Spontaneous generation of voltage in single-crystal Sm$_{0.55}$Sr$_{0.45}$MnO$_3$ during magneto-structural phase transition

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Abstract. In single-crystal Sm$_{0.55}$Sr$_{0.45}$MnO$_3$, grown by the floating zone method with the cooling in oxygen, the spontaneous generation of voltage (SGV) has been observed. Its maximum, reached 60 µV, occurs at temperature region where simultaneous destruction of the CE-type antiferromagnetic order and charge order take place in some clusters. SGV maximum decreases on ~ 40% by magnetic field 14.2 kOe. It is shown that SGV provokes of presence in sample of regions with different electrical charges.

1. Introduction

The spontaneous generation of voltage (SGV) was discovered in FeS [1], TiNi [2], FeNi [3], Ce [4], Gd$_3$(Si$_x$Ge$_{1-x}$)$_4$ [5,6] and SmMn$_2$Ge$_2$ [7]. In these materials the voltage observed between the sample ends, having the same temperature, was regarded as spontaneous since a current was not supplied on sample. SGV occurs near first-order magneto-structural phase transformation. Among them, the SGV is especially intriguing because it may result in the development of sensors, which can respond not only to changes in temperature, pressure, and/or magnetic field but most importantly to the rates of their changes without the need for a complicated analysis of signals. Furthermore, all of this can be done by a single sensor requiring no standby power.

Here we report on SGV in single-crystal Sm$_{0.55}$Sr$_{0.45}$MnO$_3$. It is known that compound Sm$_{1-x}$Sr$_x$MnO$_3$ system with $x = 0.5$ exhibits a charge-ordered state. Investigations of the neutron diffraction at 1.5 K $\leq$ T $\leq$ 300 K showed that the compound $^{154}$Sm$_{0.6}$Sr$_{0.4}$MnO$_3$ contains the clusters of three types: ferromagnetic (F), A-type antiferromagnetic (AF), and CE-type AF which are charge-order (CO) [8]. As this takes place an AF ordering of A-type disappears above $T_N = 120$ K while the AF order of CE-type clusters still exist at 150 K but are absent at 180 K. A spontaneous magnetic moment appears at Curie point $T_C = 110$ K; at the same temperature, an electrical resistivity $\rho$ exhibits a maximum. The activation energy of the conductivity changes abruptly at 180 K; in compounds possessing a CO state, this is usually interpreted as a thermal breakdown of this order. The above values of $T_C$, $T_N$ and the temperature of CO breakdown ($T_{CO}$) are close to those determined from the electron and neutron diffraction data and the temperature dependence of magnetization [9]. Runov et al. [8, 10,11] showed that the samples of Sm$_{1-x}$Sr$_x$MnO$_3$ compounds with $x = 0.25$ and 0.4 at low temperatures contain F clusters with 180 – 250 Å dimensions coexisting with large clusters up to several thousand angstroms.
in size. A the same time, no charge-ordered clusters were observed in the compound with $x = 0.25$ [8]. In work [12] the temperature dependence of the initial magnetic susceptibility in an alternating magnetic field with a frequency of 8 kHz $\chi(T)$ and paramagnetic susceptibility of the $La_{1-x}Sr_xMnO_3$ compounds with $x = 0.33, 0.4$ and 0.45 were studied. The $\chi(T)$ curves exhibit a sharp drop at high temperature. The $T_C$-values of these compounds were determined as the temperatures of minima in the $(d\chi/dT)(T)$ curves and are equal to 79, 112 and 126 K respectively. These values are close to the published data. The paramagnetic susceptibility these compositions obeys the Curie-Weiss law at temperature above $\sim 2T_C$ with the paramagnetic Curie points $\theta$ equal to 175, 194 and 250 K for $x = 0.33, 0.4$ and 0.45 respectively. In the temperature interval $T_C < T < 2T_C$ the experimental curves deviate from the Curie-Weiss law.

