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Temperature evolution of the magnetic properties of lanthanum-strontium manganites

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Abstract

The temperature dependences of the magnetization $M(T)$ for multiferroic single crystal lanthanum-strontium manganites $La_{0.875}Sr_{0.125}MnO_3$ (LSMO-0.125) and $La_{0.93}Sr_{0.07}MnO_3$ (LSMO-0.07) have been obtained. It is shown that the phase transitions (PT) in LSMO-0.07 at $T_C = 125.8(1,5)$ K and in LSMO-0.125 at $T_{C1} = 181.2$ (1.5) belong to the second order type. The phase transition in LSMO-0.125 at $T_{C2} = 157.6$ (1.5) K is the first order PT. From the $M^{-1}(T)$ curves, the values of the magnetic moments have been determined. They are equal to $\mu_1 = 2.47(1)$ μ_B/Mn and $\mu_2 = 2.82(1)$ μ_B/Mn, for LSMO-0.125 and LSMO-0.07 respectively.

Keywords: Lanthanum-strontium manganite; Multiferroic; Phase transition; Magnetic moment; Magnetization.

Introduction

A very interesting correlation between doping-induced conductivity and ferromagnetism was discovered at the end of the 20th century for the initially dielectric manganese-containing perovskites $LaMnO_3$, the so-called manganites, in which the rare-earth metal was replaced by the alkaline-earth one. Initial ternary composites $LaMnO_3$ and $AMnO_3$, where A = Ca, Sr or Ba, are antiferromagnetics whose magnetic moments are located at the sites occupied by manganese ions. In the case of quaternary stoichiometry of the $La_{1-x}A_xMnO_3$ type with intermediate compositions (with different values of x), the composite not only becomes a strong ferromagnetic, but also exhibits metallic-type conductivity observed below the Curie temperature [1]. Additionally, this compound is a material with extremely high values of dielectric permittivity (up to 10^7) and magnetocapacitance effect (up to 10^5%) even at room temperature [2].

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The structure of the cubic perovskite $LaMnO_3$ is a three-dimensional lattice consisting of regular MnO_3 octahedra connected by oxygen vertices [3,4]. In this structure, La^{3+}, which is the larger cation, is located in the center of the cube formed by the oxygen octahedra, and Mn^{3+}, which is smaller, is in the center of the octahedron. On the other hand, the structure of $La_{1-x}Sr_xMnO_3$ changes from orthorhombic to rhombohedral [5] at increasing of strontium cation concentration, and an unusual polaron-ordered state is observed in the intermediate range of concentrations (for $x=0.10$–0.15). According to the neutron diffraction data [6], this condition is associated with the ordered arrangement of aliovalent Mn^{3+}/Mn^{4+} ions in alternating (001) planes and the emergence of the corresponding superstructure.

The structure of $La_{1-x}Sr_xMnO_3$ (LSMO-x) is far from cubic perovskite. According to Ref. [7], this structure has two types of distortions, which are caused by either the mismatch between the size of the cations and the size of the corresponding free space (type 1), or by the Jahn–Teller (JT) effect (type 2) [4,8].

The JT effect manifests in the decrease in the energy of such a degenerate system due to the reduction of the symmetry removing the degeneracy of the electronic levels.

The author of Ref. [7] suggested that the second type of distortions was caused by the fact that the Mn^{3+} ion in a cubic crystalline field is degenerate in the d-orbitals, i.e., this field splits the atomic d-level to two- and three-fold degenerate levels e_g and t_{2g}. Since the first level is higher than the second one, the t_{2g} level is fully occupied by four electrons of the d-level of Mn^{3+}, while the e_g level is only partially occupied.

