Russian Journal of General Chemistry, Vol. 74, No. 4, 2004, pp. 486–488. Translated from Zhurnal Obshchei Khimii, Vol. 74, No. 4, 2004, pp. 535–537.

Atom States and Interatomic Interactions in Complex Perovskite-Like Oxides: XIX.[1] Magnetic Dilution in the $La_{0.67}Ba_{0.33}MnO_3$–$LaAlO_3$ System

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Received February 27, 2003

Abstract—Barium-doped solid solutions of lanthanum manganites in lanthanum aluminate were studied. In barium-containing magnetoresisting manganites, complete disaggregation of paramagnetic atoms does not occur even at infinite dilution, and clusters of ferromagnetically coupled manganese atoms remain in the structure.

Manganese-containing complex oxides with perovskite-like structures are being actively studied today. Particular attention is paid to perovskites doped with bivalent atoms substituting lanthanum in the structural sites with coordination number 12. This is due to the fact that, at a certain temperature, they demonstrate the so-called effect of "colossal magnetoresistance" [2–4]. This effect is associated with exchange coupling between manganese atoms in different valence states. Hence, the study of the character of such interactions can become a key to understanding the origin of "colossal magnetoresistance" and to elucidating the role of a doping element in this phenomenon. The most promising in this respect is the method of magnetic dilution, i.e., the study of magnetic properties of dilute solid solutions of isomorphous substitution, making it possible to pick out separate clusters of paramagnetic atoms in a complex oxide structure and to study the nature of the exchange within such "elementary" units constituting a magnetoresisting oxide.

In our previous works [5, 6] we studied solid solutions of $La_{0.67}A_{0.33}MnO_3$ containing calcium and strontium in lanthanum aluminate, and in this work we turned our attention to solid solutions of lanthanum manganite containing barium. We emphasize that barium(II) differs from calcium and strontium in two relevant parameters. First, it has a substantially greater ionic radius than La^{3+} (1.60 Å compared to 1.32 Å for La^{3+} in the oxygen surrounding with coordination number 12 [7]). Second, its bonds with oxygen are more ionic, which, according to J. Goodenough [8], must result in increased covalence of the Mn–O bonds.

We synthesized two series of solid solutions with the general formula $La_{1-0.33x}Ba_{0.33x}Mn_xAl_{1-x}O_3$ ($0.01 \le x \le 0.10$), carried out their X-ray phase and chemical (for manganese) analyses, and measured their magnetic susceptibility in the range 77–400 K. All the solid solutions have the structure of cubic $LaAlO_3$. The temperature and concentration dependences of magnetic characteristics of the solid solutions were plotted on the basis of magnetic susceptibility measurements.

A striking feature is that the plots of reciprocal paramagnetic component of the susceptibility vs. temperature are essentially nonlinear (Fig. 1). Only in the range of strongly dilute solid solutions ($x \le 0.01$) the plots of $1/\chi_{Mn}$ vs. T at low temperatures become linear. This means that the magnetic susceptibility of the solid solutions does not obey the Curie–Weiss law. For the $La_{1-0.33x}Sr_{0.33x}Mn_xAl_{1-x}O_3$ solid solutions studied previously [9], we also observed deviations from the Curie–Weiss law at high temperatures, but they were considerably less pronounced.

The plots of the paramagnetic component of magnetic susceptibility calculated per mole of manganese atoms (χ_{Mn}) vs. the composition of the solid solution (Fig. 2) also significantly differ from the susceptibility isotherms for Sr-doped manganites. They resemble more closely the χ_{Mn}–x plots for the calcium-containing solid solutions, since χ_{Mn} grows with x. However, for Ca-doped manganites the rate of the susceptibility growth decreases as x increases, and at high temperatures the isotherms pass through a maximum at $x \approx 0.02$, after which the susceptibility decreases [5]. The trends observed with barium-containing manganites were quite different. Their paramagnetic susceptibility grows more and more

