ORDER, DISORDER, AND PHASE TRANSITION IN CONDENSED SYSTEM

Two-Dimensional Antiferromagnetic Correlations in an $La_{1.4}Sr_{1.6}(Mn_{0.9}Co_{0.1})_2O_7$ Single Crystal

A. A. Bykov[a]*, **I. A. Zobkalo**[a,b], **A. A. Dubrovskii**[c], **O. P. Smirnov**[a], **S. E. Nikitin**[d],
K. Yu. Terent'ev[c], **S. V. Gavrilov**[a], and **K. A. Shaikhutdinov**[c]

[a] *Konstantinov St. Petersburg Nuclear Physics Institute, Russian Academy of Sciences,
Gatchina, Leningrad oblast, 188300 Russia*
[b] *St. Petersburg State University, St. Petersburg, 198504 Russia*
[c] *Kirensky Institute of Physics, Siberian Branch, Russian Academy of Sciences, Krasnoyarsk, 660036 Russia*
[d] *Max Plank Institute for Chemical Physics of Solids, Dresden 01187 Germany*
*e-mail: redi87@bk.ru
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Abstract—The temperature and field dependences of the magnetization, the electrical resistivity, and the magnetostriction of bilayer lanthanum manganite $La_{1.4}Sr_{1.6}Mn_2O_7$ single crystals and cobalt-doped $La_{1.4}Sr_{1.6}(Mn_{0.9}Cu_{0.1})_2O_7$ are measured. The magnetostriction of the cobalt-doped compound increases as compared to the initial $La_{1.4}Sr_{1.6}Mn_2O_7$ compound, and the magnetization and the magnetoresistance of the former compound change substantially. Powder and single-crystal neutron diffraction patterns are used to detect ferromagnetic ordering in $La_{1.4}Sr_{1.6}(Mn_{0.9}Co_{0.1})_2O_7$ at a temperature below $T_C \sim 45(2)$ K, and this ordering coexists with antiferromagnetic correlations, which develop at temperatures below $T_C \sim 80(5)$ K.

INTRODUCTION

As $RMnO_3$ manganites with a perovskite structure, bilayer $R_{2-2x}Sr_{1+2x}Mn_2O_7$ manganites exhibit colossal magnetoresistance; as a result, they have been attracted particular interest over decades [1–4]. However, in contrast to the $RMnO_3$ compounds (which have a very anisotropy of the magnetic and transport properties), the $R_{2-2x}Sr_{1+2x}Mn_2O_7$ compounds have a giant magnetoresistance anisotropy related to their layered structure, which leads to spin-dependent carrier tunneling between manganese–oxygen planes along crystallographic axis c in a crystal [1].

The Sr^{2+} ion in the $La_{1.4}Sr_{1.6}Mn_2O_7$ (LSMO) compound where trivalent lanthanum is doped by divalent strontium induces hole carriers in the $3d$ states of the Mn^{3+} ion, which results in the appearance of local ferromagnetism regions at the nearest Mn^{4+} ions. These regions influence the mechanisms of colossal magnetoresistance [1, 3]. This compound has tetragonal symmetry (space group $I4/mmm$), in which double layers of oxygen octahedra centered by manganese are separated by rare-earth metal (REM) layers. The results of neutron diffraction at a high pressure [5] and infrared spectroscopy [6] demonstrate at temperatures below 370 K the presence of two-dimensional ferromagnetic correlations in the double planes of the compound, which are caused by a double exchange between manganese ions $Mn^{3+}-Mn^{4+}$ through oxygen in the pairs of the nearest planes [3, 7–9]. In the temperature range from 100 to 60 K, a three-dimensional antiferromagnetic (AF) order, which is caused by an antiferromagnetic interaction between the double ferromagnetic planes, is detected; at temperatures below 80 K, the system transforms into a ferromagnetic (FM) state [3, 4, 10]. As was shown in [4], the AF and FM states coexist over the entire temperature range of FM ordering: an LSMO single crystal was shown to consist of two crystalline phases having the same symmetry ($I4/mmm$) and very close lattice parameters. The authors of [4] think that the coexistence of different crystalline phases does ensure the coexistence of two magnetically ordered phases in LSMO. However, this coexistence was not observed in [5], and magnetic AF and FM phases changed each other in the same crystalline phase. In any case, this behavior points to the sensitivity of both the crystalline and magnetic systems in LSMO to very small changes in the composition near the sharp boundary of the composition phase diagram, including a change in the sign of the exchange interaction between the MnO_2 bilayers. For example, the magnetic phase diagram of the $La_{2-2x}Sr_{1+2x}Mn_2O_7$ compounds is very sensitive to small changes in parameter x near $x = 0.30$. The scatter of the ordering temperatures is likely to be caused by certain differences in strontium substitution parameter x from 0.30.
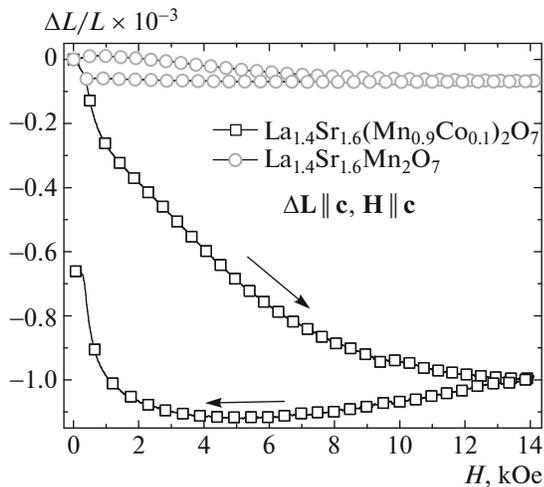
Fig. 1. Field dependences of the magnetostrictions of the compositions under study at a temperature $T = 4.2$ K. The arrows indicate the direction of changing a magnetic field.

