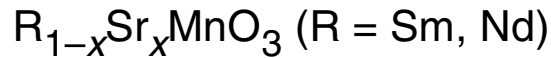


## Giant volume magnetostriction in CMR manganites



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Magnetization, ac initial magnetic susceptibility, resistance, magnetoresistance, thermal expansion and magnetostriction measurements were performed for  $R_{1-x}Sr_xMnO_3$  (R = Sm,  $x = 0.33, 0.40, 0.45$ ; R = Nd,  $x = 0.33, 0.45$ ) compounds. For all compounds in the  $T_C$  region we have observed a large volume contraction  $\Delta V/V \approx 0.1\%$  and unusual behavior of the volume magnetostriction  $\omega$ , namely, a peak of anomalous magnitude of negative volume magnetostriction on the  $\omega(T)$  curve. We have obtained a giant negative volume magnetostriction  $\sim 5 \cdot 10^{-4}$  at a relatively low magnetic field  $B = 0.9$  T and  $\sim 10^{-3}$  at a high magnetic field  $B = 13$  T for Sm samples. The magnetostriction of Nd compounds is one order of magnitude less. For all compounds the giant magnetostriction is accompanied by colossal negative magnetoresistance equal to 78, 72, and 44% at  $B = 0.9$  T for Sm compounds with  $x = 0.33, 0.40$ , and  $0.45$ , respectively. All of the observed properties are explained in the framework of an electronic phase separation model.

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**Introduction**

The discovery of high-temperature superconductors has stimulated interest in the investigation of materials with similar structure, in particular of manganites with the perovskite structure, with the general formula  $R_{1-x}A_xMnO_3$  (R = La, Nd, Pr, Sm; A = Ca, Sr, Ba, Pb). These materials have close interplay between the electronic and magnetic subsystems and the crystal lattice, resulting in anomalies of their magnetic, electric, optical, and elastic properties. Doubtless, the most interesting effects from the theoretical as well as the practical point of view are the colossal magnetoresistance (CMR) and giant magnetostriction (MS) observed in them near the Curie point  $T_C$ . Generally, CMR materials can be used as the highly sensitive and electrically readable magnetic-field sensors for the read head of the magnetic memory, and compounds with large MS – in devices that convert magnetic energy to the mechanical one. For this purpose it is necessary to stimulate a search for materials having CMR and very high MS at room temperature in the low magnetic field. There are many papers devoted to the CMR study (see the review articles [1,2] and the references cited therein), while the MS is scarcely explored [3–9]. Earlier the giant negative

volume MS  $\omega \approx -5 \cdot 10^{-4}$  has been found by us for the compound  $Sm_{0.55}Sr_{0.45}MnO_3$  in a low magnetic field of 0.9 T [10]. It is accompanied by negative CMR equal to 44% in the same magnetic field. In this work we present our results of the study of the MS, thermal expansion (TE), resistance, magnetoresistance (MR), magnetization, and ac initial magnetic and paramagnetic susceptibility for  $R_{1-x}Sr_xMnO_3$  (R = Sm,  $x = 0.33, 0.40, 0.45$ ; Nd,  $x = 0.33, 0.45$ ) compounds.

**Synthesis and experimental details**

The ceramic samples were prepared as follows: ash-free paper filters were soaked with an aqueous solution of the metal nitrates with a concentration about 1 mol/l, and then the ashes formed by burning of the dried filters were annealed at 973 K, and the powder was pressed into pellets and sintered in air at 1473 K for 12 h. The phase composition and lattice parameters were controlled by x-ray diffraction with Siemens D5000 diffractometer ( $CuK_\alpha$  radiation). The ceramic was found to be pure single-phase perovskite with the orthorhombic  $Pnma$  structure. The phase purity was also proved by a Raman spectrometry study performed with a triple monochromator system (Jobin-Yvon

T64 000): only the phonon bands characteristic for *Pnma* perovskite manganites were observed.

The magnetization measurements were performed by a vibrating magnetometer in magnetic fields up to 1 T and by the ballistic method in magnetic fields up to 4 T; the initial magnetic susceptibility in an ac magnetic field with frequency from 0.8 to 8 kHz was measured with a F-5063 ferrometer; the paramagnetic susceptibility was measured using a balance (weighing) method with electromagnetic compensation. The resistance was measured by a four-probe method; contacts to the sample were attached using a silver paste. The magnetostriction and thermal expansion were measured with strain gauges with resistance  $(92.30 \pm 0.01) \Omega$  and tensosensitivity factor 2.26. One gauge was glued to the flat surface of the sample and the other one was glued to quartz. During the measurements the gauges were arranged identically on the sample and on the quartz with respect to direction of the magnetic field.

