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Oxygen Vacancies in the Perovskite-type Ferrites. II. Mössbauer Effect in the $SrFeO_{2.5}$-$LaFeO_3$ Solid-solution System

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The Mössbauer effect was studied for the solid-solution $Sr_{1-x}LaFeO_{2.5+x/2}$ system, prepared by firing in a vacuum. The intensity of the characteristic six absorption lines of the tetrahedral-iron site in the brownmillerite-type phase ($0.0 \leq x \leq 0.20$) was weakened with an increase in the La content because of an increasing incorporation of oxygen, while the Mössbauer parameters remained constant. $SrFeO_{2.5}$ with a brownmillerite-type structure, completely changed into a cubic perovskite-type structure at the composition with $x=0.30$; however, the original absorption peaks for the tetrahedral-iron site still exist even if the intensity is considerably decreased. Moreover, new peaks came out, with Mössbauer parameters different from those for the octahedral- or the tetrahedral-iron sites. On the basis of the values of their Mössbauer parameters, the origin of the new peak can be assigned to the presence of a five-coordinated iron site surrounded by a trigonal bipyramidal polyhedron of oxygen rather than a square pyramidal one. The three kinds of iron site lead to a single octahedral one when most of Sr is replaced with La ($x \geq 0.50$). The oxygen-deficient, perovskite-type phase with a cubic symmetry may be stabilized by the presence of the mixed-coordination scheme of Fe^{3+}, *i.e.*, the octahedral, trigonal bipyramidal, and tetrahedral sites.

In the previous paper,[1] we studied the role of oxygen vacancies in the stabilization of the perovskite-type structure in the $Sr_{1-x}M_xFeO_{3-\delta}$ solid-solution system ($M=Y^{3+}$, La^{3+}, Bi^{3+}, or In^{3+}). The X-ray diffraction measurements indicated that the end member $SrFeO_{2.5}$, which is isostructural with brownmillerite, which has an orthorhombic symmetry, changed to a cubic perovskite-type structure upon the addition of M^{3+} ($0.30 \leq x \leq 0.60$) as a result of a decrease in the concentration of oxygen vacancies. Throughout the previous study, however, we could not visualize the details of an oxygen-deficient structure only by means of X-ray diffractometry. The purpose of the present work is to further clarify the contents of the defect structure with the aid of such Mössbauer spectroscopic information, observed at iron sites, as the coordination state from the surrounding oxygens, the nature of the chemical bonding, and the electric-field gradient.

$LaFeO_3$, being isostructural with $GdFeO_3$ (the space group P_{bnm}-D_{2h}^{16}), consists of four distorted sub-cells,[2] and neutron-diffraction measurements[3] have shown that it has a G-type,[4] spin-ordered antiferromagnetic structure with its Neel temperature at 750°K. The Mössbauer spectrum was first observed by Eibschutz *et al.*[5] to show an isomer shift of $+0.32$ mm/sec and

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[1] H. Yamamura and R. Kiriyama, *Nippon Kagaku Kaishi*, **1972**, 343.

[2] S. Geller and E. A. Wood, *Acta Crystallogr.*, **9**, 563 (1956).

[3] W. C. Koehler and E. O. Wollan, *J. Phys. Chem. Solids*, **2**, 100 (1957).

[4] E. O. Wollan and W. C. Koehler, *Phys. Rev.*, **100**, 545 (1955).

[5] M. Eibschutz, G. Gorodetsky, S. Shtrikman, and D. Tres, *J. Appl. Phys.*, **35**, 1071 (1964).

an internal magentic field of 519 kOe. On the other hand, MacChesney *et al.*[6] studied the $SrFeO_{3-\delta}$ system, in which $SrFeO_{2.5}$ (prepared by firing in CO_2/H_2) was found to have a brownmillerite-type structure. The Mössbauer spectrum for $SrFeO_{2.5}$ was first reported by Gallagher *et al.*[7] without sufficient discussion. According to the results of Collvile's study, $CaFeO_{2.5}$,[8] being isostructural with $SrFeO_{2.5}$ (the space group P_{cmn}-D_{2h}^{16}), has an orthorhombic symmetry, are containing two types of iron sites, (Fe_I and Fe_{II}), both of which are alternatively drawn up along the *b*-axis. The Fe_I occupies an octahedral site surrounded by 6 O^{2-}, while the Fe_{II} occupies a tetrahedral site surrounded by 4 O^{2-} ions. The crystal lattice with a perovskite-type structure is deformed by the ordering of the oxygen vacancies. The neutron-diffraction measurements[9] revealed that $CaFeO_{2.5}$ also has a G-type antiferromagnetic structure with its Neel temperature at 720°K, where the spins of Fe^{3+} in both the octahedral and tetrahedral sub-lattices all lie along the *c*-axis. Grant,[10] after having studied the Mössbauer effect of $CaFeO_{2.5}$, concluded that the electric-field gradient is axially symmetric, in which the *z*-principal axis is parallel to the crystallographic *b*-axis, and that the large quadrupole splitting both the iron sites arises from the deformation of the corresponding oxygen-octahedron and -tetrahedron.

