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Atom States and Interatomic Interactions in Perovskite-Like Oxides: XXVI.[1] Short Order in Magnetoresistive Lanthanum Manganites Doped with Various Diamagnetic Elements

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Abstract—The study of magnetic dilution of lanthanum manganites doped with alkaline-earth elements (Ca and Sr) and yttrium has shown that nonmonotonic changes in magnetic characteristics and in clustering of the manganese atom in the solid solutions are connected with the influence of two factors: the size of diamagnetic elements and the degree of ionicity of their bonds with oxygen. These factors determine the competition between ferro- and antiferromagnetic exchange between manganese atoms underlying the colossal magnetoresistance effect.

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Complex ABO_3 oxides with the perovskite structure are the subjects of elevated attention of researchers from the end of the 1960s–1970s. A possibility of practical using oxide ceramics containing diamagnetic additions resulted in the studies of perovskite-like oxides with layered structure, of Aurvillius phases, and other more complex structures. A splash of interest to canonical perovskites observed within the last years was generated mostly by two circumstances: revealing of oxygen conductivity in doped lanthanum gallates (a circumstance of utmost importance in the context of the development of SOFC technologies, oxygen sieves, etc.) and the detection of the effect of colossal negative magnetoresistance (CMR) in doped lanthanum manganites. However, the problem of the influence of the nature and concentration of doping elements on various practically important properties still remains open, and the search for optimal compositions is carried out empirically.

Functional properties of a material are known to be determined by the state of paramagnetic element atoms and the character of exchange interactions within magnetic centers, depend on the composition of a magnetoresistor. It is customary to assume that the main role in the CMR effect upon a heterovalent substitution in manganites is played by the transfer of a fraction of manganese atoms to the tetravalent state and by so-called double exchange between atoms with different valence, Mn(III)–O–Mn(IV) [2]. To optimize properties of magnetoresistors, the attempts of additional doping of manganites with diamagnetic elements are undertaken. For example, doping lanthanum manganite, $La_{0.67}A_{0.33}MnO_3$ (A is the substituting element), simultaneously with yttrium, calcium, and strontium allowed the material with the maximal CMR to be obtained [3]. This manganite has the composition $La_{2/3-x}Y_xCa_{1/3-y}Sr_yMnO_3$, in which the ratio [Ca]:[Sr]=1:1 and yttrium substitutes for 10% of lanthanum.

A decrease or an increase in the fraction of yttrium in these oxides results in an abrupt decrease in magnetoresistance. The authors of [3] associate such non-monotony in the variation of properties upon doping only with the factor of the diamagnetic particle size. From this point of view differences in the ionic radii of substituting elements may result in the distortion of perovskite lattice, which shows itself in the changes in the exchange angle between paramagnetic atoms and, as a consequence, determines the

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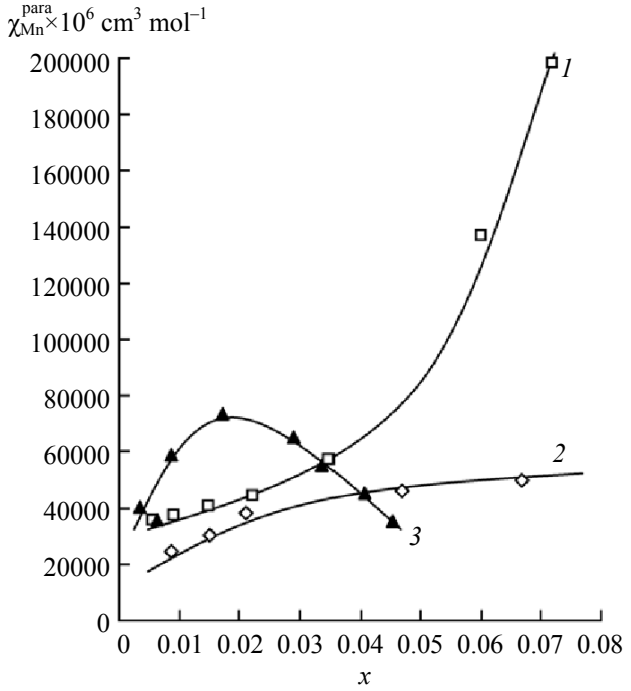


Fig. 1. Plot of paramagnetic component of magnetic susceptibility, χ_{Mn}, vs. composition at 100 K forthe systems: (*1*) xLa$_{0.33}$Ba$_{0.67}$MnO$_3$–(1–x)LaAlO$_3$; (*2*) xLa$_{0.33}$·Ca$_{0.67}$MnO$_3$–(1–x)LaAlO$_3$; (*3*) xLa$_{0.33}$Sr$_{0.67}$MnO$_3$–(1–x)LaAlO$_3$.

