Influence of heat exchange on magnetic susceptibility of lanthanum cobaltates

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An influence of thermal processes rate on temperature dependence of complex magnetic susceptibility $\chi = \chi' - i\chi''$ in ceramic perovskites $La_{1-x}Sr_xCoO_3$ (x = 0.15; 0.25; 0.35) has been studied. At increasing cooling rate, the χ value grew up as compared to the value obtained under slow (equilibrium) temperature variation. This effect is explained by thermomagnetic component $(\partial M/\partial T)(\partial T/\partial t)$ of χ value, which is due to strong dependence of magnetization M on temperature T near the Curie point.

В керамических перовскитах $La_{1-x}Sr_xCoO_3$ (x = 0,15; 0,25; 0,35) изучено влияние скорости термических процессов на температурную зависимость комплексной магнитной восприимчивости $\chi = \chi' - i\chi''$. При увеличении скорости охлаждения величина χ возрастала относительно значения, полученного в условиях медленного (равновесного) изменения температуры. Эффект объяснен термомагнитным вкладом $(\partial M/\partial T)(\partial T/\partial t$ в величину χ, обусловленным сильной зависимостью намагниченности M от температуры T вблизи точки Кюри.

The interest in lanthanum cobaltates $La_{1-x}A_xCoO_3$ (A is an alkaline-earth element) is motivated by their prospective application as high-sensitivity magnetic field sensors, as electrodes in ferro-electric capacitors [1] and in thermal cells [2]. This work concerns the influence of heat exchange conditions with environment on magnetic properties of lanthanum cobaltates. It is known [3] that in substituted lanthanum manganites, value of magnetization M is influenced by cooling rate. This influence has its maximum near the Curie temperature T_c. Besides, it is shown [4, 5] the "pyromagnetic" effect was revealed consisting in the fact that magnetization of garnet-type ferrites and yttrium-orthoferrite is changed under irradiation with pulse laser beams. As an indicator of M value variation, there was electromotive force (EMF) being registered in a detector coil around a sample under testing. The EMF generation might be explained both by magneto-elastic [4] and thermo-magnetic [5] mechanisms, i.e., by an influence of thermal pulses that occur due to irradiation of the sample.

The studies were carried out using three ceramic samples of the following chemical compositions: (1) $La_{0.65}Sr_{0.35}CoO_3$ (T_c = −50°C), (2) $La_{0.75}Sr_{0.25}CoO_3$ (T_c = −70°C) and (3) $La_{0.85}Sr_{0.15}CoO_3$ (T_c = −185°C). The initial compound $LaCoO_3$ is a non-magnetic dielectric of perovskite type structure. Substitution of La by an alkaline-earth element results in occurrence of magnetic ordering of $La_{1-x}A_xCoO_3$ within the concentration range of $0.3 \le x \le 0.5$. The Curie point is located within 220 to 250 K interval [6]. In this case, the samples are subdivided into regions enriched in charge carriers (and hence exhibiting metal type conductivity) and those depleted of charge carriers (the semiconductor conductivity type). The regions enriched in charge carriers represent a ferromagnetic state, while those poor in these

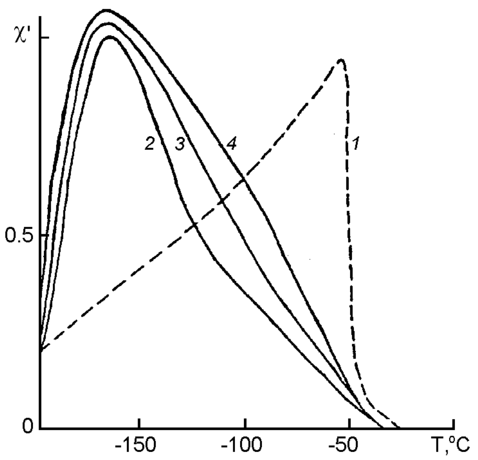

Fig. 1. Dependence $\chi'(T)$ for a $La_{0.65}Sr_{0.35}CoO_3$ sample determined at different cooling rates (K/min): 2 (*1*), 150 (*2*) 300 (*3*) and 400 (*4*). Curves (*2*) – (*4*) denote non-equilibrium processes and (*1*) represents an equilibrium process.

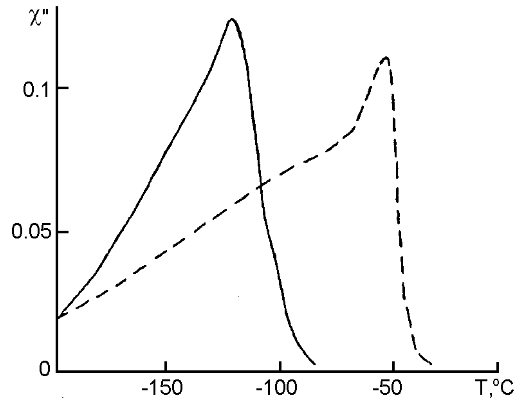

Fig. 2. Dependence $\chi''(T)$ for a $La_{0.65}Sr_{0.35}CoO_3$ sample determined at different cooling rates: 2 K/min (dotted line) and 300 K/min (solid line).

carriers are non-magnetic [7]. The nature of phase transformations and magneto-resistive effect in these compounds is still a matter under discussion [8].