## Results

**Magnetic properties.** The magnetization measurements show that magnetization isotherms at 4.2 K are saturated at a magnetic field of 2 T for the Nd compounds and are not saturated at magnetic fields up to 4 T (maximum field of measurements) for the Sm compounds. The spontaneous magnetic moment of the  $x = 0.45$  (R = Nd) compound is equal to  $3.50 \mu_B/\text{mol}$ , which is close to the value  $3.55 \mu_B/\text{mol}$  corresponding to ferromagnetic (FM) ordering of the  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions. The spontaneous magnetic moment of the  $x = 0.33$  (R = Nd) compound is equal to  $4.20 \mu_B/\text{mol}$ , which is considerably higher than the value of  $3.67 \mu_B/\text{mol}$ , corresponding to FM ordering of the Mn ions only. Apparently, this difference is due to the magnetic moment of the  $\text{Nd}^{3+}$  ions. As was shown by the neutron diffraction method for the  $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  compound, the  $\text{Nd}^{3+}$  magnetic moment reaches  $0.8 \mu_B$  and points in the same direction as the Mn magnetic moments [11]. The spontaneous magnetic moments for the Sm compounds are less than for the Nd compounds. They are equal to  $3.18 \mu_B/\text{mol}$  for  $x = 0.45$  and to  $3.30 \mu_B/\text{mol}$  for  $x = 0.33$ , values that are approximately 90% of the moment that would be expected for complete ferromagnetic ordering. It was found that Curie temperatures  $T_C$ , defined by extrapolation of the sharpest part of the magnetization curve to the temperature axis, depend on the magnetic field magnitude. This means that the FM – paramagnetic transition is strongly broadened. Conse-

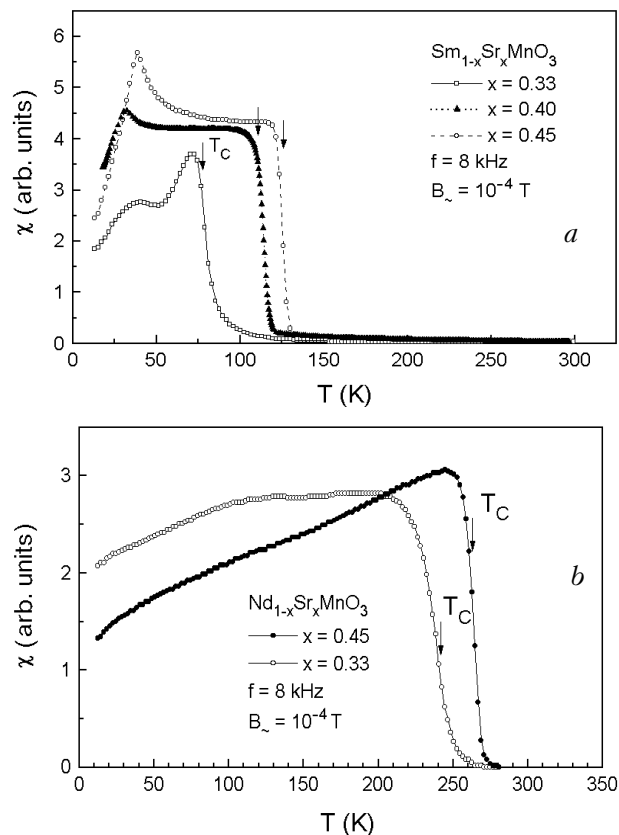


Fig. 1. Temperature dependence of the ac initial magnetic susceptibility for the Sm (a) and Nd (b) compounds.

