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State of Atoms and Interatomic Interactions in Perovskite-Like Oxides: XXII.[1] Effect of the Ca–Sr Ratio on Exchange Interactions in Lanthanum Manganites Doped with Calcium and Strontium

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Abstract—Magnetic properties of lanthanum manganites of the perovskite structure, doped with calcium and strontium in various ratios, were studied. Magnetic dilution experiments and analysis of the temperature and concentration dependences of the magnetic characteristics showed that the properties of the manganites under consideration nonmonotonically depend on the Ca–Sr ratio in the lanthanum sublattice.

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Magnetoresistive lanthanum manganites $A_{1-x}B_xMnO_3$ of the perovskite structure (where A are rare-earth and B, alkaline-earth metals) attract large researchers' attention as they exhibit colossal negative magnetoresistance (CMR). Numerous recent studies concerning CMR considerably expanded our knowledge of giant magnetoresistivity as effect caused by exchange interactions between different-valence atoms of a paramagnetic element, but the CMR mechanism is not yet understood. Attempts to get the maximal decrease in the resistance are made differently, in particular, by variation of the cationic composition of manganites. Partial substitution of lanthanum by bivalent alkaline-earth metal atoms affects the magnetoresistivity of the material differently. From the viewpoint of practical use, the problem of controlling the magnetoresistance of a material by varying its composition is particularly topical. Despite the fact that the number of synthesized and studied lanthanum manganites doped with various alkaline-earth metals is relatively large, the mechanisms responsible for the effect a substituting cation in the lanthanum sublattice on CMR have not yet been elucidated.

The most comprehensive information on the character of exchange interactions in manganites is furnished by the magnetic dilution method. This procedure makes it possible to reveal and follow the effect of particular factors on the state of transition metal atoms and exchange interactions in isomorphous substitution solid solutions.

Magnetochemical study of lanthanum manganites doped with calcium, strontium, and barium [2–4] showed that introduction of one or another dopant into the lanthanum sublattice leads to certain distortions of the perovskite structure and, as a result, to changes in the character of exchange within clusters of paramagnetic atoms, which, in turn, affects the physicochemical properties of a material, including its magnetic properties. However, the properties of magnetoresistors are influenced not only by the nature of a dopant, but also by the quiantitative ratio of the substituting atoms. Previous magnetic dilution studies of yttrium-substituted lanthanum manganites containing 10 and 20% yttrium [1] showed that the size of paramagnetic clusters and the exchange in them vary nonmonotonically with increasing dopant concentration. Introduction of ~10% Y into the lanthanum sublattice results in the presence of paramagnetic clusters of three manganese atoms of different valences with ferromagnetic exchange at infinite

[1] For communication XXI, see [1].

dilution in the solution. Apparently, specifically in this case the highest values of the magnetoresistance can be attained [5]. An increase in the fraction of yttrium to 20% not only does not improve the magnetoresistive properties of the material, but even decreases the magnetoresistance. In this case, an increase in the relative content of yttrium, capable of strongly polarizing the electron shell of oxygen atoms, leads to greater disaggregation of the paramagnetic atoms. It follows from the aforesaid that the character of interatomic interactions determining the unusual properties of magnetoresistors strongly and often unpredictably depends on the nature and amount of diamagnetic elements in the perovskite structure.

As the magnetic behavior of solid solutions based on lanthanum manganite containing calcium and strontium is cardinally different [4], the goal of this study was to examine the effect of the substituent ratio on the magnetochemical properties of lanthanum manganites doped simultaneously with strontium and calcium, $La_{1-0.33x}(Ca_ySr_{1-y})_{0.33x}Mn_xAl_{1-x}O_3$ (y = 0.3, 0.5, 0.7; $0.01 \le x \le 0.10$).

The possibility of following the dynamics of changes in cluster formation and the exchange interactions by the magnetic dilution method allows us to account for the magnetoresistive properties exhibited by lanthanum manganite on partial replacement of calcium by strontium.

For this purpose, we prepared by the ceramic technique solid solutions of lanthanum manganites with different Ca–Sr ratios and measured their magnetic susceptibility by the Faraday method in the temperature range 77–400 K.

