

# Spin-Reorientation Transition during Isoelectron Substitution in Two-Layer Manganites $(\text{La}_{1-z}\text{Pr}_z)_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$

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The transport, magnetic, and thermal properties of single crystal two-layer manganites of the Ruddlesden–Popper series  $(\text{La}_{1-z}\text{Pr}_z)_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$  ( $z = 0.1$  or  $0.4$ ) were studied. The compounds exhibit the colossal negative magnetoresistance effect in the region of a transition into a ferromagnetic state. Upon the isoelectron substitution of  $\text{Pr}^{3+}$  for  $\text{La}^{3+}$ , the Curie temperature decreases, while the easy magnetization axis rotates from the  $ab$  plane to the  $c$  axis. The observed effect is related to a change in the occupancy of  $d_{x^2-y^2}$  and  $d_{3z^2-r^2}$  orbitals as a result of stretching of the  $\text{MnO}_6$  octahedra. © 2001 MAIK “Nauka/Interperiodica”.

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In the Ruddlesden–Popper series of metal oxide compounds [1] with the general formula  $[(\text{RE},\text{AE})\text{MnO}_3]_n(\text{RE},\text{AE})\text{O}$  (where RE stands for rare-earth ions and AE, for the alkaline-earth ions), the effect of colossal negative magnetoresistance was studied for the most part in three-dimensional perovskites of the  $(\text{RE},\text{AE})\text{MnO}_3$  type ( $n = \infty$ ) [2, 3]. The discovery of the colossal negative magnetoresistance in  $[\text{La}_x\text{Sr}_{1-x}\text{MnO}_3]_2(\text{La}_x\text{Sr}_{1-x}\text{O})$  with  $x = 0.4$  [4] has drawn the attention of researchers to the Ruddlesden–Popper compounds with  $n = 2$ .

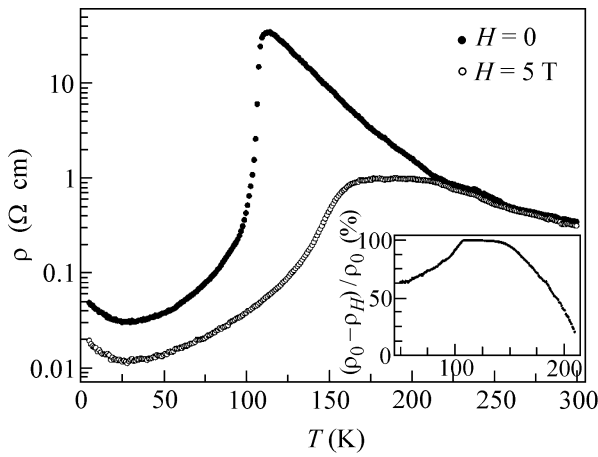
In the crystal structure of these compounds, the double perovskite layers  $[(\text{La},\text{Sr})\text{MnO}_3]_2$  in the  $ab$  plane are separated by the  $(\text{La},\text{Sr})\text{O}$  layers in the  $c$  direction. The ratio of the rare-earth ( $\text{La}^{3+}$ ) and alkaline-earth ( $\text{Sr}^{2+}$ ) ions determines the content of trivalent ( $\text{Mn}^{3+}$ ) and tetravalent ( $\text{Mn}^{4+}$ ) manganese ions. With decreasing temperature,  $[\text{La}_x\text{Sr}_{1-x}\text{MnO}_3]_2(\text{La}_x\text{Sr}_{1-x}\text{O})$  compounds exhibit magnetic ordering the type of which depends on the  $x$  value [5]. In the same layer of  $\text{MnO}_6$  octahedra, the interaction is always ferromagnetic, but the ordering of layers within one bilayer may vary including antiferromagnetic, oblique antiferromagnetic, and ferromagnetic types.