quently, it is necessary to estimate  $T_C$  for these compounds either by methods excluding the magnetic field or in a very low magnetic field. The more-exact  $T_C$  values were estimated from measurements of the ac initial magnetic susceptibility in a magnetic field of  $10^{-4}$  T at a frequency of 8 kHz. They were determined as the temperatures at which the  $\partial\chi/\partial T(T)$  curves display a minimum and they are equal to 263 and 242 K for  $x = 0.45$  and 0.33 (R = Nd) and to 126, 112, and 78 K for  $x = 0.45$ , 0.40, and 0.33 (R = Sm) compounds, respectively. As one can see from Fig. 1, a very sharp increase of the ac magnetic susceptibility takes place at  $T_C$  for all samples, while a sharp peak on the  $\chi(T)$  curve is observed in the low-temperature region ( $T < 40$  K) for Sm compounds only, and its position is practically independent of  $x$ . The paramagnetic susceptibility of Nd compounds obeys the Curie–Weiss law. A deviation from this law is observed at  $T < 2T_C$  for all Sm compounds, and this means that the magnetic state is inhomogeneous in this temperature region.

**Resistivity and magnetoresistance.** All of the compounds have a maximum on the temperature dependence of the resistivity near  $T_C$  (Fig. 2). For Sm compounds the resistivity at the maximum varies over 3–4 orders of magnitude, while for the

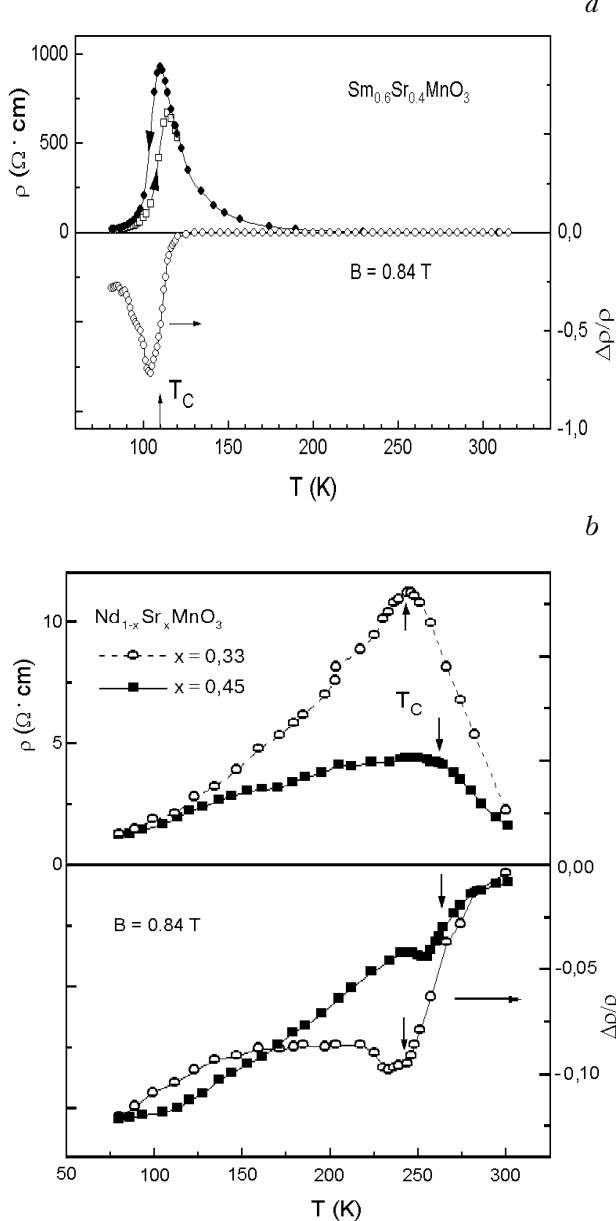


Fig. 2. Temperature dependence of the resistivity (top) and MR (bottom) for the  $\text{Sm}_{0.60}\text{Sr}_{0.40}\text{MnO}_3$  (a) and for the two Nd compounds (b).

Nd compounds it varies only several-fold. Temperature-dependent hysteresis of the resistivity is observed below  $T_C$  for the Sm compounds only. The value of the resistivity decreases and the peak position shifts to higher temperature upon application of a magnetic field. The temperature dependences of the MR for all of the compounds exhibit a peak near  $T_C$ . Figure 2,b (bottom) displays the temperature dependence of the MR for both Nd compounds in a magnetic field  $B = 0.84$  T, and Fig. 2,a (bottom) displays the same for the Sm compound with  $x = 0.40$ . One can see that for the Nd compounds the MR shows a steady drop with increasing  $T$ , interrupted by a slight increase near  $T_C$ . The MR

