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State of Transition Element Atoms in the Solid Solutions of Lanthanum Ortoferrites Containing Calcium and Strontium

Natalia V. Chezhina*, Anna V. Fedorova, Stepan M. Musatov

Sankt-Petersburg State University, Universitetskii pr. 26, Sankt-Petersburg, 198504, Russia

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Abstract With the help of magnetic dilution method lanthanum ortoferrites containing calcium and strontium were studied. The clusters of iron atoms with competing antiferro- and ferromagnetic superexchange interactions were found, which do not disintegrate at the infinite dilution of the solid solutions. They necessarily contain the atoms of bivalent doping element and accompanying vacancies in the oxygen sublattice. By the method of Mossbauer spectroscopy a small fraction of Fe^{IV} was found in calcium containing solid solutions, whereas only Fe^{III} is present in strontium containing solutions in two different surroundings by heavy metal atoms (La,Sr). Clustering seems to be the reason for the stability of perovskite structure of doped lanthanum ortoferrite.

Keywords Magnetic Dilution, Effective Magnetic Moment, Clusters, Superexchange

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1. Introduction

Rare earth ortoferrites, $RFeO_3$ (where R is a rare earth element) attracted considerable recent attention of the researchers in the context of the possibilities of their application as highly efficient magnetic materials. Doped lanthanum ortoferrites, $La_{1-x}A_xFeO_3$, (where A is an alkaline earth element) occupy a significant place among oxide semiconductors. They find use in the field of nanoelectronics, as flexible constant magnets etc[1],[2],[3]. In spite of a large number of works devoted to obtaining materials with particular characteristics, the mechanisms of the influence of diamagnetic substituents on functional properties of the materials remains obscure up to the present. Complex oxides doped with bivalent elements – calcium and strontium attract particular interest of the researchers. Introduction of alkaline earth elements in the perovskite structure may initiate a transfer of iron atoms to various valence states and is the reason for oxygen conductivity in the complex oxides based on lanthanum ortoferrite[4],[5],[6]. Recent studies show that not only the nature of the doping diamagnetic element but also its concentration has a profound effect on the physical and chemical properties of these materials. Currently the attempts are made to exert an influence on the properties of doped ortoferrites by substituting aluminium for a fraction of iron atoms[7],[8]. In this case the substitution of Al^{III} for Fe^{III} is not associated with Fe^{III} transfer to other valence states, however it results in the changes in the properties of these compounds, a decrease in the electronic and oxygen conductivity among them. The authors of[7],[8] studied Mossbauer spectra of lanthanum ortoferrites containing alkaline earth elements and found the transfer of iron atoms to various valence states – Fe^{IV} and even Fe^{V}, the latter being extremely doubtful.

The study of magnetically concentrated systems such as lanthanum ortoferrites fails to trace the influence of the nature of diamagnetic elements on the state of iron atoms and physico-chemical characteristics of materials based on $La_{1-x}A_xFeO_3$, since in the perovskite structure short and long order superexchange interactions are superimposed thus disguising the state of a paramagnetic atom and excluding the possibility to determine the interactions between the nearest atoms.

This problem may be solved with the help of magnetic dilution method based on the study of magnetic properties of the solid solutions of isomorphic substitution. Examination of temperature and concentration dependences of magnetic properties of diluted solid solutions allows the state of a paramagnetic atom and the character of super exchange interactions between magnetic centres to be determined to closer limits of accuracy.

The aim of this work was to study the state of iron atoms in the solid solutions $xLa_{0,67}Ca_{0,33}FeO_3$ – $(1-x)LaAlO_3$ and $xLa_{0,67}Sr_{0,33}FeO_3$ – $(1-x)LaAlO_3$ ($x=0.01$ – 0.15) and to determine the influence of the nature of a substituting diamagnetic element on the state of iron atoms and the character of super exchange interactions.

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* Corresponding author:
chezhina@nc2490.spb.edu (Natalia V. Chezhina)

2. Experimental

Solid solutions $xLa_{0,67}Ca_{0,33}FeO_3$ – $(1\text{-}x)LaAlO_3$ and $xLa_{0,67}Sr_{0,33}FeO_3$ – $(1\text{-}x)LaAlO_3$, where x =0,01, 0,02, 0,03, 0,04, 0,05, 0,06, 0,08, 0.15, were obtained by ceramic procedure. The starting compounds: special pure grade lanthanum and iron (III) oxides, analytical pure grade strontium and calcium carbonates, aluminium oxide obtained by thermal decomposition of analytical pure grade aluminium nitrate hexahydrate were homogenized in an agate mortar for 1 h. The quantities of the starting substances were calculated by the solid state reaction:

$$0{,}5La_2O_3+0{,}33xACO_3+0{,}5(1\text{-}x)Al_2O_3+0{,}5xFe_2O_3 = xLa_{0,67}A_{0,33}FeO_3–(1\text{-}x)LaAlO_3+0{,}33xCO_2,$$

where A is an alkaline earth element (calcium or strontium). The obtained mixtures were pressed into pellets and sintered at 1450°C in air for 50 h.

