frequency and determined from the derivative real part of permeability $d\,Re(\mu)/dT$. Maximum temperature of derivative increases by three degrees with rise of frequency from $f = 100$ Hz to 10 kHz. The imaginary part of $Im(\mu)$ has a maximum at Tg that shifts towards high frequencies and it is well fitted by the linear logarithmic dependence $T_g = 36 + 1.5 \ln f$, plotted in an inset to Fig. 1(b).

Measurement of complex permeability gives the essential information about energy dissipation of the magnetic oscillations, induced by the external variable magnetic field. A dissipation of magnetic moment is characterized by various dependences of parameter of a relaxation on temperature and frequency and depends on an exchange interaction, magnetoelastic interaction or an interaction with delocalized electrons. These interactions define three types of a relaxation in the semiconductor: the spin-spin, spin-lattice and interaction of the localized electrons spins with the band electrons.

The relaxation due to conductivity electrons arises from the exchange interaction with a localized electrons I_{sd} and the T_1 time is in inverse proportional to temperature $1/T_1 = \pi/h(I_{sd}N(E_F))^2\ kT \approx 10^{10}(I_{sd}N(E_F))^2\ T$, here $N(E_F)$ is electron density of state at Fermi level. The imaginary part of $Im(\mu)$ is mainly determined by relaxation time $Im(\mu) \sim T_1$. The imaginary part of the magnetic permeability of $Sm_XMn_{1-X}S$ solid solution is well fitted by linear function $Im(\mu(T)) \approx 60\ Im(\mu(T_g))/T$ versus inverse temperature.

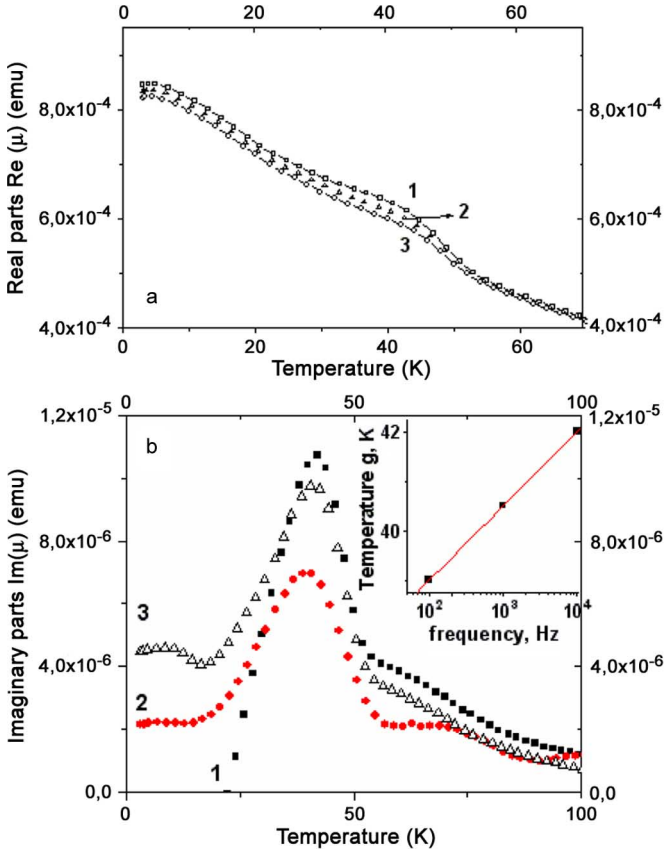

Fig. 1. Temperature dependences of real (a) and imaginary (b) parts of magnetic permeability for $Sm_{0.25}Mn_{0.75}S$ at $f = 100$ Hz (2), 1 kHz (3), 10 kHz (1) frequencies. The insert: the asperromagnetic state temperature versus frequency for the same sample.

Similar relaxation time dependence has been observed for CuMn spin glass.

These indicate that interaction of localized and delocalized electron spins causes relaxation mechanism of magnetic moment at low temperatures. Samarium ion injects electrons in d- band which establish the ferromagnetic ordering among the nearest spins of manganese ions.

