ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 9, pp. 1645–1648. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © N.V. Chezhina, A.V. Fedorova, S.M. Musatov, 2013, published in Zhurnal Obshchei Khimii, 2013, Vol. 83, No. 9, pp. 1419–1422.

Atoms State and Interatomic Interactions in Perovskite-Like Oxides: XXXII.[1] Formation of Paramagnetic Clusters in the $La_{1-0.33x}Ca_{0.33x}Fe_xAl_{1-x}O_3$ and $La_{1-0.33x}Sr_{0.33x}Fe_xAl_{1-x}O_3$ Solid Solutions

N. V. Chezhina, A. V. Fedorova, and S. M. Musatov

St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia
e-mail: avfiodorova@gmail.com

Received March 4, 2013

Abstract—Calcium- and strontium-containing lanthanum orthoferrites have been studied using magnetic dilution method. It has been shown that the iron-atom clusters with competing ferro- and antiferromagnetic exchange interactions can exist. By using Mossbauer spectroscopy, Fe(IV) atoms have been found in the $La_{1-0.33x}Ca_{0.33x}Fe_xAl_{1-x}O_3$ solid solutions and Fe(III) atoms in two different surroundings have been found in the $La_{1-0.33x}Sr_{0.33x}Fe_xAl_{1-x}O_3$ solid solutions. The compositions of paramagnetic clusters stable at the infinite dilution have been proposed basing of the magnetic susceptibility and Mossbauer spectroscopy data.

DOI: 10.1134/S107036321309003X

Recently, considerable attention has been focused on rare-earth orthoferrites $RFeO_3$ (R being a rare-earth element) due to their potential use as highly efficient magnetic materials. Doped lanthanum orthoferrites $La_{1-x}A_xFeO_3$ (A being an alkaline-earth element) occupy a special place among oxide semiconductors. They are widely applied in nanoelectronics and in fabrication of flexible permanent magnets [2–4]. The study of complex oxides doped with bivalent elements (calcium and strontium) is a topical issue due to a possibility to induce the transition of iron atoms to various valence states by introducing alkaline-earth elements into the perovskite structure; furthermore, the oxygen conductivity has been detected in complex oxides based on lanthanum orthoferrite [5–7]. Recent studies have shown that in addition to the nature of the doping diamagnetic atoms, their concentration affects significantly the physical and chemical properties of orthoferrites. The attempts are currently made to alter the properties of doped orthoferrites by a partial substitution of iron atoms with aluminum [8, 9]. In this case, a homovalent substitution of trivalent iron atoms with aluminum, not inducing Fe(III) change of the valence state, also results in the changes of these compounds properties, including decrease in the electron and ionic conductivities. In spite of a large number of published papers, the mechanism of the diamagnetic substituents influence on the functional properties of the orthoferrites has still remained unclear. The Mössbauer study of complex oxides, lanthanum orthoferrites containing alkaline-earth elements [7, 8], has revealed the transition of iron atoms to various valence states (IV, V). However, the study of magnetically concentrated systems, including complex oxides of lanthanum orthoferrites, has not allowed disclosure of the diamagnetic atoms nature influence on the iron atoms state and on the physical and chemical characteristics of the materials based on $La_{1-x}A_xFeO_3$.

In the case of a ferromagnetic oxide, this complication can be overcome taking advantage of the magnetic dilution method based on studying magnetic properties of isomorphically substituted solid solutions. The analysis of the solid solutions magnetic properties as functions of temperature and concentration allows reliable determination of the paramagnetic atoms state and the character of exchange interactions between magnetic centers.