The X-ray patterns were recorded on a DRON-3 diffractometer using FeK_α emission. All the solid solutions were single phase and had the structure of cubic lanthanum aluminate. We determined the content of iron atoms in the solid solutions after sintering by the method of atom absorption spectroscopy. The error of the chemical analysis did not exceed 3% from x in the solid solution formula.

Magnetic susceptibility of the solid solutions under study was measured by Faraday method in the temperature range 77-400 K. The error of relative measurements was 1%. Diamagnetic corrections for calculating the paramagnetic component of magnetic susceptibility were introduced with respect to the susceptibility of diamagnetic $LaAlO_3$ matrix measured over the same temperature range.

We studied the state of iron atoms by the method of Mossbauer spectroscopy. The Mossbauer examination of samples employed a WISSEL spectrometer. The measurements were performed in the absorption geometry at room temperature with $^{57}Co/Rh$ source. The isomer shift (IS) values are referenced relative to α-Fe. The experimental spectra were folded and fitted by Lorentz functions using the computer program MossFit.

3. Results and Discussion

For the solid solutions under study the temperature and concentration dependencies of paramagnetic component of magnetic susceptibility calculated per one mole of iron atoms were plotted. The plots of inverse paramagnetic component vs temperature are linear over the whole temperature interval; χ_{Fe} for both systems obeys Curie-Weiss low with small negative Weiss constants. Of utmost interest are the isotherms χ_{Fe} – x plotted for 16 temperatures measured and their comparison with the $LaFeO_3$-$LaAlO_3$ system [9] (Figure 1). It is seen from figure 1 that in the region of x>0.04 both isotherms for calcium and strontium containing solid solutions almost coincide being located higher than the dependencies for $LaFe_xAl_{1-x}O_3$. This can point to the fact that the character of long order exchange interactions is the same for both systems, but differ significantly from the exchange in the system containing no bivalent doping elements. However at a greater dilution both isotherms are moving apart. For calcium containing solid solutions the dependencies χ_{Fe} – x lie higher and for the solid solutions doped with strontium – lower than for the solid solutions $LaFe_xAl_{1-x}O_3$.

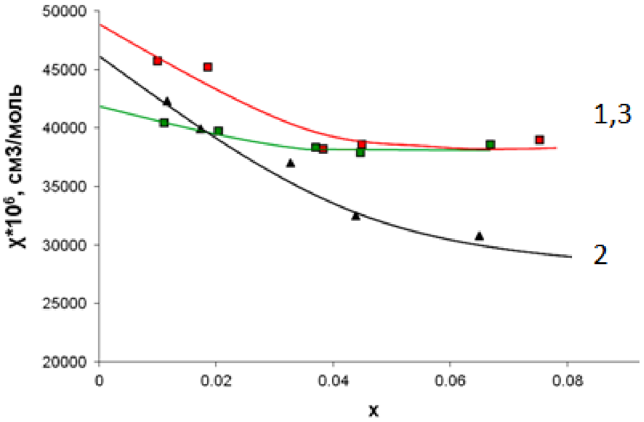

Figure 1. Plots of paramagnetic component of magnetic susceptibility vs x for the solid solutions $La_{1\text{-}0.33x}Ca_{0.33x}Fe_xAl_{1\text{-}x}O_3$ -1; $LaFe_xAl_{1\text{-}x}O_3$ -2; $La_{1\text{-}0.33x}Ca(Sr)_{0.33x}Fe_xAl_{1\text{-}x}O_3$ -3

All the isotherms of paramagnetic component of magnetic susceptibility and effective magnetic moments calculated by Curie formula $\mu_{eff} = \sqrt{\dfrac{3k\chi T}{N\beta^2}}$ were extrapolated to the infinite dilution of the solid solutions (χ_{Fe}, μ_{eff}, $x\rightarrow0$) (Figure 2.). We emphasize that the effective magnetic moment at the infinite dilution of the solid $LaFe_xAl_{1-x}O_3$ solution is 5.92 BM , does not depend on temperature, and accurately fits Fe^{III} - $3d^5$, $^6A_{1g}$[10]. The effective magnetic moments for the $La_{1\text{-}0.33x}Ca(Sr)_{0.33x}Fe_xAl_{1\text{-}x}O_3$ solid solutions under study slightly increase as the temperature increases and appear to be higher (6.0-6.22 BM) for the solid solutions doped with calcium and lower than 5.92 BM (5.35-5.68 BM) for strontium containing solid solutions.