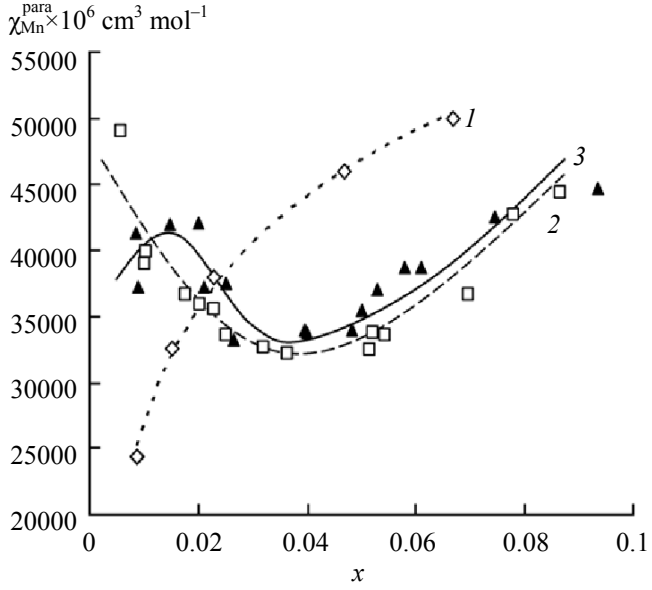


Fig. 2. Plot of magnetic susceptibility χ_{Mn} vs. composition at 100 K for the systems (*1*) xLa$_{0.33}$Ca$_{0.67}$MnO$_3$–(1–x)·LaAlO$_3$; (*2*) x(La$_{0.9}$Y$_{0.1}$)$_{0.67}$Ca$_{0.33}$MnO$_3$–(1–x)La$_{0.9}$Y$_{0.1}$AlO$_3$; (*3*) x(La$_{0.8}$Y$_{0.2}$)$_{0.67}$Ca$_{0.33}$MnO$_3$–(1–x)La$_{0.8}$Y$_{0.2}$AlO$_3$.

character of exchange interactions responsible for colossal magnetoresistance.

Since the long-range magnetic order is undoubtedly associated with short-range order interactions, with states of manganese atoms, and with interactions between the nearest neighbors, an attempt must be made to find out how the nature of a doping element and its concentration influence CMR. The answer to this question can be obtained by the magnetic dilution method. The study of magnetic properties of diluted solid solutions of isomorphous substitution makes it possible to find the state of single paramagnetic atoms and to trace the development of interatomic interactions as their concentration increases.

The previous study of magnetic dilution of lanthanum manganites doped with Ca, Sr, and Ba in lanthanum aluminate [4, 5] showed that at infinite dilution ($x\to0$) manganese atoms are in the states of single Mn(III) and Mn(IV) atoms, and the exchange interactions between them are of various character for different alkaline-earth elements incorporated into lanthanum sublattice (Fig. 1).

To find out which factors influence the effects of the short-range order in doped lanthanum manganites, we posed two problem: to carry out the magnetic dilution of manganites doped simultaneously with an alkaline-earth element (calcium or strontium) and yttrium, the content of this latter being 10 and 20 mol %; to find out how the exchange interactions in manganites vary upon simultaneous doping with calcium and strontium in various ratios.

The character of isotherms of the paramagnetic component of magnetic susceptibility χ_{Mn} (Figs. 2 and 3) for solid solutions (1) points to the fact that the pattern of magnetic dilution for the systems containing yttrium principally differs from that for manganites containing only calcium or strontium.

$$x(La_{1-y}Y_y)_{0.67}Ca(Sr)_{0.33}MnO_3 - (1-x)La_{1-y}Y_yAlO_3$$
$$(0.005 < x < 0.10;\ y = 0.10, 0.20). \qquad (1)$$

The main differences in the magnetic properties are observed in the region of the most diluted solutions, where small aggregates of manganese atoms are formed. The most important is the fact that the isotherms of the systems with various content of yttrium differ from each other.