The compound  $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$  (corresponding to  $x = 0.4$ ) exhibits the transition into a ferromagnetic state of the easy plane type at  $T_C \sim 120^\circ\text{C}$  [6]. The low (in comparison with the three-dimensional perovskites) value of the Curie temperature in the two-layer manganites is due to a lower dimensionality of the magnetic

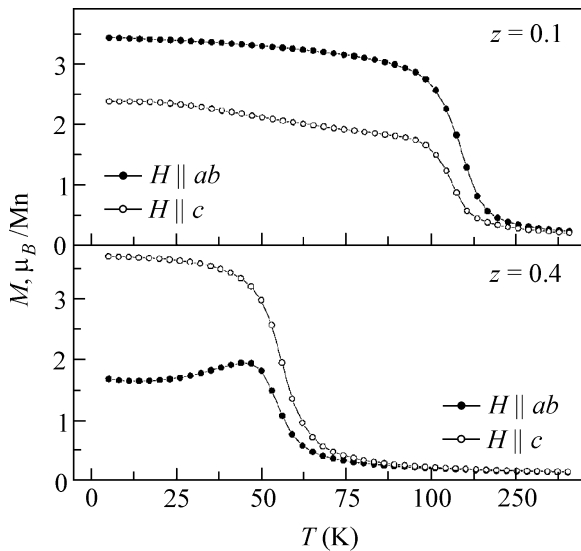
subsystem. The colossal negative magnetoresistance observed in the vicinity of  $T_C$  is characterized by a considerable anisotropy: the electron transport is effective in the  $ab$  plane and is hindered along the  $c$  axis.

At a fixed ratio of the  $\text{La}^{3+}$  and  $\text{Sr}^{2+}$  ions, a significant effect on the transport and magnetic properties of layered manganites is produced by isoelectron substitutions at the positions of both RE and AE ions. This is explained by a difference in atomic radii of the corresponding ions that leads to a change in the  $(\text{La},\text{Sr})$  layer thickness and to distortion of the manganese–oxygen octahedra. For example, the compound  $\text{La}_{1.2}(\text{Sr}_{1-y}\text{Ca}_y)_{1.8}\text{Mn}_2\text{O}_7$  exhibits a change in the ordering type from ferromagnetic to antiferromagnetic when  $\text{Ca}^{2+}$  ions (with an atomic radius of  $1.06 \text{ \AA}$ ) are substituted for  $\text{Sr}^{2+}$  ( $1.27 \text{ \AA}$ ) so that the  $y$  value increases [7].

The aim of our experiments was to study the effect of isoelectron substitution at the rare-earth ion position on the properties of  $(\text{La}_{1-z}\text{Pr}_z)_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ . For this purpose, the  $\text{La}^{3+}$  ions (with an atomic radius of  $1.22 \text{ \AA}$ ) were replaced by  $\text{Pr}^{3+}$  ( $1.06 \text{ \AA}$ ). It was established that this substitution significantly affects the transport, magnetic, and thermal properties of  $(\text{La}_{1-z}\text{Pr}_z)_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$  single crystals. The single crystals with  $x = 0.1$  and  $0.4$  were grown by the floating zone technique. These crystals possess a bulk-centered tetragonal structure belonging to the space symmetry group  $I4/mmm$ . The electric resistance was measured by a standard four-point-probe method and the magnetic properties were studied using a SQUID magnetometer, and the heat



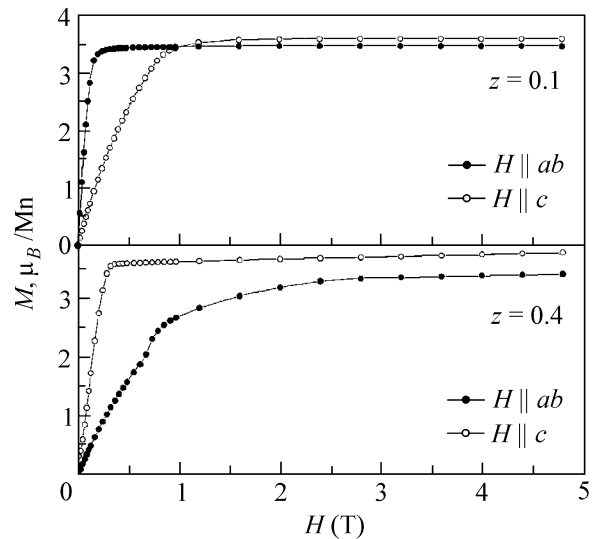
**Fig. 1.** The temperature dependence of the electric resistance  $\rho$  of a  $(\text{La}_{1-z}\text{Pr}_z)_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$  single crystal with  $z = 0.1$  measured in the  $ab$  plane with and without an applied magnetic field  $H$ . The inset shows the temperature variation of the negative magnetoresistance  $(\rho_0 - \rho_H)/\rho_0$ .