of all the Sm compounds passes through a maximum slightly below  $T_C$  and then drops as the temperature decreases. Two contributions to the MR are clearly seen from Fig. 2: one is the MR peak near  $T_C$  and other is the low-temperature MR, which is usually very small in manganite single crystals but reaches approximately 12% of the value at 80 K for our Nd samples. The low-temperature MR is usually related with intergrain spin-polarized tunneling [12] and spin-dependent scattering of polarized electrons at the grain boundaries [13]. We assume that the first mechanism is predominant for our compounds, because for manganites a strong  $p-d$  exchange takes place, and they have a large thickness of the domain wall. For example, the domain wall thickness is  $10^3 a$  (where  $a$  is the lattice parameter) according to the estimate made in [14]. In such a wide domain wall the spins turn gradually, and because of the strong  $p-d$  exchange the charge carrier spin is arranged parallel to the spin of the ion on which it is located at the time. In this case the charge carrier has not scattered. The MR peak near  $T_C$  seems to arise from a magnetoresistance contribution inside the grains. The MR of the Sm compounds is considerably larger than for the Nd compounds. For example, for the  $x = 0.45$  sample at 100 K the negative MR is 44 and 20% in magnetic fields of 0.9 and 0.4 T, respectively. The MR of the  $x = 0.33$  compound is still greater: it is equal to 78 and 52% in the same fields at 80 K, i.e., we obtained CMR in the relatively low magnetic fields and over a wide temperature region, which is important for practical device applications.

*Thermal expansion and magnetostriction.* Figure 3,a displays the temperature dependence of the TE for all Sm compounds, and Fig. 3,b – the same for the two Nd compounds. One can see that a sharp reduction  $\Delta L/L$  is observed at  $T_C$ , with a volume contraction  $\Delta V/V \approx 0.1\%$  ( $\Delta V/V = 3\Delta L/L$ ) for the  $x = 0.40$  and 0.45 ( $R = \text{Sm}$ ) compounds. A sharp change of the TE ( $\Delta V/V \approx 0.15\%$ ) is observed in a wide temperature region near  $T_C$  for the Nd compound with  $x = 0.33$  and a smoother change for compound with  $x = 0.45$ . Besides, we observed temperature-dependent hysteresis of the TE in the  $T_C$  region for all Sm compounds. This fact indicates that the phase transition at  $T_C$  is first-order. Temperature-dependent hysteresis of the TE was not observed for the Nd compounds.

The longitudinal ( $\lambda_{\parallel}$ ) and transverse ( $\lambda_{\perp}$ ) MS with respect to the applied magnetic field were measured for all compounds. The volume ( $\omega$ ) and anisotropic ( $\lambda_t$ ) MS were calculated as  $\omega = \lambda_{\parallel} + 2\lambda_{\perp}$  and  $\lambda_t = \lambda_{\parallel} - \lambda_{\perp}$ . For all of the com-

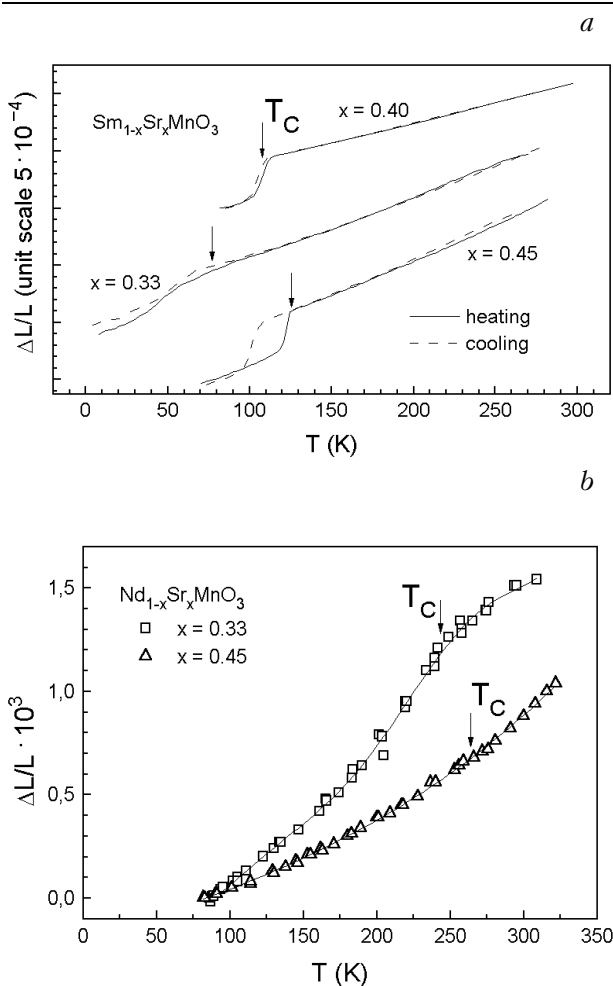


Fig. 3. Temperature dependence of the TE for the Sm (a) and Nd (b) compounds.