The extrapolation of the isotherms of magnetic susceptibility of calcium-containing manganites to the

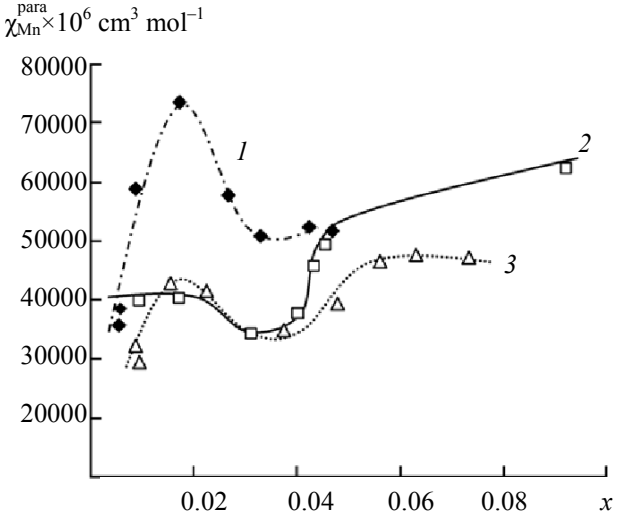


Fig. 3. Plot of paramagnetic component of magnetic susceptibility at 100 K, χ_{Mn}, vs. the composition for the systems: (*1*) $La_{1-0.33x}Sr_{0.33x}Mn_xAl_{1-x}$; (*2*) $x(La_{0.9}Y_{0.1})_{0.67}$·$Sr_{0.33}MnO_3$–$(1-x)La_{0.9}Y_{0.1}AlO_3$; (*3*) $x(La_{0.8}Y_{0.2})_{0.67}Sr_{0.33}MnO_3$–$(1-x)La_{0.8}Y_{0.2}AlO_3$.

infinite dilution ($x\to0$) results in the effective magnetic moments which in no way can be attributed to single manganese atoms, no matter in which of the possible valence states they were [Mn(II), $3d^5$, $^6A_{1g}$; Mn(III), $3d^4$, ^5E_g, or Mn(IV), $3d^3$, $^4A_{2g}$] (Fig. 4).

In this case even at infinite dilution no complete disaggregation of manganese atoms occurs as it took place in the systems containing no yttrium. Clusters of manganese atoms are retained in the solutions. An estimation of their size in the context of the HDVV model of isotropic exchange suggests that at 10% doping with yttrium in the infinitely diluted solutions clusters containing at least three heterovalent manganese atoms are preserved and in the case of 20% doping with yttrium–clusters of two manganese atoms. In other words, the introduction of yttrium results in strengthening interatomic interactions in the structure, this strengthening occurring non-monotonously as the concentration of yttrium increases, being maximal precisely for 10% of yttrium concentration (the CMR effect is maximal precisely for this concentration). The further run of the isotherms is well described within the assumption of increasing aggregates with ferromagnetic exchange in size for the 20% yttrium concentration, then the further enlargement up to clusters of four atoms with predominantly antiferromagnetic exchange, and at last, the enlargement of the size of the clusters with ferromagnetic exchange responsible for the CMR effect. The same trends are observed also for strontium-containing manganites

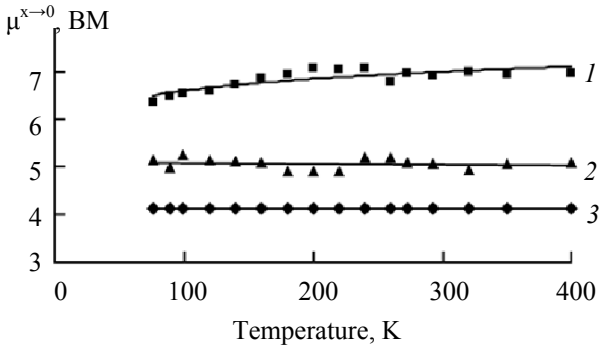


Fig. 4. Temperature dependences of the effective magnetic moments at infinite dilution: (*1*) $x(La_{0.9}Y_{0.1})_{0.67}Ca_{0.33}MnO_3$–$(1-x)La_{0.9}Y_{0.1}AlO_3$; (*2*) $x(La_{0.8}Y_{0.2})_{0.67}Ca_{0.33}MnO_3$–$(1-x)La_{0.8}Y_{0.2}AlO_3$; (*3*) $xLa_{0.33}Ca_{0.67}MnO_3$–$(1-x)LaAlO_3$.