To study the influence of specific features of heat exchange with environment on magnetic transition in lanthanum cobaltates, variations of temperature dependences of real $\chi'(T)$ and imaginary $\chi''(T)$ parts of complex magnetic susceptibility have been investigated at different cooling and heating rates of the samples. Similar studies have been carried out previously with lanthanum manganites [9]. The T_c value has been determined from the maximum in the magnetic susceptibility temperature dependence. The magnetic measurements were carried out using a setup of the Hartshorn bridge type. The amplitude of alternating (modulating) magnetic field $H(t) = H_{ac}\cos(\omega t)$ corresponded to $H_{ac} = 3$ Oe, frequency $\omega/2\pi = 1.3$ kHz (t is time). The measuring apparatus was calibrated using a reference sample of high temperature superconducting $YBa_2Cu_3O_7$ ceramics. Values of χ' and χ'' have been calculated in Sl units.

The samples prepared by conventional solid state reaction method were shaped as 15 mm long and 3.3 mm diameter cylinders. According to X-ray-phase analysis data, the samples were single-phase ones possessing hexagonal structure with the crystal lattice unit cell characterized by the parameters $a = b = 0.54287$ nm; $c = 1.32368$ nm; and $\gamma = 120°$. The samples were placed in a closed capsule where the temperature was controlled by means of a copper-constantan thermocouple at the reference junction temperature 0°C. The samples were cooled by immersion of the capsule into liquid nitrogen and warmed up again using a resistive non-inductive heater. The heating rate was regulated by varying the heater current. The various cooling rates were obtained by changing the sample-holding capsule thermal insulation extent. The temperature change rate defined over time interval Δt between its start and the thermal equilibrium state was represented as an average value $\Delta T/\Delta t$.

Figs. 1 and 2 represent dependences $\chi'(T)$ and $\chi''(T)$, respectively, obtained for the sample No.1 in cooling mode. The cooling process was started from temperatures $T > T_c$, where the sample was in paramagnetic state. It has been found that at rapid cooling of a sample from $T = 253$ K to 77 K, the maximum values of χ'_{0max} and χ''_{max} increase as compared to maximum values of these parameters, χ'_{max} and χ''_{max}, respectively, obtained under equilibrium (i.e., slow) cooling mode. The relative increment of $\chi'(T)$ maximum value at non-equilibrium process increases with rising cooling rate, reaching 12 % at $\Delta T/\Delta t = 400$ K/min. It should be noted that during measurements in non-equilibrium conditions, a significant temperature gradient is present in the samples. Besides, the thermal conductivity val-

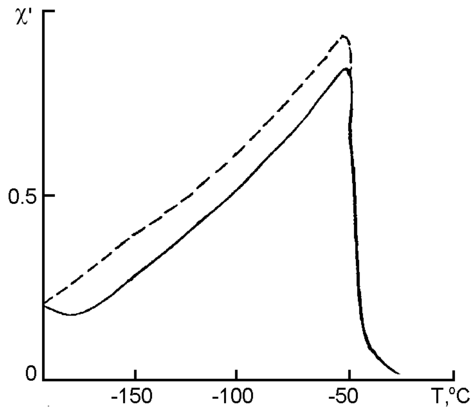

Fig. 3. Dependence $\chi'(T)$ for a $La_{0.65}Sr_{0.35}CoO_3$ sample determined at different heating rates: 2 K/min (dotted line) and 50 K/min (solid line).

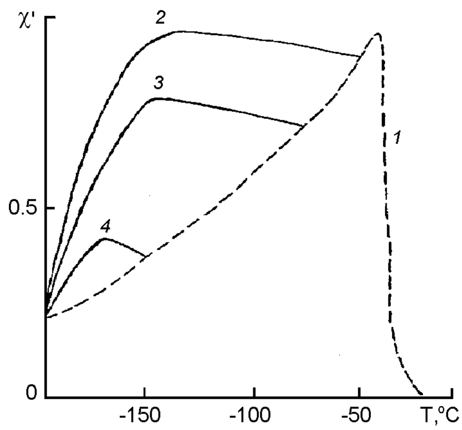

Fig. 4. Hysteresis $\chi'(T)$ obtained at rapid cooling (300 K/min) of a $La_{0.65}Sr_{0.35}CoO_3$ sample starting from $T < T_c$: curve (*2*), $T = -55$°C; curve (*3*), $T = -80$°C; curve (*4*), $T = -150$°C. Curve (*1*) denotes an equilibrium process.

