Pis'ma v ZhETF, vol.64, iss.4, pp.250 - 253

CONDUCTIVITY JUMPS AND LOW-TEMPERATURE MAGNETORESISTANCE IN NEW SEMICONDUCTING $La_{1-x}Bi_xMnO_{3+\delta}$ PEROVSKITES

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Submitted 8 July 1996
Resubmitted 25 July 1996

The abrupt jumps were observed on the temperature dependences of electrical conductivity of $La_{1-x}Bi_xMnO_{3+\delta}$ ($0.1<x<0.7$) and $La_{0.3}Bi_{0.7}Na_{0.1}MnO_{3+\delta}$ ceramics. The temperatures at which the jumps take place could be reduced by several degrees at applying external magnetic field of 15 kOe. It can be seen from the magnetization data that low-temperature poor-conducting phase is not antiferromagnetic (it is likely ferromagnetic) and hence the real-space charge ordering mechanism is not sufficient for explaining the experimental results. An interpretation in terms of magnetic phase nonuniformity is proposed. All the samples studied showed high low-temperature magnetoresistance.

PACS: 71.27.+a, 71.28.+d, 71.30.+h, 75.30.Kz

The publication of sensational results by S.Jin et al. [1, 2] on anomously large negative isotropic low-temperature magnetoresistance (MR) in hole-doped $LaMnO_3$-based perovskites attracted a broad interest not only because of its possible numerous sensor applications but also from the fundamental viewpoint. In some papers on similar compounds (Ref. [3-5], for example) published after [1, 2] the observation of resistivity ρ jumps at changing temperature T was reported. The corresponding $\rho(T)$ curves had hysteric character and moreover the jumps of ρ approximately coincided with ferromagnetic (FM) – antiferromagnetic (AFM) first-order transition on cooling and AFM-FM first-order transition on heating. Both temperatures T_+ and T_- at which the jumps of ρ take place (on heating and on cooling respectively) could be reduced by external magnetic field H.

The phenomenon observed was attributed to the real-space charge ordering effect: the periodical alignment of Mn^{3+} and Mn^{4+} at $T < T_\pm$ result in poor-conducting AFM phase. So, one can see at least three types of magnetic ordering at changing temperature: AFM at $T < T_\pm$, FM at $T_\pm < T < T_c$ (T_c is the Curie point) and paramagnetic (PM) at $T > T_c$. In this Letter we report on the observation of the similar jumps of ρ accompanied at some extent by just the opposite sequence of magnetic phases: FM at $T < T_C < T_\pm$ and PM at $T > T_c$. More or less pronounced the phenomenon was observed by us on the ceramic samples of $La_{1-x}Bi_xMnO_{3+\delta}$ with $0.1 < x < 0.7$. It is also of importance that Bi as La is threevalent, so Mn^{4+} holes if they are present could result only from some amount of superstoichiometric oxygen ($\delta > 0$) which we had no opportunity to reveal. Moreover, introduction of acceptors (partial substitution of La^{3+} by Na^+) did not change dramatically the $\rho(T)$ curves. In other words in our case the nature of conductivity jumps is likely more complicated than in [3-5].

Our samples ($x = 0$, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70) were synthesised by mixing stoichiometric proportions of La_2O_3, Bi_2O_3 and Mn_2O_3 and then heating in air at 950–1300°C for 24*h* with intermediate grindings. We had also synthesised the hole-doped $La_{0.5}Bi_{0.4}Na_{0.1}MnO_3$ samples using the same technique and corresponding amount of $NaHCO_3$. The structural and phase analyses showed

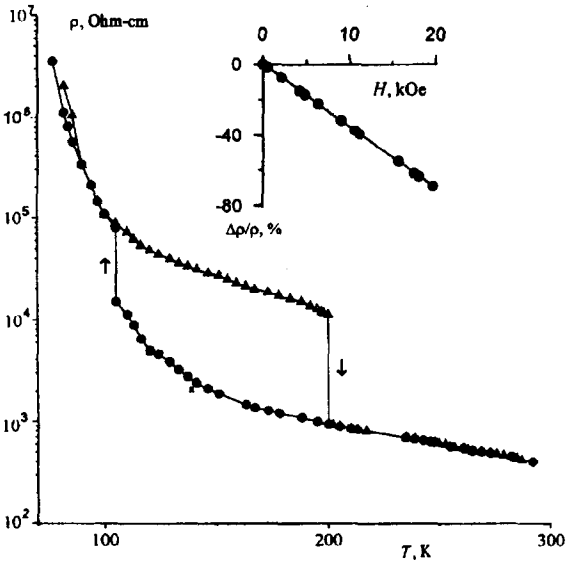

Fig.1. Resistivity ρ vs temperature T for $La_{0.5}Na_{0.1}Bi_{0.4}MnO_{3+\delta}$. Curve *1* – on heating, curve *2* – on cooling. Inset: MR at 77 K

clean single-phase patterns. The chemical composition was monitored by a X-ray microanalyser. The specific magnetization σ was measured by a vibrational magnetometer in the temperature range 77–350 K and in magnetic fields up to 20 kOe. Resistivity was measured by a standard 2 or 4 in-line contact in the same temperature and field ranges as magnetic ones.

