Pyromagnetic effect in LaAMnO perovskites

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Influence of temperature change rate on the magnetic susceptibility of polycrystalline bulk $La_{0.6}Ca_{0.2}Mn_{1.2}O_3$, $La_{0.6}Sr_{0.3}Mn_{1.1}O_3$ and $La_{0.6}(Ca_{0.5}Sr_{0.5})Mn_{1.3}O_3$ samples has been studied. It has been found that at fast cooling of the samples from the temperatures exceeding the Curie point down to 77 K, the real part value, χ', of the complex dynamic magnetic susceptibility increases as compared to that obtained under equilibrium (slow) cooling. This effect was called cryomagnetization. It is opposite to thermomagnetization observable in rare-earth magnetics. The effect is symmetric with respect to the temperature change, that is, the magnetic susceptibility drops at the sample fast heating. The χ' returns to its equilibrium value in the course of time.

Изучено влияние скорости изменения температуры на величину магнитной восприимчивости поликристаллических объемных образцов $La_{0.6}Ca_{0.2}Mn_{1.2}O_3$, $La_{0.6}Sr_{0.3}Mn_{1.1}O_3$ и $La_{0.6}(Ca_{0.5}Sr_{0.5})Mn_{1.3}O_3$. Обнаружено, что при быстром охлаждении образцов от температур, выше точки Кюри, до 77 К значение реальной части χ' комплексной динамической магнитной восприимчивости возрастает по сравнению со значением, полученным в условиях равновесного (медленного) охлаждения. Этот эффект был назван крионамагничиванием. Крионамагничивание противоположно термонамагничиванию, наблюдаемому в редкоземельных магнетиках. Данное явление симметрично относительно изменения температуры, т.е. магнитная восприимчивость уменьшается при быстром нагревании образцов. С течением времени величина χ' возвращается к своему равновесному значению.

Complex oxides of transition metals, $(La_{1-x}Sr_x)MO_{3\pm\delta}$ and $(La_{1-x}Ca_x)MO_{3\pm\delta}$ where M is a $3d$ transition metal such as Mn, Co, or Fe, are now under intensive research in connection with the "giant magnetic resistance" (GMR) revealed therein [1]. So, the relative magnetic resistance values of the order of thousand percent were attained in $La_{0.67}Ca_{0.33}MnO_y$ films [2]. Although those substances are studied for a rather long time, the mechanism of the above-mentioned phenomenon remains still unclear. Such a behavior of electric resistance is due either to homogeneous structure of the compounds or to electronic separation of phases, namely, to formation of ferromagnetic droplets in a homogeneous antiferromagnetic matrix [1].The GMR is supposed also [1] to result from double electron exchange between $3d$ ions of different valences in a homogeneous solid solution where the rare-earth and alkaline-earth ions are distributed arbitrarily over the A sites of the perovskite-like crystal lattice.

The base of such complex oxides of transition metals is formed by the initial compound $LaMnO_3$ having a strongly distorted orthorhombic unit cell of the crystal lattice. The magnetic structure of $LaMnO_3$ is an antiferromagnetic lattice consisting of ferromagnetic layers of Mn ions with oppositely oriented spins in alternating (100) planes. If trivalent La ions are substituted in part by bivalent ones (Ca, Ba, and Sr), then the $La_{1-x}A_xMO_3$ crystals take a spontaneous magnetization at $x \leq 0.5$ while at larger x values, the crystal becomes antiferromagnetic [3]. The magnetization attains saturation at $x = 0.3$ while remaining unsaturated at low x values.

Neutronographic examination [4] show that the unsaturated magnetization state is due to that the samples are either a two-

phase mixture of ferromagnetic and antiferromagnetic regions, or single-phase ones in a two-sublattice state that is characterized by a nonzero momentum, as in a non-collinear antiferromagnetic ordering or a collinear state of ferrimagnetic type. Some works testify to the first model while other, to the second one [5]. In this connection, the study of lanthanum manganites is topical.

We have found in experiment one more unique property of those substances in polycrystalline $La_{0.6}Ca_{0.2}Mn_{1.2}O_3$ (1), $La_{0.6}Sr_{0.3}Mn_{1.1}O_3$ (2) and $La_{0.6}(Ca_{0.5}Sr_{0.5})Mn_{1.3}O_3$ (3) samples with the Curie temperatures of 170, 292, and 237 K. It is known [6] that an electric polarization ΔP can be induced in dielectrics and ferroelectrics using a temperature gradient ΔT (or a heat pulse ΔQ). This is so-called pyroelectric effect. For ferromagnetics, the internal magnetic energy change dU in the course of magnetization can be written [6] as

$$dU = dQ + HdI = TdS_m + HdI, \qquad (1)$$

where H is the magnetic field strength; dI, the magnetization change; T, temperature; dS_m, the change of the magnetic entropy component. As dU is a total differential, it follows from (1) that

$$(\partial U / \partial S_m)_I = T, \quad (\partial U / \partial I)_{S_m} = H. \qquad (2)$$