It is known [8, 9, 11−16] that substitution in the manganese positions of the system can also exist, which was demonstrated for all $3d$ elements and zinc. This substitution also strongly affects the magnetotransport properties of the system. For example, the authors of [15] studied a series of polycrystalline $La_{1.4}Sr_{1.6}(Mn_{1-x}Co_x)_2O_7$ ($x = 0{-}0.2$) samples. However, data on studying single crystals samples of this composition in the limits of cobalt solubility in them are unavailable. The purpose of this work is to investigate the macroscopic properties and the magnetic structure of single-crystal $La_{1.4}Sr^{1.6}(Mn_{1-x}Co_x)_2O_7$ ($x = 0.1$; LSMCO) as functions of cobalt doping in the manganese position.

EXPERIMENTAL

$La_{1.4}Sr_{1.6}(Mn_{1-x}Co_x)_2O_7$ ($x = 0, 0.1$) single crystals were synthesized by optical zone melting on the FZ-4000 (Crystal System, Japan) setup in the Kirensky Institute of Physics. The crystal growth was performed in an oxygen atmosphere at a rate of 5 mm/h, normal pressure, and a relative rate of rod rotation of 30 rpm. For synthesis, we prepared polycrystalline samples with a cobalt content $x = 0.1, 0.2$, and 0.3. However, it was found during crystal growth that single crystals formed only at $x = 0.1$. At higher cobalt concentrations, crystal growth became unstable and the grown samples decomposed in air within a weak. Thus, for a further analysis, we only used the $La_{1.4}Sr_{1.6}(Mn_{0.9}Co_{0.1})_2O_7$ sample, which has been retaining its integrity over several years.

X-ray powder diffraction and X-ray energy dispersive microanalysis were carried out in the Resource Center of St. Petersburg State University on Rigaku Miniflex II and Zeiss Merlin devices, respectively, and demonstrated correspondence to the nominal compositions. Magnetization and electrical resistivity curves were measured with a PPMS-6000 device (Kirensky Institute of Physics), and magnetostriction measurements were performed in the International Laboratory of High Magnetic Fields and Low Temperatures (Wroclaw, Poland). Neutron diffraction experiments were carried out on a PD powder diffractometer and DPN polarized neutron diffractometer (channels 1 and 6 of the VVR-M reactor at the Konstantinov St. Petersburg Nuclear Physics Institute, respectively).

RESULTS AND DISCUSSION

The measurements performed at the liquid-nitrogen temperature showed a substantial increase in the relative magnetostriction $\Delta L/L(H)$ for doped compositions LSMCO as compared to LSMO (see Fig. 1). The authors of [17, 18] related the change in the magnetostriction induced by doping in the lanthanum position to the influence of the magnetic subsystem of REMs. Therefore, the change in the magnetostriction properties upon cobalt doping in a position inside the magnetic layers rather than between them is unexpected.