---

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

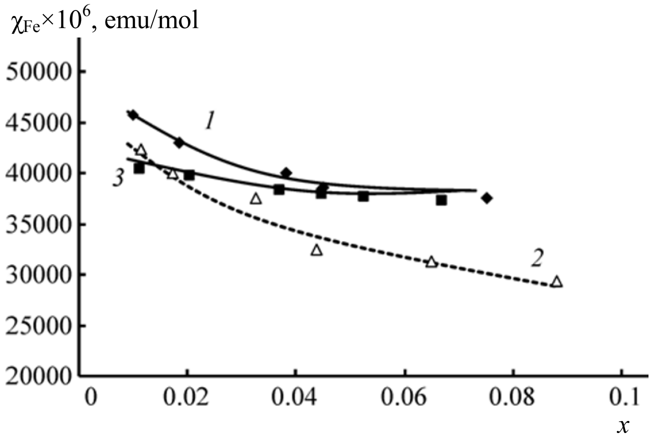

Fig. 1. Paramagnetic part of magnetic susceptibility as function of iron atoms concentration for: (*1*) $La_{1-0.33x}Ca_{0.33x}$·$Fe_xAl_{1-x}O_3$, (*2*) $LaFe_xAl_{1-x}O_3$, and (*3*) $La_{1-0.33x}Sr_{0.33x}Fe_xAl_{1-x}O_3$ solid solutions.

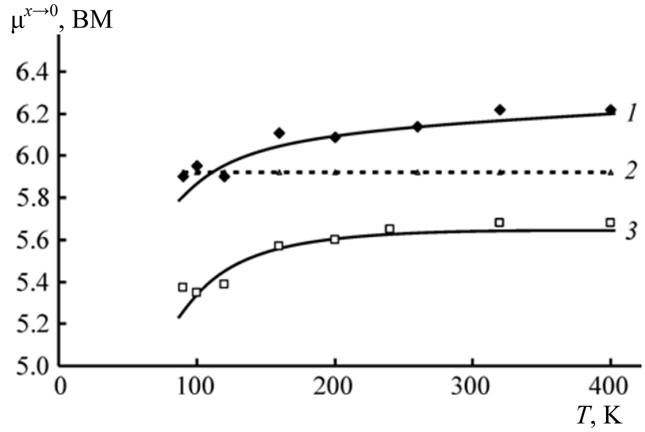

Fig. 2. The effective magnetic moment at the infinite dilution as function of temperature for: (*1*) $La_{1-0.33x}Ca_{0.33x}$·$Fe_xAl_{1-x}O_3$, (*2*) $LaFe_xAl_{1-x}O_3$, and (*3*) $La_{1-0.33x}Sr_{0.33x}Fe_xAl_{1-x}O_3$ solid solutions.

This work aimed to study the state of iron atoms in the $La_{1-0.33x}Ca_{0.33x}Fe_xAl_{1-x}O_3$ and $La_{1-0.33x}Sr_{0.33x}Fe_xAl_{1-x}O_3$ solid solutions (x = 0.01–0.15) and to reveal the influence of the substituting diamagnetic atoms nature on the iron atoms state and the exchange interactions character.

Basing on the measured magnetic susceptibility, we calculated paramagnetic part of magnetic susceptibility per 1 mol of iron atoms (χ_{Fe}) and the effective magnetic moment (μ_{eff}), and plotted their temperature and concentration dependences. By extrapolation of the magnetic susceptibility isotherms to infinite dilution ($x\to0$), we determined the effective magnetic moments at infinite dilution ($\mu^{x\to0}$).

The analysis of the magnetic properties showed that the temperature dependences of the inverse paramagnetic part of magnetic susceptibility followed the Curie–Weiss law over the whole temperature range, Weiss constants being negative, in the cases of the $La_{1-0.33x}Ca_{0.33x}Fe_xAl_{1-x}O_3$ and $La_{1-0.33x}Sr_{0.33x}Fe_xAl_{1-x}O_3$ solid solutions.

