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Low-temperature Mössbauer studies of substituted $La_{0.67}Sr_{0.33}FeO_{3-\gamma}$ lanthanum ferrite

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The valence states of Fe atoms and the formation of oxygen vacancies in substituted $La_{0.67}Sr_{0.33}FeO_{3-\gamma}$ orthoferrite have been studied in detail by low-temperature Mössbauer spectroscopy under oxygen removal. It has been shown that the averaged valence state of Fe atoms is not revealed with a decreasing measurement temperature. This makes it possible to reveal Fe^{4+} ions. The Analysis of the obtained data allows us to conclude that the presence of several Zeeman sextets associated with Fe^{3+} ions is related to the appearance of oxygen vacancies and Fe^{4+} ions in the nearest ionic surrounding of Fe ions. Using the Mössbauer data, the number of oxygen vacancies and oxygen ions has been determined for all the studied samples depending on the vacuum annealing temperature.

Keywords: perovskites, substituted lanthanum ferrites, X-ray diffraction analysis, Mössbauer spectroscopy, Fe valence states, oxygen vacancies.

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1. Introduction

Perovskite-type $R_{1-x}A_xFeO_{3-\gamma}$ orthoferrites, where R is the rare earth element and A is Ba, Ca, or Sr, are promising materials due to their unusual electrical, magnetic, and catalytic properties [1,2]. They can be used in various application fields, e.g., as cathode material for fuel elements, catalysts, chemical sensors, optoelectronic devices, magnetic memory devices, and so on [3–7]. In these systems, transition metal ions have mixed valence states, which can be caused by either the substitution of divalent ions (A) for trivalent element (R) position or the formation of oxygen vacancies [8].

$LaFeO_3$ orthoferrite, which is part of this compound family, has an orthorhombic structure with the space group $Pbnm$. Fe ions are in a trivalent state and have an octahedral oxygen environment. Oxygen anions located at the vertices of the octahedron participate in the superexchange interaction between iron ions $Fe^{3+}-O^{2-}-Fe^{3+}$, which is antiferromagnetic according to the Goodenough theory [9] and stronger than that between Fe^{4+} and Fe^{3+}, as well as Fe^{4+} and Fe^{4+} ions.

When trivalent La^{3+} is partially replaced by divalent Sr^{2+}, a homogeneous structural and charge ordering in $La_{1-x}Sr_xFeO_{3-\gamma}$ oxides is violated at the local level. The oxidation degree of Fe ions increases from Fe^{3+} to Fe^{4+} when La^{3+} cations are substituted by Sr^{2+} cations in $LaFeO_{3-\gamma}$. This weakens the antiferromagnetic order caused by the superexchange interaction of Fe^{3+} ions [10–14].

The substituted $La_{0.67}Sr_{0.33}FeO_{3-\gamma}$ lanthanum ferrite was studied by SEM, XRD, Mössbauer, and Raman spectroscopy at room temperature in our previous work [15]. It followed from the room-temperature Mössbauer study that Fe ions are manifested in the form of an averaged valence state. Heat treatment in vacuum results in an increase in the number of oxygen vacancies and a change of an averaged valence state. Oxygen leaving a lattice finishes at a temperature above 450°C, and only Fe^{3+} ions are detected. However, to study the valence states of iron and its environment in detail and to estimate an oxygen concentration in all $La_{0.67}Sr_{0.33}FeO_{3-\gamma}$ samples, low-temperature Mössbauer studies are necessary.

In the present work, the valence states of iron atoms and the formation of oxygen vacancies in the substituted $La_{0.67}Sr_{0.33}FeO_{3-\gamma}$ orthoferrite samples (synthesized and after vacuum heat treatments) have been studied by low-temperature Mossbauer spectroscopy.

2. Materials and methods

A polycrystalline $La_{0.67}Sr_{0.33}FeO_{3-\gamma}$ sample was prepared in the air by a sol-gel method using strontium, iron, and lanthanum nitrates in a stoichiometric proportion and glycine as starting reagents. The details of the preparation procedure were described in Ref. [16]. After synthesis at 1100°C for 20 h in the air, the sample and a furnace were cooled down slowly to room temperature. Then, the samples were annealed in vacuum (10^{-3} Torr) at 200−650°C for 4 h and cooled down slowly.

The Mössbauer measurements were performed at 85 K on an SM 1101 spectrometer operating in a constant acceleration mode using ^{57}Co(Rh) radioactive source. The fitting and analysis of the spectra were carried out by the model fitting of hyperfine spectral parameters using the SpectrRelax program [17].

3. Results and discussion

Since the room-temperature Mössbauer data obtained in our previous work did not provide unique information on the presence, number and behavior of Fe^{4+} ions, the number of subspectra associated with the effect of substitution of La by Sr, the effect of oxygen vacancies, and inability to estimate an oxygen concentration in the samples after a series of vacuum annealing, the Mössbauer investigations were performed at 85 K. The 85 K Mössbauer spectra of $LaFeO_3$, synthesized substituted $La_{0.67}Sr_{0.33}FeO_{3-\gamma}$, and some of its samples annealed in vacuum are presented in Figs. 1 and 2.

