

Magnetic and transport properties of $\text{Nd}_{0.2}\text{La}_{1.8-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.5, 0.4, 0.3$) and $\text{La}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$

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2001 J. Phys.: Condens. Matter 13 1571

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Magnetic and transport properties of $\text{Nd}_{0.2}\text{La}_{1.8-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.5, 0.4, 0.3$) and $\text{La}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$

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Received 7 August 2000, in final form 20 November 2000

Abstract

Lattice structure, magnetic and transport properties of polycrystalline samples of $\text{Nd}_{0.2}\text{La}_{1.8-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ in the range $0.5 \geq x \geq 0.3$ and $\text{La}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ have been investigated. A pronounced decrease of the Curie temperature T_C and the metal–insulator transition temperature T_{MI} of $\text{Nd}_{0.2}\text{La}_{1.8-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ compared to Nd-free compounds $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ with the same doping level has been observed. The shift of T_C , which is increased with decreasing Sr content, indicates a weakening of the ferromagnetic ordering for the Nd-substituted samples.

$\text{Nd}_{0.2}\text{La}_{1.2}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ orders ferromagnetically at $T_C = 75$ K and reveals a transition to an antiferromagnetic (afm) spin arrangement below $T_N = 38$ K, whereas polycrystalline samples of the composition $\text{La}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ remain ferromagnetically ordered down to 5 K. A transition to afm spin structure in a polycrystalline sample of the composition $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ has been observed for $x = 0.25$. $\text{La}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ orders ferromagnetically at 66 K in a field of 0.5 T; the transition to an afm ordering occurs below $T_N = 34$ K. In contrast to the Nd-substituted phase the afm transition only occurs for zero-field cooled measurements. At low temperature, $T < T_N$, $\text{La}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ undergoes a metamagnetic transition; the threshold field was found to depend strongly on the temperature (≈ 0.8 T at 20 K/ ≈ 3.5 T at 5 K). With the T_{MI} of 102 K the compound shows metallic behaviour clearly above T_C . It becomes insulating again at T_N , which is in line with the properties of $\text{Nd}_{0.2}\text{La}_{1.2}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$.

Large magnetoresistance ratios (MR) have been measured for $\text{Nd}_{0.2}\text{La}_{1.8-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ with $x = 0.4, 0.3$ and $\text{La}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ near T_C . Furthermore, the metamagnetic transition causes high values of MR for $\text{La}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ and $\text{Nd}_{0.2}\text{La}_{1.2}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ at low fields.

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1. Introduction

Considering the members of the *Ruddlesden–Popper* series $(\text{La,Sr})_{n+1}\text{Mn}_n\text{O}_{3n+1}$, the bilayer compounds ($n = 2$) show some deviating properties compared to the perovskites due to their more anisotropic crystal structure. The influence of interlayer tunnelling processes leads to a larger magnetoresistance ratio in a certain range of doping at low fields [1]. On the other hand, $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ exhibits a lower Curie temperature as well as a restriction of ferromagnetism to a narrower range of x compared to $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$.

Chemical substitution of La or the alkaline earth metal in both systems has been investigated concerning crystal structure and properties (see e.g. [2–8]). By incorporation of a smaller metal atom, the resulting distortion of the lattice differs in both systems. Unlike the perovskites, the MnO_6 octahedron of the bilayer structure has three symmetrically independent Mn–O bonds. The development of these bond lengths strongly affects the magnetic and transport properties [8–10].

The influence of progressive Nd substitution on properties in $(\text{La}_{1-z}\text{Nd}_z)\text{Sr}_2\text{Mn}_2\text{O}_7$ [11, 12], $(\text{La}_{1-z}\text{Nd}_z)_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ [4, 5, 11, 13] and $(\text{La}_{1-z}\text{Nd}_z)_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ [6, 7] has been described in the literature. Whereas for low values of z , the magnetic ordering is generally preserved, the long range ordering of the Mn spins in $(\text{Nd,L a})_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ is suppressed with larger z for $x = 0.3$ and $x = 0.4$. We have prepared ceramic samples of $\text{Nd}_{0.2}\text{La}_{1.8-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ with a constant low Nd content in the composition range $0.7 \geq x \geq 0.3$. The change of the magnetic properties is discussed with respect to the lattice distortion.

In contrast to $(\text{La}_{1-z}\text{Nd}_z)_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ with $z \geq 0.1$, the occurrence of antiferromagnetic (afm) interactions in $\text{La}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ is discussed controversially [14–17]. Whereas our sample of this composition orders ferromagnetically (fm), we show the occurrence of afm-like interactions in a ceramic sample of $\text{La}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$. A possible reason for the contradictory results is discussed.

2. Experiment

Samples of the composition $\text{Nd}_{0.2}\text{La}_{1.8-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ with $0.3 \leq x \leq 0.7$ and $\text{La}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ were prepared by solid-state reactions of appropriate amounts of SrCO_3 (99.9%; Merck), Mn_2O_3 (99.9%; Merck), La_2O_3 (99.99%; MaTeck) and Nd_2O_3 (99.99%; MaTeck). The powders were thoroughly mixed and pre-reacted at 800 °C for 12 h, followed by a temperature program listed in table 1.

