Connection of thermopower and giant magnetothermopower with magnetic and structural heterogeneity in $Sm_{0.55}Sr_{0.45}MnO_3$ manganite

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ABSTRACT

It was first shown that the thermoelectric power in a magnetic semiconductor $Sm_{0.55}Sr_{0.45}MnO_3$ is caused by ferromagnetic (FM) ferron-type nanoclusters and antiferromagnetic (AFM) CE-type nanoclusters with charge-orbital (CO) ordering. The presence of these clusters is caused by heavily Sr doping of a $SmMnO_3$ compound, which replaced Sm ions. Thermoelectric power S and magnetothermopower $\Delta S/S$ has been studied in three samples: ceramics and two single-crystal samples. One of single-crystals was cooled in the air, another one was cooled in an oxygen atmosphere. The annealing in oxygen closes oxygen vacancies and, thus, increases the fraction of the CE-type AFM phase with the CO ordering which displaces the oxygen ions. $S(T)$ curves of single-crystal sample cooled in the air and ceramic sample have a sharp increase starting from Curie temperature (T_C) region and a slow decline till 325 K. At the same time $\{\Delta S/S\}(T)$ curves have a sharp minimum near $T_C=126$ K, reaching the giant absolute value of 87% in the magnetic field $H=14.17$ kOe. This means that thermopower almost vanish with thermal destruction of FM clusters, i.e. thermopower is caused by these clusters in which crystal lattice is compressed. Oxygen cooled single-crystal's $S(T)$ curves have a broad maximum near 270 K, including Neel temperature of CE-type clusters $T_{NCE}=240$ K. $\{\Delta S/S\}(T)$ curve has a sharp minimum at the T_{NCE} reaching the absolute value of 50% in $H=13.2$ kOe. The decrease of S is caused by destruction of CO order displacing oxygen ions in CE-type AFM clusters. Thus changed crystal lattice in nanoclusters of ferron type or AFM of CE-type makes the main contribution in thermopower in these three samples.

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1. Introduction

The usage of thermoelectric devices in various devices is primarily because of their primitive structure. It is only necessary to make a closed electrical circuit and a temperature gradient on the working sample. Furthermore, it is an environmentally friendly energy source. Efficiency is small in modern thermoelectric devices and therefore they cannot compete with other sources of electricity. In our work we find new materials, in which the thermopower increases with the doping level. Therefore, a sample of a sufficiently small size can replace a bulky battery thermoelectric generator.

Coefficient of efficiency for thermoelectric materials has next view:

$$ZT = S^2\sigma/k \tag{1}$$

where S is the coefficient of thermopower, σ is the electrical

conductivity and k is the coefficient of the heat conductivity. At present ZT of the best thermoelectric materials is not more than one. This value is 10% of efficiency of Carnot cycle. Since last century Bi_2Te_3, with some dopes or prepared in different ways, is the best thermoelectrical material. So, the carrier concentration was adjusted to increase the value of S; melting was used to reduce the heat conductivity [1,2], and also crystalline defects and nanostructures were induced [3]; thin films were prepared to the control of the transportation of phonons and electrons [4].

As will be shown in this article, the value of thermopower in magnetic semiconductors can be strongly changed by the doping. This is due to the fact that magnetic semiconductors have the special magnetic impurity state that do not have nonmagnetic one. Nagaev showed [5] that in magnetic semiconductors the electron of donor or the hole of acceptor because the gain in the s–d exchange energy is localized near impurity ion and maintain FM order around its among magnetic ions. This nanoscale quasi-particle is called ferron. In nondegenerate magnetic semiconductor individual ferrons exists in which one electron of the impurity is localized in the ferron. In degenerate magnetic

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semiconductors electron density in the ferrons is raised. In FM semiconductors ferrons exist near Curie temperature T_C, where they achieve the maximum dimension and fall quickly at $T > T_C$. This destruction accelerates by the magnetic field. In AFM semiconductors ferrons exist from $T = 0$ K. Coulomb repulsion and interfacial energy define the topology of magnetic two-phase state. Therefore ferrons have the form of spheres, symmetrically arranged in a matrix. Yanase and Kasuya showed that crystal lattice is compressed inside the ferrons [6], therefore thermopower inside the ferrons is different from the matrix's one. It is known that certain compounds of manganite, for example in $Re_{(0.5+x)}Sr_{(0.5-x)}MnO_3$ ($0 \leq x \leq 0.1$, Re is rare-earth ion), contain the nanosized clusters with a charge-orbital ordering, displacing the oxygen ions, so that the orthorhombic structure in them is stronger distorted than in the matrix [7,8]. Therefore thermopower inside these clusters is different from the matrix's. These clusters have the AFM structure of CE-type which is composed of a bundle of spin-FM chains, each with the zigzag geometry, and with AFM interchain coupling [8].

As it will be shown in this article, these two types of the nanoparticles (ferrons and AFM of CE-type clusters with CO ordering) determine the value of the thermopower in magnetic semiconductors.

In this paper thermopower S and magnetothermopower $\Delta S/S = \{S_H - S_{H=0}\}/S_{H=0}$ have been studied on three samples of $Sm_{0.55}Sr_{0.45}MnO_3$: two single-crystal and one polycrystalline sample. During the preparation the one of the single-crystal samples was cooled in the air, and the other one was cooled in the oxygen atmosphere. The annealing in oxygen performed during preparing the samples closes broken Mn–V–Mn bonds (here V is vacancy of oxygen) and, thus, increases the number of the clusters with charged-orbital ordering. All the samples have ferron-type nanoclusters.