The Mössbauer spectrum of $LaFeO_3$ is a typical Zeeman sextet related to the magnetic ordering of strontium ferrite and has narrow resonance lines, Fig. 1. Hyperfine parameters of the spectrum (isomer shift $\delta = 0.433 \pm 0.002$ mm/s, quadrupole shift $\varepsilon = -0.037 \pm 0.002$ mm/s, and hyperfine magnetic field $H_{\text{hf}} = 557.45 \pm 0.14$ kOe) are in a good agreement with the known literature data [18] and correspond to Fe atoms being in a trivalent high spin state in an octahedral oxygen environment.

As was shown in our earlier work [15], a very wide distribution $p(H_{\text{hf}})$ of the hyperfine magnetic field H_{hf} is observed for the synthesized $La_{0.67}Sr_{0.33}FeO_{3-\gamma}$ sample measured at room temperature, which is caused by two factors. The first factor is the random distribution of Fe^{4+} ions over Fe ion positions and the appearance of oxygen vacancies in the substituted $La_{0.67}Sr_{0.33}FeO_{3-\gamma}$ ferrite structure. This distribution of Fe^{4+} ions and vacancies in the structure results in strong local heterogeneity in the Fe atom environment and, as a consequence, in a wide distribution $p(H_{\text{hf}})$. The second factor is a fast electron transfer between Fe^{3+} and Fe^{4+} ions at room temperature, leading to an averaged valence state of Fe ions. Based on the fact that the linewidths of the 85 K Mössbauer spectrum strongly decrease (Fig. 2) as compared to the room-temperature Mössbauer spectrum, one can conclude that the averaged valence state of Fe ions is not revealed with a decreasing temperature. This testified to the freezing of the electron transfer process.

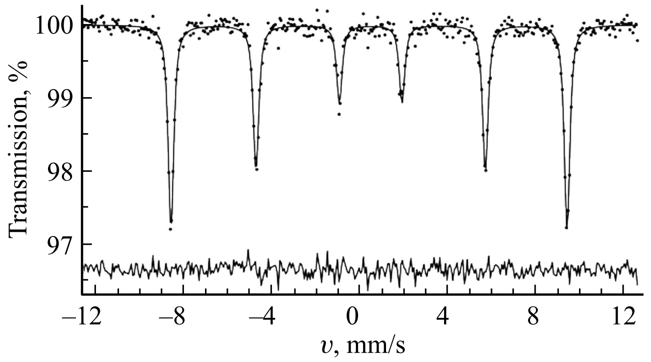

Figure 1. The 85 K Mössbauer spectrum of synthesized $LaFeO_3$ and the result of its model fitting.

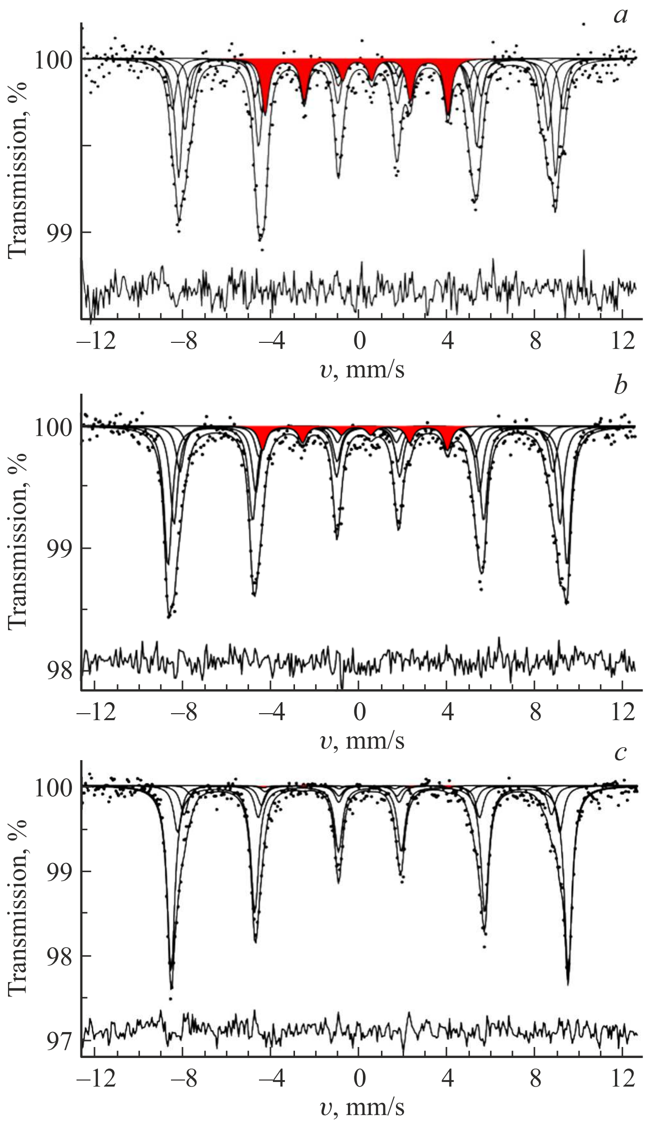

Figure 2. Result of the model fitting of the 85 K Mössbauer spectra of the $La_{0.67}Sr_{0.33}FeO_{3-\gamma}$ samples: synthesized (*a*) and annealed in vacuum at 300°C (*b*) and 650°C (*c*). The subspectrum for Fe^{4+} ions is marked in red.