The sintering processes were interrupted several times to homogenize the powders in a ball mill. Before the final sintering, the powders were pressed into pellets using an organic binder, which is completely evaporated during the high temperature treatment. After each sintering step the samples were quenched from 1200 °C to room temperature.

Table 1. Sample preparation conditions for $\text{Nd}_{0.2}\text{La}_{1.8-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ and $\text{La}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$.

	$T = 1350\text{ }^\circ\text{C}$	$T = 1400\text{ }^\circ\text{C}$	$T = 1450\text{ }^\circ\text{C}$	$T = 1500\text{ }^\circ\text{C}$	Achieved density
$\text{Nd}_{0.2}\text{La}_{0.4}\text{Sr}_{2.4}\text{Mn}_2\text{O}_7$	97 h	138 h			67%
$\text{Nd}_{0.2}\text{La}_{0.6}\text{Sr}_{2.2}\text{Mn}_2\text{O}_7$	97 h	138 h			68%
$\text{Nd}_{0.2}\text{La}_{0.8}\text{Sr}_{2.0}\text{Mn}_2\text{O}_7$	97 h	158 h			68%
$\text{Nd}_{0.2}\text{La}_{1.0}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$	97 h		48 h		70%
$\text{Nd}_{0.2}\text{La}_{1.2}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$	97 h	158 h	90 h		82%
$\text{La}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$	48 h		66 h	114 h	73%

Table 2. Atomic parameters of $\text{La}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ at room temperature. Space group $I4/mmm$ (No 139) $a = 3.865(1)$ Å, $c = 20.373(1)$ Å, $Z = 2$. $R_{\text{exp}} = 7.72\%$, $R_p = 11.91\%$, $R_{\text{Bragg}} = 6.28\%$.

	Site	x	y	z	n	U (Å ²)
La(1)	2b	0	0	1/2	0.63(6)	0.028(1)
Sr(1)	2b	0	0	1/2	0.37(6)	0.028(1)
La(2)	4e	0	0	0.318(1)	0.44(4)	0.023(1)
Sr(2)	4e	0	0	0.318(1)	0.56(4)	0.023(1)
Mn	4e	0	0	0.097(1)	1	0.024(9)
O(1)	2a	0	0	0	1	0.02(1)
O(2)	4e	0	0	0.197(1)	1	0.06(1)
O(3)	8g	0	1/2	0.096(1)	1	0.04(1)

The resulting products of the composition $\text{Nd}_{0.2}\text{La}_{1.8-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ are prepared without detectable impurity phases, whereas the La compound showed small traces of the perovskite in the XRD pattern. Opposite to $\text{La}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$, the temperature treatment above 1350 °C was found to be not necessary for the phase formation of the Nd-substituted phases. However, at higher temperatures the quality of the samples was significantly improved concerning a better crystallinity and homogeneity (sharper 00 l reflections) as well as improved densities up to 82%.

The powder patterns were obtained on a diffractometer PW 1820 (Philips) with monochromatic Co K α radiation ($\lambda = 1.7903$ Å). Silicon was used as an internal standard. A Rietveld analysis was carried out with the sample of the nominal composition $\text{La}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$. The powders were prepared for the measurement by sieving through a 15 μm mesh. The x-ray data were collected in the Bragg–Brentano geometry between 20 and 130° with a step width of 0.03°. The calculation was carried out using the program X’pert Plus (program for crystallography and Rietveld analysis). Furthermore the La:Sr ratio of the as-prepared $\text{La}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ was determined by EDX measurements (EDAX system).

Low-temperature magnetic and magnetotransport properties were measured in a vibrating sample magnetometer and a Lake Shore ac susceptometer, respectively. The resistance (R) was measured in dependence on temperature (T) and magnetic field (H) by the usual four-probe technique on long sample rods of typical dimensions of $8 \times 2 \times 1$ mm³. The magnetoresistance ratio (MR) is determined as $\text{MR} = [R(H) - R(0)]/R(0)$.

3. Results and discussion

3.1. Structural aspects

The XRD patterns of all compositions reveal no changes of the lattice symmetry of the Nd-substituted samples compared to the pure La compounds. The lattice parameters a and c , indexed in the tetragonal space group $I4/mmm$, of both systems are compared in figure 1. Their non-monotonic development as a function of x has already been described for $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ and $\text{Nd}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ [18]. As can be seen in figure 1, the smaller atomic radius (r_A) of Nd compared to La leads to a constant shortening of both lattice parameters of the Nd substituted samples with $x \geq 0.5$ in $\text{Nd}_{0.2}\text{La}_{1.8-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$. With the occurrence of the *Jahn–Teller* distortion ($x \leq 0.4$), the shortening of the a axis as well as the increase of the c axis are even more pronounced for the Nd-substituted compounds, which indicates a larger distortion. For the composition $\text{Nd}_{0.2}\text{La}_{1.2}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$, this behaviour results in a larger c axis compared to the La compound of the same doping level.