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

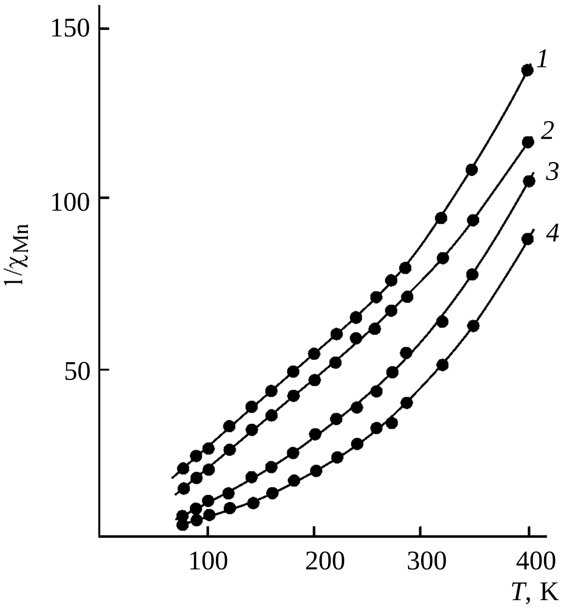

Fig. 1. Temperature dependences of reciprocal paramagnetic component of the magnetic susceptibility of the $La_{1-0.33x}Ba_{0.33x}Mn_xAl_{1-x}O_3$ solid solutions. x: (*1*) 0.0091, (*2*) 0.0201, (*3*) 0.0601, and (*4*) 0.0719.

intensively as x increases, and this growth is observed over the entire temperature range. This fact suggests active formation of ferromagnetic clusters of manganese atoms in the barium-containing solid solutions.

The temperature dependences of the effective magnetic moment (μ_{eff}) (Fig. 3) are complex. For dilute solid solutions, there is a “plateau” in the μ_{eff}–T plot in the temperature range 150–300 K. A similar temperature dependence of μ_{eff} was also observed for strontium-containing solid solutions. However, as the concentration increases, the second inflection in the μ_{eff}–T curve disappears. In this case, the effective magnetic moment decreases substantially as the temperature increases, namely, from 15 to 6 μB. It also suggests formation of large clusters of manganese atoms with the number of atoms $n > 4$, and a sharp decrease in μ_{eff} with increasing temperature shows that the exchange parameter J is temperature-dependent. At low temperatures, $J \gg 0$, whereas as the temperature increases the ferromagnetic component in the exchange interactions decreases and the antiferromagnetic exchange is enhanced.

The extrapolation of magnetic characteristics to the infinite dilution of the solid solution leads to the value μ_{eff} ~5.6 μB within the range 77–320 K. A further increase in temperature results in the decrease in the magnetic moment to ~4.6 μB (T 400 K). The magnetic characteristics of regular solid solutions at $x \rightarrow 0$

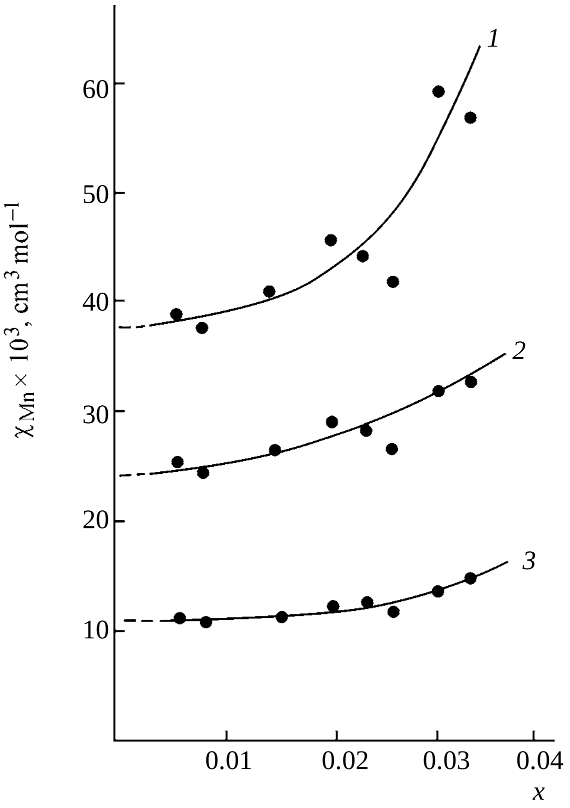

Fig. 2. Plots of χ_{Mn} vs. manganese concentration in the $La_{1-0.33x}Ba_{0.33x}Mn_xAl_{1-x}O_3$ solid solutions at (*1*) 100, (*2*) 160, and (*3*) 320 K.