In a general case, the 85-K Mössbauer spectra of $La_{0.67}Sr_{0.33}FeO_{3-\gamma}$ consist of several subspectra, the hyperfine parameters of which suggest that one of them with the smallest isomer shift and hyperfine magnetic field belongs to Fe^{4+} ions, and the other belong to Fe^{3+} ions (Fig. 2). The presence of several Zeeman sextets applying to Fe^{3+} ions in the spectra is caused by the appearance of oxygen vacancies and Fe^{4+} ions in the nearest Fe atom cation environment in the substituted lanthanum ferrite. As a result of vacuum heat treatment of the synthesized sample, the number of oxygen vacancies and Fe^{3+} ions changes, which leads to the corresponding change in the Mössbauer spectra.

According to electrical neutrality, the crystal-chemical formula of La$_{0.67}$Sr$_{0.33}$FeO$_{3-\gamma}$ can be presented in the form

$$\mathrm{La}^{3+}_{1-x}\mathrm{Sr}^{2+}_{x}\mathrm{Fe}^{3+}_{1-y}\mathrm{Fe}^{4+}_{y}\mathrm{O}^{2-}_{3-\gamma} \Rightarrow (\mathrm{La}^{3+}_{1-x}\mathrm{Sr}^{2+}_{x}) \times (\mathrm{Fe}_{1-x+2\gamma})^{3+}\mathrm{Fe}^{4+}_{x-2\gamma})(\mathrm{O}^{2-}_{3-\gamma}\square_{\gamma}), \qquad (1)$$

where $x, y = x - 2\gamma$ and $\gamma = (x - y)/2$ are the numbers of Sr^{2+} and Fe^{4+} ions and oxygen vacancies ($\square$) per formula unit of ferrite, respectively.

The appearance of an oxygen vacancy in the nearest environment of Fe^{3+} ion results in the breaking of a Fe^{3+}–O^{2-}–Fe exchange coupling, which leads to a decrease in the hyperfine magnetic field H_{hf} and a change in the isomer shift of the spectrum [19,20]. In its turn, the appearance of a Fe^{4+} ion in the nearest cation environment of Fe^{3+} ions leads to the weakening of the exchange coupling and, correspondingly, to a decrease in the field H_{hf}. We supposed almost similar additive changes in the hyperfine field and isomer shift of the subspectra of Fe^{3+} ions with increasing the number m of either breaking or weakening of an exchange coupling produced by the appearance of either oxygen vacancies or Fe^{4+} ions:

$$H_{\mathrm{hf}}(\mathrm{Fe}^{3+}; m) = H_{\mathrm{hf}}(\mathrm{Fe}^{3+}; 0) + m\Delta H_{\mathrm{hf}}(\mathrm{Fe}^{3+}), \qquad (2)$$

$$\delta(\mathrm{Fe}^{3+}; m) = \delta(\mathrm{Fe}^{3+}; 0) + m\Delta\delta(\mathrm{Fe}^{3+}). \qquad (3)$$

Here $H_{\mathrm{hf}}(\mathrm{Fe}^{3+};0)$ and $\delta(\mathrm{Fe}^{3+};0)$ are the values of the hyperfine field and isomer shift, respectively, for the subspectrum of Fe^{3+} ions with all six exchange couplings with Fe^{3+} ions surrounding them, $\Delta H_{\mathrm{hf}}(\mathrm{Fe}^{3+})$ and $\Delta\delta(\mathrm{Fe}^{3+})$ are the variations of the hyperfine field and isomer shift with either breaking or weakening of one exchange coupling.

As for the quadrupole shift ε, the same value was taken for all subspectra of Fe^{3+} ions because possible relation between ε and the presence of vacancies and Fe^{4+} ions turns out to be essentially ambiguous. In a general case, with the same number m different arrangements in their crystallographic positions relative to Fe^{3+} ions and each other are possible, which lead to essentially different values of ε.

Taking into account possible numbers of oxygen vacancies (γ) and Fe^{4+} ions (y), the experimental spectra were fitted suggesting the presence of four Fe^{3+} subspectra and one Fe^{4+} subspectrum (Fig. 2). A small contribution of Fe^{4+} ions to the experimental spectrum and statistics in the experimental spectrum do not allow us to reveal analogous subspectra of Fe^{4+} ions differing by their hyperfine parameters.

