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Magnetic Properties of Iron Atoms in the Perovskite-like Oxides

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Abstract—Magnetic and structural characteristics of magnetically diluted complex oxides $La_{2-x}A_xMO_4$ (M is Fe; A is Sr, Ba) were studied. An essential dependence of magnetic susceptibility on the composition of dia- and paramagnetic components of the structure and also the tendency of heterovalent iron atoms to form clusters were found.

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To study the magnetic behavior of iron atoms in a two-dimensional perovskite-like structure, complex oxides of the specified compositions $La_{1.85}Sr_{0.15}FeO_4$, $La_{1.85}Ba_{0.15}FeO_4$, and $La_{0.75}Sr_{1.25}FeO_4$ were synthesized, and their magnetic dilution was carried out. This method makes it possible to study valence and spin states of single atoms and also the character of interatomic interactions on the formation of solid solutions of a paramagnetic oxide in a corresponding diamagnetic matrix. In this case $LaSrAlO_4$ and $LaBaAlO_4$ are the diamagnetic solvents. The chemical composition of the oxide was selected in such a manner as to obtain various states of iron atoms. These should be Fe(II) and Fe(III) for $La_{1.85}Sr(Ba)_{0.15}FeO_4$ and Fe(III) and Fe(IV) for $La_{0.75}Sr_{1.25}FeO_4$.

The $y[La_{1.85}Sr(Ba)_{0.15}FeO_4]$–$(1 - y)LaSr(Ba)AlO_4$ solid solutions ($0 < y < 0.7$) were obtained by the ceramic technique. Over this concentration range the solid solutions must have the structure of the solvent. $LaSrAlO_4$ has a layered two-dimensional structure similar to K_2NiF_4, in which aluminum atoms are in the octahedral surrounding of oxygen atoms. Owing to a larger size of barium atoms $LaBaAlO_4$ has a distorted structure (like in β-K_2SO_4), and aluminum atoms are in isolated oxygen tetrahedra.

Therefore, setting up a required composition of the solution, we gain the possibility of studying behavior of various valence states of iron atoms in various crystal fields, and also of deciding whether there are differences in the magnetic characteristics at such a small iron content. Often 3*d* elements enter an oxide ceramics as dopants and thus exert a strong influence on its properties.

Of greatest interest are the $y(La_{0.75}Sr_{1.25}FeO_4)$–$(1 - y)$·$LaSrAlO_4$ solid solutions, which should contain a poorly studied state of Fe(IV).

In the $La_{1.85}Ba_{0.15}FeO_4$–$LaBaAlO_4$ system the exchange inside clusters containing Fe(II) and Fe(III) atoms is ferromagnetic. At the infinite dilution μ_{eff} of 5.3–5.4 BM corresponds to the magnetic moment of a $Fe(II)_{S1}$–O–$Fe(III)_{S5/2}$ dimer with J 6 cm^{-1} (Fig. 1). In the $La_{1.85}Sr_{0.15}FeO_4$–$LaSrAlO_4$ system the clusters are retained even at infinite dilution; μ_{eff} at infinite dilution corresponds to a cluster of three Fe(III) atoms, the exchange between them being also ferromagnetic (Fig. 2). The μ_{eff} at infinite dilution of the $La_{0.75}Sr_{1.25}FeO_4$–$LaSrAlO_4$ system also does not depend on temperature, but it is substantially lower. This is associated with the formation of trimers containing two Fe(III) and one Fe(IV) atoms.

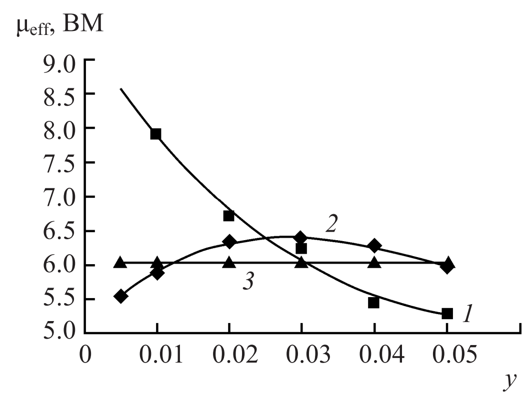

Fig. 1. Plot of the effective magnetic moment vs. the composition for the systems: (*1*) $y(La_{1.85}Sr_{0.15}FeO_4)$–$(1- y)LaSrAlO_4$; (*2*) $y(La_{1.85}Ba_{0.15}FeO_4)$–$(1 - y)LaBaAlO_4$; and (*3*) $y(FeO_{1-x})$–$(1- y)MgO$.