Thus, the magnetic structure of $Sm_{1-x}Sr_xMnO_3$ compounds is more complicated as compared to that of the $La_{1-x}Sr_xMnO_3$ system. Compounds of the former system with $x$ close to 0.5, in contrast to $La_{1-x}Sr_xMnO_3$ compounds, contain charge-ordered clusters. This order exhibits thermal breakdown at higher temperatures than does the magnetic order in the F and A-type AF phases of the sample. In the compounds with $x = 0.4$ and 0.45 at $T > T_C$ the magnetization isotherms exhibit a jump like increase in the interval of field strengths between $H_{C1}$ and $H_{C2}$ and than reach saturation. In the interval $H_{C1} < H < H_{C2}$ the magnetization exhibits a metastable behavior and conclusion was made that transformation of charge-ordered clusters with CE-type AF order into F state at the threshold field $H_{C1}$ occurs. This conversion is analogous to a first-order phase transition. This magnetic transition coexists with structure transition since in CO clusters the crystal lattice is subjected to larger orthorhombic distortion than in F clusters.

2. Experimental methods

The $Sm_{0.33}Sr_{0.45}MnO_3$ single crystal was grown by the floating zone method with cooling at the oxygen atmosphere. It is known that preparation of the manganite samples in the oxygen atmosphere improves their quality since the torn connections Mn-V-Mn (V is oxygen vacancy) are restored and the Curie point is raised [13]. That’s why an anneal and cooling of single-crystal are produced in the oxygen atmosphere. Such preparation raises the $T_C$ up to 134 K and paramagnetic Curie point $\theta$ up to 270 K that will be shown in section 3. Two parallelepiped-shaped samples were cut from single crystal by electric discharge machining. The longest side of samples was parallel to $ab$-plane. The $dc$ voltage across the sample was measured by standard two-probe method with use a B7-65 microvoltmeter. The sample was subjected to the temperature and magnetic field variations at rates 1.13 - 17.5 K/min for former and 170 kOe/min for second. The field was applied and the voltage were measured along the longest side of sample. The misorientation between the directions of the magnetic field vector and crystal axis were less than $\pm 5^\circ$. The magnetization was measured using SQUID-magnetometer and pm susceptibility was obtained using the Faraday day method.

3. Results and discussion

Figure 1 shows the temperature dependence of magnetization $M$ measured in weak magnetic field $H = 100$ Oe of the $Sm_{0.33}Sr_{0.45}MnO_3$ single crystal. One can see from this Figure that the $M$-value abruptly decreases at temperature $T_C = 134$ K that is the Curie point of the F clusters. The figure 2a shows the SGV along $c$-axis and along $ab$-plane of this sample as function of temperature upon cooling at 17.5 K/min. The SGV anisotropy is essentially absent in $ab$-plane as our measurements are shown. The small difference of SGV measured along $c$-axis and $ab$-plane is presents as shown figure 2a. The maximum of SGV observes at $T_C \sim 255$ K. Figure 2b shows SGV along $c$-axis of the sample cooling with the rate 1.13 K/min and heating with the rate 1.38 K/min. From comparison figures a and b one can see that the SGV value near 255 K almost does not depend from the cooling rate, but the forms of their $SGV(T)$ curves are distinguished. At rate 17.5 K/min the maximum is observed on its while at rate 1.13 K/min is plateau. This maximum and the plateau onset observe at
Figure 1. The temperature dependence of the magnetization $M$ of the Sm$_{0.55}$Sr$_{0.45}$MnO$_3$ single-crystal sample in weak magnetic field of 100 Oe.

Figure 2a. Sm$_{0.55}$Sr$_{0.45}$MnO$_3$ single-crystal sample. The temperature dependence of spontaneous generation of voltage along the $c$-axis and along $ab$-plane upon cooling at the rate 17.5 K/min.

Figure 2b. Sm$_{0.55}$Sr$_{0.45}$MnO$_3$ single-crystal sample. The temperature dependence of spontaneous generation of voltage along the $c$-axis cooling with the rate 1.13 K/min and heating with the rate 1.38 K/min.

$T_m = 255$ K which far exceeds the Curie point $T_C = 134$ K. Here the $T_m$-value is closer to paramagnetic Curie point $\theta = 270$ K. (The $\theta$-value was determined by extrapolation of the $1/\chi(T)$ curve up to intersection with $T$-axis as demonstrates Figure 3. Here $\chi$ is paramagnetic susceptibility).