The t_{ann} dependencies of relative intensities of all subspectra of Fe^{3+} and Fe^{4+} ions obtained by model fitting of the experimental Mössbauer spectra are shown in Fig. 3. As it is seen, the intensity of the subspectrum corresponding to Fe^{4+} decreases and tends to zero at $t_{\mathrm{ann}} = 650^\circ$C (Fig. 3, a). The contributions to the spectrum from different Fe^{3+} states are also redistributed with an increase in the vacuum annealing temperature. The relative intensity of the subspectrum $I(\mathrm{Fe}^{3+};0)$ corresponding to Fe^{3+} ions with all six Fe^{3+}–O^{2-}–Fe^{3+} exchange couplings ($m = 0$) increases notably, and the intensities of the subspectra of Fe^{3+} ions with broken or weakened couplings ($m = 1, 2, 3$) decrease (Fig. 3, b). The behavior of the relative intensities of the subspectra observed in the experiment (Fig. 3) indicates a decrease in the number of Fe^{4+} ions in the sample and a decrease in the probability of breaking or weakening of Fe^{3+}–O^{2-}–Fe exchange couplings under vacuum annealing. In this case, the main changes occur in the temperature range of 200–400°C. The changes become slower with a subsequent increase in the temperature t_{ann}.

If one supposes that the probabilities of the Mössbauer effect are similar for ^{57}Fe nuclei belonging to Fe^{3+} and Fe^{4+} ions, not only the number of Fe^{4+} ions ($y = I(\mathrm{Fe}^{4+})$) but also the number of oxygen vacancies ($\gamma = (x - y)/2$) and O^{2-} anions ($3 - \gamma$) per formula unit can be determined from the relative intensities of their subspectra (1) for each sample. The t_{ann} dependencies of the number of oxygen vacancies (γ) and oxygen ions ($3 - \gamma$) per formula unit of the substituted La$_{0.67}$Sr$_{0.33}$FeO$_{3-\gamma}$ lanthanum ferrite are shown in Fig. 4, a. The number of vacancies in the sample increases (from 0.083 ± 0.005 to 0.162 ± 0.004) and, correspondingly, the number of O^{2-} anions decreases (from 2.917 ± 0.005 to 2.837 ± 0.004) with an increasing t_{ann} temperature.

Supposing random distribution of oxygen vacancies and Fe^{4+} ions over their crystallographic positions, the probabilities of the appearance of an oxygen vacancy ($p(\square)$) in the nearest anion environment of Fe^{3+} ion and Fe^{4+} ion ($p(\mathrm{Fe}^{4+})$) in the cation environment of Fe^{3+} ion are:

$$p(\square) = \gamma/3 = (x - y)/6, \qquad (4)$$

$$p(\mathrm{Fe}^{4+}) = x - 2\gamma = y. \qquad (5)$$

In this case, the probability of the appearance of either an oxygen vacancy or Fe^{4+} ion, i.e., of either breaking or weakening of exchange couplings $p(\square\mathrm{Fe}^{4+})$ is

$$p(\square \vee \mathrm{Fe}^{4+}) = p(\square) + p(\mathrm{Fe}^{4+}) - p(\square)p(\mathrm{Fe}^{4+}) = x/6 + y5/6 - xy/6 + y^2/6. \qquad (6)$$

By using the relative intensity of the subspectrum of Fe^{4+} ion obtained from the model fitting and the number of Sr^{2+} ions (x) specified from the synthesis, the probabilities $p(\square)$, $p(\mathrm{Fe}^{4+})$, and $p(\square \vee \mathrm{Fe}^{4+})$ can be determined. Their t_{ann} dependencies are shown in Fig. 4, b. It is seen from the figure that the total probability of either breaking or weakening of an exchange coupling decreases with increasing t_{ann} in spite of an increase in the probability