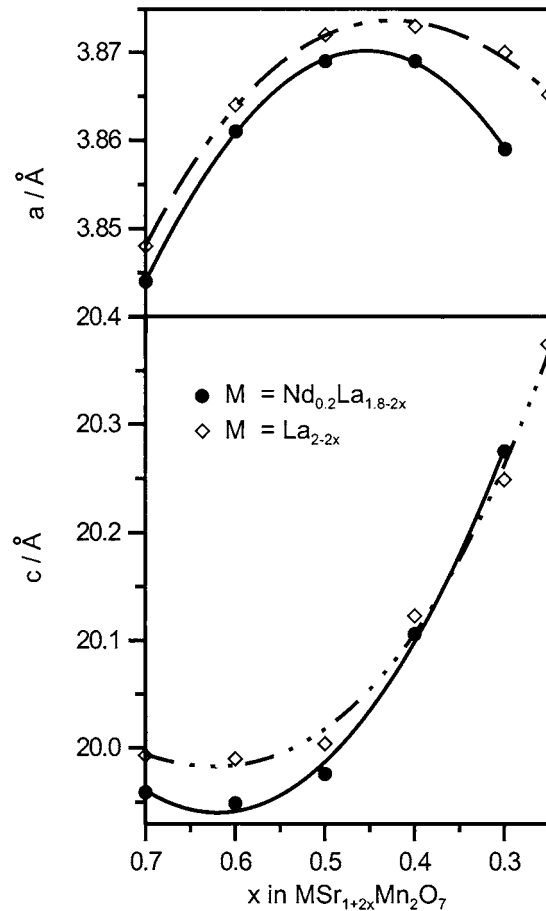


Figure 1. Lattice parameters a and c of $\text{Nd}_{0.2}\text{La}_{1.8-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ and $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ indexed in the space group $I4/mmm$ as a function of x .

The atomic parameters of $\text{La}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ are listed in table 2. The x-ray diffraction data, refined profiles and difference profiles are shown in figure 2. The refined site occupations of La and Sr confirm the agreement of the obtained product with the starting composition $\text{La}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$. This result is in line with the EDX measurements leading to a formula $\text{La}_{1.49(4)}\text{Sr}_{1.49(4)}\text{Mn}_2\text{O}_7$. As can be seen in table 2, the La atoms occupy with a slight preference the perovskite site (1) and the Sr atoms the rock salt position (2).

3.2. Magnetic and transport properties

Magnetic transition temperatures, the temperatures of the metal-insulator transition T_{MI} and the saturation magnetization M_S , measured in a field of 8 T, for the compositions $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ and $\text{Nd}_{0.2}\text{La}_{1.8-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ are listed in table 3. The Néel temperatures T_N were estimated from the maximum derivative of the $M(T)$ curves, the Curie temperatures T_C were obtained from extrapolation of M^2-T plots to $M = 0$ and T_{MI} corresponds to the maximum or minimum of the $\rho(T)$ curves.

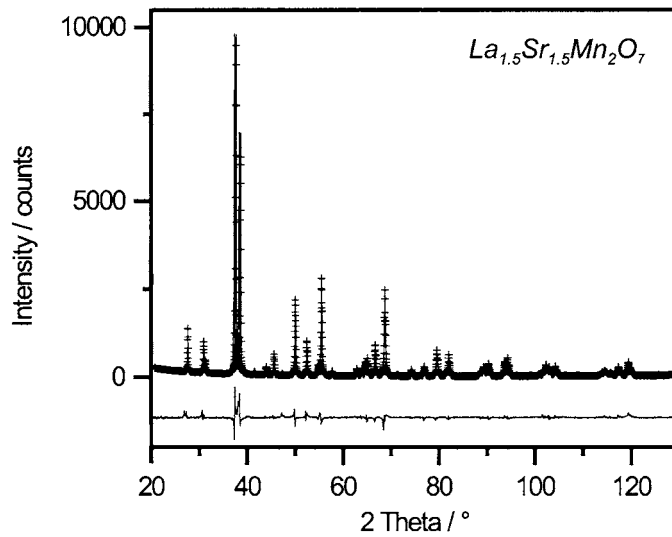


Figure 2. X-ray diffraction data (Co $K\alpha$), refined profiles (crosses) and difference profiles for $\text{La}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$.

3.2.1. $x = 0.5$. The temperature dependence of magnetization is rather similar for $\text{Nd}_{0.2}\text{La}_{0.8}\text{Sr}_{2.0}\text{Mn}_2\text{O}_7$ and $\text{La}_{1.0}\text{Sr}_{2.0}\text{Mn}_2\text{O}_7$ (not shown here). A decrease of $T_N = 212$ K for $\text{Nd}_{0.2}\text{La}_{0.8}\text{Sr}_{2.0}\text{Mn}_2\text{O}_7$ compared to $T_N = 230$ K for $\text{La}_{1.0}\text{Sr}_{2.0}\text{Mn}_2\text{O}_7$ was observed (table 3). According to literature data [19], this tendency is continued up to $\text{Nd}_{1.0}\text{Sr}_{2.0}\text{Mn}_2\text{O}_7$, which shows a Néel temperature of about 137 K. The spin structure with antiferromagnetically aligned Mn spins within the bilayers has been reported for $\text{La}_{1.0}\text{Sr}_{2.0}\text{Mn}_2\text{O}_7$ [20] as well as for $\text{Nd}_{1.0}\text{Sr}_{2.0}\text{Mn}_2\text{O}_7$ [19]. Opposite to the compounds with lower Sr content, the nature of the magnetic ordering seems to remain unchanged with progressive Nd content for $\text{La}_{1-y}\text{Nd}_y\text{Sr}_{2.0}\text{Mn}_2\text{O}_7$. This result is consistent with the data reported by Moritomo *et al* [12] for $y = 0.15, 0.25$ and 0.5 .