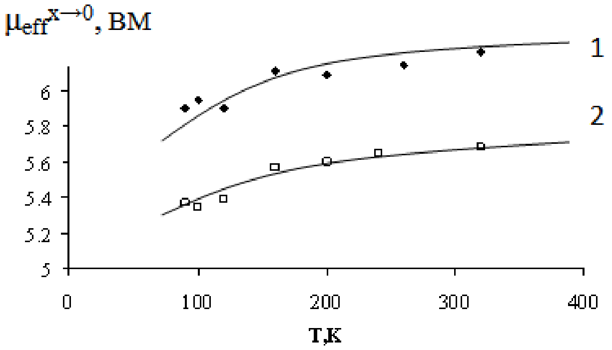

Figure 2. Plots of effective magnetic moments at infinite dilution ($\mu_{eff}^{x\rightarrow0}$) of the solid solutions $La_{1\text{-}0.33x}Ca_{0.33x}Fe_xAl_{1\text{-}x}O_3$ -1; $La_{1\text{-}0.33x}Ca(Sr)_{0.33x}Fe_xAl_{1\text{-}x}O_3$ -2

Table 1. Parameters of Mossbauer spectrum for the $0{,}15La_{0,67}Ca_{0,33}FeO_3$ –$0{,}85LaAlO_3$ solid solution

Singlets					
n	A(imp.)	Γ(mm/s)	IS(mm/s)		%
1	0.004+/-0.001	0.253+/-0.117	-0.099+/-0.034		7.00
Doublets					
n	A(imp.)	Γ(mm/s)	IS(mm/s)	QS(mm/s)	%
1	-0.017+/-0.001	0.366+/-0.028	0.340+/-0.008	0.197+/-0.016	93.00

Table 2. Parameters of Mossbauer spectrum for the $0{,}15La_{0,67}Sr_{0,33}FeO_3$ –$0{,}85LaAlO_3$ solid solution

Doublets					
n	A(imp.)	Γ(mm/s)	IS(mm/s)	QS(mm/s)	%
1	-0.25+/-0.008	0.294+/-0.039	0.376+/-0.029	0.252+/-0.014	68.05
2	-0.013+/-0.008	0.266+/-0.091	0.237+/-0.045	0.278+/-0.022	31.95

If undersized μ_{eff} for strontium containing systems may be, in principle, associated with iron atoms appearing in other oxidation states (Fe^{IV}, Fe^{II}), $\mu_{eff}^{x\to 0}$ equal to 6.0-6.22 MB for calcium containing solid solution cannot be ascribed to single iron atoms no matter in which oxidation state they are. It is evident that we were to determine the oxidation states of iron atoms in the systems under study. With this aim in view Mossbauer spectra were recorded for the solid solutions containing Ca and Sr with x=0.15. The spectra are given in Figures 3 and 4, their parameters are given in tables 1 and 2.