The lanthanum strontium manganite undergoes two structural transitions, however, the data on them greatly differs. According to the results obtained by the authors of Refs. [5,9,10], the high-temperature structural transition in LSMO-0.125 occurs at $T=270$ K from one orthorhombic structure to another, accompanied by the appearance of cooperative distortions of the second type. With a further decrease in temperature, a transition back to the initial structure occurs at $T=150$ K with the suppression of these distortions. At the same time, it follows from the results of Refs. [6,11,12] that the first transition occurs from the orthorhombic phase (*Pbnm*) to the monoclinic one ($P2_1/c$); the second transition is from the monoclinic phase to the triclinic one ($P1$) [13]. For example, according to the data in [14], LSMO-0.125 in a high-temperature paramagnetic phase belongs to the orthorhombic space group *Pnma* and has the parameters $a=5.5624(6)$ Å, $b=7.7360(6)$ Å, $c=5.5478(6)$ Å, while according to the results of [15], this phase in LSMO-0.2 belongs to the rhombohedral space group $R\bar{3}c$ and has the following unit cell parameters: $a \approx 5{,}5$ Å, $c \approx 1{,}34$ Å, $\gamma=120^{\circ}$.

$La_{1-x}Sr_xMnO_3$ crystals have become a model object for studying colossal magnetoresistance [16], which is often associated with the charge and phase separation and with the percolation of the nanoregions with metallic-type conductivity [17]. It was predicted that inhomogeneous states could occur even above the Curie temperature [17].

The presence of unusual magnetocapacitance properties provides opportunities for practical applications of this type of manganites. For example, the authors of Ref. [2] proposed, for achieving high values of permittivity and magnetocapacitance effect, to modulate the properties of charge inhomogeneities in doped manganites LSMO-x. Extremely high values of permittivity (up to 10^7 in the 0.1–1 kHz frequency range) and magnetocapacitance effect (up to 10^5%) were detected even at room temperature. The authors of [2] suggest that this may be due to the strong interaction between charge, spin and lattice degrees of freedom, leading to charge and phase separation before the percolation threshold [17].

Despite extensive studies in this field, the microscopic origin of this behavior has not yet been found. The study carried out by the authors of Ref. [5] can be considered one of the more successful attempts; a full T–x phase diagram was constructed for LSMO-x with the x concentrations from 0 to 0.45 and in a wide temperature range (4.2–1050 K), and detailed investigations of the electrical and magnetic properties of LSMO-x single crystals were examined in detail in the above-noted range of concentrations. Temperature studies of the properties of LSMO-0.07 and LSMO-0.125 [5] have revealed that these compounds undergo a variety of magnetic and structural transformations, which include the appearance of antiferromagnetic and ferromagnetic orderings, structural transitions between strongly and weakly distorted orthorhombic phases, transition to the rhombohedral phase and transition to polaron ordering. According to Ref. [6], the polaron phase is an ordered arrangement of the Mn^{3+} and Mn^{4+} ions in which one of the two alternating atomic layers of the (001) plane contains, as in pure LMO, only the Mn^{3+} ions, while the second one contains both types of ions, i.e., holes [5].

Nevertheless, the temperatures of these transitions, the magnetic moments of the materials, the type of

phase transitions (PT), and the practical effect of the application of a strong magnetic field remain unclear.

The goal of this study is to obtain the information on the temperature evolution of the magnetic properties of the LSMO-0.07 and LSMO-0.125 compounds in the 4–240 K temperature range, i.e., exactly where the unusual macroscopic properties of these materials are observed.

The experimental part

The studies were carried out on a vibration magnetometer in the International Laboratory of High Magnetic Fields and Low Temperatures (Wroclaw, Poland). The weight of single-crystal samples was 121.95 mg for LSMO-0.125 and 152.8 mg for LSMO-0.07, respectively. The magnetic field was applied along the *c* axis; the measuring field was 0.2 T. The temperature dependences of the magnetization of the samples were obtained in the 4–240 K temperature range.