Table 3. Magnetic transition temperatures T_C , T_N measured in a field of 0.5 T and metal–insulator transitions T_{MI} without applied field. The value of magnetization M_S was obtained in an applied field of 8 T at temperatures between 10 and 20 K.

Compound	Magnetic transition temperatures/ M_S	T_{MI}
$x = 0.5$	$\text{La}_{1.0}\text{Sr}_{2.0}\text{Mn}_2\text{O}_7$ $T_N = 230$ K	—
	$\text{Nd}_{0.2}\text{La}_{0.8}\text{Sr}_{2.0}\text{Mn}_2\text{O}_7$ $T_N = 212$ K	—
$x = 0.4$	$\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ $T_C = 134$ K/ $M_S = 64$ emu g^{-1}	134 K
	$\text{Nd}_{0.2}\text{La}_{1.0}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ $T_C = 98$ K/ $M_S = 72$ emu g^{-1}	96 K
	$\text{La}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ $T_C = 125$ K/ $M_S = 71$ emu g^{-1} ^a	124 K
$x = 0.3$	$\text{Nd}_{0.2}\text{La}_{1.2}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ $T_C = 75$ K; $T_N = 38$ K/ $M_S = 75$ emu g^{-1}	79 /38 K
$x = 0.25$	$\text{La}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ $T_C = 66$ K/ $T_N = 34$ K $M_S = 63$ emu g^{-1}	102/34 K

^a T_C of $\text{La}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ was measured in a field of 0.05 T.

3.2.2. $x = 0.4/0.3$. Figures 3(a) and (b) show the temperature dependence of magnetization and of resistance for $\text{Nd}_{0.2}\text{La}_{1.8-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ with $x = 0.4$ and 0.3 . The shift of both

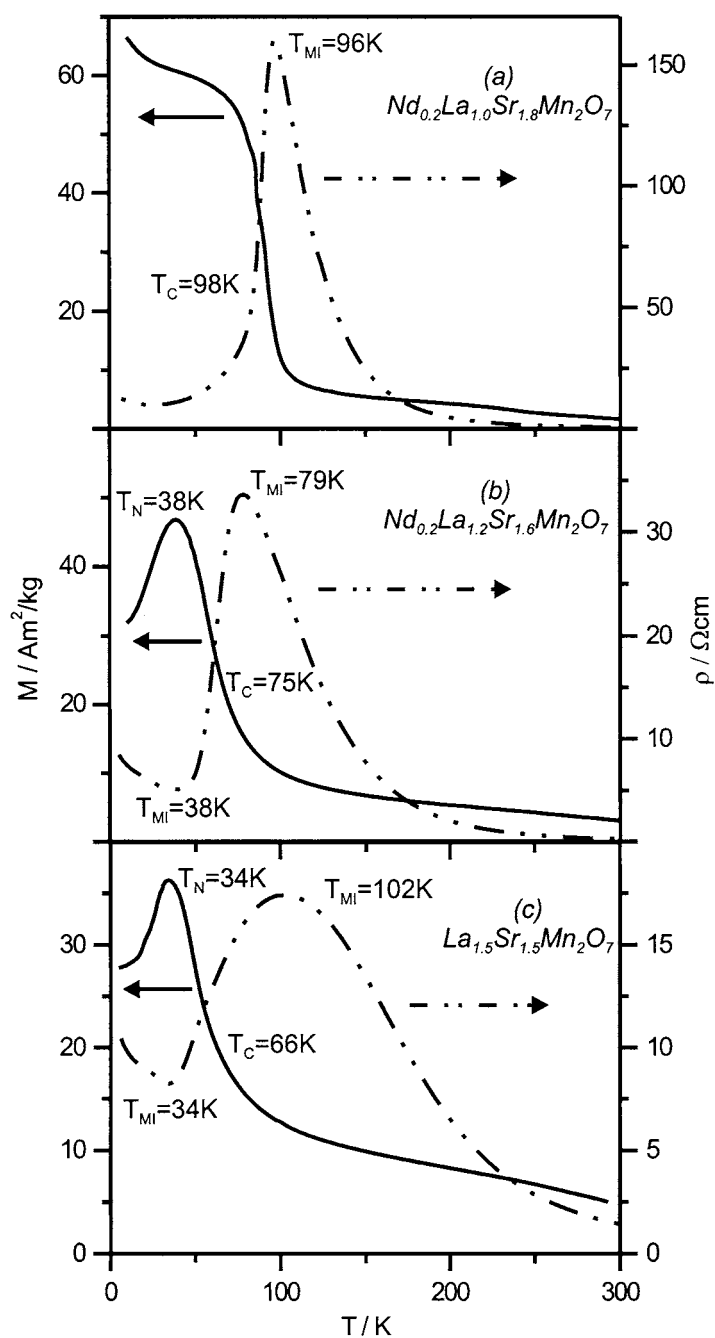


Figure 3. Temperature dependence of magnetization measured at 0.5 T (solid line) and resistance (dashed line) of (a) $\text{Nd}_{0.2}\text{La}_{1.0}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$; (b) $\text{Nd}_{0.2}\text{La}_{1.2}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ and (c) $\text{La}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ obtained after zero-field cooling.

transition temperatures T_C and T_{MI} to lower values for the Nd-containing compounds compared to $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ is confirmed as described in the literature [4, 5, 7, 11, 13, 21]. The Curie temperature T_C of $\text{Nd}_{0.2}\text{La}_{1.0}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ is 36 K lower compared to $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$.