**Fig. 2.** The temperature dependence of the magnetization  $M$  of the  $(\text{La}_{1-z}\text{Pr}_z)_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$  single crystals with  $z = 0.1$  and  $0.4$  measured with the magnetic field ( $H = 0.5$  T) applied in the  $ab$  plane and along the  $c$  axis.

capacity was measured with a quasiadiabatic microcalorimeter. All these physical characteristics were measured in the temperature range from 4 to 300 K.

Figure 1 shows the temperature dependence of the resistance  $\rho$  of a  $(\text{La}_{0.9}\text{Pr}_{0.1})_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$  single crystal ( $z = 0.1$ ) measured in the  $a$  direction without an applied magnetic field and in a field of 5 T. In the absence of the magnetic field, the initial semiconductor-like variation of the resistance changes for a decrease at  $T_C = 107$  K. Some increase in the sample resistance at low temperatures ( $T < 25$  K) can be related to the scattering on magnetic impurities. When the magnetic field is applied, a



**Fig. 3.** The field dependence of magnetization of the magnetization  $M$  of the  $(\text{La}_{1-z}\text{Pr}_z)_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$  single crystals with  $z = 0.1$  and  $0.4$  measured at  $T = 5$  K with the magnetic field ( $H = 0.5$  T) applied in the  $ab$  plane and along the  $c$  axis.

maximum in the temperature dependence of the sample resistance shifts toward higher temperatures, the negative magnetoresistance  $(\rho_0 - \rho_H)/\rho_0$  in the phase transition region reaching almost 100%.

Figure 2 shows the temperature dependence of the magnetization  $M$  of the  $(\text{La}_{0.6}\text{Pr}_{0.4})_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$  ( $z = 0.1$ ) and  $(\text{La}_{0.6}\text{Pr}_{0.4})_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$  ( $z = 0.4$ ) single crystals measured for the magnetic field applied in the  $ab$  plane and along the  $c$  axis. A sharp increase in the magnetization, typical of the transition into a ferromagnetic state, is observed on decreasing the temperature to  $T \sim 107$  K ( $z = 0.1$ ) and  $T \sim 65$  K ( $z = 0.4$ ). Note that, in the sample with  $z = 0.1$ , the magnetization along the  $a$  axis exceeds that in the  $c$  direction, whereas a reverse situation is observed in the sample with  $z = 0.4$ .

The experimental curves of  $M(T)$  are consistent with the field dependence of magnetization measured at  $T = 5$  K (Fig. 3). As is seen, the sample with  $z = 0.1$  occurs in a ferromagnetic state of the easy plane type, while the sample with  $z = 0.4$  exhibits the easy axis state. The saturation of magnetization in both cases is attained at a field strength of about 1 T, whereby the magnetization reaches a level of  $\sim 3.6\mu_B$ .

Figure 4 shows the plots of the heat capacity versus temperature for the  $(\text{La}_{0.9}\text{Pr}_{0.1})_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$  and  $(\text{La}_{0.6}\text{Pr}_{0.4})_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$  single crystals, which confirm the presence of a phase transition at  $T = 107$  K ( $z = 0.1$ ) and  $T = 65$  K ( $z = 0.4$ ). At low temperatures, the heat capacity of the samples studied contains linear and cubic components with respect to the temperature:  $C = \gamma T + \beta T^3$ . A linear contribution to the heat capacity can be related both to the conduction electrons and ferromagnetic magnons in the two-dimensional magnetic

Characteristics of  $(\text{La}_{1-z}\text{Pr}_z)_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$  manganites with  $z = 0.1$  and  $0.4$