Comparison of the χ_{Fe}–x isotherms for the studied solid solutions with that of the $LaFe_xAl_{1-x}O_3$ system [10] (Fig. 1) showed that the magnetic susceptibility isotherms were similar in the cases of the calcium-containing and strontium-containing systems, and that χ_{Fe} decreased with increasing iron concentration. At $x > 0.04$, the isotherms for solid solutions containing calcium and strontium almost coincided and were located above the plot for $LaFe_xAl_{1-x}O_3$. It pointed at the same character of exchange interactions in the systems containing calcium and strontium, while the interactions were substantially different in the case of the system free of bivalent doping element.

The analysis of the effective magnetic moments at the infinite dilution, $\mu^{x\to0}$ (Fig. 2), revealed that $\mu^{x\to0}$ values for $La_{1-0.33x}Ca_{0.33x}Fe_xAl_{1-x}O_3$ and $La_{1-0.33x}Sr_{0.33x}$·$Fe_xAl_{1-x}O_3$ depended on temperature and were in the ranges of 6.0–6.22 and 5.35–5.68 BM, respectively. The effective magnetic moment at the infinite dilution in the case of $LaFe_xAl_{1-x}O_3$ solid solution (5.92 BM) was independent of temperature and corresponded to the $3d^5$, $^6A_{1g}$ state of Fe(III) atoms. Lower $\mu^{x\to0}$ values for strontium-containing systems (as compared to $LaFe_xAl_{1-x}O_3$) could be explained by presence of iron atoms in other oxidation states [Fe(IV) and Fe(II)], whereas $\mu^{x\to0}$ values of calcium-containing solid solutions, 6.0–6.22 BM, could not correspond to isolated iron atoms in any of the possible oxidation states.

Solid solutions containing calcium and strontium (x = 0.15) were studied by Mössbauer spectroscopy (Figs. 3 and 4).

The study of the iron atoms state in the solid solutions showed that the Mössbauer spectrum of the $0.15La_{0.67}Ca_{0.33}FeO_3$–$0.85LaAlO_3$ solid solution contained a doublet (0.340), assigned to Fe(III) in the octahedral surrounding of oxygen atoms. In the same spectrum, there was a singlet line with the isomer shift of –0.099 in the region typical of Fe(IV). The latter line was weak; the fraction of iron in that state was 7%. Such a line was absent in the spectrum of the strontium-containing sample, which contained two

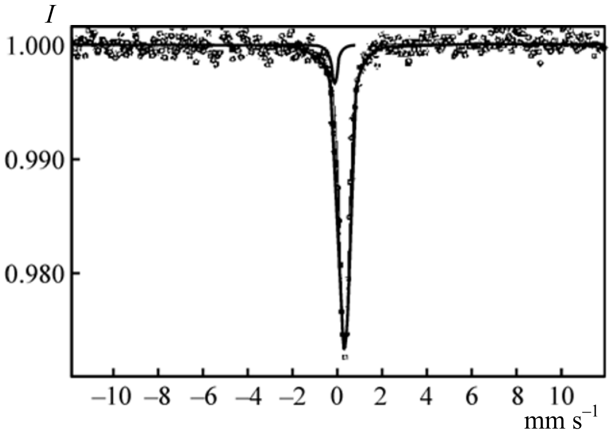

Fig. 3. Mössbauer spectrum of $0.15La_{0.67}Ca_{0.33}FeO_3$–$0.85LaAlO_3$.

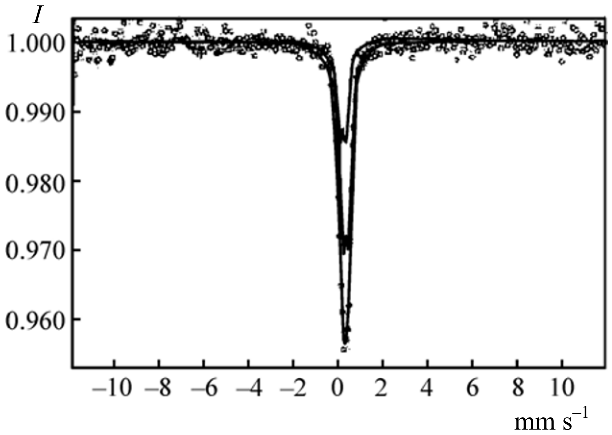

Fig. 4. Mössbauer spectrum of $0.15La_{0.67}Sr_{0.33}FeO_3$–$0.85LaAlO_3$.

doublets (0.367 and 0.237) differing in their isomer shifts and quadrupole splitting, however being typical of Fe(III). The ratio of the doublets intensities was 2:1, corresponding to different surroundings of iron by heavy lanthanum and strontium atoms.