From the magnetic susceptibility data, we calculated the paramagnetic term of the magnetic susceptibility and effective magnetic moment and plotted their temperature and concentration dependences.

Of the greatest interest, from the viewpoint of changes in the character of exchange interactions, is the dependence of the paramagnetic term of the magnetic susceptibility on the manganese content of solid solutions (Fig. 1). Comparison of the isotherms for all the systems reveals the following trends: The magnetic susceptibility and the course of the concentration dependence vary nonmonotonically with variation of the manganite composition. The isotherms of the solid solutions doped solely with calcium or with strontium strongly differ both from each other and

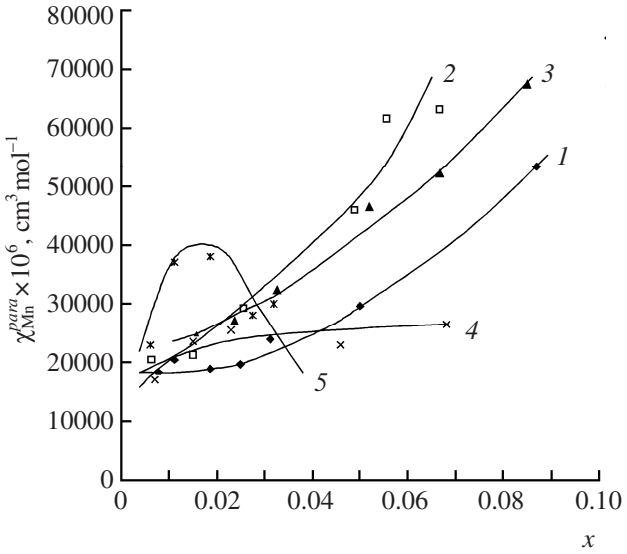

Fig. 1. Magnetic susceptibility χ_{Mn} at 140 K as a function of composition for the systems (*1*) $La_{1-0.33x}(Ca_{0.5}Sr_{0.5})_{0.33x}Mn_xAl_{1-x}O_3$, (*2*) $La_{1-0.33x}(Ca_{0.7}Sr_{0.3})_{0.33x}Mn_xAl_{1-x}O_3$, (*3*) $La_{1-0.33x}(Ca_{0.3}Sr_{0.7})_{0.33x}Mn_xAl_{1-x}O_3$, (*4*) $La_{1-0.33x}Ca_{0.33x}Mn_xAl_{1-x}O_3$, and (*5*) $La_{1-0.33x}Sr_{0.33x}Mn_xAl_{1-x}O_3$.

from those of the systems containing both diamagnetic elements. In the case of strontium-substituted manganites, the ferromagnetic exchange prevails at low manganese concentrations, but even at $x > 0.02$ the amount of clusters with antiferromagnetic exchange considerably increases, and the susceptibility maximum is observed in the isotherm. Antiferromagnetic interactions in calcium-containing manganites are less pronounced, as indicated by a slight increase in the magnetic susceptibility at $x > 0.03$.

For solid solutions containing both strontium and calcium, the magnetic susceptibility isotherms have a similar shape. In all these systems, the magnetic susceptibility is virtually independent of the content of the paramagnetic in a narrow concentration range ($0 < x < 0.02$), but further increase in x leads to an increase in the susceptibility, suggesting enhancement of the ferromagnetic exchange interactions.

The temperature dependence of the effective magnetic moment μ_{eff} (Fig. 2) also is in favor of this conclusion. The temperature dependence of the effective magnetic moment for all the solutions is similar, and, as seen from Fig. 2, at low x μ_{eff} is virtually independent of temperature. With an increase in the content of the paramagnetic element, the decrease in μ_{eff} with increasing temperature becomes