(Fig. 5), but the sizes of clusters and the exchange in them are somewhat different: at the 10% yttrium concentration we have clusters of three and two manganese atoms with ferromagnetic exchange, whereas at the 20% doping with yttrium the clusters of two manganese atoms remain in the solution with the same valence and antiferromagnetic exchange, i.e. the nonmonotony in the manganese atom aggregation is preserved.

The non-monotony of clustering in the solid solutions containing various amount of yttrium is embodied in the EPR spectra recorded at room temperature (Fig. 6). The general view of the absorption line points to the fact that the spectrum contains signals of Mn(II) and Mn(IV) against the background of a wide line of the exchange type. As the concentration increases, the signals of single atoms gradually disappear, and only the wide line is observed. In the solid solutions containing 10% of yttrium this happens at lower concentrations than in the case of the 20% doping with yttrium.

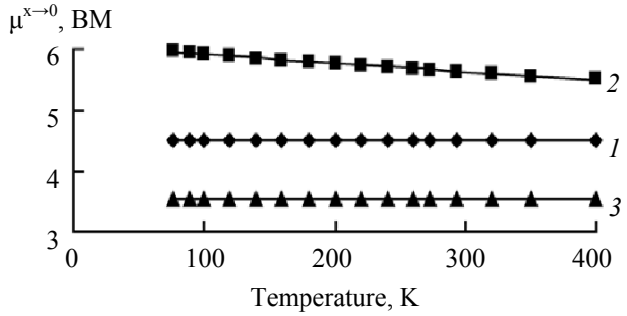


Fig. 5. Temperature dependences of the effective magnetic moment at infinite dilution for solid solutions: $x(La_{1-z}Y_z)_{0.67}$·$Sr_{0.33}MnO_3$–$(1-x)La_{1-z}Y_zAlO_3$; z: (*1*) 0, (*2*) 0.1, (*3*) 0.2.