The X-ray diffraction study of the solid solutions containing calcium and strontium and the comparison of their unit cell parameters with those of diamagnetic $LaAlO_3$ solvent showed that the unit cell parameter increased as alkaline-earth element was introduced in the perovskite structure. That increase was more substantial in the case of strontium as compared to calcium effect (3.91 and 3.78 Å, respectively).

Taking into account the results of the magnetochemical and Mössbauer experiments, we concluded that paramagnetic clusters stable at the infinite dilution were formed in the $La_{1-0.33x}Ca(Sr)_{0.33x}Fe_xAl_{1-x}O_3$ solid solutions. Similar behavior was previously observed in the cases of lanthanum manganite solid solutions doped with calcium (or strontium) and yttrium [11, 12]. In the strontium-doped solid solutions of lanthanum manganites, all iron atoms were found in the +3 oxidation state. The appearance of some Fe(IV) fraction in the $La_{1-0.33x}Ca_{0.33x}Fe_xAl_{1-x}O_3$ solid solutions was due to structural factors: calcium and lanthanum had close ionic radii of 1.34 and 1.36 Å, respectively [13]. Relatively large Fe(III) atoms induced strong local distortions in the perovskite structure. If so, the appearance of smaller Fe(IV) atoms could stabilize the structure. In the case of calcium-containing solid solutions, the formation of sufficiently stable clusters, not dissociating at infinite dilution and evidently containing bivalent element atoms and associated vacancies of the oxygen sublattice, could result in the fact that not only Fe(III)–O–Fe(IV), but also Fe(III)–O–Fe(III) exchange might be ferromagnetic at the expense of local distortions of the nearest surrounding [14].

Therefore, the introduction of bivalent atoms into the $LaFe_xAl_{1-x}O_3$ orthoferrite enhanced the iron atom clustering, the cluster size and the character of exchange in the clusters depending on the nature of the alkaline-earth element. An essential difference of magnetic properties of solid solutions containing alkaline-earth elements from those of $LaFe_xAl_{1-x}O_3$ meant that the resulting paramagnetic clusters contained calcium or strontium atoms. Noteworthily, in the most concentrated $La_{1-0.33x}Ca(Sr)_{0.33x}Fe_xAl_{1-x}O_3$ solid solution at x of 0.10 only three lanthanum atoms of a hundred were substituted for calcium or strontium.

With more of iron atoms (x) in the solid solution, the size and the number of various clusters increased, and the difference in magnetic behavior between the systems containing calcium and strontium were eliminated. However, the isotherms of the paramagnetic part of magnetic susceptibility were located above that of the $LaFe_xAl_{1-x}O_3$ system. This meant that in the heterovalently doped solid solutions, the ferromagnetic component was retained in the exchange interactions between iron atoms within the whole concentration range.

EXPERIMENTAL

We prepared the $La_{1-0.33x}Ca_{0.33x}Fe_xAl_{1-x}O_3$ and $La_{1-0.33x}Sr_{0.33x}Fe_xAl_{1-x}O_3$ solid solutions ($x = 0.01, 0.02,$

0.03, 0.04, 0.05, 0.6, 0.08, and 0.15) by the ceramic procedure. The initial substances: lanthanum oxide (special pure grade), calcium and strontium carbonates (analytical pure grade), aluminum oxide prepared by thermal decomposition of aluminum nitrate hexahydrate (analytical pure grade), and iron(III) oxide (analytical pure grade) were homogenized in an agate mortar for 1 h. The amounts of the starting substances were calculated according to solid-phase reaction equation:

$$0.5La_2O_3 + 0.33x ACO_3 + 0.5(1-x)Al_2O_3 + 0.5x Fe_2O_3 = La_{1-0.33x}A_{0.33x}Fe_xAl_{1-x}O_3 + 0.33x CO_2$$

with A being an alkaline-earth element (calcium or strontium), x = 0.01, 0.02, 0.03, 0.04, 0.05, 0.6, 0.08, or 0.15.