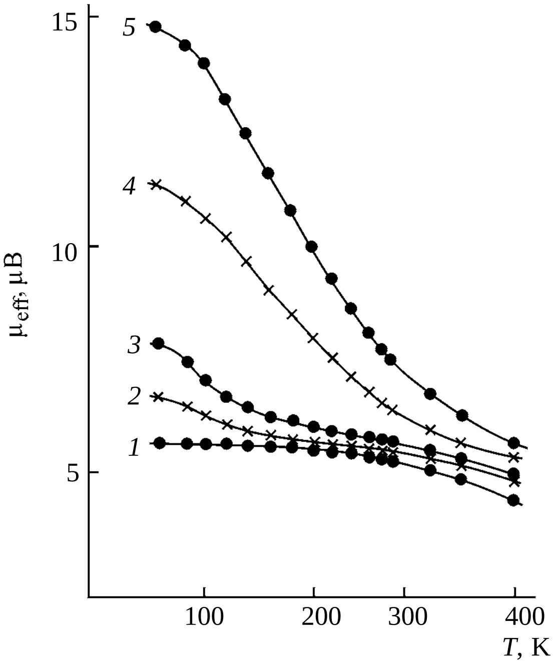

Fig. 3. Temperature dependences of the effective magnetic moment of $La_{1-0.33x}Ba_{0.33x}Mn_xAl_{1-x}O_3$ solid solutions. x: (*1*) 0.0091, (*2*) 0.0201, (*3*) 0.0601, (*4*) 0.0719, and (*5*) 0.0871

must correspond to single paramagnetic atoms, i.e., in our case, to Mn(III) (μ_{eff} ~4.9 μB) and Mn(IV) (μ_{eff} ~3.88 μB) in a certain ratio. It was precisely this pattern that was observed in the calcium- and strontium-containing solid solutions [5, 6]. A too high μ_{eff} value at $77 \le T \le 320$ K could be associated with the presence of bivalent manganese, but two reasons are against this suggestion. First, essential (more than 30 mol%) quantities of Mn(II) must result in a substantial nonstoichiometry by oxygen and, consequently, in destabilization of the cubic perovskite structure. Second, the effective magnetic moment of Mn(II) ($^6A_{1g}$ ground state) is independent of temperature [as also those of Mn(III) (^5E_g) and Mn(IV) ($^4A_{2g}$)]. Consequently, it is impossible to describe the decrease in μ_{eff} at high temperatures. It is most probable that the value of μ_{eff} and its temperature dependence at $x \to 0$ result from the fact that even at infinite dilution ferromagnetically coupled clusters, e.g., Mn(III)–Mn(IV), do not completely disaggregate. According to the Heisenberg–Dirac–van Vleck model [10], the effective magnetic moment of such a cluster at the exchange parameter $J \ge +50$ cm^{-1} appears to be 5.61 μB and must decrease at high temperatures.

Therefore, it may be concluded that the formation of ferromagnetic clusters in solid solutions of Ba-doped manganites occurs more intensively than in the Ca- and Sr-doped solid solutions. Evidently, this is not associated with magnetic exchange coupling, as its energy does not exceed 1 kJ mol^{-1}, but is determined by the increased degree of covalence of the Mn–O bonds due to essentially ionic character of the competing Ba–O bonds.

EXPERIMENTAL

The $La_{1-0.33x}Ba_{0.33x}Mn_xAl_{1-x}O_3$ solid solutions were obtained by the ceramic technique from a mixture of chemically pure grade oxides La_2O_3, MnO_2, Mn_2O_3, and Al_2O_3 and analytically pure grade barium carbonate, taken in stoichiometric amounts. The thoroughly ground mixture was pelletized and calcined in air for 50 h. The calcination time necessary to obtain homogeneous samples was determined by X-ray phase analysis and magnetic susceptibility measurements.

We recorded the X-ray patterns of the samples on a URS-50N diffractometer (CuK_α radiation). The manganese content was determined by atomic absorption spectroscopy on an AASIN spectrophotometer (Germany). The optical density of sample solutions was measured at a wavelength λ 279.5 nm. The accuracy of the analysis was 3% of x in the solid solution formula.

The magnetic susceptibility was measured by the Faraday method in the range 77–400 K at 15 fixed temperatures. The accuracy of relative measurements was 1%.

ACKNOWLEDGMENTS

The authors are grateful to A.I. Drobyshev for his help in carrying out the chemical analysis.

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