Differentiating the first expression with respect to I and the second one with respect to S_m, we obtain

$$(\partial T / \partial I)_{S_m} = (\partial H / \partial S_m)_I. \qquad (3)$$

Substituting the value $dS_m = dQ/T$, we obtain the magnetic analog of Clapeyron-Clausius formula or the relationship for magnetocaloric effect as

$$\Delta I = (1 / T)(dT / dH)_I \Delta Q. \qquad (4)$$

It follows therefrom that under action of heat pulse ΔQ, the ferromagnetics should take a magnetization pulse ΔI, that is, the "pyromagnetic effect" also being referred to as "thermomagnetization". In the case of a ferromagnetic, $(dT/dH)_I > 0$. For antiferromagnetics, $(dT/dH)_I < 0$ [7], that is why the magnetization should increase at the sufficiently sharp temperature drop.

Unlike to the pyroelectric effect, the thermomagnetization can be revealed only in the presence of a certain effective magnetic field in the sample induced by an external field or a residual one, or else, as in
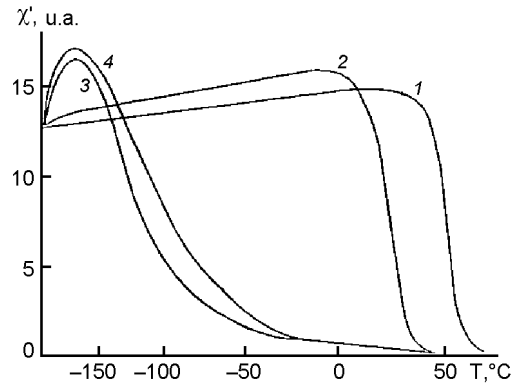

Fig. 1. Temperature dependence of magnetic susceptibility for $La_{0.6}Sr_{0.3}Mn_{1.1}O_3$ sample at different cooling rates (K/min): 2 (*1*), 50 (*2*), 100 (*3*) and 200 (*4*). Curve 1 is the equilibrium process; curves *2* through *4*, non-equilibrium ones.

lanthanum manganites, by the field formed due to spontaneous magnetization of the sample at temperatures lower than the Curie point. That is why this phenomenon is not similar to the pyroelectric effect. The thermomagnetization is revealed usually [8] basing on the shape of temperature dependence of the induction e.m.f. that is measured using a coil arranged around the sample, since the e.m.f. is in proportion to ΔI derivative with respect to time. To reveal and evaluate the thermomagnetization effect in lanthanum manganite samples, the apparatus was used by means of which the magnetic susceptibility was determined in [9]. In that manner, the measurement procedure was improved, because not only the induced voltage value was determined but also its sign, that is, the magnetization sign, see Fig. 1.

The effect revealed consisted in that at fast cooling of the samples from the temperatures exceeding the Curie point (being near the room temperature) down to liquid nitrogen temperature (77 K), the real part value, χ', of the complex dynamic magnetic susceptibility $\chi = \chi' - \chi''$ increased, that is, the sample magnetization increased as compared to that obtained under equilibrium (slow) cooling. The maximum magnetization change relative to the spontaneous magnetization value amounted up to 15 %, or, in SI units, to $\chi'_{max} = 12.4$ for the Sample 1, $\chi'_{max} = 17.1$ for the Sample 2 and $\chi'_{max} = 17.1$ for the Sample 3. The effect is symmetric with respect to the temperature change, that is, the magnetic susceptibility drops at the sample fast heating as compared to the
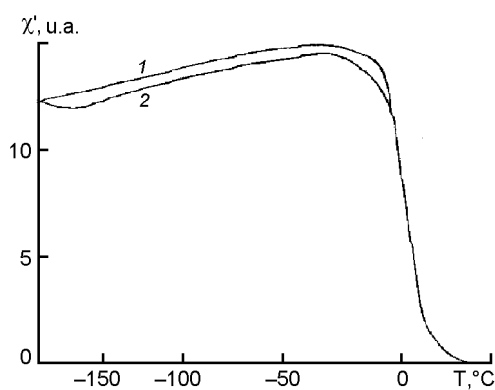
Fig. 2. Temperature dependence of magnetic susceptibility $La_{0.6}(Ca_{0.5}Sr_{0.5})Mn_{1.3}O_3$ sample at different heating rates (K/min): 2, equilibrium process (*1*), 50, non-equilibrium process (*2*).

Fig. 3. Temperature dependence of magnetic susceptibility at fast cooling (200 K/mm) started at different temperatures $T \le T_c$ (°C): 20 (*1*), -13 (*2*), -48 (*3*), equilibrium process (2 K/mm) (*4*).

Fig. 4. Temperature dependence of resistivity for $La_{0.6}Sr_{0.3}Mn_{1.1}O_3$ sample: equilibrium process, heating rate 2 K/min (*1*); fast heating, 200 K/min (*2*); fast cooling, 200 K/min (*3*).

