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Negative imaginary component of AC magnetic susceptibility, metastable states, and magnetic relaxation in $La_{0.6}Sr_{0.35}MnTi_{0.05}O_3$

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Off-stoichiometric $(La_{0.6}Sr_{0.35})(MnTi_{0.05})$ MnO_3 manganite was studied with in-phase (real, χ') and out-of-phase (imaginary, χ'') components of ac susceptibility measurements. Short- and long-time relaxation effects, manifested by the revealed negative χ'', were observed. The effects are explained at the frame of Landau theory of phase transitions where a coexistence of stable and metastable states is considered. It is supposed that the appearance of negative χ'' is an intrinsic feature of magnetic materials with impurities, defects and vacancies blocking nucleation and growth of new phase.

Keywords: Metastable state; relaxation; magnetic ac susceptibility; magnetic losses.

Most noteworthy feature of lanthanum manganites is a colossal magnetoresistivity (CMR)[1] and large magnetocaloric effect (MCE)[2,3] observed in the vicinity of Curie temperature (T_C). Possible applications of manganites are considered in Ref. 4. CMR and connection between magnetic and electronic systems are explained by the extended double exchange (DE) model.[1] Later, the DE model was complemented by electron–phonon interaction caused by Jahn–Teller splitting of external manganese *d*-orbitals.[5] Properties of manganites depend on doping/substitution in *A* (Ln)– and *B* (Mn)–positions of perovskite ABO_3 cell. Defects, vacancies and nonstoichiometry also cause the essential changes of properties of materials. For examples, anti-site defects and Griffiths phase (ferromagnetic (FM) clusters located inside the paramagnetic matrix) were recently revealed in nonstoichiometric self-doped $(La, Pr)_{1-x}MnO_{3+\delta}$ oxides.[6,7] Post-growth incorporation of vanadium impurities in $MoTe_2$ caused an (anomalous) diamagnetism in $MoTe_2$.8 Defect structure of Fe-0.06 wt.% Ti–N alloys[9] and nonstoichiometry of $La_{0.9-x}Sr_{0.1}MnO_3$ manganites[10] caused an appearance of anomalous negative imaginary (out-of-phase) component (χ'') of ac susceptibility. Negative χ'' in pyrochlore $Eu_{1-x}Fe_xTi_2O_7$,[11] $Gd_5(Ge_{4-x}Si_x)$ alloys,[12] polycrystalline (Gd, Dy) Al_2 (Ref. 13) and $Nd_{0.5}Sr_{0.5}MnO_3$ (Ref. 14) was associated with slow spin relaxation. Importance of relaxation and switching energy efficiency in sub-nm spintronic devices was underlined in theory.[15]

Here, we report the study of off-stoichiometric $(La_{0.6}Sr_{0.35})(MnTi_{0.05})MnO_3$ manganite. The short- and long-time magnetic relaxations were observed. It was manifested by the revealed negative imaginary part of ac susceptibility. The feature is explained in the terms of Landau theory of phase transitions. It was suggested that the appearance of negative χ'' component is the result of blocking of nucleation and growth of paramagnetic phase (at warming) caused by the vacancies and defects of crystal lattice.

Nonstoichiometric $(La_{0.6}Sr_{0.35})(MnTi_{0.05})MnO_3$ manganite was fabricated by conventional solid state technique. For the measurements, the same sample as in Ref. 16 was used. X-ray Cu-Kα diffraction (XRD) measurements were

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performed with diffractometer D/MAX-2500V/PC (Rigaku, Japan). Magnetization measurements were performed with SQUID magnetometer (Quantum Design MPMSXL) in temperature region of 10–300 K. Susceptibility measurements were carried out with AC7000 LakeShore susceptometer in temperature region of 77–300 K in effective ac magnetic field of 10 A/m and at frequency of 85 Hz.

According to XRD analysis, the sample belongs to rhombohedral $R\bar{3}c$ singony and contains a small amount of Mn_3O_4 oxide (Fig. 1). The presence of "parasitic" Mn_3O_4in $(La_{0.6}Sr_{0.35})(Ti_{0.05}Mn)O_3$ is caused by the excess of atoms in the B — position of the perovskites ABO_3 cell (see Ref. 17). Also, some amount of manganese (y), being in divalent state, was observed by X-ray absorption near the edge spectroscopy (XANES). Noted Mn^{2+} ions occupy the A-position of ABO_3 cell thus forming the anti-site defects (see Ref. 16 on the item). Finally, the chemical formula can be written as $(La_{0.6}Sr_{0.35}Mn_y)(Ti_{0.05}Mn_{1-y})O_3$.