Results and discussion

Fig. 1a shows the temperature dependence of magnetization for the LSMO-0.07 sample under cooling. It is easy to notice that the curve changes its behavior in the vicinity of 130 K, and this temperature, according to the phase diagram obtained in Ref. [5], corresponds to the PT from the high-temperature paramagnetic phase to the low-temperature non-collinear one, accompanied by the emergence of spontaneous and residual magnetization. This indicates that the magnetic structure is weakly ferromagnetic rather than purely antiferromagnetic [5].

In this case, let us represent the temperature dependence of magnetization $M(T)$ as the following power function:

$$(T_C - \mathrm{T})^{\beta} \tag{1}$$

where T_C is the PT temperature, β is the critical exponent.

It follows from the analysis of the data in Fig. 1a that this description (curve *2*) is in sufficiently good agreement with the experimental curve. The following values were obtained for the parameters of function (1): $T_C = 125.8(1.5)$ K, $\beta = 0.280(8)$. We also determined the PT temperature using the following procedure: the $M(T)$ dependence in the paramagnetic phase was approximated by a straight line to the region of low temperatures (curve *3* in Fig. 1a), and the intersection point with the approximating curve was found (see formula (1)). The obtained temperature value coincides with the above-listed value of T_C within ± 0.5 K.

Fig. 1b shows the temperature dependence of magnetization $M(T)$ for the LSMO-0.125 sample under cooling. It can be clearly seen that two anomalies are observed on the curve: the first one near 180 K, and the second one near 157 K; notice that the function $M(T)$ increases sharply below this temperature, and then practically does not change in the region below 100 K. Thus, we can conclude that two magnetic phase transitions are observed in the LSMO-0.125 sample. In the 150–190 K temperature range, the $M(T)$ dependence was also approximated by function (1) and the following parameters were obtained: $T_{C1} = 181.2(1.5)$ K and $\beta_1 = 0.440(13)$, which is sufficiently close to the value of the critical exponent equal to 0.5 for the mean field theory. The value of T_{C1}, obtained from the intersection point of line *3* (linear approximation of $M(T)$ of the paramagnetic phase to the low-temperature region) and curve *2* (power dependence of magnetization with the parameters T_{C1} and β_1), turned out to be similar to the case with the LSMO-0.07 sample, close (with greater accuracy than 0.5 K) to the value of $T_{C1} = 181.2$ K, determined from formula (1). This temperature value is in good agreement with the result obtained in Ref. [5].

The second PT was approximated by a step function with $T_{C2} = 157.6$ (1.5) K. This transition apparently corresponds to the transition to the polaron or the polaro n-ordering phase [5,6].

Thus, based on the character of the temperature dependences of $M(T)$, and the values of the critical exponents obtained for the LSMO-0.07 and LSMO-0.125 samples, it can be assumed that the PT at 125.8 K in the first sample and at 181.2 K in the second one are the second order phase transitions, while the PT in the second sample (LSMO-0.125) at 157.6 K is the first order phase transition. The final stage of our study involved constructing the temperature dependence of the reverse magnetization $1/M$ for both samples (Fig. 2); the slopes of these curves in the paramagnetic phase (high-temperature regions) were used to estimate the values of the magnetic moments of manganese ions in both samples.

The following formula was used to assess the values of the magnetic moments in both compounds:

$$\frac{1}{M} = \frac{k_B T}{N\mu^2 B} \tag{2}$$

where μ (in Bohr magnetons μ_B) is the magnetic moment; M is the magnetization; B (in Oe) is the applied