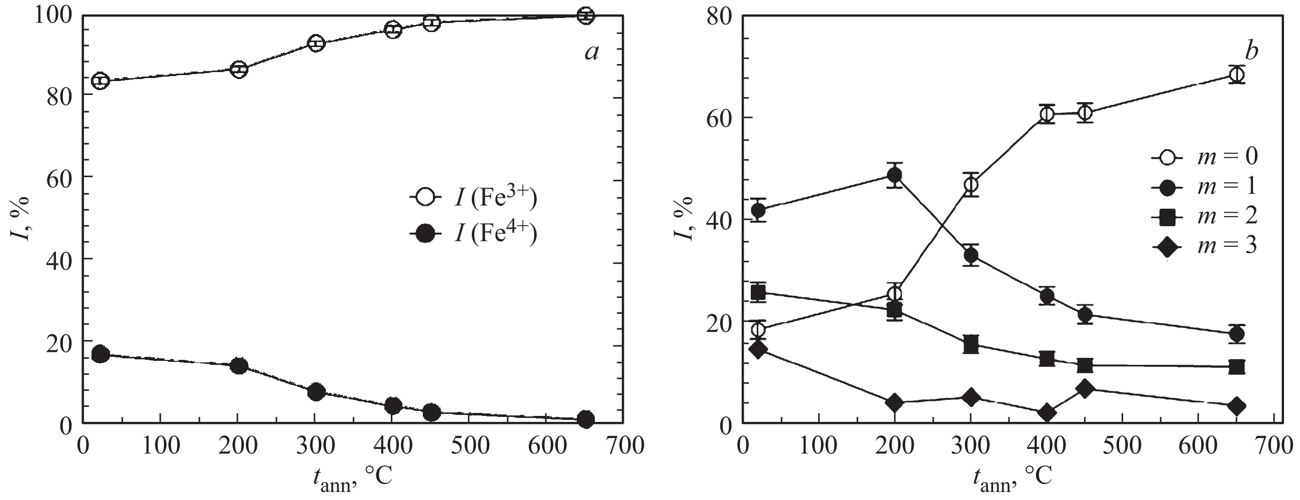

Figure 3. Annealing t_{ann} temperature dependencies of the relative intensities of the subspectra for all Fe^{3+} ions and Fe^{4+} ions (*a*) and Fe^{3+} ions with $m = 0, 1, 2, 3$ with either breaking or weakening of exchange couplings in their nearest environment (*b*).

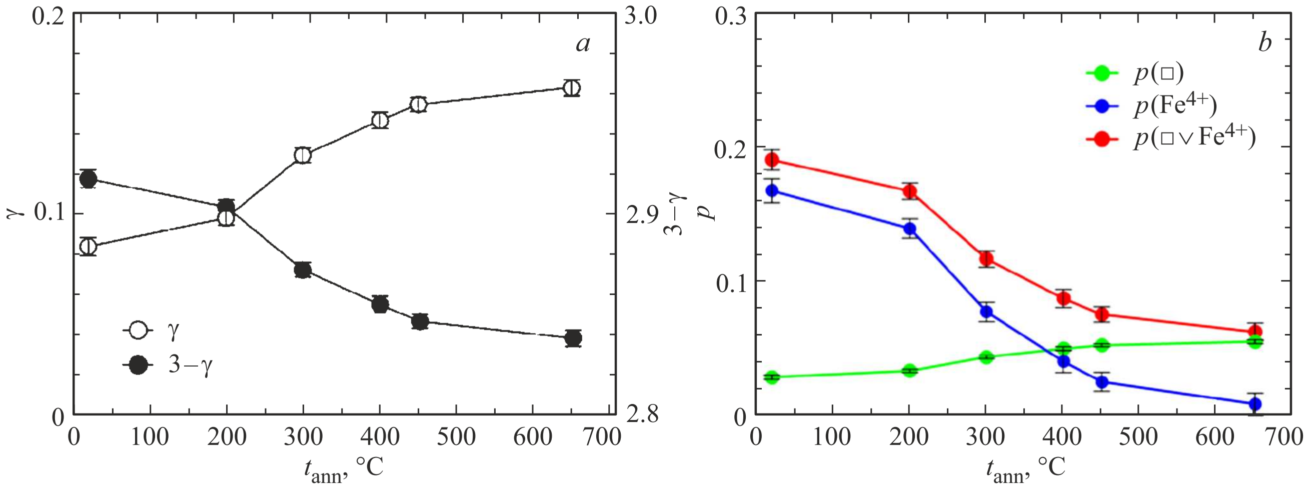

Figure 4. The t_{ann} dependencies of the number of oxygen vacancies (γ) and oxygen ions ($3-\gamma$) per formula unit of the substituted lanthanum ferrite (*a*) and the probability of the appearance of oxygen vacancies ($p(\Box)$) (green lines), Fe^{4+} ions ($p(\mathrm{Fe}^{4+})$) (blue lines), and either oxygen vacancies or Fe^{4+} ions ($p(\Box \vee \mathrm{Fe}^{4+})$) (red lines) in the nearest environment of Fe^{3+} ions (*b*).

of the appearance of oxygen vacancies, i.e., the probability of breaking of an exchange coupling. It should be noted that the weakening of exchange couplings caused by the presence of Fe^{4+} ions plays the main role at low t_{ann} temperatures, and the breaking of exchange couplings caused by the presence of oxygen vacancies is crucial at higher t_{ann} temperatures.

The dependencies of the relative intensities $I(\mathrm{Fe}^{3+}; m)$ of the subspectra of Fe^{3+} ions on the number m of either breaking or weakening of exchange couplings caused by the appearance of either oxygen vacancies or Fe^{4+} ions in the nearest Fe^{3+} cation environment for the synthesized and annealed in vacuum samples are shown in Fig. 5. The binomial distributions taking into account the appearance of only oxygen vacancies ($P_6^m(\Box)$), only Fe^{4+} ions ($P_6^m(\mathrm{Fe}^{4+})$), and either oxygen vacancies or Fe^{4+} ions ($P_6^m(\Box \vee \mathrm{Fe}^{4+})$) which are calculated according to (4)–(6), are shown in Fig. 5 as well. The dependencies $I(\mathrm{Fe}^{3+}; m)$ are well described by binomial distributions calculated from the intensities of the subspectra of Fe^{4+} ions when the suggested equidistant changes in the hyperfine magnetic field $H_{\text{hf}}(\mathrm{Fe}^{3+}; m)$ (2) and the isomer shift $\delta(\mathrm{Fe}^{3+}; m)$ (3) caused by both breaking of exchange couplings and weakening of these coupling are taken into account. Each of these mechanisms individually does not describe the experimentally observed distributions of the intensities of the subspectra of Fe^{4+} ions (Fig. 5).