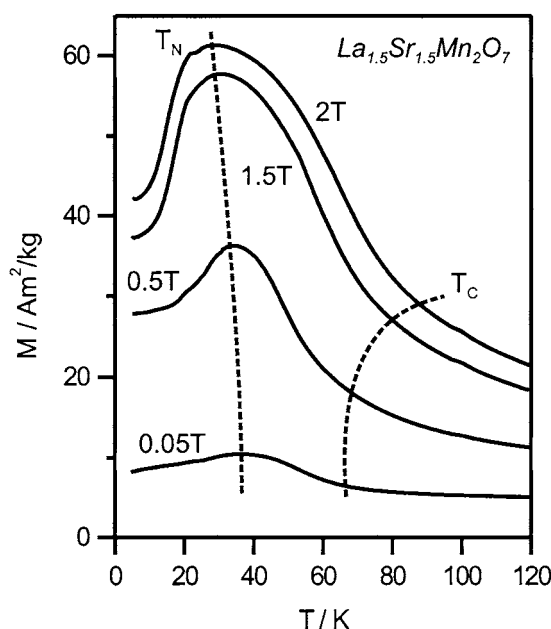


Figure 4. Temperature dependence of magnetization of $\text{La}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ at different magnetic fields obtained after zero-field cooling. The magnetic transition temperatures T_C and T_N are marked.

The temperature of the metal–insulator transition T_{MI} of 96 K is near the transition to ferromagnetic ordering (table 3; figure 3(a)). The magnetic ordering of $\text{La}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ is still controversially discussed, either as ferromagnetically ordered bilayers which are aligned antiferromagnetically to the adjacent ones (afm interbilayer coupling) [10, 22] or as a ferromagnetically ordered phase [6, 17]. Our measurements on a ceramic sample of this composition do not indicate an antiferromagnetic ordering. Unlike the La compound, a drop of the magnetization of $\text{La}_{1.2}\text{Nd}_{0.2}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ below T_C , at $T_N = 38$ K, is clearly shown in figure 3(b). The compound orders ferromagnetically at 75 K, which is about 50 K lower compared to the La compound. The spin structure below T_N is assumed to be the above mentioned antiferromagnetic interbilayer coupling according to the results by Moritomo *et al* [6, 7] for $(\text{La}_{1-z}\text{Nd}_z)_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ ($z = 0.1/0.2$). Our ceramic sample shows a metamagnetic transition towards ferromagnetism in a field of about 0.35 T at 20 K [23], which is in line with the results obtained on a single crystal [6]. The metal–insulator transition occurs at 79 K, but the compound becomes insulating again below 34 K.

3.2.3. $\text{La}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$. $\text{La}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ shows a similar temperature dependence of magnetization compared to $\text{Nd}_{0.2}\text{La}_{1.2}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ (figure 3(c)). In a field of 0.5 T the phase orders ferromagnetically at 66 K and a drop of the magnetization occurs at $T_N = 34$ K. In particular, T_C was found to depend relatively strongly on the applied magnetic field (figure 4). Opposite to the behaviour of $\text{Nd}_{0.2}\text{La}_{1.2}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$, the ‘antiferromagnetic’ ordering of $\text{La}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ occurs, however, only for zero-field-cooled measurements. The presence of a magnetic field of 0.5 T during cooling suppresses the transition at T_N ; the compound remains ferromagnetic down to 5 K (not shown here). As can be seen in figure 5, the field dependence of magnetization at 20 K shows a metamagnetic transition, i.e. a transition to

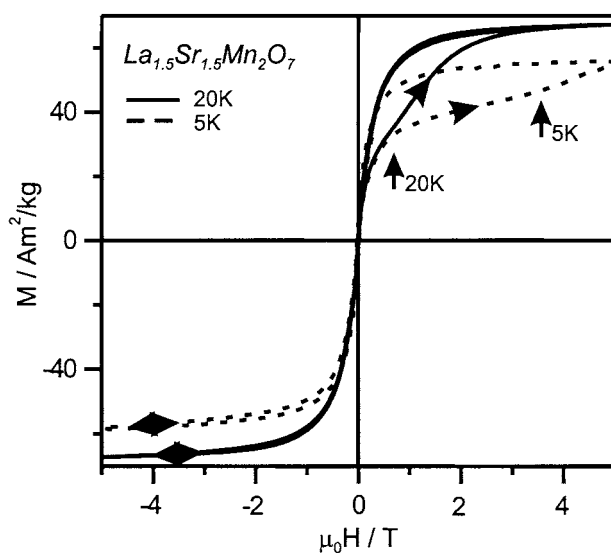


Figure 5. Field dependence of magnetization of $\text{La}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ at 20 K (solid line) and 5 K (dashed line), respectively. The virgin branch as well as the metamagnetic transition at both temperatures observed after zero-field cooling are marked. After passing the field cycling the value of magnetization remains unchanged at both temperatures.

positive curvature, in a field of about 0.8 T, which is shifted to about 3.5 T at 5 K. In agreement with the observation for the temperature dependence of magnetization, the transition is only observed in the virgin branch; for 20 K after applying a magnetic field of 5 T the sample shows ferromagnetic-like behaviour. At 5 K, after passing the same field cycling, the value of magnetization of $\text{La}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ is significantly reduced compared to 20 K (figure 5), which suggests that the metamagnetic transition needs larger fields to be completed and a canted afm spin arrangement is frozen at this low temperature.

