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Mössbauer Study of the Thermal Decomposition Products of $SrFeO_4$

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The thermal decomposition products of $SrFeO_4$ were studied by ^{57}Fe-Mössbauer-effect and X-ray-diffraction measurements. Below 300 °C in air, an amorphous Fe^{3+} product was formed. The Fe^{4+} or Fe^{5+} state was not observed in the process. A single-phase product with a perovskite structure was obtained in air at temperatures above 400 °C. The products obtained between 400 and 650 °C showed cubic symmetry, but above 700 °C they showed tetragonal distortion. Two kinds of Fe^{3+}-ion sites were detected in the tetragonal $SrFeO_x$ compounds. All the products obtained under the oxygen pressures from 50 to 500 atm and at temperatures from 300 to 900 °C showed cubic symmetry. The Fe^{3+}/Fe^{4+} ratio in those products was determined from the relative intensities of the Mössbauer absorptions.

Regarding the abnormal valence states of iron, several works have been reported. As examples of hexavalent iron compounds, K_2FeO_4, $SrFeO_4$, and $BaFeO_4$ are known[1-3] and their magnetic properties have been investigated.[4-6] It is well known that tetravalent iron, Fe^{4+}, is formed easily in alkaline-earth orthoferrate, $RFeO_x$ ($R=$Ca, Sr, Ba; $2.5<x\leqq 3.0$).[7-17]

The present author and his associates have prepared pure samples of the three hexavalent iron compounds and investigated their magnetic properties.[5,6] The decomposition products of K_2FeO_4 and $BaFeO_4$ have also been investigated. In the case of K_2FeO_4, no intermediate valence state was observed between the hexavalent and trivalent states.[18] By the decomposition of

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$BaFeO_4$ in the low temperature range, two new phases were found with the composition of $BaFeO_x$ $(2.5<x<3.0)$.[19] As for the decomposition of $SrFeO_4$, there has been no detailed report except for a brief paper by Scholder *et al.*, which reported that a perovskite, $SrFeO_3$, was formed by heating $SrFeO_4$ in an oxygen atmosphere at about 700 °C.[20] As will be reported in this paper, perovskite-type $SrFeO_x$ compounds with various oxygen deficiencies were obtained by heating $SrFeO_4$ under different conditions.

There have been several reports concerning the perovskite-type $SrFeO_x$ system. All of the $SrFeO_x$ samples used in the previous works were prepared by the ordinary ceramic method; α–Fe_2O_3 and strontium carbonate or strontium formate were treated under various oxygen pressures and temperatures. Watanabe[7] measured the magnetic susceptibility and electrical conductivity of $SrFeO_x$ compounds containing Fe^{4+} ions, and suggested the combined effect of the double exchange and the usual exchange interactions in these compounds. The Mössbauer-effect of the $SrFeO_x$ $(2.5<x<3.0)$ compounds was measured by Shirane *et al.*[8] They found that the isomer shift of the tetravalent-state iron in $SrFeO_{2.86}$ was about 0.0 mm/s relative to that of pure iron. MacChesney *et al.*[9,10] prepared $SrFeO_x$ $(2.5<x\leqq3.0)$ compounds by equilibrating $SrFeO_{2.50}$ at oxygen pressures ranging from 0.2 to 855 atm. They also studied the crystallographic and magnetic properties of $SrFeO_x$ $(2.5\leqq x\leqq3.0)$ compounds by means of X-ray-diffraction, Mössbauer-effect, susceptibility, and resistivity measurements.

The present work was undertaken in order to investigate equilibrium phases in a lower temperature range for the $SrFeO_x$ system. As a starting material, the hexavalent iron compound, $SrFeO_4$, has a definite merit; the equilibrium state is attained more rapidly in fine particles of the decomposition products than in those of the other starting materials thus far used. X-ray-diffraction and Mössbauer-effect measurements were carried out in order to examine each of the products. The ratios of Fe^{3+} ans Fe^{4+} ions in the perovskite-type products were estimated by the curve resolutions of the Mössbauer spectra.