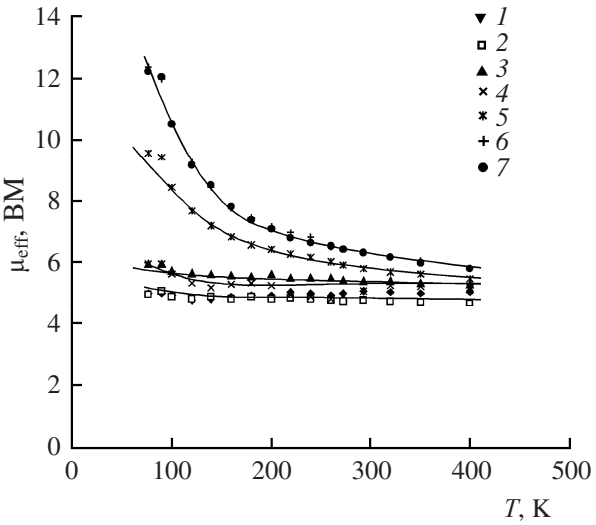

Fig. 2. Effective magnetic moment as a function of temperature for the system $La_{1-0.33x}(Ca_{0.7}Sr_{0.3})_{0.33x}Mn_xAl_{1-x}O_3$. *x*: (*1*) 0.0063, (*2*) 0.0150, (*3*) 0.0194, (*4*) 0.0267, (*5*) 0.0489, (*6*) 0.0523, and (*7*) 0.0667.

more and more pronounced. This trend suggests coarsening of clusters of manganese atoms, in which the exchange is ferromagnetic at low temperatures, and with increasing temperature the exchange parameter changes sign.

Thus, comprehensive analysis of magnetic characteristics of solid solutions containing either calcium only or strontium only, or doped with both elements simultaneously, allows a conclusion that partial substitution of calcium by strontium enhances the ferromagnetic exchange within paramagnetic clusters. This phenomenon affects the shape of the magnetic susceptibility isotherms and is responsible for their location between those of the manganites containing solely calcium or strontium.

Extrapolation of the magnetic susceptibility to zero concentration of the paramagnetic in the systems leads to the following effective magnetic moments $\mu^{x=0}$.

$\mu^{x=0}$, BM	4.6	4.5	4.4
Ca–Sr	0.3 : 0.7	0.5 : 0.5	0.7 : 0.3

The $\mu^{x=0}$ values obtained are intermediate between the spin-only values of the magnetic moments of Mn^{III} and Mn^{IV} [$\mu_{S.O.}(Mn^{III})$ 4.9 BM; $\mu_{S.O.}(Mn^{IV})$ 3.88 BM] and suggest that, as in the case of manganites doped with calcium only or with strontium only, at infinite dilution the system contains only separate manganese atoms, with the fraction of Mn^{III} growing with an increase in the fraction of strontium in lanthanum positions. This is quite explicable, because the ionic radius of strontium is appreciably larger than that of calcium, which leads to an increase in the parameter of the structure and hence to the expansion of octahedral cavities occupied by manganese atoms.

A slight increase in the paramagnetic term of the magnetic susceptibility at small *x* suggests that, at $x < 0.02$, two types of dimers, Mn^{III}–Mn^{IV} and Mn^{III}–Mn^{III}, responsible for the ferro- and antiferromagnetic contribution to the exchange, respectively, are formed in the solution. Further increase in the fraction of manganese leads to coarsening of paramagnetic clusters to tetramers and higher oligomers and to the increase in the paramagnetic term of the exchange.

Thus, at Ca–Sr ratios of 0.7:0.3, 0.5:0.5, and, to a lesser extent, 0.3:0.7, clusters of two manganese atoms are initially formed in the dilute solid solutions, and the competition of the antiferromagnetic and ferromagnetic exchange in these clusters results in that the quantities μ_{eff} and χ_{Mn}^{para} become essentially independent of the concentration.

At a low content of the paramagnetic element in the system with a Ca–Sr ratio of 0.3:0.7, μ_{eff} reaches ~ 6 BM and tends to slightly decrease, suggesting prevalence of the ferromagnetic exchange. In solid solutions with a Ca–Sr ratio of 0.5:0.5, the effective magnetic moment does not exceed 5 BM at the same *x*. This fact suggests virtually full compensation of the antiferromagnetic exchange in dimers formed by Mn atoms of the same valence and ferromagnetic exchange in Mn^{III}–Mn^{IV} dimers.