Suggesting the additivity of changes of the hyperfine field and isomer shift of Fe^{3+} ions when the number m of breaking or weakening of exchange couplings increases ((2) and (3)), the values of $H_{\text{hf}}(\mathrm{Fe}^{3+}; 0)$ and $\delta(\mathrm{Fe}^{3+}; 0)$ are determined from the model fitting for the subspectrum of Fe^{3+} ions with six Fe^{3+}–O^{2-}–Fe^{3+} exchange couplings.

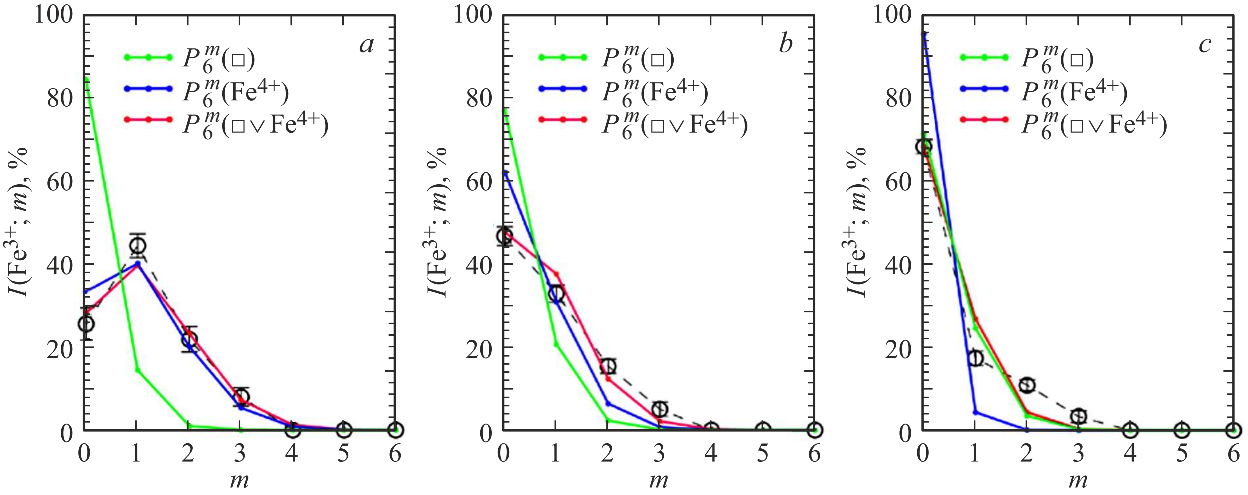

Figure 5. The dependencies of the relative intensities $I(\mathrm{Fe}^{3+}; m)$ (open circles connected by dotted lines) of the subspectra of Fe^{3+} ions on the number m of either breaking or weakening of exchange couplings in the nearest Fe^{3+} ion environment for the synthesized (*a*) and annealed in vacuum at 300°C (*b*) and 650°C (*c*) samples. The binomial distributions taking into account the appearance of only oxygen vacancies ($P_6^m(\square)$) (green lines), only Fe^{4+} ions ($P_6^m(\mathrm{Fe}^{4+})$) (blue lines), and either oxygen vacancies or Fe^{4+} ions ($P_6^m(\square \vee \mathrm{Fe}^{4+})$) (red lines).