Experimental

Using a pure sample of K_2FeO_4 obtained by a previously-reported procedure,[18] $SrFeO_4$ was prepared according to the method of Scholder *et al.*[3]

To a mixed solution of strontium hydroxide and strontium acetate, a 0.5% potassium hydroxide solution containing K_2FeO_4 was added. The filtered precipitate of $SrFeO_4$ was stored in a desiccator after having been washed with chilled alcohol and acetone successively. In the preparation of $SrFeO_4$, the distilled water, from which the carbon dioxide had been expelled, was used in order to prevent the formation of strontium carbonate. All of the reactions were carried out at about 0 °C in order to avoid the reduction of Fe^{6+} ions. By the X-ray-diffraction technique, the sample was confirmed to be a single phase of $SrFeO_4$. The particle shape of $SrFeO_4$, observed by means of an electron microscope, was granular, with a diameter of 2—4 μ. The measurements of the magnetization and the Mössbauer-effect were carried out at 80 K in order to be sure of the absence of any ferromagnetic impurity and any iron ion other than the Fe^{6+} ions.[6]

This pure sample of $SrFeO_4$ was then heated under the oxygen pressures from 0.2 to 500 atm. For the heating in air or in an oxygen atmosphere, the sample was spread thinly on a boat made of porcelain or platinum; it was heated then below 1200 °C for 50 hr and cooled rapidly to room temperature. For some of the samples, the heating period was prolonged to 1500 hr, but no difference was observed in the experimental results of the X-ray-diffraction and Mössbauer-effect measurements. For the heating under high oxygen pressures, the sample was placed in a test tube of silica or gold; this test tube was put in a cone-seal hydrothermal reaction vessel made of Stellite. These samples were quenched to cold water with the reactor after being kept at temperatures below 900 °C for 50 hr under oxygen pressures of less than 500 atm.

The phase identification of the products obtained was accomplished by X-ray-diffraction techniques. In the measurements of the lattice parameters of cubic or tetragonal $SrFeO_x$ compounds, the (200) reflections were used. The Mössbauer-effect measurements were carried out using an apparatus consisting of an Elron driving unit, AME–20, and a Northern Scientific Co. 1024–channel pulse-height analyzer, NS–600. The temperature of the absorber was varied between 4.2 and 293 K. The gamma-ray source, ^{57}Co embedded in Cu metal, was always kept at room temperature. The calibration of the velocity scale was made by using pure Fe and α-Fe_2O_3 as standard absorbers. The isomer shift is expressed relative to pure Fe metal. The ratios of the Fe^{3+} and Fe^{4+} ions, and the isomer shifts and quadrupole splittings of the products were estimated from the ^{57}Fe Mössbauer spectra by using a Curve Resolver-310 (Du Pont Co.).

Results and Discussion

X-Ray-diffraction Measurements. Strontium fer-

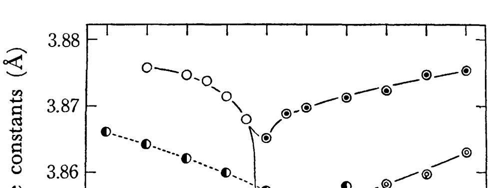

Fig. 1. Lattice parameters of the perovskite-type $SrFeO_x$ $(2.5<x<3.0)$ products obtained by heating $SrFeO_4$ at various conditions. The abscissa shows the heating temperature.

○: a_0 of a cubic $SrFeO_x$ phase obtained in air.
◎: a_0 of a tetragonal $SrFeO_x$ phase obtained in air.
⊙: c_0 of a tetragonal $SrFeO_x$ phase obtained in air.
◐: a_0 of a cubic $SrFeO_x$ phase obtained under the oxygen pressures of 50 atm.
●: a_0 of a cubic $SrFeO_x$ phase obtained under the oxygen pressures of 500 atm.

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rate, $SrFeO_4$, began to decompose abruptly at about 70 °C in air. The products formed below 300 °C in air showed no X-ray-diffraction peak. The products obtained by heating $SrFeO_4$ in air or in an oxygen atmosphere at temperatures from 400 to 650 °C consisted of a single phase of a cubic perovskite structure, while those formed above 700 °C were a single phase of a tetragonal perovskite structure. The products obtained under the oxygen pressures from 50 to 500 atm and at temperatures from 300 to 900 °C were a single phase of a cubic perovskite structure.