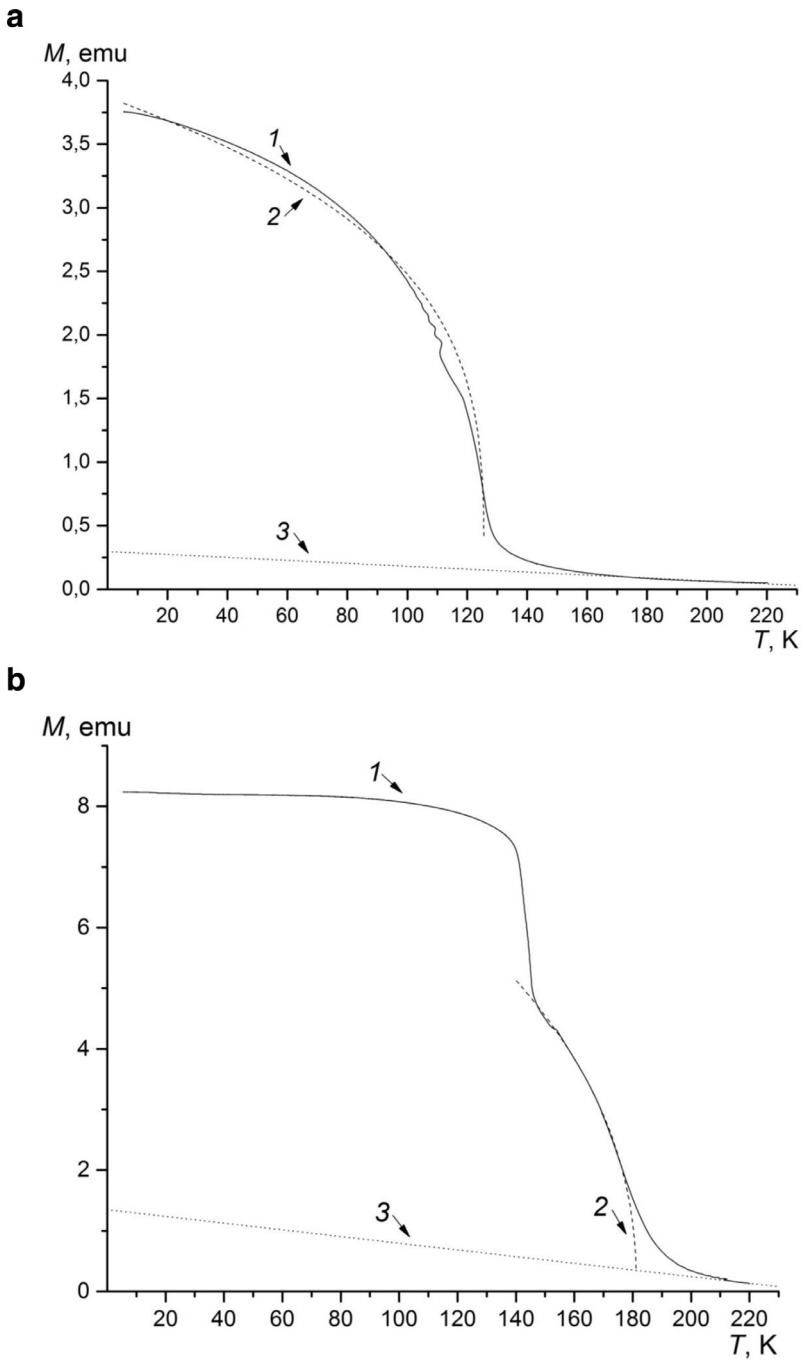

Fig. 1. Experimental temperature dependences of magnetization for samples with the LSMO-0.07 (a) and LSMO-0.125 (b) compositions under cooling (*1*) and their approximations in the high-temperature (*2*) and low-temperature (*3*) regions.

measuring magnetic field; k_B is the Boltzmann constant, N is the number of magnetic atoms per unit of volume.

The slopes of the $M^{-1}(T)$ dependences (lines *2* in Fig. 2) were determined for the experimental curves *1* in the high-temperature region; upon substitution into formula (2), the magnetic moments for both compounds were calculated. They were as follows: $\mu_1 = 2.47(1)\ \mu_B$/Mn and $\mu_2 = 2.82(1)\ \mu_B$/Mn for LSMO-0.125 and LSMO-0.07, respectively.