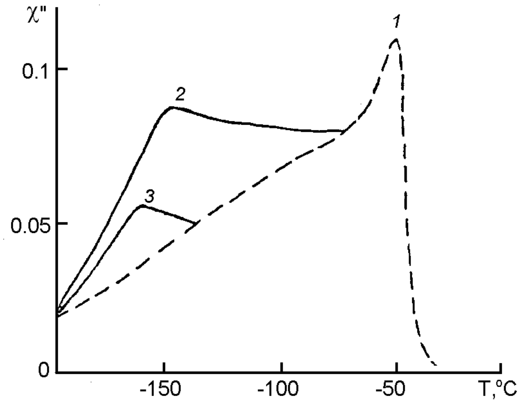

Fig. 5. Hysteresis $\chi''(T)$ obtained at rapid cooling (300 K/min) of a $La_{0.65}Sr_{0.35}CoO_3$ sample starting from $T < T_c$: curve (*2*), $T = -70$°C; curve (*3*) $T = -135$°C. Curve (*1*) denotes an equilibrium process.

ues for a ceramic sample [10] and for a measuring thermocouple junction [11] differ by more than an order of magnitude. The temperature registered in this experiment denotes a temperature inside the measurement cell and at the sample surface. Therefore, shifts of maximums in curves $\chi'(T)$ and $\chi''(T)$ corresponding to the non-equilibrium process should not be considered as a depression of the Curie point.

The discovered effect is symmetrical with respect to temperature variation, since the χ'_{max} value decreases at rapid (50 K/min) heating-up of samples as compared to $\chi'_{0\ max}$ (see Fig. 3). Moreover, the curve $\chi'(T)$ represents a minimum within the temperature range near 77 K. That minimum is an evidence that decrease of χ'_{max} at rapid temperature elevation is caused not by different heating degrees of near-surface and interior sample regions, but due to some other physical factors. In the course of time, the χ' and χ'' values which correspond both to rapid cooling and rapid heating-up, respectively, come back to their equilibrium values at a specific temperature, when $dT/dt = 0$. The $\chi'(T)$ and $\chi''(T)$ dependences determined in conditions of equilibrium cooling and heating-up coincide with one another. Similar data have also been obtained with samples No.2 and 3 having lower T_c values.

Figures 4 and 5 present the curves of $\chi'(T)$ and $\chi''(T)$ temperature hysteresis loops for the sample No.1, respectively; the curve 1 is obtained during slow heating up from 77 K, and curves *2*, *3* and *4* are obtained during cooling at the 300 K/min rate, starting from temperatures below T_c.

The data were confirmed by image of oscillograph-produced curves, and by the fact that the bridge was practically not disbalanced during rapid temperature variations with no sample in the measuring coil. Moreover, a similar increase of χ'_{max} и χ''_{max} has been observed after a sample (having temperature 20°C) has been placed into the measuring cell cooled preliminarily down to 77 K, thus excluding any peak effects of instrumental origin. The χ'_{max} value thus determined exceeded χ''_{0max} by 15 %.

The result obtained may be explained by simple considerations that follow. Taking into account the experimental conditions and the operational principle of χ measuring setup, the unbalance signal being measured can be expressed as

$$U = \varepsilon_1 - \varepsilon_2 \sim dM/dt = \quad (1)$$
$$= (\partial M/\partial H)(\partial H/\partial t) + (\partial M/\partial T)(\partial T/\partial t) =$$
$$= \chi_0(\partial H/\partial t) + (\partial M/\partial T)(\partial T/\partial t) =$$
$$= \chi_0(\partial H/\partial t) + \Delta U,$$

where ε_1 is EMF induced within detector coil that surrounds a sample; ε_2, EMF induced within the compensating coil; ΔU, thermomagnetic contribution to the signal being measured. At slow temperature change, i.e., when $\partial T/\partial t = 0$, it follows from (1) that

$$U \sim \chi_0(\partial H/\partial t). \quad (2)$$

For ferromagnetics that possess a single magnetic sublattice, the condition $(\partial M/\partial T) < 0$ is valid below the Curie point. At rapid cooling of samples, $(\partial T/\partial t) < 0$ and consequently, $\Delta U > 0$ and $U > U_0$, according to (1). At rapid heating-up, $\Delta U < 0$ and $U < U_0$, which is in conformity with experimental data.

Thus, thermomagnetic effects in the studied lanthanum cobaltates, as well as in substituted lanthanum manganites [9], cause a significant influence on magnetic measurements. The discovered effect is similar to "pyro-magnetic" one registered previously in other kinds of magnetics [4, 5]. Difference from data in [4, 5] consisted in the fact that thermal pulses have been formed by means of heat exchange processes rather than by electromagnetic radiation. This made it possible to neglect the potential contribution of susceptibility value of which occurs due to interaction between electromagnetic radiation and the magnetic spin subsystem, as well as to study the processes that occur both at heating and cooling of samples.

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Вплив теплообміну на магнітну сприйнятливість кобальтитів лантану

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У керамічних перовскітах $La_{1-x}Sr_xCoO_3$ (x = 0,15; 0,25; 0,35) вивчено вплив швидкості термічних процесів на температурну залежність комплексної магнітної сприйнятливості $\chi = \chi' - i\chi''$. При збільшенні швидкості процесів охолодження величина χ зростала відносно значення, отриманого в умовах повільної (рівноважної) зміни температури. Ефект пояснено термомагнітним внеском $(\partial M/\partial T)(\partial T/\partial t)$ у величину χ, обумовленим сильною залежністю намагніченості M від температури T поблизу точки Кюрі.