Fig.1 shows the typical $\rho(T)$ behaviour for all the compounds studied. The $La_{0.5}Bi_{0.4}Na_{0.1}MnO_3$ ceramics has been chosen for plotting because it shows the maximum value of $T_+ - T_-$ (about 100 K). For the other samples this value is smaller (it is minimal for $x = 0.7$: $T_+ - T_- \approx 18$ K) though both T_+ and T_- lie in the same temperature range (80–200 K). The resistance at room temperature varies from 3 Ohm.cm for $x = 0.7$ to $5 \cdot 10^2$ Ohm·cm for $La_{0.5}Bi_{0.4}Na_{0.1}MnO_3$. In all cases at T_+ and T_- ρ changes immediately (similar to [3–5]). The ratio of resistivities on the right and on the left from T_+ or T_- was maximal for $x = 0.4 (\approx 12)$ and minimal for $x = 0.6$ (≈ 2). The $\ln\rho$ curves plotted vs $1/T$ are the straight lines with the slope corresponding to the activation energy of 0.08–0.12 eV. It is of interest to note that activation energies above and below $T_\pm$ are approximately equal and hence they are hardly caused by structural transition. All the samples showed rather high negative isotropic MR at low temperatures. MR $[\rho(H) - \rho(H = 0)]/\rho(H = 0) \equiv \Delta\rho/\rho$ grows sharply on approaching to 77 K so that its maximum should lie below 77 K. The typical field dependence of $\Delta\rho/\rho$ is shown on the inset to fig.1. Since the $\rho(H)$ curves have no saturation ($\Delta\rho(H) \propto H$) one can expect that at higher fields (60–100 kOe) the value $\rho(0)/\rho(H)$ will be comparable to the values of [1, 2].

One can see from fig.2 that T_+ and T_- depend on external magnetic field. For example, for $x = 0.7$ the value $T_+(H = 0) - T_+(H = 18.8\,\text{kOe}) \equiv \Delta T$ is about 4 K. It is also seen that the abrupt change of resistance for all the fields takes place on reaching just the same values of ρ, i.e. the higher MR the higher ΔT.

Fig.3 presents the typical magnetization data for all the samples studied. Though we had no opportunity to measure magnetization σ at $T \to 0$ K, one can suppose that the magnetic ordering below $T_\pm$ is likely to be FM with $T_c \approx 100$ K. Spontaneous magnetization σ_s extrapolated to zero field at 77 K (20–40 emu/g)

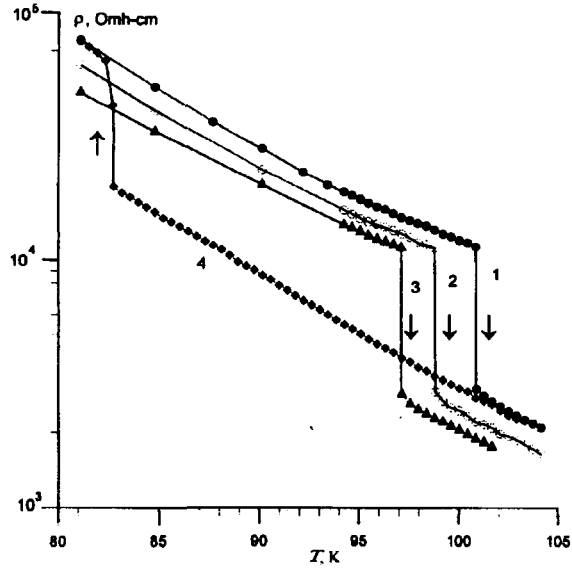

Fig.2. Resistivity ρ vs temperature T of a sample $x = 0.7$ at different magnetic fields H. On cooling: *1* – $H = 0$, *2* – $H = 11.1$ kOe, *3* – $H = 18.8$ kOe. On heating: *4* – $H = 0$

is 20-50 % of the theoretical value for the magnetically uniform FM manganites at $T = 0$ K.