Three types of clusters: FM one, A-type of AFM clusters, and CE-type of AFM clusters with charged-orbital ordering, were found in $^{154}Sm_{0.55}Sr_{0.45}MnO_3$ using neutron diffraction [9]. A-type of AFM clusters disappears at the temperature more than $T_{NA} = 120$ K, CE-type of AFM clusters disappears near bigger 180 K. Spontaneous magnetic moment appears at the temperature $Tc = 110$ K. Temperature dependence of the activation energy has a sharp jump near bigger $T = 180$ K. In compound with charge-orbital ordering this jump is connected with thermal destruction of the charge-orbital order. Transition temperatures got in [9] is close to the transition temperatures got in [10] from data of electron and neutron diffraction and the temperature dependence of magnetization. In works [9,11,12] are shown that in there are FM clusters of 180–200 Å and several thousand Å in the low-temperature region in $Sm_{0.6}Sr_{0.4}MnO_3$.

The giant magnetoresistance and magnetostriction effects were observed earlier at the temperature $T > Tc$ in $Sm_{0.55}Sr_{0.45}MnO_3$. These effects are explained by electron phase separation, caused by strong s–d change [13].

2. Experimental methods

The single crystal $Sm_{0.55}Sr_{0.45}MnO_3$ samples were grown by crucibleless floating zone melting. One sample was cooled in an oxygen atmosphere and other in an air. The phase composition and lattice parameters were controlled using a Siemens D5000 X-ray diffractometer. The samples were single-phase perovskites with an orthorhombic structure (space group *Pnma*). Polycrystalline sample was prepared and was analyzed by Kaul and Gorbenko. The synthesis was conducted by standard ceramic technology. The phase composition and lattice parameters were controlled using a Siemens D5000 X-ray diffractometer. The sample was

single-phase perovskite with the orthorhombic structure (space group *Pnma*) and lattice constants at the temperature $T = 300$ K: $a = 5.424(1)$ Å, $b = 7.678(2)$ Å, $c = 5.434(2)$ Å. The orthorhombic parameter evaluated from the lattice constants is equal to 0.2%. This means that the structure is close to the cubic structure. A single-phase state of the synthesized sample was confirmed by the Raman spectroscopy measurements performed on a Jobin-Yvon T64000 spectrometer with triple monochromator. The Roman spectra showed the presence of the phonon modes characteristic of the orthorhombic manganites with *Pnma* symmetry.

During the measurements of the thermopower S and magnetothermopower $\Delta S/S$, a heater made from a thin constantan wire was wound on one parallelepiped-shaped sample end to produce the temperature gradient of 5 K. Three copper–constantan thermocouples were brought to both ends and the middle of the sample which measured theirs temperatures. Electrical measurements were carried out by analog-to-digital converter NI-9211. The sample was placed into an evacuated inset which was lowered into Dewar flask with liquid nitrogen. The sample temperature T was regulated by an electric furnace that was bifilarly wound on the inside surface of the evacuated inset. The Dewar flask with the inset was disposed between electromagnet poles, which allowed us to study the influence of magnetic field on the thermopower. We also studied the sample magnetization using a SQUID magnetometer and the paramagnetic susceptibility by the weight method with electromagnetic compensation. The thermopower and magnetization M were measured on two samples cut from the single crystal in the parallelepiped shape ($10 \times 3 \times 2$ mm^3). The polycrystalline sample has the same dimensions and shape. The longest edge was parallel to the c axis or to the ab plane of the orthorhombic structure and was parallel to magnetic field H during the measurements. Curves $M(T)$ and $M(H)$ and also $S(T)$, $S(H)$, $\{\Delta S/S\}(T)$, and $\{\Delta S/S\}(H)$ are almost indistinguishable for the two parallelepipeds, which indicated small magnetic and crystallographic anisotropies in them.

3. Results and discussions

3.1. Magnetic behavior

In our work [13] the Curie temperature T_C determined from the initial magnetic susceptibility χ_i, measured in an alternating magnetic field with a frequency of 8 kHz as a temperature of a sharp drop χ_i. It is equal to 126 K for all three samples studied in this work. Should be taken that notion of the Curie temperature of this compound is highly conditionally: this is Curie temperature of the FM nanoclusters. Notice that the determination T_C was made in small magnetic field, where the contribution in the initial magnetic susceptibility from AFM clusters is negligibly small. The dependence of the paramagnetic susceptibility from temperature $\{1/\chi\}(T)$ fulfils the Curie–Weiss law from $T > 290$ K with the paramagnetic Curie points 225 K, 270 K, 230 K for single-crystal cooled in the air, single-crystal cooled in the oxygen and ceramic samples correspondingly. Thus, the paramagnetic susceptibility fulfils the Curie–Weiss law at the temperatures exceeding the Cutie temperature Tc in ~ 2 times. It is possible that this is connected with the presence of CE-type AFM clusters in the temperature region between Tc and the paramagnetic Curie temperature. This is corroborated by fact that paramagnetic Curie point of the sample annealing in oxygen is highest.

Fig. 1a–c shows the dependences of magnetization from the temperature and the magnetic fields of the single-crystal sample cooled in the oxygen atmosphere. As is seen from the Fig. 1a, the transition to the paramagnetic phase is washed away. It is caused by existence of the three types of clusters in the sample. It is seen