Figure 2 shows the dependences of electrical resistivity ρ_c measured along crystallographic axis c, the magnetization, and the inverse magnetic susceptibility of the compositions under study in a magnetic field and without it. The electrical resistivity peak of LSMCO is seen to be strongly broadened as compared to LSMO; that is, the metal−insulator transition, which was attributed to the transformation of an AF dielectric matrix into a conducting metallic matrix [1, 2], is smoother in the doped compound. Moreover, this transition takes place at a lower temperature. Both compositions (LSMO, LSMCO) exhibit a colossal magnetoresistance, which manifests itself in a substantial decrease in the electrical resistivity in a magnetic field. An applied magnetic field of 50 kOe shifts this transition toward high temperatures. The rapid increase in the electrical resistivity in LSMCO when temperature decreases below approximately 30 K, which is not detected in LSMO, is also worth noting. The peak of the electrical resistance measured along axis c ($\mathbf{R} \parallel \mathbf{c}$) in LSMO at 110 K is likely to be caused by the fact that the ferromagnetic correlation radius reaches a certain critical value, which ensures a current; as a result, the semiconductor behavior of the temperature dependence of electrical resistance changes into metallic behavior. The authors of [4, 5] noted the existence of a ferromagnetic order in LSMO in the temperature range 60−105 K, whereas the resistance peak is located at 110 K, i.e., above this range. In our case, the curve of the resistance of LSMO has a small peak at $T \approx 70{-}80$ K, which is thought to be related to the fact that the maximum ordering moment is reached in the AF phase.
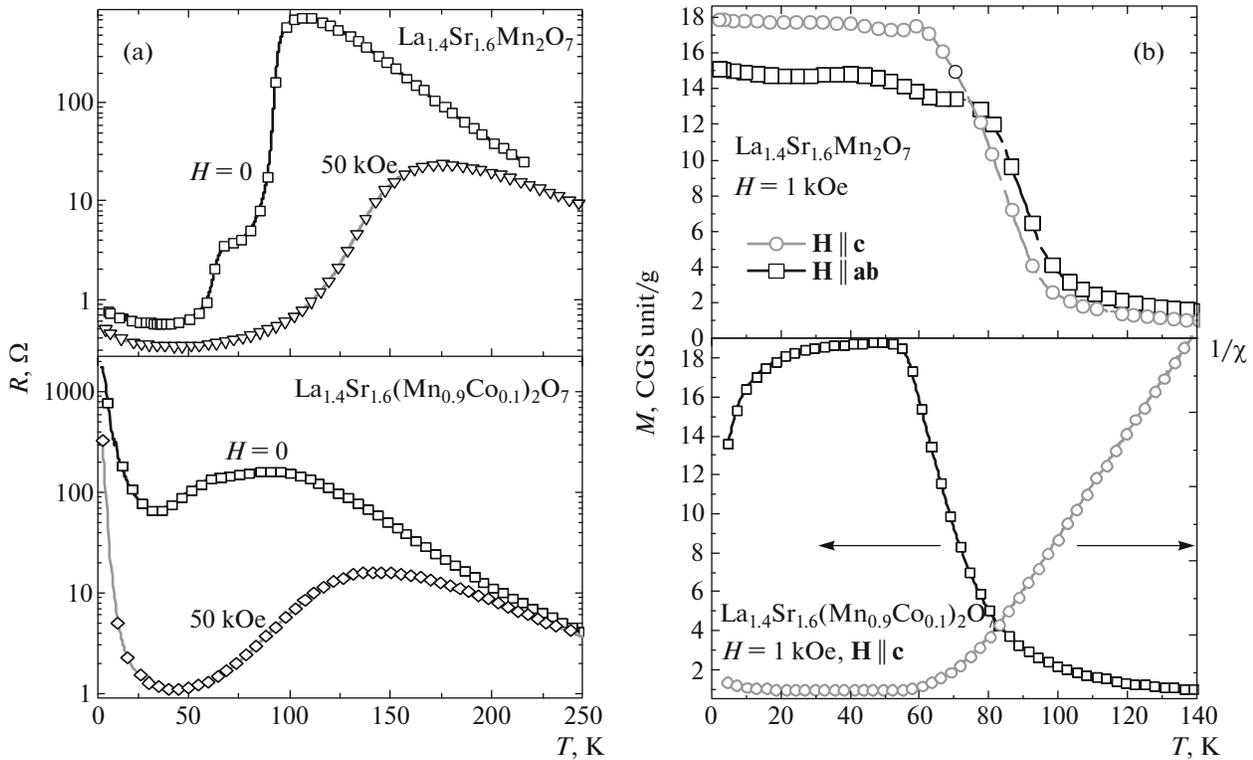
Fig. 2. Temperature dependences of the electrical resistance (along axis *c*), the magnetic moment, and the inverse magnetic susceptibility of the compositions under study.