Magnetization behavior under external magnetic field confirms formation of nonuniform magnetic structure. Curve measurements M (H) are presented in Fig. 2 in two limit case for $T < T_g$ and $T > T_g$. M (H) dependence for compound $Sm_XMn_{1-X}S$ with $X = 0.1$ is linear function and representative for polycrystalline antiferromagnetic. Nonlinear dependence of magnetization versus field is observed for $Sm_{0.25}Mn_{0.75}S$ at $H < 4$ T and get on the linear dependence at the high fields. At decreasing magnetic field the remanent magnetic moment $M\,(H = 0) = 0.22\ emu/g$ is found. The origin of the moment is associated with the canted antiferromagnet, arisen from competition of ferromagnetic and antiferromagnetic interaction on the surface boundary of Mn-Sm clusters.

III. Electric Properties $Sm_XMn_{1-X}S$

The electrical resistivity of the synthesized $Sm_XMn_{1-X}S$ samples was measured by the four-probe technique at temperatures of 80–300 K. The resistivity of the MnS pure single crystals is independent of temperature at $T < T_N$ as shown in

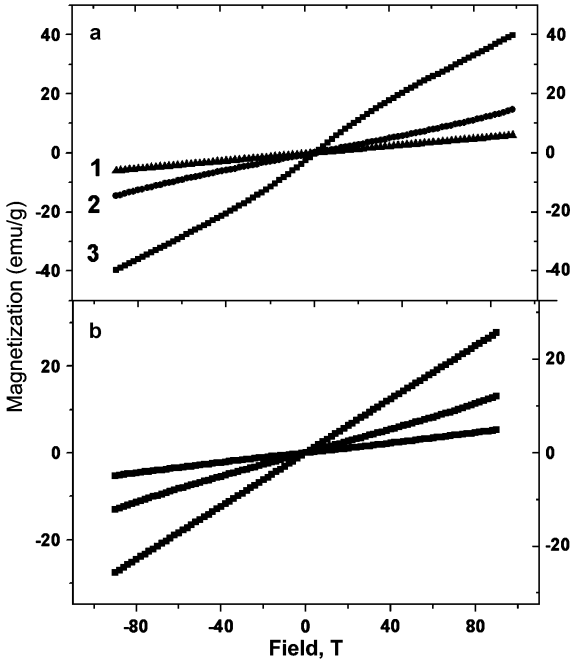

Fig. 2. Field dependences of the magnetization in two limit case for $T < T_g(T = 5\ K)$ (a) and $T > T_g(T = 50\ K)$ (b) for compounds $Sm_XMn_{1-X}S$ with $X = 0.1(1); 0.2(2); 0.25\ (3)$.

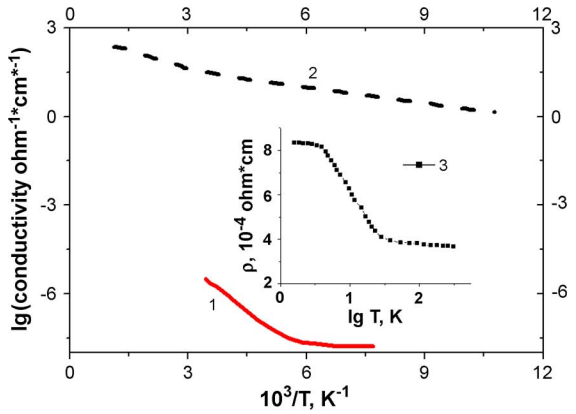

Fig. 3. Temperature dependences of conductivity for MnS (1) and for SmS (2) at different pressure and lattice constant: $P = 0\ kBar$, $a = 0.597\ nm$ (2). Insert: resistivity versus lgT for SmS at $P = 10\ kBar$, $a = 0.57\ nm$ (3) [2].

Fig. 3 and behaves analogously to semiconductors up to 500 K with values of the activation energy are equal to $E_a = 0.2\ eV$. The temperature dependences (in the range 80–1000 K) of the electrical conductivity in SmS indicate that the absolute gap Δ between the 4f levels and the conduction band edge of SmS is $\Delta = 0.23 - 0.25\ eV$ (Fig. 3) [2].

Some experimental results indicate that the golden phase of SmS could be a narrow-gap semiconductor. Evidence for a gap comes from the activation behavior of the electrical resistivity, plotted in Fig. 3 [2], and point contact measurements [9]. The estimations from the point-contact spectra show a possible gap of about 6.4 meV [9].