The Mössbauer effect for the $Sr_{1-x}La_xFeO_{3-\delta}$ system, prepared by firing under a high oxygen pressure, was studied by Shimony *et al.*[11] and by Gallagher *et al.*[12] In their investigation, however, attention was paid only to the mixed valencies of Fe^{3+} and Fd^{4+}, not to the generated lattice defect. On the other hand, only a few studies of the defect structure using Mössbauer spectroscopy have been published. Sawatzky *et al.*[13] determined the extent of the distribution of Fe^{3+} for octahedral and tetrahedral sites in the inverse spinel $CoFe_2O_4$. On the other hand, Elias *et al.*[14] successfully confirmed the occurrence of the tetrahedral Fe^{3+} site due to the presence of iron vacancies even in the wüstite phase ($Fe_{1-x}O$); their results are consistent with the results of the neutron-diffraction study.[15]

Experimental

Preparation of the Samples. The solid-solution samples were prepared by ball milling mixed particles of graduated pure reagents, (α-Fe_2O_3, $SrCO_3$ and La_2O_3) in the desired proportions, and by then firing at 900°C and 1000°C in air for 5 hr. The samples thus obtained were refired at 1100°C in a vacuum ($\sim 10^{-3}$ mmHg) and then cooled to room temperature, while the same degree of vacuum was maintained, after a given firing period. The method of preparation has been described in greater detail in the previous paper.[1]

X-Ray Diffractometry. X-ray powder diffractometry using cobalt-$K\alpha$ radiation was used for the assignment of the structure as well as for the determination of the lattice constant of the specimens.

Measurements and Analysis of Mössbauer Spectra. The Mössbauer spectrum was taken using a spectrometer equipped with 400-channel pulse-height analyzer (a RAH-403 type; Hitachi Co., Ltd.), calibration with either iron foil or α-Fe_2O_3. The source used was cobalt-57, with 14.4 keV γ-radiation, dispersed in either palladium or copper; it was driven at a constant acceleration speed (±10 mm/sec) for all the measurements at room temperature. The absorbers were prepared by grinding the oxide samples into fine particles and by then evenly spreading them on a square aluminium plate 0.50 mm thick with a circular hole 20 mm in internal diameter; both sides of the powder compact thus molded were sealed with cellophane. The thickness of the powder compact was chosen so that it contained about 15—20 mg of total iron per square centimeter of the cross section. The isomer shifts are given in values relative to metallic iron for all the samples.

The energy levels of magnetic hyperfine splitting between the ground state and first excited one of iron-57 under the presence of an axially symmetric electric-field gradient is given by the following equation:

$$E = -g\mu_n H m_I + (-1)^{|m_I|+1/2}\varepsilon, \qquad (1)$$

where μ_n, H, m_I, and ε are the nuclear magneton, the internal magnetic field, the magnetic quantum number, and the electric quadrupole parameter respectively. Fig. 1 shows diagramatically the energy levels of iron-57. In this figure, each energy level is denoted as *J, K, L, M, N,* or *O*, in the order of ascending energy. Therefore, the quadrupole parameter (ε) is given by:

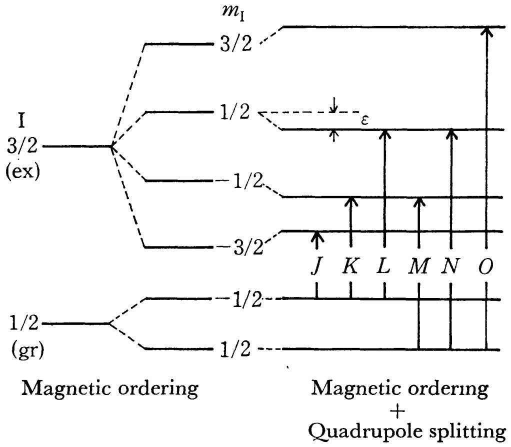

Fig. 1. Energy levels of iron-57 in the Mössbauer spectrum. I, m_I and ε are nuclear spin quantum number, magnetic quantum number of iron-57 and quadrupole parameter, respectively.

$$\varepsilon = \frac{1}{4}\{(O-N)-(K-J)\}. \qquad (2)$$

On the other hand, an isomer shift (I.S.) closely correlated

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[6] J. B. MacChesney, R. C. Sherwood, and J. F. Potter, *J. Chem. Phys.*, **43**, 1907 (1965).