Summarising the $\sigma(T, H)$ and $\rho(T, H)$ data briefly described above one can find that the effect has features both of ordinary FM manganites (large negative linear MR in the vicinity of T_c) and systems with first-order AFM-FM transition due to charge ordering (the $\rho(T)$ jumps at $T_\pm$). One can suppose that the samples studied being chemically single-phase are magnetically nonuniform below $T_\pm$, so that the appearance of the second poor-conducting phase (it is likely AFM as in ref.[3–5]) result in abrupt increase of ρ. If it is so, we have AFM inclusions in FM (at $T < T_c$) or PM (at $T_c < T < T_\pm$) matrix. Another opportunity is the first-order transition to nonuniform FM(PM)-AFM state (phase separation) theoretically grounded in [6]. In the latter case nucleation of insulator AFM inclusions results from redistribution of charge carriers promoting FM "double exchange" interaction between localised spins. The carriers abandon the regions with the lower concentration of charged defects and they become AFM due to the superexchange. Spacially-nonuniform magnetic state can explain the low values of σ_s(77 K) measured and abnormarlly high for FM susceptibility observed in high fields.

Further, it is necessary to estimate the approximate amount of AFM phase sufficient to cause $\rho(T)$ jumps by a factor of 2–10 observed at $T_\pm$. The standard effective-medium method [7] leads to the following self-consistency equation for the effective conductivity $G \equiv \rho^{-1}$ of the nonuniform sample,

$$\langle (G_{mm'} G)/(G_{mm'} + \chi G) \rangle = 0, \qquad (1)$$

where $G_{mm'}$ – a random quantity, describing the conductance between sites m and m' in the random resister network. The symbol $\langle\rangle$ denotes the configuration averaging and $\chi = d - 1$, where d is the spatial dimension of the problem considered. For our case of two phases with different conductivities (1) can be simplified ($d = 3$) to

$$f(G_1 - G)/(G_1 + 2G) + (1 - f)(G_2 - G)/(G_2 + 2G) = 0, \qquad (2)$$

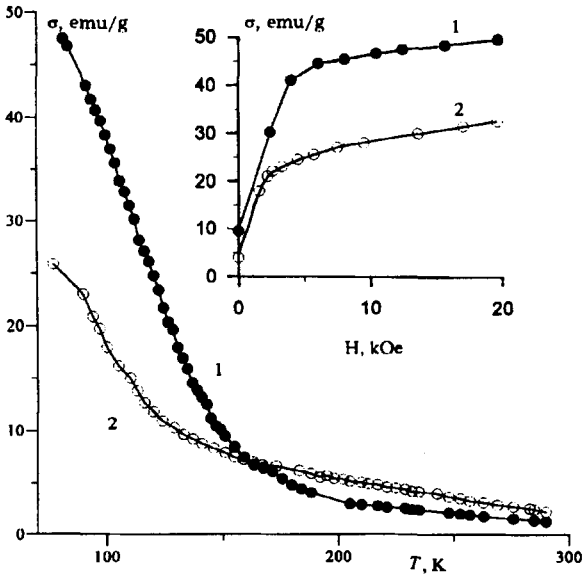

Fig.3. Magnetization σ vs temperature T: *1* – $x = 0.7$, $H = 16.6$kOe, *2* – $La_{0.5}Bi_{0.4}Na_{0.1}MnO_{3+\delta}$, $H = 18.5$kOe. Inset: σ(77 K) vs H for the same samples

where $f = V_{AFM}/V$ – the volume fraction of the AFM phase, G_1 and G_2 – conductivities of AFM and FM phases respectively. The exact values of G_1 and G_2 are unknown for this case. According to the data published G_1/G_2 at temperature interval corresponding to $T_\pm$ may vary by several orders of magnitude $10^{-6} - 10^{-2}$. Nevertheless, one can obtain from (2) that for relatively small volume fraction of AFM phase ($f < 1/2$) below the percolation threshold ($f_c = 2/3$) and at $G_1 \ll G_2$ the relative height of the conductivity jump G/G_2 is nearly independent from G_1/G_2: $G/G_2 \approx 1 - (3/4)f - (9/4)f^2 - \ldots$ (below $f_c\,\rho$ is mainly determined by the better conducting phase). Exact calculation using (2) gives f for $2 < G/G_2 < 10$ about 20–50% that is in accordance with the low values of σ_s(77 K) measured. We did not notice any peculiarities in the $\sigma(T)$ behaviour that should be at $T_\pm$, but may be the accuracy of our experiments was insufficient for this.

In conclusion, we have observed $\rho(T)$ jumps on a variety of substances given by the formula $La_{1-x}Bi_xMnO_{3+\delta}$. In contrast to the data obtained earlier on the other perovskite manganites the low-temperature phase is not AFM but likely FM and so the results can not be explained simply by the charge ordering mechanism. We had supposed that peculiarityes of $\rho(T, H)$ behaviour are due to the abrupt appearence of spatially-nonuniform magnetic ordering below $T_\pm$.

This work was supported by Grant (96-02-19065-a) from the Russian Basic Investigations Foundation.

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Edited by Steve Torstveit