pounds we observed unusual behavior of the volume MS in the  $T_C$  region, namely, a peak of anomalous magnitude of negative volume MS on the  $\omega(T)$  curve. As one can see from Fig. 4,a, which displays the temperature dependences of the volume and anisotropic MS for the  $x = 0.40$  ( $R = \text{Sm}$ ) compound,  $\omega$  is negative in the  $T_C$  region and very large  $|\omega| \approx 5 \cdot 10^{-4}$  at  $B = 0.9$  T. At a high magnetic field of 13 T it reaches  $|\omega| \approx 10^{-3}$  for all the Sm compounds. The anisotropic MS is very small for all of the Sm compounds and changes sign near  $T_C$  for the compounds with  $x = 0.40$  and  $0.45$ . In the  $T_C$  region the volume MS isotherms are not saturated in magnetic fields up to 1 T, and clear hysteresis is observed during increase and decrease of magnetic field. The MS of the Nd compounds is one order of magnitude less than for the Sm compounds. For the  $x = 0.33$  compound changes  $\omega$  sign at 160 K: it is positive below this temperature and negative above it (Fig. 4,b). The  $\omega(T)$  curve has an abrupt minimum at  $T_C$ , with  $|\omega|$  being equal to  $7 \cdot 10^{-5}$  at  $B = 0.9$  T. The  $\lambda_t$  is positive and equal to  $3 \cdot 10^{-5}$  at 80 K in the same magnetic field, and it drops continuously to

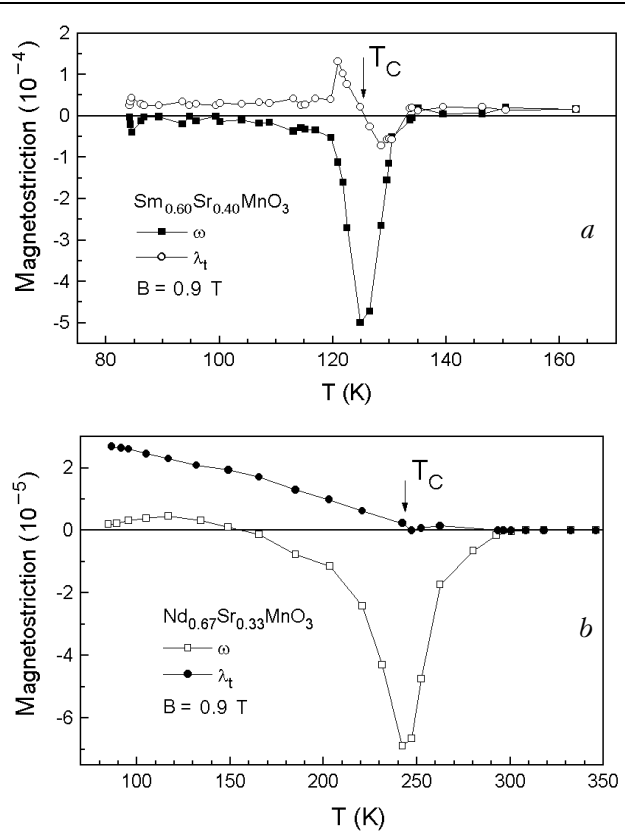


Fig. 4. Temperature dependence of the volume anisotropic MS for the  $\text{Sm}_{0.60}\text{Sr}_{0.40}\text{MnO}_3$  (a) and  $\text{Nd}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  (b).

zero near  $T_C$ . For the  $x = 0.45$  compound the volume and anisotropic MS behavior is similar, but the MS value is less than for the  $x = 0.33$  compound ( $|\omega| = 1.5 \cdot 10^{-5}$  at  $B = 0.9$  T near  $T_C$ ). For both compounds the volume MS isotherms are not saturated in magnetic fields up to 1 T, and no hysteresis is observed during increase and decrease of the magnetic field.