[7] P. K. Gallagher, J. B. MacChesney, and D. N. E. Buchanan, *ibid.*, **41**, 2429 (1964).

[8] A. A. Colville, *Acta Crystallogr.*, **B26**, 1469 (1969).

[9] T. Takeda, Y. Yamaguchi, S. Tomiyoshi, M. Fukase, M. Sugimoto, and H. Watanabe, *J. Phys. Soc. Japan*, **24**, 446 (1968).

[10] R. W. Grant, *J. Chem. Phys.*, **51**, 1156 (1969).

[11] U. Shimony and J. M. Knudsen, *Phys. Rev.*, **144**, 361 (1966).

[12] P. K. Gallagher and J. B. MacChesney, Symposia of the Faraday Soc., No. 1, The Mössbauer Effect, (1968), p. 40.

[13] G. A. Sawatzky, F. van der Woude, and A. H. Morrish, *J. Appl. Phys.*, **39**, 1204 (1968).

[14] D. J. Elias and J. W. Linnett, *Trans. Faraday Soc.*, **65**, 2673 (1969).

[15] W. L. Roth, *Acta Crystallogr.*, **13**, 140 (1960).

with the contribution of s-electron density manifests itself as a shift of the nuclear energy levels and, therefore, is given by the following equation:

$$\text{I.S.} = \frac{4}{5}\Pi Ze^2R^2\left(\frac{\delta R}{R}\right)\{|\Psi_a(0)|^2-|\Psi_s(0)|^2\} \quad (3)$$

$$= \frac{1}{12}(3J+2K+L+M+2N+3O), \quad (4)$$

where $e|\Psi(0)|^2$ is an expression for the charge density at the nucleus and whose R and δR are, respectively, the ground-state radius of iron-57 and the difference in nuclear radius between the ground-state and the excited-one. The Mössbauer velocity was obtained by multiplying the respective pair peaks, J—O, K—N, and L—M, by the transition probabilities of 3, 2, and 1 respectively.

Results and Discussion

At first, the structural knowledge on the $Sr_{1-x}La_xFeO_{3-\delta}$ solid-solution system obtained by X-ray diffractometry will be briefly described. The content of oxygen vacancies (δ) varies with the content of La (x), as may be understood from the formula. The X-ray powder patterns of the sample with x=0.0—0.20 could be indexed on the basis of a brownmillerite-type structure with orthorhombic symmetry. It is noticeable that the intensity of fairly strong peaks with an even larger k number in Miller indices (hkl) (*e.g.*, (161), (080), and (280)) decreased with an increase in x. On the other hand, the respective pair peaks, such as (200)—(002), (240)—(042), and (341)—(143), in the brownmillerite-type phase approached each other with an increase in x, resulting in the appearance of the corresponding peaks of (110), (111), and (211) in the cubic perovskite-phase with a further increase in x. The rather broad diffraction pattern and no splitting of the peak due to $K\alpha_1$ and $K\alpha_2$ radiation at a high diffraction angle for the cubic perovskite phase in the compositional range of x=0.30—0.60 suggest that the structure is a little random as a result of its vacancies. The lattice constant *versus* the composition is plotted in Fig. 2. In the unit-cell parameter of the brownmillerite-type phase, the a-axis decreased rapidly, whereas the c-axis increased slowly, with an increase in the La content, the two meeting at x=0.30. In Fig. 2, the lattice constant in the cubic perovskite-type phase is given, for comparison, as a value 2 times the actual lattice constant, a_0.[16] On the other hand, the tendency of the b_0 parameter to increase over the region with x=0.20 resulted in 15.85 Å, which was approximately equal to 15.94 Å ($=a_0\times4\sqrt{2}$).[16] This fact allows us to consider the phase with x=0.20 as a pseudotetragonal structure formed as an intermediate phase during the transformation between the two phases. Over the compositional range of x=0.30—0.60, the cubic perovskite-type structure was preferable; its lattice constant was 3.926 Å at the composition of x=0.30, larger than that of 3.850 Å for $SrFeO_3$ prepared by firing under a high oxygen pressure, after MacChesney *et al.*[6] The lattice constant in the cubic phase decreased linearly with an increase in the contents of La. The further addition of La (x=0.80—1.0) distorted the cubic lattice to a $LaFeO_3$-type structure with an orthorhombic symmetry. Thus, it seems likely that the presence of oxygen vacancies of the solid-solution plays an important role in the stabilization of a perovskite-type structure with cubic symmetry.