The results of magnetic measurements also demonstrated significant differences in the behavior of the magnetizations of LSMO and LSMCO (Fig. 2b). As the temperature decreases, the magnetization of LSMO increases starting from $T \sim 100$ K, which can also be related to the fact that the ferromagnetic correlations reach a critical value (as in the case of the beginning of decrease in the electrical resistance). The magnetization of LSMCO exhibits similar behavior but at lower temperatures. A decrease in the ferromagnetic ordering temperature was detected in our neutron measurements. However, the behavior of magnetization in the doper compound changed as compared to LSMO, where the magnetization became maximal and remained constant down to the very low temperatures: the magnetization decreased when the temperature decreased to $T \sim 30$ K. Note that a paramagnetic character of the magnetic susceptibility is observed at temperatures above 80 K, and a deviation from the linear dependence $1/\chi$ takes place when a temperature $T \sim 80$ K is approached. The temperature dependence of resistance also has a maximum at this temperature; that is, a metal–insulator transition occurs. At low temperatures (below 30 K), the magnetic susceptibility and the magnetic moment of the LSMCO compound change their behavior into AF behavior.

Figure 3 shows the field dependences of the magnetoresistance measured along axis *c* and the magnetic

moment at temperatures of 2 and 4.2 K. A positive magnetoresistance is observed at low fields in the field dependence of the magnetoresistance of LSMO when a magnetic field is applied along the *ab* plane, and this magnetoresistance is discussed in more detail in [19]. The appearance of a positive magnetoresistance is attributed to the decrease in the hopping integral that is induced by an increase in the angle between the magnetic moments of manganese atoms in neighboring double layers. In high fields, this angle begins to decrease and the resistance begins to behave similarly to the curve plotted for a field along the easy magnetization axis; that is, it decreases logarithmically. A positive magnetoresistance was not observed in LSMCO and the decrease is sharper and takes place in fields higher than 40 kOe. This difference is associated with a harder magnetic nature of LSMCO, which is seen in the field dependences of magnetization. This specific feature also influences the behavior of the magnetoresistance of LSMCO measured along and across the easy magnetization axis. As is seen in the temperature dependences of the magnetization of LSMCO (Fig. 2), the field dependences of LSMCO also demonstrate a substantial anisotropy in the system. A higher coercive force for the easy plane than along the easy magnetization axis also leads to a sharper decrease in the resistance in higher fields for the magnetization curve. The high magnetic rigidity of
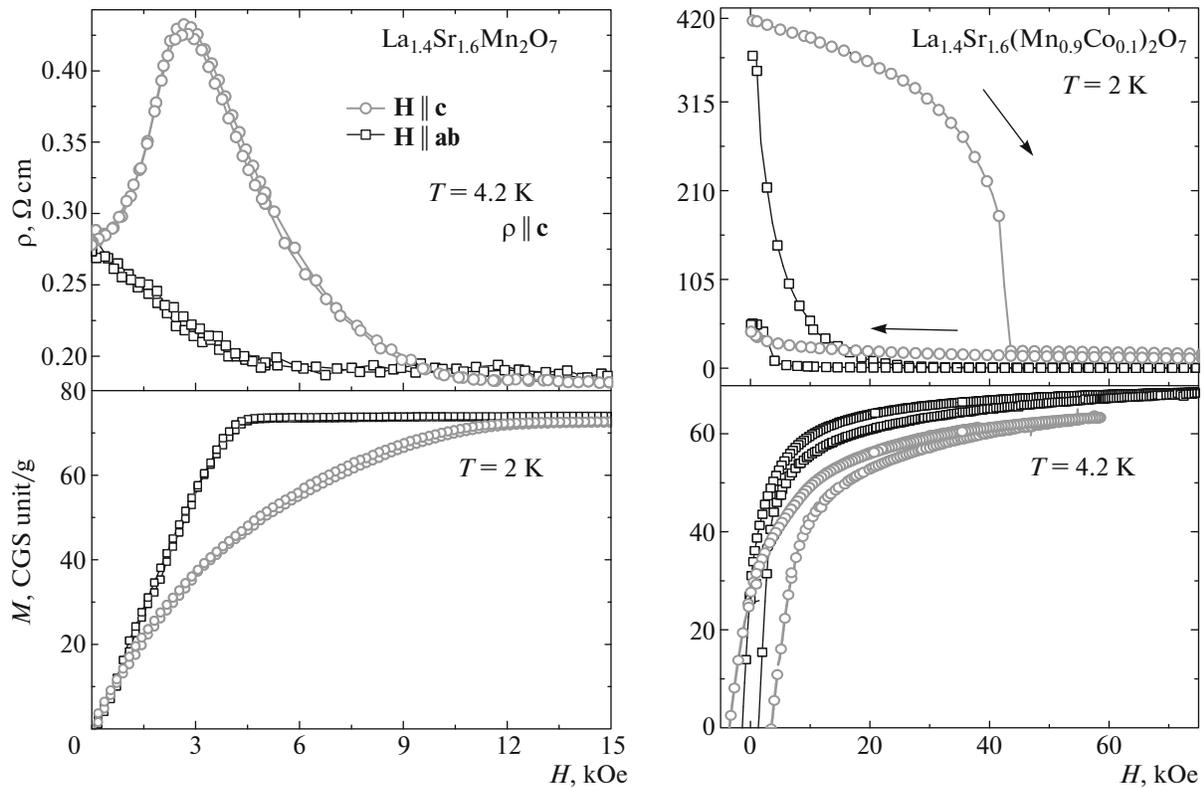
Fig. 3. Field dependences of the magnetoresistance and the magnetization at low temperatures along and across the easy magnetization axis for the compositions under study.