Obviously, the threshold composition for the occurrence of an afm coupling in $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ is close to $x = 0.3$. Thus, the above mentioned controversial discussion of magnetic ordering in $\text{La}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ may result from slight deviations of the La:Sr ratio. Our results concerning $\text{La}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ agree with a recent work by Chi *et al* [17], which shows fm ordering in a sample of this composition prepared by ceramic methods. These authors further mentioned that the afm ordering has only been observed on single-crystalline samples. The determination of the exact metal stoichiometry for the appearance of afm ordering remains difficult. On the one hand, the phase pure preparation of ceramic samples is problematical; on the other hand, the bilayer compounds melt incongruently and no information about phase relations in the liquidus region are known. Due to our experiences in crystal growth, it is difficult to control the La:Sr ratio of the molten rod by applying the floating zone method. However, with a further decrease of the Sr content, the afm-like ordering clearly occurs in ceramic samples without Nd substitution. Although our sample of the nominal composition $\text{La}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ contains traces of a secondary phase, the ‘afm’ ordering is obviously a bulk property of the major phase.

The metal–insulator transitions of $\text{La}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ occur at $T_{MI1} = 102$ K which is, however, 36 K higher than T_C , while T_{MI2} of 34 K, where the compound becomes insulating again, corresponds to the appearance of ‘antiferromagnetic’ ordering. A pronounced broadening of the maximum of the resistance curve is observed in comparison with the samples of larger Sr content (figures 3(a)–(c)).

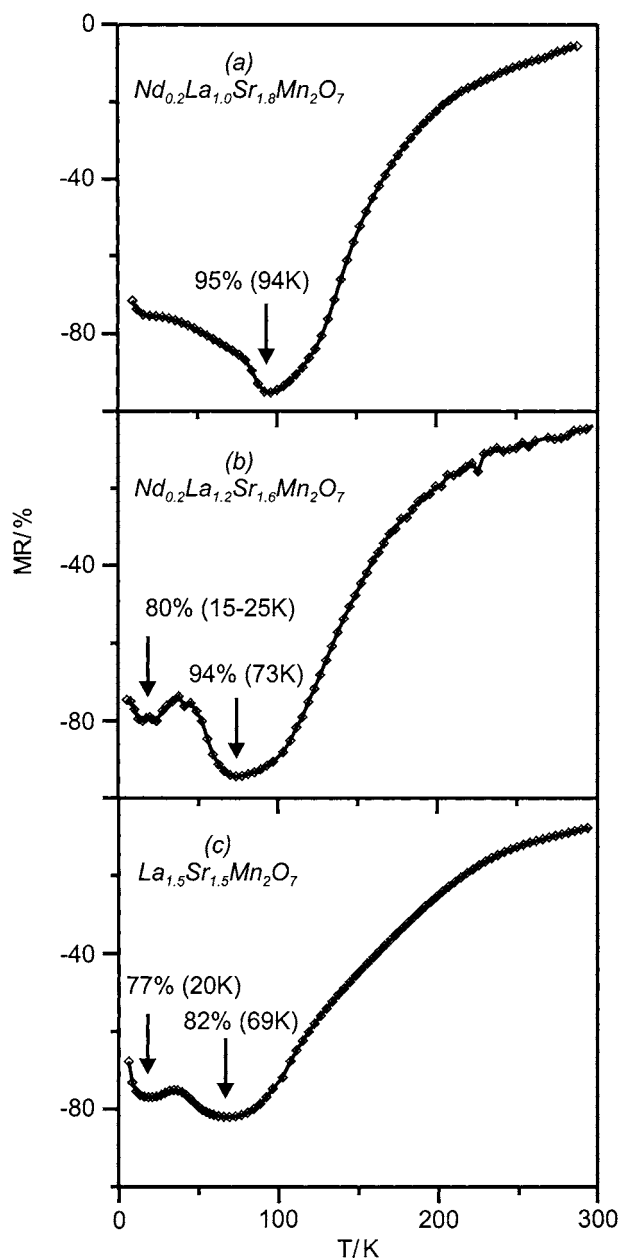


Figure 6. Temperature dependence of magnetoresistance for the samples with low Sr content obtained in an applied field of 5 T: (a) $Nd_{0.2}La_{1.0}Sr_{1.8}Mn_2O_7$; (b) $Nd_{0.2}La_{1.2}Sr_{1.6}Mn_2O_7$ and (c) $La_{1.5}Sr_{1.5}Mn_2O_7$. For $La_{1.5}Sr_{1.5}Mn_2O_7$, the large MR at low temperatures is only observed after zero-field cooling (ZFC).