	$T_C$ , K	$\gamma$ , mJ/(mol K <sup>2</sup> )	$\beta$ , mJ/(mol K <sup>4</sup> )	$\Theta$ , K	$\Delta S_{\text{magn}}$ , mJ/(mol K <sup>2</sup> )
$(\text{La}_{0.9}\text{Pr}_{0.1})_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$	107	50	0.344	409	1
$(\text{La}_{0.6}\text{Pr}_{0.4})_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$	65	56	0.449	385	0.9

subsystem of  $(\text{La}_{1-z}\text{Pr}_z)_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$  [8], while the cubic term is due to phonons. The  $\gamma$  and  $\beta$  coefficients for the samples with  $z = 0.1$  and  $0.4$  are given in the table. The table also presents the values of the Debye temperature  $\Theta_D$  determined using the relationship  $\beta = 12\pi^4 Rv/5\Theta_D^3$ , where  $R$  is the universal gas constant and  $v$  is the number of atoms per formula unit. In a broad range of temperature, except the phase transition region, the phonon contribution to the heat capacity is described by three Einstein modes. This circumstance allows a part of the entropy  $\Delta S_{\text{magn}}$  related to the magnetic system ordering to be separated. The corresponding values are also indicated in the table.

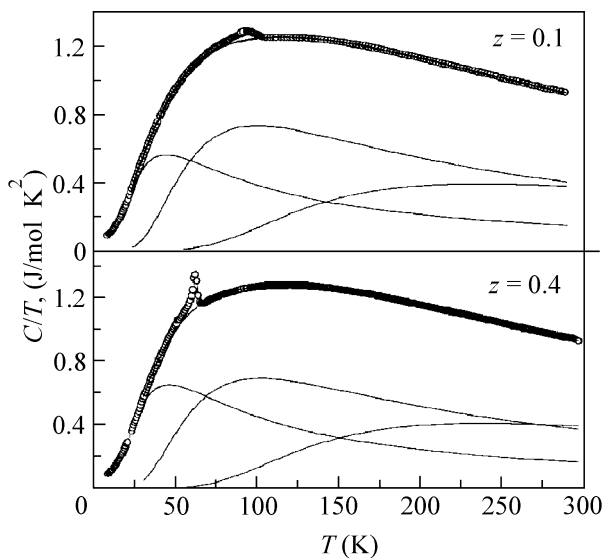
The experimental data presented above indicate that an increase in the Pr content is accompanied by a decrease in the temperature of ferromagnetic ordering, while the magnetization vector exhibits reorientation from the  $ab$  plane to the  $c$  axis. This behavior is related to the fact that the isoelectron substitution of  $\text{Pr}^{3+}$  for  $\text{La}^{3+}$  decreases the (La-Pr,Sr) layer thickness and increases the distance from  $\text{Mn}^{3+}/\text{Mn}^{4+}$  ions to the apical  $\text{O}^{2-}$  ions. Stretching of the  $\text{MnO}_6$  octahedra in the  $c$  direction leads to a change in the order of the partly filled  $e_g$  orbitals. In  $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ , the  $3d_{x^2-y^2}$  orbital

lies below the  $3d_{3z^2-r^2}$  orbital [5]; Apparently, the same situation takes place in  $(\text{La}_{0.9}\text{Pr}_{0.1})_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ . Predominant filling of the  $3d_{x^2-y^2}$  orbital favors the electron transport in the  $ab$  plane and accounts for a rather high temperature of the ferromagnetic ordering due to the exchange involving the conduction electrons. For  $z = 0.4$ , the stretching of the  $\text{MnO}_6$  octahedra in the  $c$  direction favors predominant filling of the  $3d_{3z^2-r^2}$  orbital. In this case, the electron transport in the  $ab$  plane is hindered. This, together with the absence of electron transport along the  $c$  axis, leads to a decrease in contribution of the conduction electrons to the exchange and, hence, to the corresponding decrease in the temperature of ferromagnetic ordering.

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**Fig. 4.** The temperature dependence of the heat capacity of the  $(\text{La}_{1-z}\text{Pr}_z)_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$  single crystals with  $z = 0.1$  and  $0.4$ . Thin solid curves show the of three Einstein modes approximating the phonon contribution.

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