$\chi'(t)$ change under equilibrium heating, see Fig. 2. Note that the χ' returned to its initial value in the course of time. The $\chi'(t)$ dependences obtained at equilibrium cooling and heating conditions coincided with one another. If the fast cooling is started from temperatures below the Curie point (T_c), a second maximum arises in the $\chi'(t)$ dependences (the first one being at the Curie point). This evidences an increased magnetic ordering of the system as compared to the system state at equilibrium temperature change, see Fig. 3.

One possible explanation of the effect revealed can be based on the model of two-phase ferro-antiferromagnetic state that is used to describe the properties of lanthanum manganites [10] where a non-trivial phase separation takes place, namely, the electronic one. In this case, the phase regions, i.e. ordered ferromagnetic and antiferromagnetic ones, are mixed together. At low concentrations of charge carriers (holes), ferromagnetic electrically conductive regions are present inside the dielectric antiferromagnetic phase as droplets that are not connected electrically. The conductivity between those droplets is of the tunnel type. The resistivity of such a sample ρ is about 10^5 Ω·m. As the carrier concentration increases, the ferromagnetic phase volume grows, the droplets become fused together, and the electric conductivity type becomes metallic. This dynamic equilibrium phase separation varies under external actions (temperature, magnetic and electric fields) due to variation of the antiferromagnetic phase. Thus, it can be stated that, due to negative sign of the antiferromagnetic
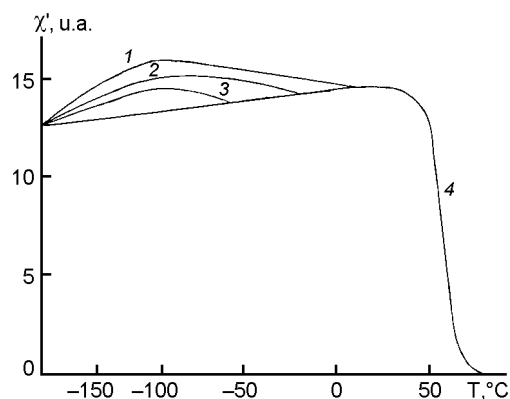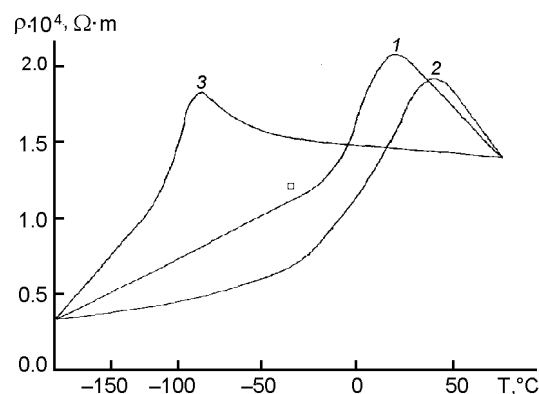
phase magnetocaloric effect ($dT/dH < 0$), and under action of a short-term fast cooling that forms a negative thermal pulse, the samples pass to the non-equilibrium state where the magnetization increases. In the course of time, the samples are returned to the initial state due to spin fluctuations. This process in reflected in the plot as the return of χ' to its equilibrium value.

The resistivity of the samples at room temperature was about 10^{-1} Ω·cm, as measured using the four-probe scheme. Near T_c, the resistivity ρ dropped both at fast cooling and at fast heating (from a temperature below T_c) as compared to the value obtained at a slow temperature change. The maximum decrease of ρ near the Curie point was about 12 % of the ρ value obtained at the equilibrium sample heating, see Fig. 4. This effect can be explained by a specific shape

of the $\rho(t)$ dependence that contains a maximum when measured in the equilibrium state both under cooling and heating. As the sample is heated fast, its temperature changes non-uniformly, because its near-surface region is heated more than the inner one. As the near-surface region attains the temperature corresponding to the $\rho(t)$ maximum, its resistance will be shunted by that of the inner region having a higher conductance. As the inner region attains the temperature of the $\rho(t)$ maximum, its conductance will be shunted by that of the near-surface one that has a higher temperature. That is why the resistance of the sample as a whole does not attain the $\rho(t)$ value. A similar consideration is true for the sample under fast cooling. In the course of time, the specific resistance ρ returns to its equilibrium value, like χ'.

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Піромагнітний ефект у перовскітах LaAMnO

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Вивчено вплив швидкості зміни температури на величину магнітної сприйнятливості полікристалічних об'ємних $La_{0,6}Ca_{0,2}Mn_{1,2}O_3$, $La_{0,6}Sr_{0,3}Mn_{1,1}O_3$ і $La_{0,6}(Ca_{0,5}Sr_{0,5})_{0,1}Mn_{1,3}O_3$ зразків. Виявлено, що при швидкому охолодженні зразків від температур, вищих за точку Кюрі, до 77 К значення реальної частини її комплексної динамічної магнітної сприйнятливості збільшується відносно значення, отриманого в умовах рівноважного (повільного) охолодження. Це явище є симетричним відносно зміни температури, а саме: сприйнятливість зменшується при швидкому нагріванні зразків. З часом величина її повертається до свого рівноважного значення.