Temperature dependence of magnetization (M) is presented in Fig. 2. The $M(T)$ was measured in a field-cooled sample at warming rate in magnetic field of 50 Oe. Curie temperature (Tc), defined as the inflection point on the M on T dependence, equals to about 175 K. We assign for decrease of magnetization at low temperature with T decrease. Noted kink in the $M(T)$ is attributed to competition between the magnetization and magnetic domain orientation processes. The above anomaly was also observed in Refs. 18–20 and disappeared in the field of 1.0 T due to the orientation of domain magnetic moments along the applied field.

Temperature dependencies of real χ' and imaginary χ'' components of ac susceptibility are presented in Fig. 3. With increasing temperature, the χ' component at first increases and then decreases which is typical for ferromagnetics. At the same time, imaginary part of ac susceptibility demonstrates an unusual behavior. Namely, a large wide bell-shaped negative χ'' peak at low temperatures and weak sharp negative χ' peak at temperatures just below Tc are observed. Intensity of the peaks is very dependent on the sample prehistory. The wide and sharp imaginary χ'' peaks were also observed in Refs. 9–14, respectively. Also, negative magnetic after-effect was observed in Ref. 9.

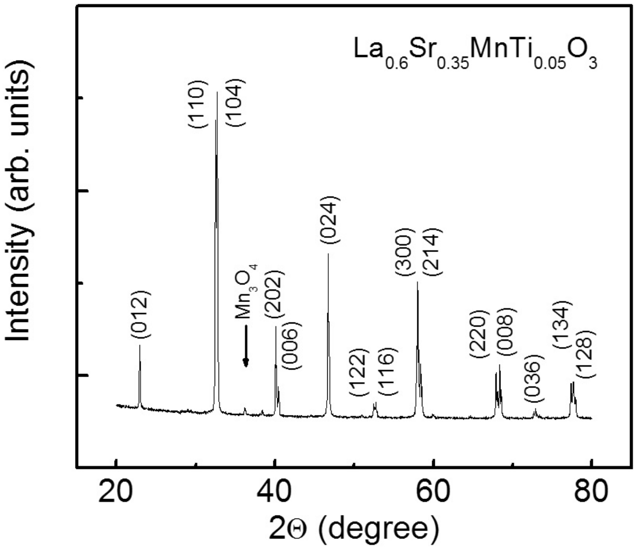

Fig. 1. XRD pattern of the $(La_{0.6}Sr_{0.35})(MnTi_{0.05})O_3$ perovskites.

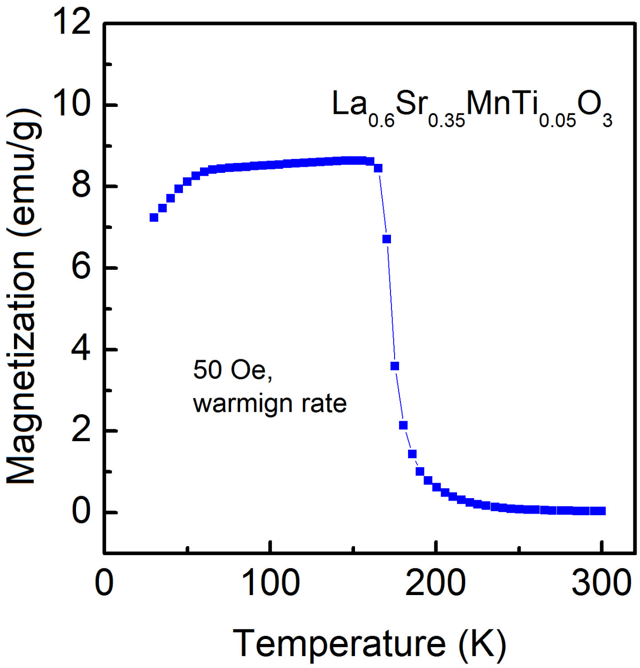

Fig. 2. Temperature dependence of magnetization of the $(La_{0.6}Sr_{0.35})(MnTi_{0.05})O_3$ oxide.