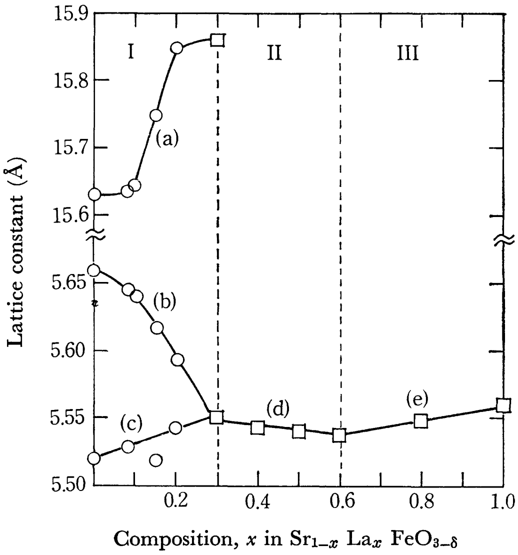

Fig. 2. Lattice constants in the system $Sr_{1-x}La_xFeO_{3-\delta}$ prepared by firing at 1100°C in vacuum: (a), (b), and (c) are the lattice constants of b-, a- and c-axis for the brownmillerite-type orthorhombic phase (region I), respectively and (d) and (e) are the lattice constants for the cubic perovskite-type phase (region II) and pseudocubic $LaFeO_3$-type one (region III).

The Mössbauer spectrum of $SrFeO_{2.5}$ at room temperature is shown in Fig. 3(a). It is understandable in terms of a couple of six-line patterns arising from types of iron sites having both different magnetic hyperfine splitting and quadrupole splittings. The quadrupole splitting must occur as a result of the destruction of the spherical symmetry built by the surrounding ions around iron, because the Fe^{3+} ion itself is in a spherically symmetrical $^6A_1$ state. Generally, the relation between ΔE_Q, the quadrupole splitting observed above the Neel point, and ε, the quadrupole parameter observed below it, are given by the following equation:

$$\varepsilon = \frac{1}{4}\Delta E_Q(3\cos^2\theta-1), \quad (5)$$

where θ is the angle between the magnetic field and the principal axis of the electric-field gradient. The idea proposed by Grant[10] in his Mössbauer study on $CaFeO_{2.5}$ may be also true for $SrFeO_{2.5}$; that is, the electric-field gradient at both the iron tetrahedral and octahedral sites may be axially symmetric, with the z-principal axis parallel to the crystallographic b-axis. On the other hand, the antiferromagnetic spins of both the iron sites in $SrFeO_{2.5}$ are supposed to be along the

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[16] When the lattice constants for the brownmillerite-type phase with an orthorhombic symmetry and for the cubic perovskite-type one are assumed to be a_0, b_0, c_0, and a^* respectively, the relations among them are given by the following equations; $a_0\simeq c_0\simeq 2a^*$ and $b_0\simeq 4\sqrt{2}a^*$.

c-axis. Therefore, Eq. (5) may be simplified to:

$$\varepsilon = -\frac{1}{4}\Delta E_Q \qquad (6)$$

Since the Mössbauer spectra are measured below the Neel point in this work, ΔE_Q can be calculated using the observed values of ε with the aid of Eq. (6). The presently-observed absorption lines are here denoted as *J*, *K*, *L*, *M*, *N*, and *O* in the order of ascending energy, as has been described above, together with additional symbols showing the coordination numbers of the iron sites. Therefore, for example, the third line from the left in the tetrahedral iron site is expressed by 4L (Fig. 3(a)).

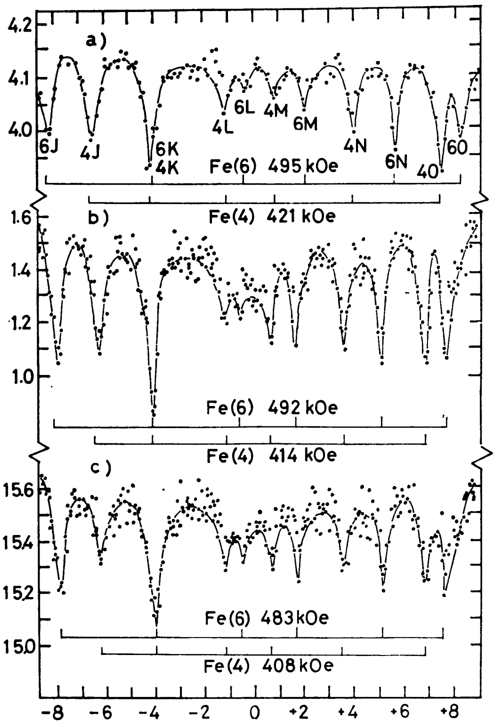

Fig. 3. Mössbauer spectra in the system $Sr_{1-x}La_xFeO_{3-\delta}$ ($0.0 \leq x \leq 0.10$) prepared by firing in a vacuum: a), b) and c) are the spectra for the composition of x=0.0, 0.07 and 0.10, respectively. Number in parentheses is coordination number of oxygen.