The lattice constants were measured using the (200) reflections; the results are depicted in Fig. 1. It has been known in the $SrFeO_x$ $(2.5<x\leqq3.0)$ system with the perovskite structure that the lattice constants decreased with an increase in the Fe^{4+}-ion concentration, for the Fe^{4+} ion has a smaller ionic radius than the Fe^{3+} ion. According to Clevenger,[13] the ionic radii of the Fe^{3+} and Fe^{4+} ions are 0.67 Å and 0.59 Å respectively.

Mössbauer-effect Measurements. The Mössbauer spectrum, measured at room temperature, of the decomposition products obtained by heating $SrFeO_4$ for 4 hr at 160 °C in air consisted of a narrow single-line absorption at −0.86 mm/s and a broad symmetric doublet. The narrow single-line absorption is characteristic of the Fe^{6+} state. This absorption disappeared when the amorphous product was heated at 160 °C for more than 10 days. The Mössbauer spectra of the amorphous decomposition product measured at room temperature and at 4.2 K are shown in Fig. 2. At room temperature, a broad symmetric doublet was observed. The isomer shift and quadrupole splitting of the doublet were $+0.35\pm0.02$ mm/s and 0.57 ± 0.02 mm/s respectively. A set of six broad absorptions with the internal magnetic field of 480 ± 5 kOe appeared at 4.2 K. These Mössbauer parameters are characteristic of the Fe^{3+} state. All of the iron ions in the amorphous product were trivalent. No intermediate valence state, the Fe^{5+} or Fe^{4+} ion, was detected in any decomposition product in this work. Judging from the Mössbauer spectra and from the fact that no X-ray diffraction peak was observed, it seems that the product consists of ultrafine particles which show superparamagnetism at room temperature. The broad line-width is caused by the inhomogeneity of the crystallographic circumstances of the iron ions. These results observed in the thermal decomposition process of $SrFeO_4$ are very similar with those found in the case of K_2FeO_4.[18]

The Mössbauer absorption spectra of the products with a cubic perovskite structure obtained by heating $SrFeO_4$ below 600 °C in air are shown in Fig. 3 (spectra measured at room temperature) and in Fig. 4 (at 4.2 K). The results show that most of the iron ions in the cubic perovskite phase obtained at lower temperatures were in trivalent state and that the Fe^{4+}-ion concentration increased gradually with the increase in the heating temperature up to 600 °C. Besides, it was found that, in these products with a cubic perovskite structure, there was only one kind of species for each of the Fe^{3+} and Fe^{4+} ions. In Fig. 3, the results of the curve resolutions obtained by fitting the paramagnetic Mössbauer spectra with Lorentzian curves using a Curve Resolver-310 (Du Pont Co.) are represented by broken lines. The paramagnetic spectrum of the Fe^{3+} ions was composed of a symmetric doublet with an isomer shift of $+0.22\pm0.02$ mm/s, and with a quadrupole splitting of 0.63 ± 0.02 mm/s, while that of the Fe^{4+} ions was composed of a singlet with an isomer shift of $+0.07\pm0.02$ mm/s.

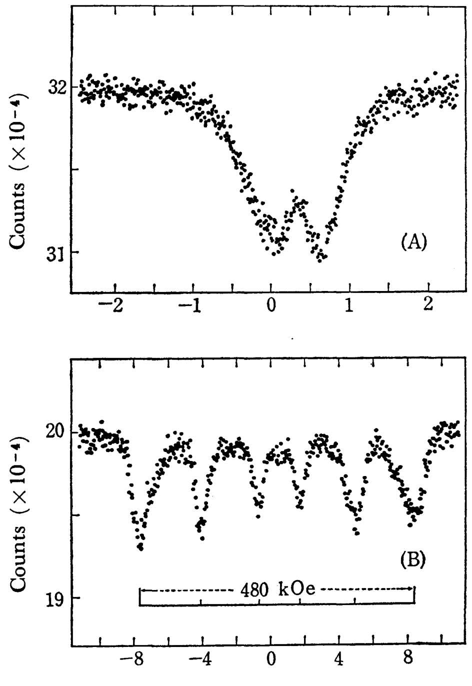

Fig. 2. ^{57}Fe Mössbauer absorption spectra at 293 K(A) and 4.2 K(B) of an amorphous product obtained by heating $SrFeO_4$ at 160 °C in air for 10 days.