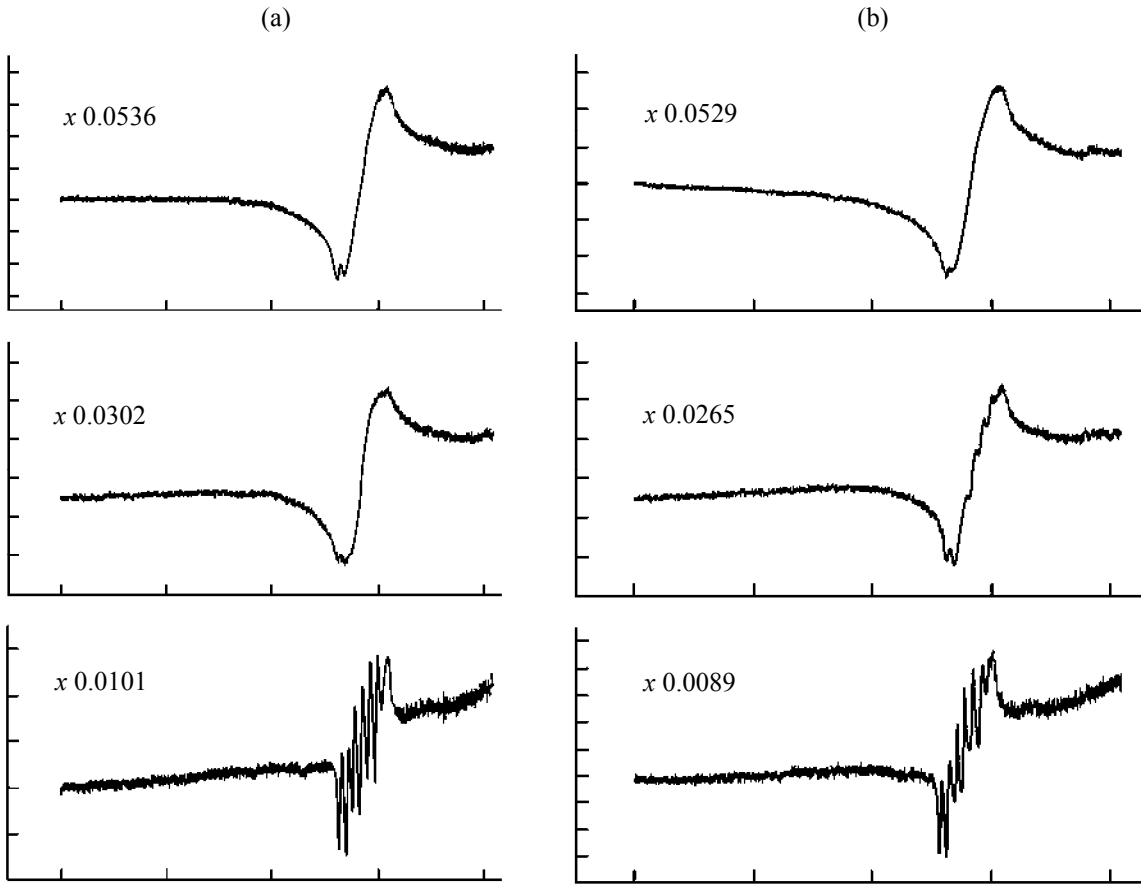


Fig. 6. EPR spectra of $x(La_{1-z}Y_z)_{0.67}Ca_{0.33}MnO_3$–$(1–x)La_{1-z}Y_zAlO_3$ solid solutions; z: (a) 0.1 and (b) 0.2.

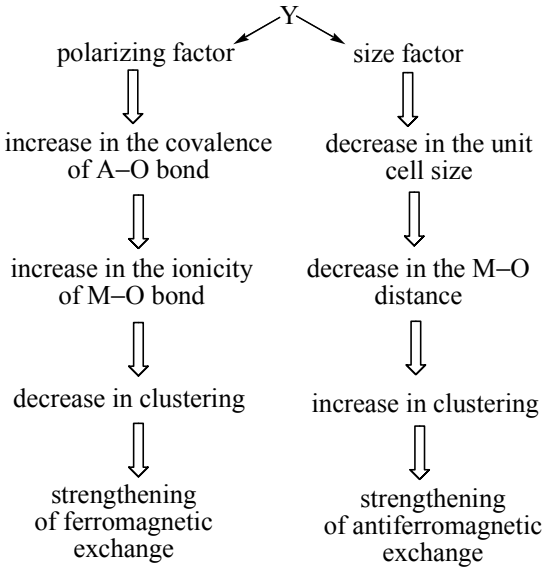
A number of conclusions follow from these data. First, these are sufficiently high dilution of solid oxides doped with an alkaline-earth element and yttrium, at which the difference in magnetic data is observed. This difference is associated with the short-range order and can be detected at low concentrations of paramagnetic atoms. Second, as on studying the influence of the nature of alkaline-earth element on magnetic characteristics of manganites we concluded that an alkaline-earth element is included into the cluster and influences its size and the character of exchange interactions, the last data on clustering in manganites point to the fact that yttrium atoms also are in the immediate vicinity of the cluster, take part in its formation, and influence the exchange.

The question arises, what is the reason for the non-monotony of yttrium influence. It is common practice to take into account only the factor of the particle size of a doping element and its concentration. But this does not account for the fact that the introduction of 10% of yttrium into the lanthanum sites results in an abrupt increase in CMR, and 20% of yttrium equally abruptly decrease it.

In the course of studying a large number of oxide systems we came to the conclusion that there are at least two factors determining the influence of diamagnetic elements on magnetic characteristics of paramagnetic oxides. These are their size and a polarizing effect on the oxygen atomic orbitals. This latter affects the degree of ionicity of transition element-oxygen bonds. An increase in the covalence of transition element-oxygen bonds results in an increase in its clustering in a solid solution, and the antiferromagnetic exchange, which is the result of overlapping orbitals, must be strengthened as the bond covalence increases, whereas the ferromagnetic exchange is determined by the interaction via two perpendicular orbitals of oxygen and is not immediately associated with the overlapping.