The most important feature of these solutions is mutual arrangement of the magnetic susceptibility isotherms in relation to the composition of the diamagnetic sublattice of the complex oxides and especially the fact there is no definite regularity in the position of the isotherms. As seen from Fig. 1, the magnetic susceptibility reaches the highest values at a Ca–Sr ratio of 0.7:0.3 and the lowest values, at the 0.5:0.5 ratio. In the latter case, the magnetic susceptibility isotherms at low concentrations of the paramagnetic lie even lower than for the manganites doped with calcium only. In other words, with partial replacement of calcium by strontium, the magnetic characteristics vary nonmonotonically.

The ascent of the magnetic susceptibility isotherms suggests the formation of clusters of the growing size

in which the exchange interactions, at least at low temperatures, are strongly ferromagnetic. This fact indicates that the exchange not only between manganese atoms of different valences (Mn^{III}–Mn^{IV}), but also between those of the same valence appears to be ferromagnetic. This is possible if the MnOMn angle is less than 180° [6], which is favored by introduction into the lanthanum sublattice of relatively large strontium atoms distorting the nearest surrounding of the manganese atoms. However, the temperature dependence of μ_{eff} indicates that the exchange parameter J changes with temperature from ferromagnetic to antiferromagnetic and is associated with the nonrigidity of paramagnetic clusters. As the sizes of the calcium and lanthanum atoms are close, an increase in the calcium content does not distort the nearest surrounding of the paramagnetic atoms, and in this case the distortions are associated only with the relatively large size of the manganese atoms. Therefore, introduction of calcium into the lanthanum positions increases the nonrigidity of the paramagnetic clusters.

In other words, the character of exchange interactions is determined by two opposite trends associated with both the size and the polarizing ability of alkaline-earth metal atoms. Firstly, the cluster size grows with increasing strontium content because the Mn–O bonds become more covalent. This fact is responsible for the steeper shape of the isotherms for solid solutions with a Ca–Sr ratio of 0.3:0.7 at $x <$ 0.02. It should be noted that, in the system containing strontium only, clusters of manganese atoms with the number of paramagnetic atoms $n > 4$ appear at x 0.02, whereas in the calcium-containing solid solutions they appear only at $x > 0.05$ [4]. Secondly, owing to the large size of strontium atoms, relatively rigid ferromagnetic clusters are formed.

Enhancement of the interatomic interactions favors, on the whole, the formation of ferromagnetic clusters and hence should lead to enhancement of CMR. However, the formation of more and more rigid clusters which do not change the geometry with temperature, apparently, adversely affects CMR. In this case, presumably, the Ca–Sr ratio of 0.5:0.5 is optimal for ensuring, on the one hand, sufficient clusterization and, on the other hand, still appreciable nonrigidity of the clusters.

It is quite obvious that the explanation suggested in [5] for the nonmonotonicity of the properties of magnetoresistors with different degrees of substitution of lanthanum by calcium, strontium, and yttrium and based solely on the size of the dopant atoms is insufficient. Changes in the characteristics of the Mn–O bond should also be taken into account.

EXPERIMENTAL

Solid solutions $La_{1-0.33x}(Ca_ySr_{1-y})_{33x}Mn_xAl_{1-x}O_3$ with various Ca–Sr ratios were prepared by the ceramic technique. Stoichiometric amounts of the starting compounds [ultrapure grade lanthanum and manganese(III) oxides, analytically pure grade calcium and strontium carbonates, γ-Al_2O_3 prepared by thermal decomposition of ultrapure grade aluminum nitrate] were ground for 1 h in a jasper mortar and calcined at 1500°C for 50 h.

X-ray phase analysis of the solid solutions was performed on a DRON-3 X-ray diffractometer using CuK_α radiation. The manganese content was determined by atomic absorption spectroscopy. The analytical error was 3% of x in the formula of the solid solution.

The magnetic susceptibility was measured by the Faraday method in the temperature range 77–400 K. The measurement error did not exceed 1%.

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