The Mössbauer parameters of $SrFeO_{2.5}$, *i.e.*, the isomer shifts, quadrupole splittings, and internal magnetic fields, were calculated to be +0.235 mm/sec, +0.391 mm/sec, and 495 kOe for the octahedral iron site, and +0.160 mm/sec, −0.280 mm/sec, and 421 kOe for the tetrahedral one, respectively. The higher velocity of the isomer shift, accompanied by a larger internal magnetic field, for the octahedral site than those for the tetrahedral one may be explained by the contribution of covalency in Fe–O bonding, this being also found in the cases of spinels[17] and garnets.[18] Both the values of the isomer shift indicate that two types of iron in this solid-solution are three valency states. Accordingly, the relation between the substituted La content and the oxygen one for the solid-solution system in the present study may be presented by x in the composition: $Sr_{1-x}La_xFeO_{2.5+x/2}$.

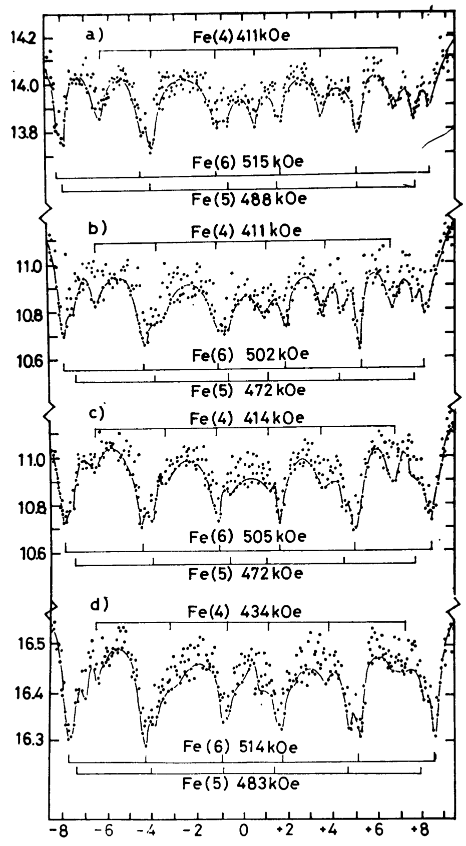

Fig. 4. Mössbauer spectra in the system $Sr_{1-x}La_xFeO_{3-\delta}$ ($0.15 \leqq x \leqq 0.40$) prepared by firing in a vacuum: a), b), c) and d) are the spectra for the composition of x=0.15, 0.20, 0.30 and 0.40, respectively. Number in parentheses is coordination number of oxygen.

The Mössbauer spectra for x=0.07 and x=0.10 are shown in Fig. 3(b) and 3(c) respectively. The respective intensities of the 4M-, 4N-, and 4O-peaks decreased with an increase in the La content. This fact may be attributed to a change in the coordination state of Fe^{3+} from a tetrahedral site to an octahedral one occurring as a result of the incorporation of oxygen due to La substitution. No change was observed in the values of the internal magnetic field and quadrupole splitting, whereas the isomer shift for the octahedral, Fe^{3+} site had a tendency to move toward the higher-velocity side when the content of Sr decreased in the compositional range from x=0.0 to 0.10.

The Mössbauer spectrum for the composition with x=0.15 revealed a broad line with an asymmetric form, as is shown in Fig. 4(a). In addition, new absorption lines appeared between the 4O and 6O lines, and between the 4K and 6K lines. This means the appearance of new six lines different from the lines for the octahedral and tetrahedral Fe^{3+} sites. If only the amount of oxygen incorporated by the addition of La controls the change from a tetrahedral site to an

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[17] T. Mizoguchi and M. Tanaka, *J. Phys. Soc. Japan*, **18**, 1301, (1963).

[18] W. J. Nicholson and G. Burns, *Phys. Rev.*, **133**, 1568 (1964).

octahedral one, the peak intensity for the tetrahedral site must be only two-thirds that for the octahedral site at the composition of $x=0.15$. Experimental evidence, however, indicated that the intensities for the two sites were nearly equal. The values of the isomer shift, the quadrupole splitting, and the internal magnetic field for the sample with $x=0.15$ were $+0.380$ mm/sec, $+0.109$ mm/sec, and 515 kOe for the octahedral site, $+0.136$ mm/sec, -0.150 mm/sec, and 411 kOe for the tetrahedral site and $+0.326$ mm/sec, $+0.326$ mm/sec, and 488 kOe for the new peak, respectively. It is noticeable that the isomer shift and the internal magnetic field for the new peak both fall between those for the octahedtal site and those for the tetrahedral site.