It is well known that imaginary part of ac susceptibility is connected with the energy losses. The losses are caused by remagnetization processes and (almost) always positive. At the same time, magnetic as well as the electrical component of electromagnetic field may be negative if the (non)equilibrium state was excited by an external field as it is performed in the optical laser.[21] Negative χ'' in $Gd_5(Ge_{4-x}Si_x)$ alloys was explained by the release of the energy at returning of system to ground state from the initially excited one.[12] Authors attributed an appearance of negative χ'' to anomalous relaxation processes in the low-temperature ferromagnetic phase. Negative χ'' in Fe–Ti–N alloys was caused by high density of dislocation and attributed to anomalous motion of domain walls.[9] In vacancy-doped $La_{0.9-x}Sr_{0.1}MnO_3$ perovskites, the appearance of negative χ'' was connected with the sample inhomogeneity.[10]

Ulyanov *et al.*[14] observed the negative χ'' response in $Nd_{0.5}Sr_{0.5}MnO_3$ manganites just below the Tc in applied ac magnetic field of 10 A/m and at frequency of 85 Hz (see, also, Ref. 22). Negative χ'' in $Nd_{0.5}Sr_{0.5}MnO_3$ was related to

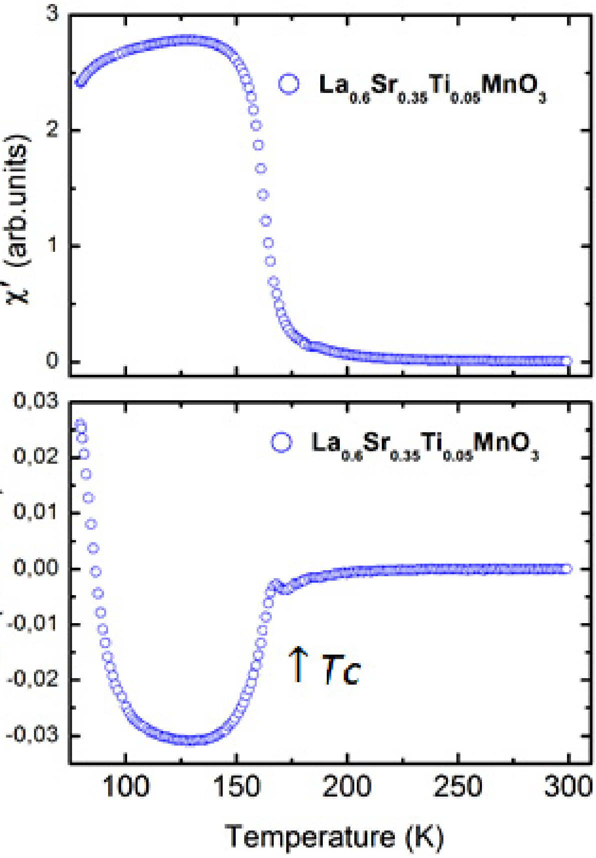

Fig. 3. Temperature dependence of real χ' and imaginary χ'' components of ac susceptibility of $(La_{0.6}Sr_{0.35})(MnTi_{0.05})O_3$ manganites.

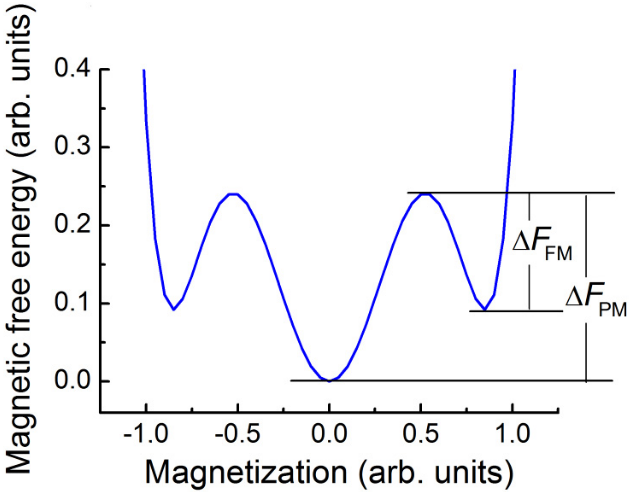

Fig. 4. Dependence of magnetic free energy on magnetization (order parameter) at temperatures lower but close to T_C.

short-time relaxation of magnetic domains from metastable to stable state, and anomaly was explained at the frame of Landau theory of phase transitions[23] (see, also, Refs. 24–26), where the metastable state in ferroelectrics, ferromagnetics and ferroelectric nanofibers, respectively, were carefully considered).