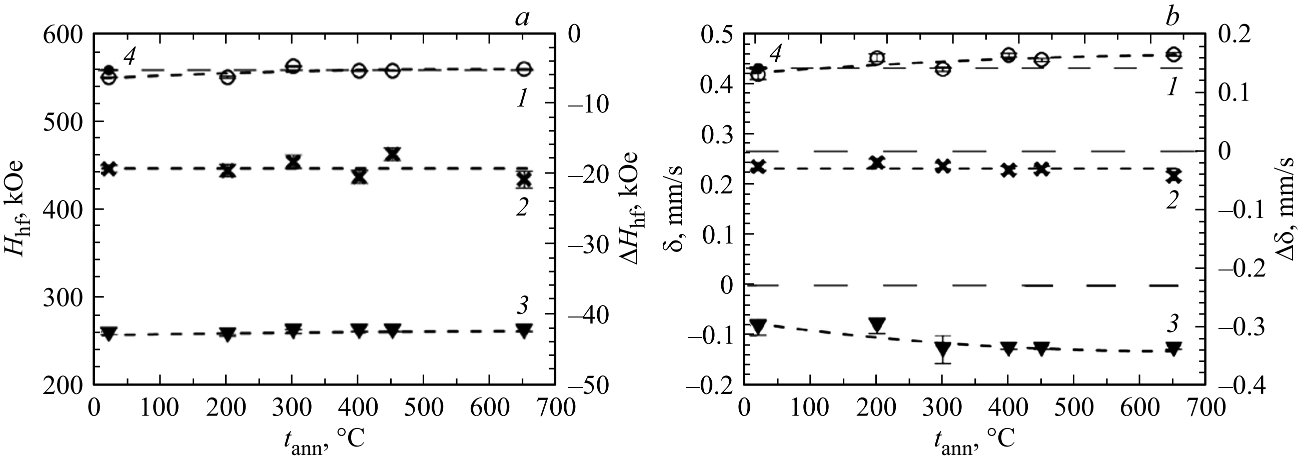

Figure 6. The t_{ann} dependencies of the hyperfine parameters of the subspectra of Fe^{3+} and Fe^{4+} ions: $H_{\mathrm{hf}}(\mathrm{Fe}^{3+}; 0)$, $\Delta H_{\mathrm{hf}}(\mathrm{Fe}^{3+})$, $H_{\mathrm{hf}}(\mathrm{Fe}^{4+})$ (*a*) and $\delta(\mathrm{Fe}^{3+}; 0)$, $\Delta\delta(\mathrm{Fe}^{3+})$, $\delta(\mathrm{Fe}^{4+})$ (*b*). *1* — $H_{\mathrm{hf}}(\mathrm{Fe}^{3+}; 0)$, $\delta(\mathrm{Fe}^{3+}; 0)$; *2* — $\Delta H_{\mathrm{hf}}(\mathrm{Fe}^{3+})$, $\Delta\delta(\mathrm{Fe}^{3+})$; *3* — $H_{\mathrm{hf}}(\mathrm{Fe}^{4+})$, $\delta(\mathrm{Fe}^{4+})$; *4* — $H_{\mathrm{hf}}(\mathrm{LaFeO_3})$, $\delta(\mathrm{LaFeO_3})$.

The changes in the hyperfine field $\Delta H_{\mathrm{hf}}(\mathrm{Fe}^{3+})$ and isomer shift $\Delta\delta(\mathrm{Fe}^{3+})$ when one exchange coupling is broken or weakened are also determined for all samples of the substituted lanthanum ferrite (Fig. 6).

The obtained hyperfine parameters of the subspectra of Fe^{3+} and Fe^{4+} ions depend weakly on the vacuum annealing temperature (Fig. 6). The values of $H_{\mathrm{hf}}(\mathrm{Fe}^{3+}; 0)$ and $\delta(\mathrm{Fe}^{3+}; 0)$ are close to the corresponding values of H_{hf} and δ for unsubstituted $\mathrm{LaFeO_3}$ ferrite, in which all Fe^{3+} ions participate in all six $\mathrm{Fe}^{3+}{-}\mathrm{O}^{2-}{-}\mathrm{Fe}^{3+}$ exchange couplings. The Breaking or weakening of one exchange coupling leads to a decrease in both the hyperfine magnetic field (on average, by 19.2 ± 0.4 kOe) and the isomer shift (on average, by 0.029 ± 0.003 mm/s). As for the quadrupole shifts ε of the subspectra components, their average values are small and negative: -0.01 ± 0.01 mm/s for Fe^{3+} ions and -0.02 ± 0.02 mm/s for Fe^{4+} ions.

4. Conclusion

The valence states of Fe atoms and the formation of oxygen vacancies in the substituted $\mathrm{La_{0.67}Sr_{0.33}FeO_{3-\gamma}}$ orthoferrite were studied in detail by low-temperature Mössbauer spectroscopy under gradual oxygen removal. The averaged Fe valence state was shown to be not revealed when decreasing the measurement temperature. This testifies to the freezing of the electron transfer process between Fe ions. The hyperfine parameters of the partial Mössbauer spectra obtained by their model fitting allowed us to conclude that one of them with the smallest isomer shift and hyperfine magnetic field belongs to Fe^{4+} ions and the others belong to Fe^{3+} ions. The presence of several Zeeman sextets associated with Fe^{3+} ions in the spectra is caused by the appearance of oxygen vacancies and Fe^{4+} ions in the nearest Fe atom cation environment in the substituted lanthanum ferrite. The appearance of an oxygen vacancy breaks a $Fe^{3+}-O^{2-}-Fe$ exchange coupling and results in a decrease in the hyperfine magnetic field and a change in the isomer shift of the spectrum. The appearance of Fe^{4+} ions in the nearest cation environment of Fe^{3+} ions leads to the weakening of a $Fe^{3+}-O^{2-}-Fe$ exchange coupling and, correspondingly, to a decrease in the hyperfine field. The total probability of either breaking or weakening of exchange coupling decreases with increasing the vacuum annealing temperature, the number of Fe^{4+} ions decreases, and the concentration of oxygen vacancies increases. The weakening of exchange couplings caused by the presence of Fe^{4+} ions plays the main role in the change of Fe^{3+} subspectra at low annealing temperatures, and the breaking of exchange couplings caused by the presence of oxygen vacancies is crucial at higher annealing temperatures. As a result of the model fitting of the Mössbauer spectra, the numbers of oxygen vacancies and Fe^{4+} ions were determined for all samples depending on the vacuum annealing temperature. The obtained data on the relative intensities of the subspectra for different Fe ions confirm the validity of assumption made in this work on the random distribution of oxygen vacancies and Fe^{4+} ions over their crystallographic positions in the structure of the substituted $La_{0.67}Sr_{0.33}FeO_{3-\gamma}$ orthoferrite.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] M.B. Salamon, M. Jaime. Rev. Mod. Phys. **73**, 583 (2001). https://doi.org/10.1103/REVMODPHYS.73.583