The Mössbauer spectrum for the sample with $x=0.20$, with a pseudotetragonal perovskite-type structure, is shown in Fig. 4(b); three kinds of six absorption line also appear, and a new line appears in the neighborhood of the 6*N* line besides the splitting which has already occurred in the sample with $x=0.15$. The sample with $x=0.30$ revealed an exact cubic perovskite-type structure. According to a discussion on the basis of the crystal structure, the central metal ion in the cubic perovskite-type structure must be surrounded by six oxygen ions. Nevertheless, it is interesting that the presently-observed oxygen-deficient perovskite-type phase with cubic symmetry possesses measurable amount of the tetrahedral iron site and the "X-site" in addition to the octahedral site (Fig. 4(c)).

In the sample with the composition of $x=0.40$ (Fig. 4(d)), the absorption line from the tetrahedral iron site was still recognized even if its intensity was weakened. For the sample with $x=0.50$ (Fig. 5(a)) and $x=0.80$ (Fig. 5(b)), however, broad six line arose only from the octahedral site, in which the half-height width values of the respective line were four times (for $x=0.50$) and two times (for $x=0.80$) the value in $LaFeO_3$ (Fig. 5(c)). In spite of such a situation regarding the intensity of the absorption lines of the octahedral site, little change for that of the tetrahedral site occurred. These facts allow us to say that an increase in the oxygen content in the solid-solution plays no role in the occurrence of change from the tetrahedral site to the octahedral one over the compositional range from $x=0.50$ to $x=1.0$.

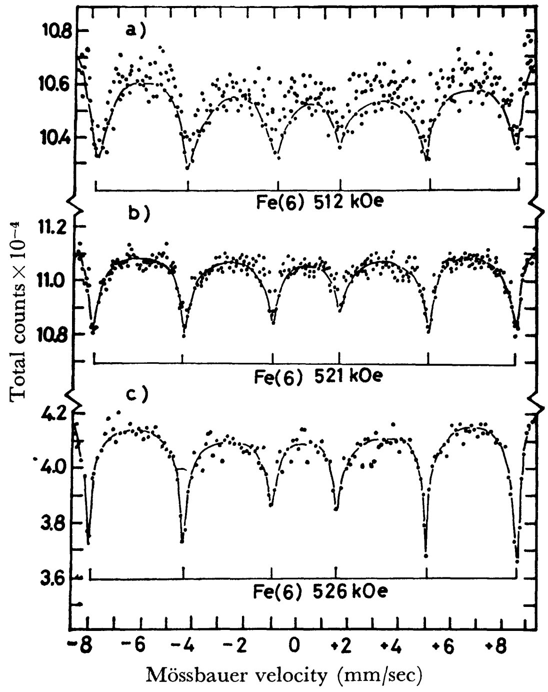

Fig. 5. Mössbauer spectra in the system $Sr_{1-x}La_xFeO_{3-\delta}$ ($0.50 \leq x \leq 1.0$) prepared by firing in a vacuum: a), b), and c) are the spectra for the composition of $x=0.50$, 0.80 and 1.0, respectively. Number in parentheses is coordination number of oxygen.

To clarify the details of the present oxygen-deficient structure, it seems important to discuss the assignment of the unknown peak for "X-iron site" which appeared in all the samples with the composition of $x=0.15$—0.40. The characteristics of the new unknown pattern may be summarized as follows:

(1) The value of the isomer shift falls between that for the octahedral site and that for the tetrahedral site, regardless of the composition.

(2) The value of the internal magnetic field is also between that for the octahedral site and that for the tetrahedral site.

(3) No measurable change in the intensity of the new peak is observed over the entire range of composition of the solid-soltuion presently treated.

(4) The magnitude and the direction of the quadrupole splitting in the brownmillerite-type phase are almost equal to those for octahedral site, the magnitude being decreased considerably in the cubic perovskite-type phase.

The possible origins for the occurrence of the new peaks are as follows:

(1) The presence of a different phase containing Fe^{3+}.

(2) The existence of Fe^{2+} occurring as a result of firing at a fairly high temperature in a vacuum and/or of the substitution of La^{3+}.

(3) The presence of a tetrahedral or octahedral site with an environment slightly different from the brownmillerite-type phase of $SrFeO_{2.5}$.

(4) The presence of Fe^{4+} remained unchanged even under a fairly high degree of vacuum.

(5) The formation of five-coordinated Fe^{3+} as an intermediate during the course of the transformation from a tetrahedral site to an octahedral one.