The temperature dependence of magnetoresistance has been measured for the samples of the compositions $Nd_{0.2}La_{1.8-2x}Sr_{1+2x}Mn_2O_7$ with $x = 0.3/0.4$ and $La_{1.5}Sr_{1.5}Mn_2O_7$ (figure 6). MR_{max} is obtained in the vicinity of the ferromagnetic transition temperature, which indicates that the main effect is based on the ‘usual’ CMR mechanism for all samples. For

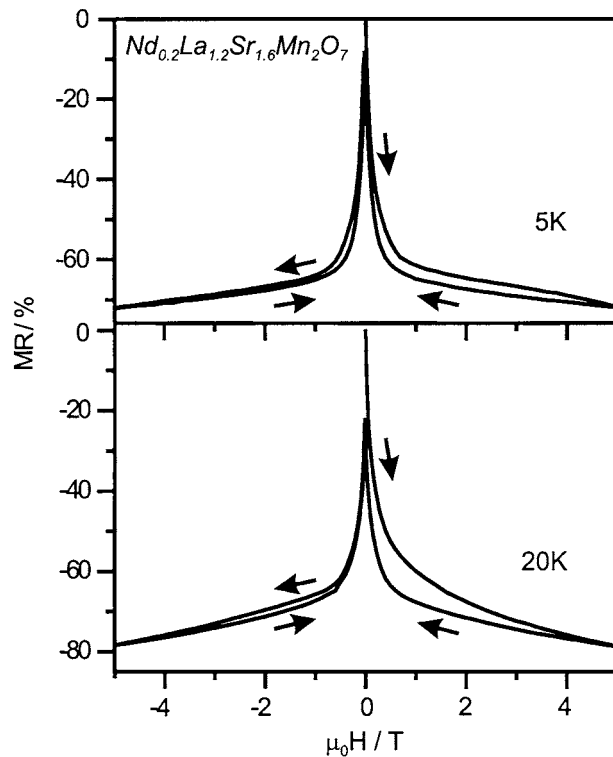


Figure 7. Field dependence of magnetoresistance of $\text{Nd}_{0.2}\text{La}_{1.2}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ at 5 K and 20 K measured after zero-field cooling.

both compositions showing an 'afm' ordering, a second peak of the MR ratio has been observed at low temperatures. Concerning $\text{Nd}_{0.2}\text{La}_{1.0}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$, MR_{max} is 14% higher than the value obtained by Zhang *et al* [5], which might be attributed to the higher density of our sample.

The field dependences of magnetoresistance of $\text{Nd}_{0.2}\text{La}_{1.2}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ and $\text{La}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ at low temperatures are drawn in figures 7 and 8. A large magnetoresistance has been found in magnetic fields of $H < 0.5$ T where the spontaneous magnetic moments of the grains align. (Both compounds, though essentially antiferromagnetic, also show a ferromagnetic contribution in their magnetization loops (figure 5, and [23]), indicating an ordered canted structure with a spontaneous magnetic moment for the Mn spins.) Aligning the grains' magnetization vectors leads to an increase of the spin-polarized transport through the grain boundaries which are present in our ceramic samples. Thus, grain boundary transport causes a contribution to the MR [24]. However, an additional MR effect results from the improved interbilayer transport due to the metamagnetic transition from the afm to the fm spin structure. The two parts of the MR can be separately observed on the first branches of $\text{MR}(H)$ curves of $\text{La}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ in figure 8. If the field of 5 T has been applied, only the grain boundary effect being typical for the ferromagnetic state remains, corresponding to the stability of the fm state at low temperature observed in the magnetization loops (figure 5). For $\text{Nd}_{0.2}\text{La}_{1.2}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$, the lower value of the critical field for the metamagnetic transition produces a superposition of both MR effects at $T < T_N$. However, a grain boundary MR below 30%, probably less, can be estimated [23].

Comparing the slightly Nd-substituted samples with the corresponding La compounds, a pronounced shift to a lower Curie temperature T_C occurs for all compositions, which indicates

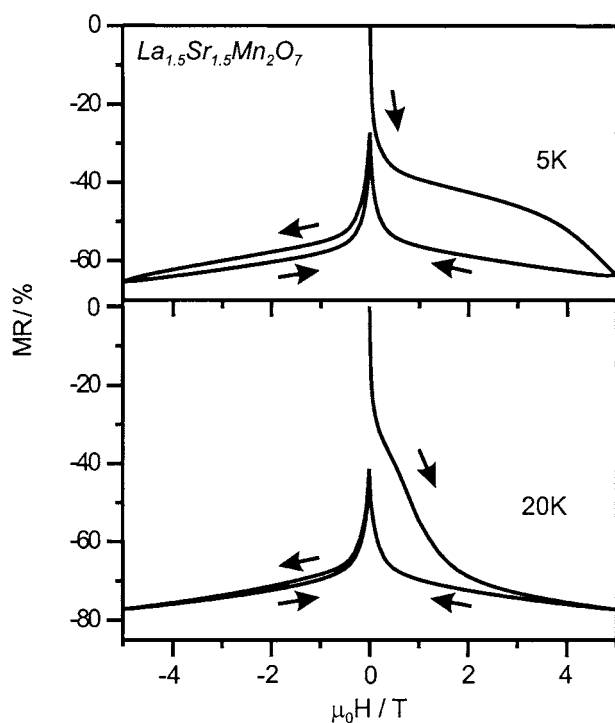


Figure 8. Field dependence of magnetoresistance of $\text{La}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ at 5 and 20 K measured after zero-field cooling.