The homogenized mixtures were molded into pellets using an acrylic resin mold, and then the pellets were sintered for 50 h at 1450°C.

The X-ray analysis confirmed the homogeneity of the prepared samples. The X-ray diffraction patterns were recorded with DRON-3 diffractometer using Fe-K_α radiation. The quantity of iron atoms was determined by the atomic absorption method.

The magnetic susceptibility of the solid solutions was measured by the Faraday method in the temperature range of 77–400 K. The solid solutions with iron atom concentration x = 0.15 were investigated by Mössbauer spectroscopy. The state of iron atoms was studied by Mössbauer spectroscopy at room temperature with Wissel spectrometer. The ^{57}Co source in Rh matrix was used. The isomer shifts were related to α-Fe. The experimental spectra were processed using the Möss Fit software package.

ACKNOWLEDGMENTS

The authors are grateful to V.G. Semenov and V.V. Panchuk for the Mössbauer spectroscopy experiments.

REFERENCES

1. Chezhina, N.V. and Korolev, D.A., *Russ. J. Gen. Chem.*, 2012, vol. 82, no. 3, pp. 347–353.
2. Ciambelli, P., Cimino, S., and Lisi, La.L., *Appl. Catal. (B),* 2001, p. 193.
3. Pecchi, G. and Reyes, P., *Catalysis Today*, 2008, vols. 133–135, p. 420.
4. Ahn, K.H. and Wu, X.W., *Phys. Rev. (B),* 1996, vol. 54, no. 21, p. 299.
5. Ahmed, M.A. and El-Dek, S.I., *Mater. Sci. Eng. (B),* 2006, vol. 128, p. 30.
6. Martin, L.W., Chu, Y.-H., and Ramesh, R., *Mater. Sci. Eng. (R),* 2010, vol. 68, p. 89.
7. Hudspeth, J.M., Stewart, G.A., Studer, A.J., and Goossens, D.L., *J. Phys. Chem. Solids*, 2011, vol. 72, p. 1543.
8. Yaremchenko, A.A., Patrakeev, M.V., Kharton, V.V., Marques, F.M.B., Leonidov, I.A., and Kozhevnikov, V.L., *Solid State Sci.*, 2004, vol. 6, p. 357.
9. Cihlar, J., Del Favero, D., Cihlar, Ja., Jr., Buchal, A., and Van Herle, J., *J. Eur. Ceramic Soc.*, 2006, vol. 26, p. 2999.
10. Brach, B.Ya., Dudkin, B.N., and Chezhina, N.V., *Zh. Neorg. Khim.*, 1979, vol. 24, no. 8, p. 2064.
11. Chezhina, N.V. and Fedorova, A.V., *Russ. J. Gen. Chem.*, 2010, vol. 80, no. 2, pp. 203–206.
12. Chezhina, N.V. and Fedorova, A.V., *Russ. J. Gen. Chem.*, 2010, vol. 80, no. 5, pp. 909–914.
13. Shannon, K.D. and Prewitt, C.T., *Acta Crystal. (B),* 1969, vol. 25, p. 925.
14. Kalinnikov, V.T. and Rakitin, Yu.V., *Vvedenie v magnetokhimiyu. Metod staticheskoi magnitnoi vospriimchivosty* (Introduction to Magnetochemistry. Method of Static Magnetic Susceptibility), Moscow: Nauka, 1980.