No different phase containing Fe^{3+} with magnetic ordering, however, was confirmed by either X-ray diffractometry or magnetic measurements. The possibility of (2) and (3) can also be ruled out because the value of the isomer shift is between those for the octahedral and tetrahedral Fe^{3+} sites. On the other hand, Fig. 2 shows that the length of the *b*-axis in the brownmillerite-type structure increased with an increase in the content of incorporated oxygen, suggesting an increase in the over-all coordination number of Fe^{3+}; thus, one more of the possibilities (4) may be ruled out. The most probable reason for the occurrence of the octahedral iron site may be the existence of small amounts of $LaFeO_3$ in the brownmillerite-type phase.

The values of the isomer shift and the internal magnetic field of $LaFeO_3$, however, indicate that it is different from the values for the "X-iron site". The above anomalies in the Mössbauer parameters may be explained by the fifth possibility, that is, the presence of the five-coordinated Fe^{3+}.

Van Loef,[19] in his Mössbauer study of spinels and garnets, suggested that the values of the isomer shifts and the internal magnetic fields have a close relation to the form of oxygen-coordinated polyhedron. The results in the present work support his idea. The possible form of the five-coordinated polyhedron may be a regular trigonal bipyramidal rather than a square pyramidal because of the fairly small quadrupole splitting.

TABLE 1. MÖSSBAUER PARAMETERS IN THE SYSTEM $Sr_{1-x}La_xFeO_{3-\delta}$ PREPARED BY FIRING IN A VACUUM

Comp. (x)	C.N.	H_{int} (kOe)	I.S. (mm/sec)	ε (mm/sec)
0.0	6	495	0.235	0.391
	4	421	0.160	−0.287
0.07	6	492	0.339	0.340
	4	414	0.204	−0.285
0.10	6	483	0.367	0.340
	4	408	0.190	−0.298
0.15	6	515	0.380	0.109
	5	488	0.326	0.226
	4	411	0.136	−0.150
0.20	6	502	0.367	0.104
	5	472	0.284	0.066
	4	411	0.079	−0.025
0.30	6	505	0.380	0
	5	472	0.285	0.068
	4	414	0.136	−0.028
0.40	6	514	0.385	0
	5	483	0.275	0
	4	434	0.248	0
0.50	6	512	0.386	0
0.80	6	512	0.385	0
1.00	6	526	0.396	0.056

Remarks
C.N.: oxygen coordination number around iron
$H_{int.}$: internal magnetic field
I.S. : isomer shift relative to metallic iron
ε : quadrupole parameter

The Mössbauer parameters obtained in the present work are summarized in Table 1. The isomer shift and the quadrupole splitting for the three types of iron sites against the composition are also plotted in Fig. 6 and 7. The isomer shift for the octahedral Fe^{3+} site increased abruptly with an increase in the concentration of La and then stayed constant over the cubic perovskite-type phase, approaching that of $LaFeO_3$ when the concentration of La increased further. The isomer shift for the tetrahedral site showed a more complicated variation with the composition. It decreased rapidly up to $x=0.20$ and then increased linearly above $x=0.20$, nearly coinciding with the expected value for the octahedral site estimated by extraporation to $x=0.50$, where the Mössbauer pattern showed only a broad six-line pattern for the octahedral iron site.

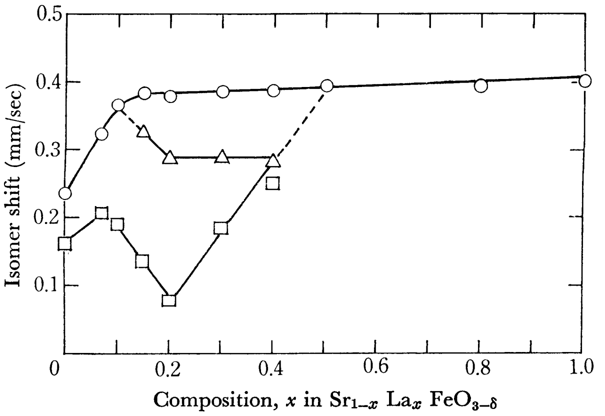

Fig. 6. Isomer shifts *vs*. composition in the system $Sr_{1-x}La_xFeO_{3-\delta}$ prepared by firing in a vacuum.
○: isomer shift for the octahedral Fe^{3+} site
△: isomer shift for the trigonal bipyramidal Fe^{3+} site
□: isomer shift for the tetrahedral Fe^{3+} site