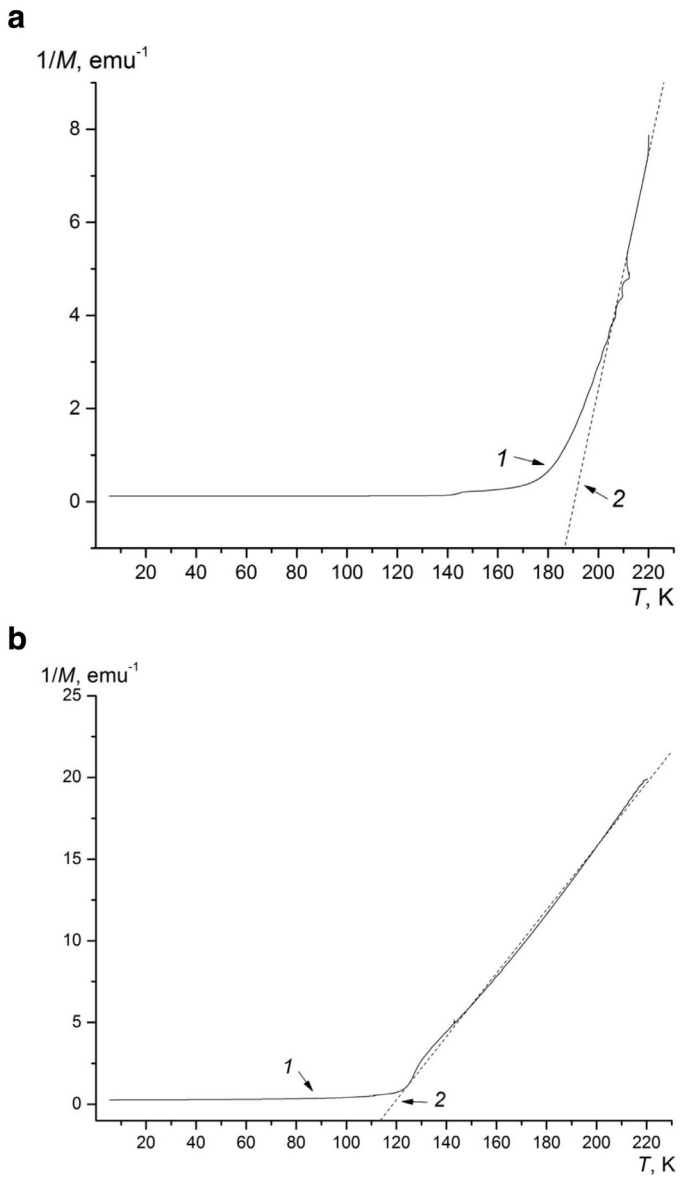

Fig. 2. Experimental temperature dependences of reverse magnetization (*1*) for the LSMO-0.0125 (a) and LSMO-0.07 (b) samples and their approximations in the high-temperature region (2).

Conclusion

We have studied the temperature evolution of magnetization in the single crystals of the $La_{0.875}Sr_{0.125}MnO_3$ and $La_{0.93}Sr_{0.07}MnO_3$ compositions and have established that a single magnetic PT has been observed in LSMO-0.07 $T_C = 125.8(1.5)$ K, and two magnetic PTs have been observed in LSMO-0.125 at $T_{C1} = 181.2(1.5)$ K и $T_{C2} = 157.6(1.5)$ K.

We have determined the values of the critical exponents $\beta = 0.280(8)$ for $La_{0.93}Sr_{0.07}MnO_3$ and $\beta_1 = 0.440(13)$ for $La_{0.875}Sr_{0.125}MnO_3$.

Based on the obtained experimental data and the critical exponent values we can conclude that the PTs at the T_C and T_{C1} temperatures are the second order phase transitions, and the PT in LSMO-0.125 at T_{C2} is the first order phase transition.

We have obtained the estimates for the magnetic moments, which have the following values

$\mu_1 = 2.47(1)$ μ_B/Mn and $\mu_2 = 2.82(1)$ μ_B/Mn for LSMO-0.125 and LSMO-0.07, respectively.

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