a weakening of the ferromagnetic ordering for the Nd-substituted samples. Zhang *et al* [4] discussed, for the solid solution series of the composition $\text{Nd}_z\text{La}_{1.2-z}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$, mostly lattice effects for samples with $z < 0.6$. They mentioned that the influence of a decreasing Mn–O–Mn bond angle which is observed for perovskites resulting from decreasing atomic radius may also be of relevance in the bilayer phases. The second effect is the lengthening of the apical Mn–O bond distance (the unshared oxygen). The influence of lattice distortions on the magnetic ordering has also been described by Moritomo *et al* [13] for $(\text{La}_{1-z}\text{Nd}_z)_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ and Akimoto *et al* [8] for $(\text{La}_{1-z}\text{Nd}_z)_{1.2}(\text{Sr}_{1-y}\text{Ca}_y)_{1.8}\text{Mn}_2\text{O}_7$. The distortion of the MnO_6 octahedra is considered with respect to the splitting and occupation of the e_g orbitals.

Furthermore, the influence of the Nd moments which interact with $\text{Mn}^{3+}/\text{Mn}^{4+}$ spins is discussed in the literature [5, 19].

However, a significant change of the Mn–O–Mn bond angle from 180° does probably not occur in the bilayer phases. No deviations from the tetragonal symmetry of the lattice have been found in our samples, which is expected in case of a pronounced reduction of this bond angle. Furthermore, structural investigations of the bilayer compounds under internal pressure (chemical substitution with metal atoms of lower atomic radius) [9] or under external pressure [10] also revealed an almost constant bond angle near 180° with changing composition or pressure.

The observed shortening of the a axis (figure 1) indicates a reduced Mn–O bond length in [100]. To preserve the bond-valence sum of Mn, an increase of a Mn–O distance in the c direction follows, despite the observed reduced length of the c axis. It is generally found that the apical bond distance Mn–O (unshared oxygen) is increased with internal pressure [8, 9, 25],

leading to a weakening of the interaction between adjacent bilayers. On the other hand, for a slight Nd substitution in $(\text{La}_{1-z}\text{Nd}_z)_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ an increase of the apical Mn–O distance within the bilayer has been observed [8]. As a general tendency, an increasing difference between the transition temperatures of corresponding La- and Nd-containing samples with decreasing Sr content from 16 K for $\text{La}_{0.8}\text{Nd}_{0.2}\text{Sr}_{2.0}\text{Mn}_2\text{O}_7$ to 50 K for $\text{La}_{1.2}\text{Nd}_{0.2}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ can be derived from our data. This is correlated to the increasing c/a ratio of the lattice parameters (figure 1), leading to the conclusion that the elongation of the Mn–O₆ octahedra is the main feature which influences T_C in our samples.

Obviously, the interbilayer distance strongly affects the kind of magnetic ordering. For the compounds $\text{La}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ and $\text{La}_{1.5}\text{Ca}_{1.5}\text{Mn}_2\text{O}_7$ [26, 27] the influence of the lattice becomes obvious: The c axis of the Ca compound is about 1.04(1) Å shorter compared to the corresponding Sr compound. The resulting shorter distance between the bilayers completely suppresses the antiferromagnetism and leads to a Curie temperature of ~200 K. This conclusion is consistent with the results obtained for $\text{La}_{1.2}(\text{Sr}_{1-y}\text{Ca}_y)_{1.8}\text{Mn}_2\text{O}_7$ showing a reduced T_C for $y = 0.2$ and the occurrence of afm ordering with higher Ca content y [8].

The participation of the Nd spins in magnetic ordering of $\text{Nd}_{1.0}\text{Sr}_{2.0}\text{Mn}_2\text{O}_7$ depends on the lattice site as has been shown by Battle *et al* [19]: An antiferromagnetic interbilayer ordering of the Nd moments occurs below 28 K between the rock salt layers, whereas the Nd spins on the perovskite blocks are magnetically frustrated. A contribution of Nd moments to *ferromagnetic* ordering in our samples can be derived from the temperature dependence of magnetization: the value of magnetization M_S at 20 K of the compositions $\text{Nd}_{0.2}\text{La}_{1.8-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ with $x = 0.3$ and 0.4 is larger than that of the La compounds with the same doping level (table 3). Furthermore, an upward curvature of the M – T curve of $\text{Nd}_{0.2}\text{La}_{1.0}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ can be observed below 30 K (figure 3(a)).

Acknowledgments

The authors thank Mrs W Höppner for preparative help. This work is part of a research project supported by the SMWK (Sächsisches Ministerium für Wissenschaft und Kunst) and a personal grant (KD) also from SMWK. For financial assistance, the Fonds der Chemischen Industrie is gratefully acknowledged. This work was also supported by DFG (SFB 422).

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