Appearance of small negative peak of χ'' in $(La_{0.6}Sr_{0.35})(MnTi_{0.05})O_3$ oxide near the Tc can be explained using the model presented in Ref. 14 and attributed to relaxation effect. Namely, let us consider the uniaxial ferromagnets showing the first-order phase transition. At low temperature, a magnetic free energy (F) demonstrates a single minimum potential (F_{FM}) which corresponds to FM state with magnetization $M \neq 0$ (For simplicity, we do not distinguish the states with antiparallel magnetization because their potentials are equal to each other). With increase of temperature, the second potential minimum (F_{PM}) appears at $M = 0.0$. The minimum corresponds to paramagnetic (PM) state. With subsequent increase of temperature, the volume of FM phase decreases while an amount of PM phase increases. Relative volume of FM and PM states depends on potential barriers between the state and surface boundary energy between the FM and PM domains. At temperature lower but close to T_C the ferromagnetic and paramagnetic states became metastable and stable, respectively, because the minimum, corresponding to FM state is higher than that of PM one (see Fig. 4). Domains of metastable state can transfer to stable one because of thermal fluctuations if the sample is kept during long time at fixed temperature. With subsequent increase of temperature, the volume of FM phase decreases but the metastable state cannot be empty until the reaching of liability boundary (spinodal line) where the potential barrier between the FM and PM states disappears. If a sample is excited by ac magnetic field with sufficiently high energy, E_{ac}, some domains can overcome the barrier ΔF_{FM} and pass from high-energy metastable FM state to low-energy stable PM one with energy release $\Delta E = \Delta F_{FM} - \Delta F_{PM}$. Thus, electromagnetic system receives the energy at every period, and it is manifested by an appearance of negative χ''. If the energy of excited field is high, the both, ΔF_{FM} and ΔF_{PM}, barriers can be overcame and system absorbs the energy which manifested as positive χ''.

Appearance of wide bell-shaped negative χ'' susceptibility peak observed at low temperature can be explained by the following. The measurements were performed not in zero magnetic field but really in Earth magnetic field, H_E (= 0.3–0.5 Oe), and in exciting ac field equaled to 10 A/m (≈ 0.12 Oe). In small magnetic field the spins orient almost chaotically with negligible advantage along the Earth field (stable state) and opposite the field (metastable state). Potential barriers between the states can be overcome due to exciting of sample by ac magnetic field with release of energy. Similar picture is observed on $M(T)$ dependence at low temperature (Fig. 2). Namely, with increase of temperature in weak magnetic field the spins of metastable domains change the orientation and particles pass to stable one causing the increase of magnetization. The above feature is attributed to long-time relaxation of magnetization of the system.

Observation of negative χ'' depends on sample prehistory, on nucleation and growth conditions of high temperature PM phase (when heating) and on amplitude of ac magnetic field. The growth conditions of PM domains depend on quality of the samples. Impurities, vacancies, defects and anti-site defects prevent the nucleation and growth of paramagnetic domains. Due to it, the FM domains can be observed even near the spinodal line thus causing the observation of negative χ''. It is confirmed by the observation of negative χ'' caused by (a) small amount of Mn_3O_4 impurity oxide, cation vacancies (due to off-stoichiometry) and anti-site defects as in this work; (b) defect structure of Fe-0.06 wt.% Ti–N alloys[9]; (c) second phase observed in RAl_2 (Ref. 13); (d) small amount of Mn_2O_3 oxide and vacancies in $La_{0.9-x}$ $Sr_{0.1}MnO_3$.[10]

Summary, negative imaginary component of ac susceptibility is revealed in perovskite-like $(La_{0.6}Sr_{0.35})(MnTi_{0.05})$ MnO_3 manganite. The effect demonstrates the release of energy by sample at transfer of metastable magnetic domains with higher magnetic energy to the stable state with lower energy. It is supposed that the observed unusual feature is a common one for ferromagnetics placed in weak dc magnetic and excited by weak ac field. The observed features are attributed to long- and short-time relaxation effects. The negative χ'' component can be observed in magnetic materials containing the impurities, defects and vacancies blocking the nucleation and growth of paramagnetic phase inside the ferromagnetic one. The finding should be taken into account at designing of new functional materials.

Recently, the negative imaginary component of ac susceptibility was observed in $Pr_{0.6}7Ba_{0.33}Mn_{1-x}Ru_xO_3$ manganites[27] and explained with model presented in Ref. 14.

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