LSMCO also results in the fact that its forward and backward magnetization curves coincide in fields higher than 40 kOe, and the forward and backward magnetoresistance curves also coincide with each other in these fields. The curves of LSMO obtained for a magnetic field applied along and across the easy axis coincide in the fields that are higher than 10 kOe.

To reveal the nature of this change in the properties of cobalt-doped LSMCO, we performed neutron diffraction investigations. Their results demonstrate that the magnetic properties of LSMCO and LSMO are similar. The powder and single-crystal neutron diffraction patterns of these compounds exhibit an increase in the intensities of the (101), (103), and (105) peaks at a temperature below 45(2) K, which should be attributed to the appearance of an FM order. Figure 4a (at the top) shows the temperature dependences of the (105) peak intensity obtained for the LSMCO single crystal and the magnetic moment of manganese (M) calculated from the powder diffraction data. The calculations demonstrate that the magnetic moment at manganese ions is directed along axis c, so that the value and the direction of the magnetic moment in the ferromagnetic LSMCO phase correlate well with the results obtained for LSMO [4, 5].

In contrast to the plain LSMO compound (where an AF order was detected [4, 5]), an AF was not observed in LSMCO. It is important that significant diffuse scattering, the intensity of which increases with decreasing temperature, is seen near the positions of forbidden nuclear reflections at temperatures below 80(5) K (Fig. 4a). Figure 4b shows the map of neutron scattering in the ($0kl$) plane at a temperature $T = 1.5$ K. The peaks in forbidden and "non-Bragg" positions belong to the contribution of neutrons with a wavelength $\lambda/2$ and to scattering by impurities, respectively. The presence of narrow discontinuous "rods" along axis c^* (indicated by the arrow) at this temperature is noteworthy. The appearance of such narrow rods in our case should be attributed to the existence of two-dimensional magnetic ordering in the ab plane, and weak correlations between the FM bilayers cause diffuse magnetic scattering of this type. Taking into account the results from [4, 5], we can conclude that these correlations serve as a precursor of the three-dimensional AF ordering that is characteristic of LSMO and is not achieved in LSMCO (at least, down to the very low measurement temperatures); therefore, they can be considered as AF correlations. Figure 2a (at the bottom) shows the temperature dependences of