On the other hand some experiments indicate that there may not be a gap but rather a pseudogap, and the hybridization does not occur over the whole Brillioun zone. Although the temperature dependence of the resistivity in the golden phase of SmS is

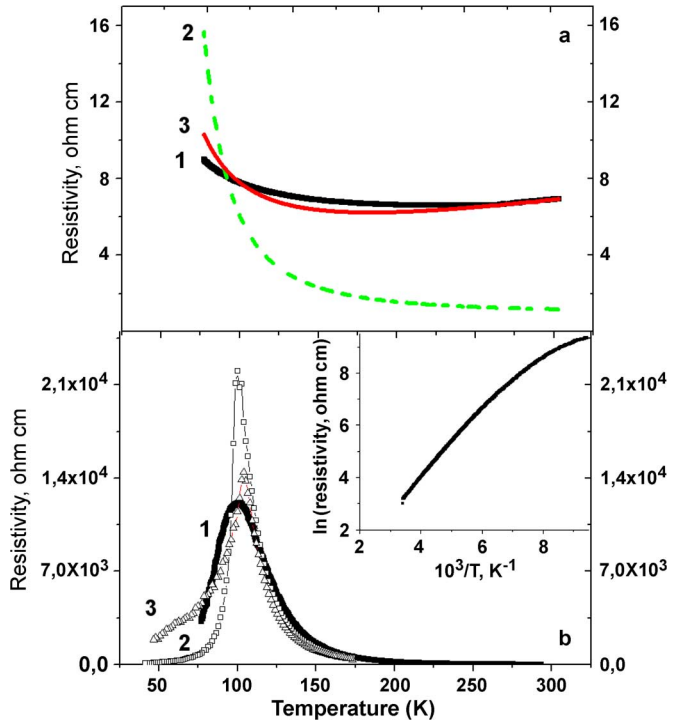

Fig. 4. Electrical resistivity vs temperature for $Sm_XMn_{1-X}S$ with $X = 0.15$ compound (1) and fitting function $\rho = 1/enu$, where $u = el^2\omega p/k_BT\ \exp(-Ea/k_BT)$ (2, 3) for several parameters $n = 0.1$, $E_a = 410\ K$ (2), $n = 0.01$, $E_a = 186\ K$ (3) (a); for $X = 0.2$ compound (1) and calculated in terms of Anderson disordered model using function (1) with $\rho_0 = 0.5\ ohm\ cm$, $W = 3.1\ eV$ (2), $W = 3\ eV$, $\langle S^z \rangle = 0$ (3) (b). Inset: resistivity vs 1/T at $T > 100\ K$.

semiconductor-like (Fig. 3), the resistivity is increased only in severel time with cooling from room temperature to $T = 4\ K$. Band structure calculations of golden SmS produce a pseudogap at the Fermi level with a peak just above and a shoulder below the Fermi level with predominantly of f character [4]. When the density of states at E_F is small compared to the giant density of states of the f peaks, the resistivity may nevertheless appear activated over a certain temperature range.

In Fig. 4 the temperature dependence of the resistivities for solid solution $Sm_XMn_{1-X}S$ with $X = 0.15$ (a) and $X = 0.2$ (b) are shown. One can clearly see a gradual change of the temperature dependence of resistivity which can be divided into two regions: the first extends from 80 to 220 K and the second occupies the range 220–300 K. In firth region resistivity decreases at the heating from $T = 80\ K$ and beginning from 220 K the resistivity rises with increasing temperature. It may be explained using a process of electron hopping between Sm^{2+} and Sm^{3+} ions from occupied to empty 5d level by thermal hopping with activation energy E_a. The main part of this energy results from difference in the energies of local spin order d-f interaction and a deformation of elastic system near samarium ion. The impurity conductivity relies as disorder diffusion process and drift mobility expressed by $u = el^2\omega_p/k_BT\ \exp(-E_a/k_BT)$, where ω_p is phonon frequency and l is the distance between samarium ions that is approximately equal to $l = x^{1/3}$ [10]. Theoretical resistivity dependencies on temperature simulated by $\rho = 1/enu$, are presented in Fig. 4 for two fitting parameter: concentration of 5d electrons (n) and E_a activation energy