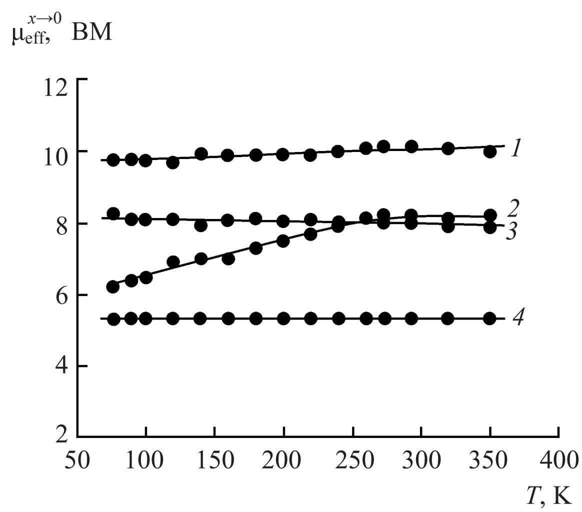

Fig. 2. Plot of the effective magnetic moment at infinite dilution vs. temperature for the systems: (*1*) $La_{1.85}Sr_{0.15}FeO_4$–$LaSrAlO_4$; (*2*) $LaFeO_3$–$LaGaO_3$; (*3*) $La_{0.75}Sr_{1.25}FeO_4$–$LaSrAlO_4$; and (*4*) $La_{1.85}Ba_{0.15}FeO_4$–$LaBaAlO_4$.

Therefore, the examination of magnetic characteristics of iron-containing oxide systems has shown that we succeeded to stabilize Fe(IV) atoms in the magnetically diluted $y(La_{0.75}Sr_{1.25}FeO_4)$–$(1 - y)LaSrAlO_4$ solid solutions and to prove that these atoms, along with Fe(III) atoms, enter the composition of the clusters stable even at infinite dilution. The interactions within the clusters are ferromagnetic and those between the clusters–antiferromagnetic. This accounts for the competition between two contributions to the magnetic susceptibility.

EXPERIMENTAL

We synthesized solid solutions by the ceramic technique from the stoichiometric mixture of corresponding starting components (oxides and carbonates). A thoroughly ground mixture was pressed into pellets and sintered at 1800 K for 50 h. The optimal duration of sintering was found from the X-ray and magnetic susceptibility data. As the result we obtained samples having the structure of the solvent: $LaBaAlO_4$ (β-K_2SO_4 type) and $LaSrAlO_4$ (K_2NiF_4 type). The powder diffraction patterns were recorded on a DRON-3 diffractometer using CuK_α emission. We measured the magnetic susceptibility by the Faraday method in the temperature range 77–400 K.

Thus we have synthesized a series of solid solutions with a set of iron concentrations in the range from 0.5 up to 7 mol %. All the obtained solid solutions were analyzed for the content of a paramagnetic component by the method of atomic absorption spectroscopy.

The magnetic susceptibility of the compounds under study was measured by the Faraday method. The measurements of magnetic susceptibility of each sample were carried out at 16 fixed temperatures from 77 up to 400 K. The errors of the relative measurements were 1–2%. We introduced the diamagnetic corrections for determining the paramagnetic component of magnetic susceptibility calculated per 1 mole of the paramagnetic atom (χ_{Fe}), taking into account the experimental susceptibilities of diamagnetic matrices. The selected procedures of extrapolation of magnetic characteristics to the infinite dilution provided for the error of no more than 3%.