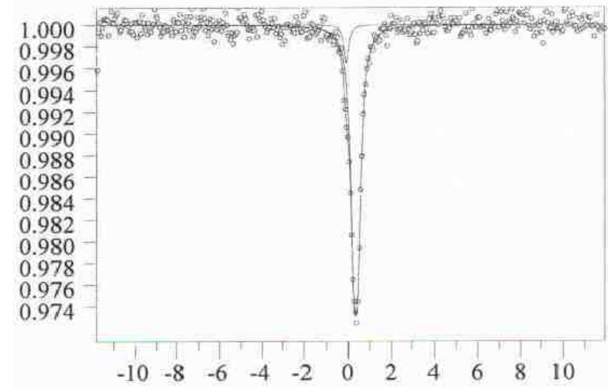

Figure 3. Mossbauer spectrum of $0{,}15La_{0,67}Ca_{0,33}FeO_3$ –$0{,}85LaAlO_3$

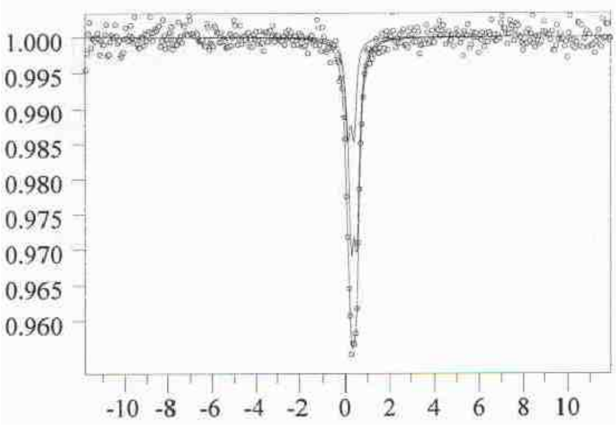

Figure 4. Mossbauer spectrum of $0{,}15La_{0,67}Sr_{0,33}FeO_3$ –$0{,}85LaAlO_3$

A doublet typical for iron (III) in the octahedral surrounding of oxygen atoms is observed in the spectrum of calcium containing solid solution. However in the same spectrum there is a singlet line with isomeric nuclear shift -0.099 falling to the region typical for iron (IV). This line has a low intensity, and the fraction of iron in this state is only 7%. There is no such a line in the spectrum of strontium containing sample, where two doublets are observed differing by their isomeric shift and quadrupole splitting, but also typical for Fe^{III}. The ratio of the intensities of both doublets is about 2:1, which can be associated with different surrounding of iron atoms with heavy atoms of lanthanum or strontium.

We must emphasize that the possibility of Fe^{IV} appearing in calcium containing solid solutions is confirmed by the fact that the lattice parameter is slightly decreasing as x increases (a=3.79 Å in $LaAlO_3$ and a=3.78 Å in $0{,}1La_{0,67}Ca_{0,33}FeO_3$ –$0{,}9LaAlO_3$), whereas in $0{,}1La_{0,67}Sr_{0,33}FeO_3$ –$0{,}9LaAlO_3$ a =3.91 Å, as could be anticipated upon introduction of greater Sr and Fe atoms into $LaAlO_3$. Calcium and lanthanum have close ionic radii ($r_{(Ca2+)}$= 1.34Å, $r_{(La3+)}$=1.36Å[11]). Relatively large Fe^{III} atoms ($r_{Fe(III)}$= 0,645 Å , $r_{Al(III)}$= 0,585 Å) give rise to strong local distortions in the structure. In this respect the emergence of smaller Fe^{IV} atoms may appear as a stabilizing factor.

In other words in the strontium containing system all the atoms of iron are in the oxidation state +3. Consequently in this system μ_{eff} (x→0) also does not fit single iron atoms. This means that in both solid solutions no complete disaggregation of iron atoms occurs at the infinite dilution as we could see for the $LaFe_xAl_{1-x}O_3$ system. Such a behavior was observed in the solid solutions of lanthanum manganite doped with calcium or strontium and yttrium [12],[13]. The formation of sufficiently rigid clusters, which do not disintegrate at the infinite dilution and include bivalent atoms and vacancies in the oxygen sublattice in the calcium containing solid solutions may result in the fact that not only the exchange Fe^{III}-O-Fe^{IV} but also Fe^{III}-O-Fe^{III} may become ferromagnetic at the expense of local distortions of the nearest surrounding [10].

Therefore it is evident that introduction of bivalent element atoms into the structure of the solid solution results in an increase in iron atom clustering, the size and the character of exchange interactions depending on the nature of an alkaline earth element. The clusters must include also Ca or Sr atoms and vacancies accompanying them, otherwise such a drastic difference in the magnetic characteristics of the solid solutions in comparison with the LaFe$_x$Al$_{1-x}$O$_3$ system could not be observed. We must take into account the fact that in the most concentrated solid solution La$_{1-0.33x}$Ca(Sr)$_{0.33x}$Fe$_x$Al$_{1-x}$O$_3$ at x=0.10 only three lanthanum atoms out of one hundred are replaced with strontium or calcium.

An increase in the iron content in the solid solution results in an increase in the size and quantity of various clusters, and the difference in the magnetic behavior of calcium and strontium containing systems becomes leveled, however the isotherms of magnetic susceptibility lie higher than for the LaFe$_x$Al$_{1-x}$O$_3$ system. This points to the fact that a ferromagnetic component in the superexchange interactions between iron atoms is preserved over the whole concentration interval in the solid solutions with a heterovalent doping.

4. Conclusions

The study of magnetic dilution of lanthanum ortoferrites doped with alkaline earth elements showed that the introduction of heterovalent doping elements into the sublattice of lanthanum results in an increase in iron atoms clustering in the solid solution in comparison with the LaFe$_x$Al$_{1-x}$O$_3$ system. The sizes and the exchange interactions in the clusters stable even at the infinite dilution depend on the nature of the doping element. Introduction of relatively small calcium atoms (compared to strontium) results in a fraction of iron (IV) appearing in the solid solution, which seem to stabilize the structure, whereas in the strontium containing solid solutions only two kinds of Fe^{III} surrounding with heavy metal atoms show themselves in the Mossbauer spectra. The clusters include also the atoms of a doping element and accompanying vacancies in the oxygen sublattice.

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