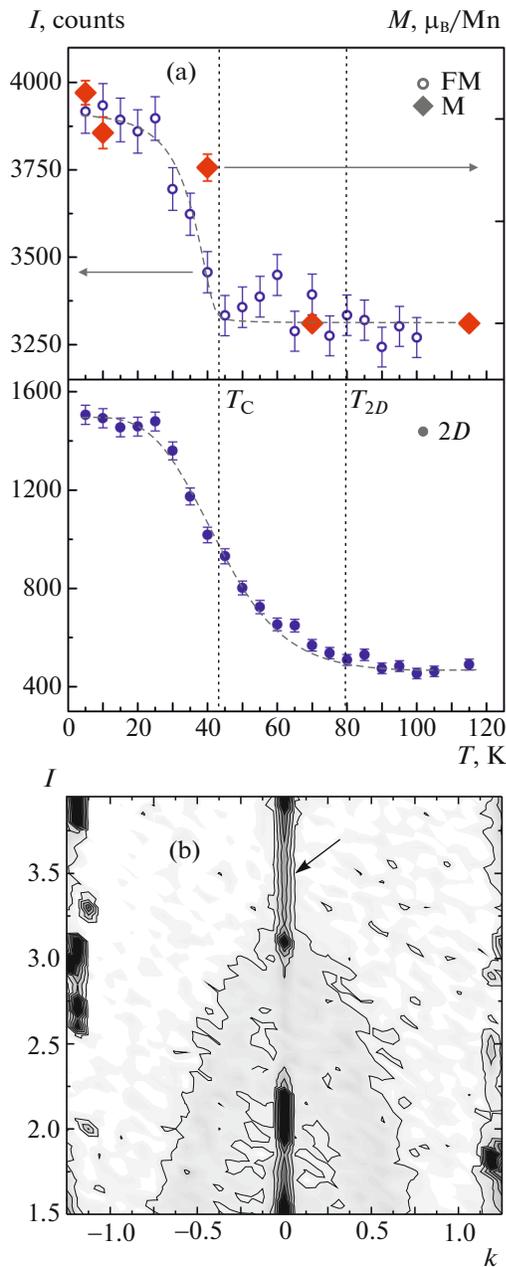
Fig. 4. (Color online) (a) Temperature dependences of the neutron scattering in LSMCO: (at the top) dependence of the (105) reflection intensity combined with the dependence of the ferromagnetic moment component M_z calculated from powder neutron diffraction data; (at the bottom) temperature dependence of the diffuse scattering intensity near (001). (b) Neutron scattering map in the (0kl) plane at $T = 1.5$ K. The arrow indicates a rod in the [001] direction.

the integrated intensities of the rods along the [00l] direction, i.e., the correlation intensity in the *ab* plane. The radius of these two-dimensional FM correlations is estimated at about 20a at $T = 1.5$ K.

Thus, our neutron diffraction experiments demonstrate that a FM order appears in LSMCO at a tem-

perature below $T_C \sim 45(2)$ K and AF correlations between the FM bilayers develop below $T_{2D} \sim 80(5)$ K. These correlations reach their maximum at a temperature of about 30 K. It is the maximum in the development of AF correlations that causes the anomalous behavior of the resistance and the magnetization in LSMCO.

CONCLUSIONS

The magnetic correlations in bilayer manganites are being extensively studied in the formation of magnetic and transport properties [1, 3, 7–9, 16, 20]. The detected substantial change in the macroscopic properties at helium temperatures is thought to be related to the appearance of such AF correlations along axis *c*. These are experimentally observed in the form of diffuse scattering near 001 reflex. The change in the interaction of pairs of magnetic planes is considered to be caused by chemical compression, as in [17–19]. Our magnetostriction measurements support this conclusion, since such changes occur when the manganese–oxygen planes are doped by cobalt. An additional influence could also be induced by the decrease in the double exchange in the CuO_2 bilayers that is caused by the doping of $La_{1.4}Sr_{1.6}Mn_2O_7$ with cobalt, which has two electrons more than manganese [13, 15]. However, we think that this influence can only decrease the magnetic ordering temperature and, correspondingly, shift the metal–insulator transition temperature in the LSMCO system toward low temperatures.

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