[2] Y. Tokura. Contribution to Colossal Magnetoresistance Oxides / Ed. Y. Tokura. Gordon & Breach, London (1999).

[3] E.A. Tugova, V.F. Popova, I.A. Zvereva, V.V. Gusarov. Phys. Chem. **32**, 674 (2006). https://doi.org/10.1134/S1087659606060137

[4] S. Petrovic, A. Terlecki, L. Karanovic, P. Kirilov-Stefanov, M. Zduji, V. Dondur, D. Paneva, I. Mitov, V. Rakic. Appl. Catal. B Environ **79**, 186 (2008). https://doi.org/10.1016/J.APCATB.2007.10.022

[5] S.N. Tijare, M.V. Joshi, P.S. Padole, P.A. Mangrulkar, S. Rayalu, N.K. Labhsetwar. Int. J. Hydrogen Energ. **37**, 10451 (2012). https://doi.org/10.1016/J.IJHYDENE.2012.01.120

[6] Z. Wei, Y. Xu, H. Liu, C. Hu, J. Hazard. Mater. **165**, 1056 (2009). https://doi.org/10.1016/J.JHAZMAT.2008.10.086

[7] J. Faye, A. Bayleta, M. Trentesauxb, S. Royera, F. Dumeignil, D. Duprez, S. Valange. Appl. Catal. B Environ **126**, 134 (2012). https://doi.org/10.1016/J.APCATB.2012.07.001

[8] J.B. Yang, W.B. Yelon, W.J. James, Z. Chu, M. Kornecki, Y.X. Xie, X.D. Zhou, H.U. Anderson, Amish G. Joshi, S.K. Malik. Phys. Rev. B **66**, 184415 (2002). https://doi.org/10.1103/PhysRevB.66.184415

[9] J.B. Goodenough. Magnetism and Chemical Bond / Ed. F. Albert Cotton. Interscience, London (1963).

[10] R.B. da Silva, J.M. Soares, José. A.P. da Costa, J.H. de Araújo, A.R. Rodrigues, F.L.A. Machado. JMMM **466**, 306 (2018). https://doi.org/10.1016/J.JMMM.2018.07.040

[11] U. Shimony, J.M. Knudsen. Phys. Rev. B **144**, 361 (1966). https://doi.org/10.1103/PhysRev.144.361

[12] M. Takano, J. Kawachi, N. Nakanishi, Y. Takeda. J. Solid State Chem. **39**, 75 (1981). https://doi.org/10.1016/0022-4596(81)90304-2

[13] S.E. Dann, D.B. Currie, M.T. Weller, M.F. Thomas, A.D. Al-Rawwas. J. Solid State Chem. **109**, 134 (1994). https://doi.org/10.1006/JSSC.1994.1083.

[14] A.D. Al-Rawwas, C.E. Johnson, M.F. Thomas, S.E. Dann, M.T. Weller. Hyperfine Interact. **93**, 1521 (1994). https://doi.org/10.1007/BF02072903

[15] V. Sedykh, O. Rybchenko, V. Rusakov, S. Zaitsev, O. Barkalov, E. Postnova, T. Gubaidulina, D. Pchelina, V. Kulakov. J. Phys. Chem. Solids **171**, 111001 (2022). https://doi.org/10.1016/j.jpcs.2022.111001

[16] V.D. Sedykh, O.G. Rybchenko, A.N. Nekrasov, I.E. Koneva, V.I. Kulakov. Phys. Solid State **61**, 1099 (2019). https://doi.org/10.1134/S1063783419060210

[17] M.E. Matsnev, V.S. Rusakov. AIP Conf. Proceed. **1489**, 178 (2012). https://doi.org/10.1063/1.4759488

[18] J.C. Grenier, F.M. Pouchar. Mater. Res. Bull. **17**, 55 (1982). https://doi.org/10.1016/0025-5408(82)90183-0

[19] G.A. Sawatzky, F. van der Woude. J. Phys. Colloq. **35**, 47 (1974).

[20] V.I. Nikolaev, V.S. Rusakov. Mössbauer studies of ferrites, Moscow State University Publisher, Moscow, 1985. (in Russian).