A substitution of yttrium atoms for a fraction of lanthanum atoms results in a decrease in the unit cell

parameter of the solvent (and of pure manganite). In this case the average M–O distance decreases, the orbital overlapping is strengthened and increases in its absolute value, and the clustering increases. The small yttrium atom stronger than lanthanum polarizes the oxygen orbitals, which results in an increase in the ionicity of M–O bonds, thus increasing the contribution of the ferromagnetic exchange.



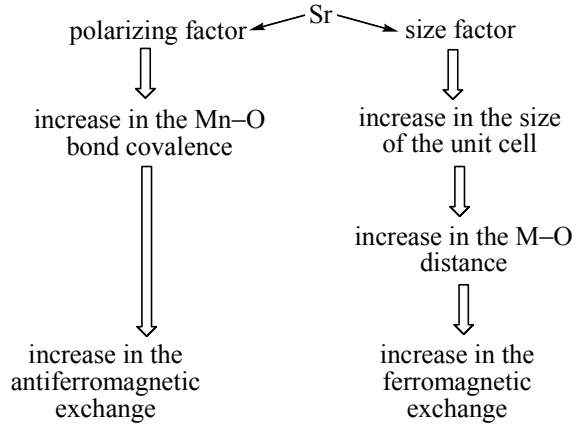
Therefore, the introduction of yttrium into lanthanum sites leads simultaneously to opposite results, one of the tendencies appearing to prevail at a certain concentration. In this case at 10% of yttrium a maximal clustering (the size factor) and a maximal ferromagnetic exchange (polarizing factor) are observed. The difference in the behavior of the systems containing calcium and strontium is determined by the same reasons: strontium, being larger and forming a more ionic bond with oxygen, acts in the opposite direction as compared to yttrium. As the result all the effects observed for calcium-containing systems appear to be less pronounced, but they show themselves in the same directions.

The study of magnetic dilution of solid solutions (2) of lanthanum manganites simultaneously doped with calcium and strontium in various ratios [6] in the same concentration range (x = 0.01–0.10) showed that the changes in magnetic properties occur non-monotonously as the ratio between alkaline-earth elements varies.

$$x\mathrm{La}_{0.67}(\mathrm{Ca}_y\mathrm{Sr}_{1-y})_{0.33}\mathrm{MnO}_3–(1–x)\mathrm{LaAlO}_3. \qquad (2)$$

As is seen from Fig. 7, the isotherms of magnetic susceptibility have nothing in common with the isotherms for manganites doped only with calcium or only with strontium. The simultaneous introduction of calcium and strontium atoms into the perovskite structure results in strengthening ferromagnetic exchange interactions. This is proved by the grows of isotherms of χ_{Mn} in the concentration range $x > 0.02$. The curve for the ratio [Ca]:[Sr]= 0.5:0.5 appears to be the lowest.

It is easy to show that even in this case the both factors noted above, the size of alkaline-earth atoms and their polarizing ability, are acting.