As figure 3 shows, the $1/\chi(T)$ curve obeys the Curie-Weiss law at temperature above $\sim 2T_C$. Clearly in the temperature interval $T_C < T < 2T_C$ the clusters, obtained by magnetic order, are presented. It should be noted that the magnetocaloric effect maximum of this composition was observed at $T \sim 245$ K which is near to $T_m$. 
Figure 3. The temperature dependence of the paramagnetic susceptibility $\chi$ of the Sm$_{0.55}$Sr$_{0.45}$MnO$_3$ single-crystal sample.

Figure 4. The temperature dependence of spontaneous generation of voltage along the $c$-axis of the Sm$_{0.55}$Sr$_{0.45}$MnO$_3$ single-crystal sample in some magnetic fields.

Figure 4 shows the magnetic field influence on SGV-value. From this Figure we notice that the maximum SGV-value decreases on ~ 45% at $H = 14.2$ kOe. We established that the maximum SGV
value do not exchange for the time 24 hours. It is obvious that SGV is nonequilibrium process with big relaxation time. We emphasize that the maximum SGV-value is bigger than in another compounds mentioned above and can to be source to supply a nanoobjects with electricity.

The SGV behavior outlined above is connected with the presence in sample the clusters of three types: F, AF of A-type and AF of CE-type with charge-ordering. The maximum on SGV(T) curve can be caused by the simultaneous destruction of charge-ordering and AF order of CE-type since at $T > \sim 140$ K the clusters of this type remain. Obviously, the generation of spontaneous voltage necessitates the presence in sample the regions with the opposite charges. In cluster with charge ordering Mn-ions, occupied by electrons (Mn$^{3+}$), alternate with Mn-ions without electron (Mn$^{4+}$). They are fixed in the cluster. So, there is voltage between cluster and paramagnetic host deprived of charge carriers. These clusters are symmetric disposed in sample from Coulombic repulsion if they are identical. In this case the electrical field from each cluster compensates the electrical field from neighboring clusters. As a whole the spontaneous voltage is absent. But the cluster sizes can distinguish and in this case the spontaneous generation of voltage can be. Obviously the distribution of cluster sizes wider in the temperature region of the phase transition from AF of CE-type phase to paramagnetic phase than in smaller temperature that explains the SGV maximum in $T = T_m$. It should be noted that SGV was observed at $T < T_m$ up to 78 K which is minimal temperature of measurement. Here the F clusters occur in which the electrical charges are localized from s-d exchange gain. As point out above, at low temperatures in these compounds F clusters were observed by Runov et al. [8,10] with 180 – 250 Å dimensions coexisting with large clusters up to several thousand angstroms in size that can be the case of SGV. It is known [14] that the external magnetic field near phase magnetic transition increases the clusters sizes and by doing so decreases SGV.

References
[1] Takahashi T and Yamada O 1976 J. Phys. Chem. Solids 17 161
[2] Johnson A D and Katz P I 1977 J. Appl. Phys. 48 73
[3] Koval Yu N and Molin A L 1980 Fiz. Met. Metalloved. 49 1099
[4] Kokorin V V and Chernenko V A 1985 Fiz. Met. Metalloved. 60 285
[5] Levin E M, Pecharsky V K and Gschneidner K A 2001 Phys. Rev. B 63 4110
[6] Zou M, Tang H, Schlagel D L, Lograsso T A, Gschneidner K A and Pecharsky V K 2006 J. Appl. Phys. 99 304
[7] Zou M, Sampaio J A, Pecharsky V K and Gschneidner K A 2009 Phys. Rev. B 80 2403
[8] Runov V V, Chernyshov D Yu, Kurbakov A I, Runova M K, Trunov V A, Okorokov A I 2000 J. Exp. and Theor. Phys. 91 1017
[9] Martin C, Maignan A, Hervieu M and Raveau B 1999 Phys. Rev. B 60 12191
[10] Runov V V, Glattli H, Kopitsa G V, Okorokov A I and Runova M K 1999 JETP Lett. 69 353
[11] Runov V, Glattli H, Kopitsa G Okorokov and Runova M 2000 Physica B 276-278, 795
[12] Abramovich A I, Koroleva L I and Michurin A V 2002 J. Exp. and Theor. Phys. 95 917
[13] Koroleva L I 2003 Magnetic Semiconductors. (Moscow: Publishing of Phys. Dept. of MSU)
[14] Nagaev E L 2002 Colossal Magnetoresistance and Phase Separation in Magnetic Semiconductors (Singapore: Imperial College Press)