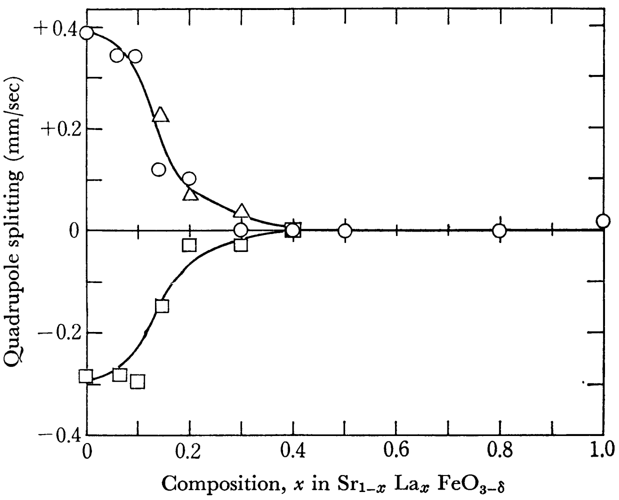

Fig. 7. Quadrupole splitting *vs*. composition in the system $Sr_{1-x}La_xFeO_{3-\delta}$ prepared by firing in a vacuum.
○: quadrupole splitting for the octahedral Fe^{3+} site
△: quadrupole splitting for the trigonal bipyramidal Fe^{3+} site
□: quadrupole splitting for the tetrahedral Fe^{3+} site

The relation between the quadrupole splitting and the composition seems to be valuable enough to discuss on the basis of crystal symmetry. Though the values of the quadrupole splitting for all the sites over the entire compositional range of $x=0.0$—0.10, in which the brownmillerite-type phase was preferable, are comparable to that of $SrFeO_{2.5}$, they considerably decreased with the progress of the structural transformation from the orthorhombic phase to the tetragonal one, and then show no quadrupole splitting when the cubic perovskite-type is attained. No internal magnetic field dependence on the composition was observed; these values for octahedral, tetrahedral, and trigonal bipyramidal sites were found to be ~510, ~480, and ~410 kOe respectively.

It is necessarily uncommon for the trigonal bipyra-

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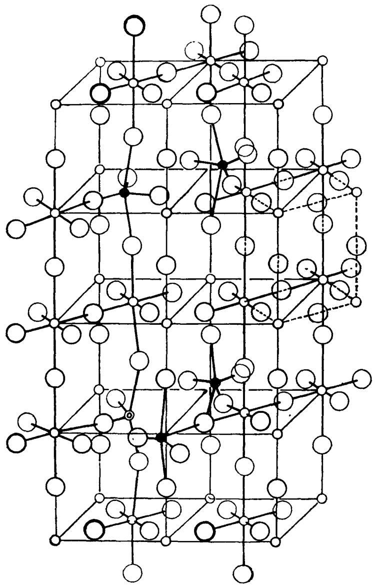
[19] J. J. Van Loef, *Physica*, **32**, 2102 (1966).



○: Oxygen, ∘: iron (6), •: iron (5), ◎: iron (4)

Fig. 8. Imaginative oxygen-deficient cubic perovskite-type structure in the system $Sr_{1-x}La_xFeO_{3-\delta}$ prepared by firing in a vacuum, where large cation, Sr or La ion is omitted for simplicity. The primitive unit cell is represented in dashed line. Number in parentheses is coordination number of oxygen.

midal polyhedron of oxygen to be present as a result of the absence of oxygen along the direction [110] out of the cubic perovskite-type structure. The imaginative oxygen-deficient cubic perovskite-type structure with octahedral, trigonal bipyramidal, and tetrahedral iron site is shown in Fig. 8. The reported Mössbauer spectroscopic measurements, together with the nuclear ferromagnetic resonance spectroscopic measurements, however, have already indicated that magneto plumbite, $BaFe_{12}O_{19}$, with layer structure, has a trigonal bipyramidal iron site.[20-22] The isomer shift for the trigonal bipyramidal iron site in $BaFe_{12}O_{19}$ was found to be between that for the octahedral site and that for the tetrahedral site, as in the present study. On the other hand, the quadrupole splitting and the internal magnetic field were larger and smaller than the values for both the octahedral and tetrahedral sites. In this case, however, the presence of the five-coordinated iron site may be expected because one of the anion sites is replaced by barium in the $BaFe_{12}O_{19}$.

Wadsley[23] has studied the importance of transition metal-oxygen mixed coordination schemes associated with an anion-deficient phase. Negas and Roth[24] have discussed the stoichiometry and the stability of $SrMnO_{3-\delta}$ from the standpoint of variation in the coordination scheme of the manganese cation and suggested the presence of a trigonal bipyramidal manganese site in addition to a normal octahedral site, without, however, reporting any data on this idea. In summary, it may be shown that the presence of an ion deficiency in the crystal lattice contributes to the change in the coordination number. Accordingly, the traditional thinking that vacancies exist as simple holes is not applicable for an oxygen-deficient perovskite-type structure. This idea may be sometimes true for an oxide solution.

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