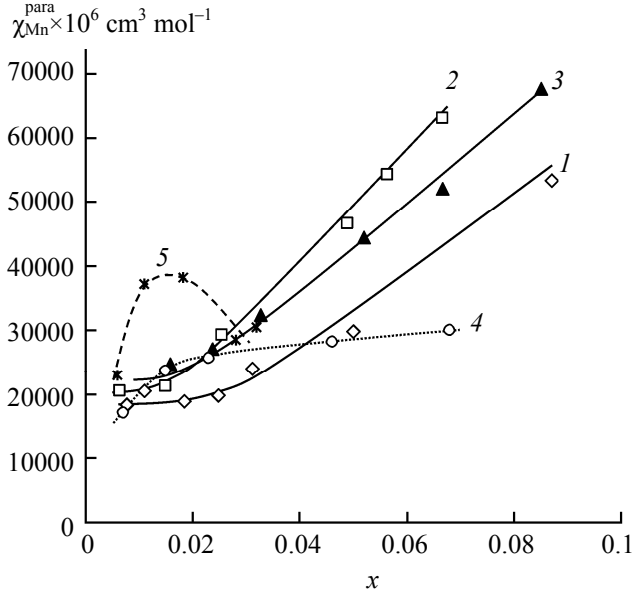


Fig. 7. Plot of paramagnetic component of magnetic susceptibility vs. the composition of the solid solutions at 140 K: (*1*) $x\mathrm{La}_{0.67}(\mathrm{Ca}_{0.5}\mathrm{Sr}_{0.5})_{0.33}\mathrm{MnO}_3–(1–x)\mathrm{LaAlO}_3$; (*2*) $x\mathrm{La}_{0.67}(\mathrm{Ca}_{0.7}\mathrm{Sr}_{0.3})_{0.33}\mathrm{MnO}_3–(1–x)\mathrm{LaAlO}_3$; (*3*) $x\mathrm{La}_{0.67}\cdot(\mathrm{Ca}_{0.3}\mathrm{Sr}_{0.7})_{0.33}\mathrm{MnO}_3–(1–x)\mathrm{LaAlO}_3$; (*4*) $x\mathrm{La}_{0.67}\mathrm{Ca}_{0.33}\mathrm{MnO}_3–(1–x)\mathrm{LaAlO}_3$; (*5*) $x\mathrm{La}_{0.67}\mathrm{Sr}_{0.33}\mathrm{MnO}_3–(1–x)\mathrm{LaAlO}_3$.

As strontium is introduced into the sites of calcium, the size of the unit cell increases, the Mn–O distance increases also, the overlapping decreases, and the contribution of the ferromagnetic component to the exchange increases. However, in this case the ionicity of A–O bonds increases, which results in an increase in the antiferromagnetic exchange. As the result we seem to arrive at the fact that the both factors are equalized at the ratio 1:1. Evidently it has determined the fact that this very ratio was used the doped manganites in [3].

Therefore we can state that the main role in the effect of colossal magnetoresistance is not played by simple ferromagnetic exchange between heterovalent manganese atoms, but by a certain balance between ferromagnetic and antiferromagnetic interactions. Their relative contributions are determined by the nature of doping diamagnetic elements, their size and polarizing power. The influence of the doping elements shows itself in the interactions of the short-range order within small aggregates of 4–8 atoms of manganese localized around or in the vicinity of the doping elements.

EXPERIMENTAL

Solid solutions under study were characterized by the methods of X-ray analysis and atom absorption spectroscopy. The X-ray analysis was carried out with the help of a DRON-3 X-ray diffractometer using FeK_α emission. The absence of any additional peaks from the X-ray patterns points to single-phase nature of the samples. We determined the concentration of manganese atoms by atom absorption spectroscopy, the error of the analysis was 3%.

For all the solid solutions the magnetic susceptibility was measured by Faraday method in the temperature range 77–400 K. The error of the measurements did not exceed 1%.

We synthesized doped lanthanum manganites by the sol–gel and ceramic methods.

Solid solutions of lanthanum manganite doped with yttrium (1). Sol-gel method of the synthesis. The starting components, special-purity grade lanthanum, yttrium, and manganese oxides, calcium and strontium carbonates, and γ-Al_2O_3 obtained by thermal decomposition of special-purity grade aluminum nitrate were dissolved in nitric acid (1:1) with addition of hydrogen peroxide on continuous heating on a sand bath. After dissolving the starting substances and decreasing the acidity with ammonium hydroxide, we added citric acid and ethylene glycol. We heated the mixture on a sand bath up to its transformation into a gel, and then decomposed the gel in a muffle by heating up to 200°C at a rate 4 deg min^{-1}. The obtained mixture was sintered at 800°C up to the complete removal of organic components; the powders were pressed into pellets and sintered at 1450°C for 50 h.

$x La_{0.67}(Ca_ySr_{1-y})_{0.33}MnO_3$–$(1-x)LaAlO_3$ solid solutions (2) (y = 0.3, 0.5, 0.7). Ceramic method**.** We mixed the stoichiometric mixture of the starting components and ground it in a jasper mortar for 1 h. We pressed the obtained mixtures into pellets in an organic-glass mold and sintered in air at 1450°C for 50 h.

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