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LETTERS TO THE EDITOR

Magnetic Susceptibility of Dilute $La_{0.67}Sr_{0.33}MnO_3$–$LaAlO_3$ Solid Solutions

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The complex oxide $La_{0.67}Sr_{0.33}MnO_3$ with the perovskite structure is a so-called "colossal magnetoresistor," one of the series of $La_{0.67}A_{0.33}MnO_3$ oxides (A = Ca, Sr, Ba, Pb). At present these oxides are extensively studied with the aim to obtain the best electrophysical characteristics by optimizing their composition [1, 2]. The basis of magnetoresistance as a cooperative phenomenon is formed by exchange interactions between manganese atoms in different oxidation states [Mn(III) and Mn(IV)]. To reveal the nature of their exchange interactions and the effects of substituents (Ca and Sr), we earlied studied magnetic dilution in the $La_{0.67}Ca_{0.33}MnO_3$–$LaAlO_3$ system [3]. In this work we focused on the magnetic susceptibility of manganite solid solutions in which lanthanum was partially substituted by strontium.

Solid solutions $La_{0.67}Sr_{0.33}MnO_3$–$LaAlO_3$ ($La_{1-0.33x}Sr_{0.33x}Mn_xAl_{1-x}O_3$) were obtained by the ceramic procedure as described in [4]. The manganese content was determined colorimetrically by the color of permanganate ions with the accuracy ~3%. The magnetic susceptibility was measured in the range 77–400 K.

The plots of the paramagnetic susceptibility calculated per 1 mol of manganese atoms vs. the concentration of the latter in the solid solutions have a maximum in the region of x ~0.025 over the entire temperature range. The effective magnetic moment μ_{eff} is temperature-dependent for all the solid solutions studied. For very dilute solutions (x 0.008 and 0.011) this dependence manifests itself in the fact that μ_{eff}, being constant up to ~300 K, begins to decrease noticeably as the temperature is raised further. A similar μ_{eff}–T dependence is observed for an indefinitely dilute solid solution. Since for any oxidation state of manganese, which can occur in the solid solutions under study [Mn(III), Mn(IV), or even Mn(II)], the ground states are either nondegenerate [Mn(IV) $^4A_{2g}$, Mn(II) $^6A_{1g}$] or doubly degenerate [Mn(III) ^5E_g], and the effective magnetic moment for the octahedral surrounding of the paramagnetic atom is independent of temperature, we are to suggest that even on infinite dilution the manganese atoms do not disaggregate completely. Thus, even at x 0 some aggregates of manganese atoms linked by ferromagnetic superexchange are present in the solid solutions. The nature of the superexchange is evidenced by, first, the values of μ_{eff}, which are higher than those for Mn(III) and Mn(IV) and, second, by the decrease in μ_{eff} with increasing temperature.

The temperature changes in μ_{eff} for $x > 0.02$ are the most interesting. At low temperatures, μ_{eff} in the region of the maximum in the magnetic susceptibility isotherms attains 6.9 BM and decreases with increasing temperature. Such high μ_{eff} values point to formation of rather large ferromagnetically linked clusters of manganese atoms, in which the exchange parameter appears to be positive regardless of the two manganese atoms have different [Mn(III)–O–Mn(IV)] or the same [Mn(III)–O–Mn(III)] valences. The same phenomenon has also been observed in the $La_{0.67}Ca_{0.33}MnO_3$–$LaAlO_3$ solid solutions [3], however, in strontium-substituted solid solutions the magnetic moment much less varied with temperature, from 6.8 to 5.6 BM in the range 77–400 K against 7– 4.5 BM for calcium-substituted systems. Moreover, the μ_{eff}–T dependence is nonmonotic and shows two regions of a sufficiently abrupt decrease in μ_{eff}: 77–200 and 300–400 K, between which μ_{eff} decreases only slightly. All this suggests that the nature and energy of the magnetic superexchange in manganese clusters vary with temperature.

It is interesting that the region of the plateau in the μ_{eff}–T plot coincides, according to [1], with the temperature range where in a pure lanthanum manganite doped with strontium, as well as in solid solutions containing very little Al (up to 3 mol%), the low-temperature coherent ferromagnetism passes

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to the high-temperature incoherent ferromagnetism responsible for colossal magnetoresistance.

Therefore, we can point out two main differences between calcium- and strontium-substituted solid solutions. First, on dilution of strontium-substituted manganite its manganese atoms do not disaggregate completely, i.e. the interaction between manganese atoms in this compound is characterized by a higher energy incompatible with the energy of local magnetic exchange. Second, while the exchange parameter does vary with temperature in the strontium-substituted solid solution, this variation does not change the sign of the exchange parameter ($J > 0$, the exchange remains ferromagnetic over the entire temperature range studied). The latter can be accounted for by the fact that strontium atoms, being more sizable than lanthanum and calcium atoms, more rigidly fix distortions of MnOMn angles, and these distortions are not completely taken off by increasing temperature, leaving room for ferromagnetic exchange between manganese atoms with the same oxidation state. The presence of the plateau in the μ_{eff}–T plot in the very region of the transfer between different metal ferromagnetic states in the pure magnetoresistor points to a certain correlation between changes in the exchange parameters of relatively small clusters and the phenomenon of colossal magnetoresistance, which testifies that research into dilute solid solutions does allows the nature of this phenomenon to be understood on a molecular level.

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