## Discussion

At present there are different ideas concerning the nature of the CMR effect in manganites. Nevertheless, one should note that the behavior of  $\rho$  and the CMR in manganites is similar to that in usual magnetic semiconductors of the EuSe and  $\text{CdCr}_2\text{Se}_4$  type, where it was explained by the existence of a magnetic two-phase state (MTPS) [15]. As is well known, in magnetic semiconductors the charge carrier energy is minimal when the total ordering in the crystal is FM. For this reason, on account of the gain in the  $s-d$  exchange energy the electrons produce FM microregions (droplets) in an antiferromagnetic (AFM) semiconductor and stabilize these droplets by their self-localization in them (insulating MTPS). As the impurity concentration increases, such FM droplets

in an insulating AFM host increase in size, and at a sufficiently high doping level they undergo percolation. In the process, another MTPS is formed: the insulating AFM droplets are located in a conducting FM host (conducting MTPS). So the  $R_{1-x}Sr_xMnO_3$  ( $R = Sm, Nd$ ) compounds are heavily doped AFM semiconductors  $RMnO_3$  ( $R = Sm, Nd$ ) in which, as we propose, MTPS is realized at low temperatures. It is confirmed by the following facts: (i) the spontaneous magnetization at 4.2 K is less than expected for full FM ordering (including rare-earth ions), (ii) the existence of the low-temperature peak on the  $\chi(T)$  curves for Sm compounds, which can be due to distortion of the magnetic ordering in an AFM part of crystal, (iii) independence of the peak temperature from  $x$  — the concentration of Sr ions. We suppose that a conducting MTPS takes place in our compounds, because they have metallic type of conductivity at low temperatures. Their resistivity at 80 K is  $\sim 10^0$  and  $\sim 10\text{--}10^2 \Omega\cdot\text{cm}$  for the Nd and Sm compounds respectively, but these high values of the resistivity can be connected with the properties of the grain boundaries. In the case of a conducting MTPS there are two mechanisms by which the impurity–magnetic interaction can influence the resistance: (i) the scattering of charge carriers, which reduces their mobility; (ii) the formation of band tails, consisting of localized states. The decrease of the charge carrier mobility and their partial localization in band tails are most prominent in the  $T_C$  region. The MR is caused by suppression of the impurity–magnetic scattering and band tails by the magnetic field [16].

At present there is no theory that can explain the MS and TE of manganites. We propose that the MTPS is also the reason for the MS and TE anomalies. Yanase and Kasuya showed that the lattice parameters decrease in the FM part of crystal, since this results in screening of the new charge distribution and lowers its energy by increasing the overlap of the charge clouds of the central ion and its nearest neighbors [17]. The lattice contraction in  $La_{1-x}Ca_xMnO_3$  manganites near  $T_C$  has been confirmed by a neutron diffraction study [18]. In the absence of magnetic field the FM part of the crystal breaks down thermally in the  $T_C$  region, and an excess TE of the sample takes place, as was observed in the present work (Fig. 3). It is known that the imposition of an external magnetic field at  $T \geq T_C$  increases the degree of FM order near the impurities more strongly than on the average over the crystal, since the effect of the field is intensified by the  $s$ – $d$  exchange. That is, a magnetic field

restores the FM parts of crystal which were destroyed by heating, and a corresponding compression of the lattice occurs. However, the process of field-induced production of the FM clusters occurs in a limited temperature range not far above  $T_C$ . For this reason, the curves  $\omega(T)$  pass through a minimum and  $|\omega|$  drops rapidly as the temperature increases further (Fig. 4).

## Conclusions

In summary, we have found a close relationship between the magnetic, transport and elastic properties of Sm and Nd manganites. Near the Curie point for all of the investigated compounds we have observed: (1) a maximum on the temperature dependence of the resistivity; (2) a maximum on the temperature dependence of the absolute value of the magnetoresistance; (3) an abrupt minimum on the temperature dependence of the negative volume MS; (4) a large volume contraction; (5) CMR and giant MS, both effects being observed at low magnetic fields, which is important for practical device applications. We have explained the above-described properties by the existence of a magnetic two-phase state, just like that in the usual magnetic semiconductors of the EuSe and  $CdCr_2Se_4$  type.

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