for fixed $\omega_p = 100$ K phonon frequency. Maximum of phonon mode intensity is observed near the Brillioun zone boundary. The frequency of acoustic phonon mode at X point is 66 cm^{-1} in SmS [11] and optical mode 100 cm^{-1} in MnS that proves the validity of ω_p magnitude using in our simulations. The best fit to experimental results achieves at $n = 0.01$, $E_a = 186$ K, $l = 1$ nm. According to these results the relation between divalent and trivalent samarium ions is $Sm^{+3}/Sm^{+2} = 1/15$ and the activation energy is closely to Debye temperature, that is 230 K for MnS.

The minimum of the electrical resistivity may be also explained in terms of the single impurity Anderson model which takes into account the crystal-field splitting of the $4f$ ground-state multiplet, and assumes a strong Coulomb repulsion and the redistribution of the single-particle spectral weight within the Fermi window. If hybridization strength G is smaller as compared to crystal field splitting D than the high-temperature maximum in R (T) appears [12]. For temperatures below the maximum, ρ (T) drops to a minimum and then rises logarithmically as T_0 is approached. This minimum and the subsequent low-temperature upturn are of a purely electronic origin and appear in systems with small T_0 coherence temperature and large crystal-field splitting. The minimum temperature is related to T_m by $T_{min} = T_{max}/3 = D/9k_B$ [12] and splitting of the $4f$ ground-state multiplet is $D = 0.2$ eV that in order to exceed splitting of the $4f$ multiplet in $Sm_xMn_{1-x}S$ compound.

The temperature dependence of the electrical resistivity shows a sharp maximum for $X = 0.2$ (Fig. 4) that may be interpreted as temperature induced metal-insulator transition due to magnetic ions spin density fluctuations.

Using ideas and methods of Anderson localization theory authors [13] obtain simple formulas, which connect the mobility edge with short-range order characteristics of the magnetic subsystem—static spin correlators.

$$\rho = \rho_0 \exp\left\lfloor \left(\left(1 - \langle S_0 \cdot S_1 \rangle / S^2\right) / \left(1 + \langle S^z \rangle / S\right) \right) (W/4kT) \right\rfloor . \quad (1)$$

W is the conductivity band width, $\langle S_0 \cdot S_1 \rangle$ is spin-spin correlator between nearest neighbors, and $\langle S^z \rangle$ is average magnetization. We used the Monte Carlo (MC) method for calculation the magnetic characteristics for $18 \times 18 \times 18$, $22 \times 22 \times 22$ lattice with 50000–100000 Monte Carlo steps per site with periodical boundary conditions. Spin-spin correlator and magnetization were simulated for ferromagnetic and for AFM with random ferromagnetic and antiferromagnetic exchange. Using MC results for $\langle S_0 \cdot S_1 \rangle$ and $\langle S^z \rangle$ we fit formule (1) to experimental data with one parameter W. The best agreement is achieved for the band width with $W = 3$ eV and spontaneous magnetization tends to zero. A random-bond model with off-diagonal disorder depending on an instant spin configuration gives a quantitative description of the experimental dependence ρ (T).

IV. Conclusion

The relaxation maximum of magnetic moment in $Sm_XMn_{1-X}S$ compound with $X = 0.25$ is found. Temperature associated with relaxation maximum increases logarithmically with frequency. Temperature behaviors of real part of magnetic permeability in zero field and magnetic moment for $H = 0.05$ T field are different at $T < T_g$. Nonlinear magnetization dependence on field and remanent magnetic moment reveal for compound with $X = 0.25$ at $T < T_g$. These effects are explained in term of a nonuniform magnetic structure, consisting of domain with canted antiferromagnetic. The magnetic moment relaxation is associated with exchange spin interaction of localized and delocalized electrons. Electron state is better described in the disordered Anderson model. Change in the carrier mobility causes minimum of the resistivity associating with change in the conductivity type from hopping to band type for $X = 0.15$. Formation of a nonuniform magnetic order at $T = 100$ K leads to shift of the mobility edge that explained the electrical resistivity peak for $X = 0.2$ compound.

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