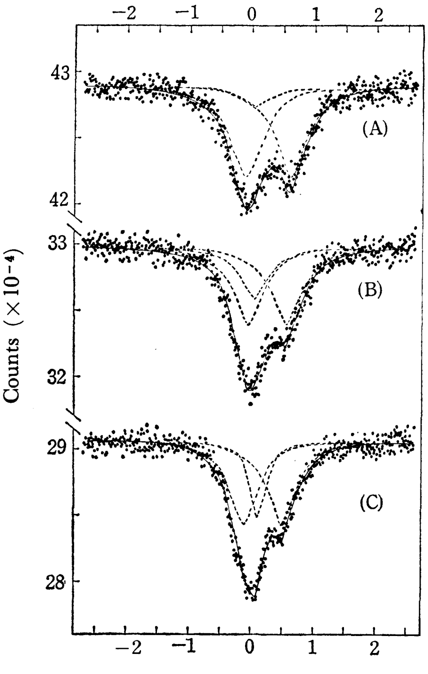

Fig. 3. ^{57}Fe Mössbauer absorption spectra at 293 K of cubic perovskite $SrFeO_x$ compounds obtained by heating $SrFeO_4$ in air at 400 °C(A), 500 °C(B), and 600 °C(C).

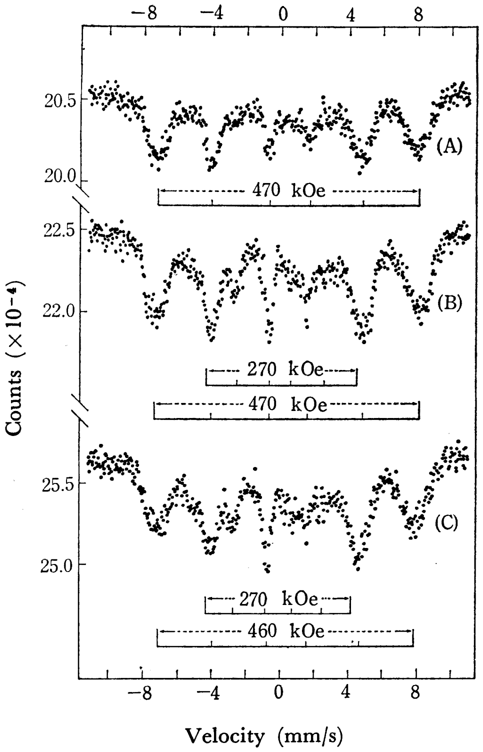

Fig. 4. ^{57}Fe Mössbauer absorption spectra at 4.2 K of cubic perovskite SrFeO$_x$ compounds obtained by heating SrFeO$_4$ in air at 400 °C(A), 500 °C(B), and 600 °C(C).

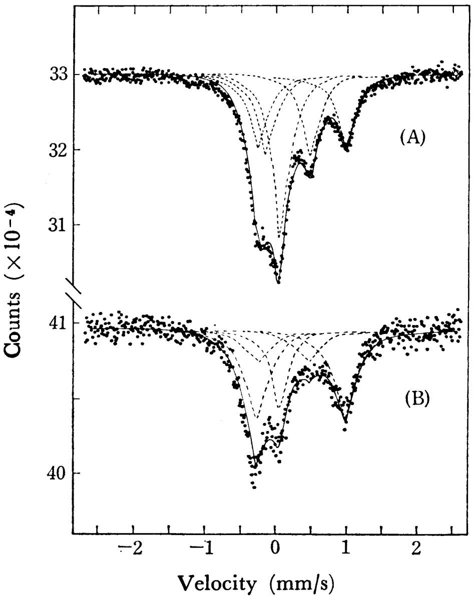

Fig. 5. ^{57}Fe Mössbauer absorption spectra at 293 K of tetragonal perovskite SrFeO$_x$ compounds obtained by heating SrFeO$_4$ in air at 800 °C(A) and 1200 °C(B).

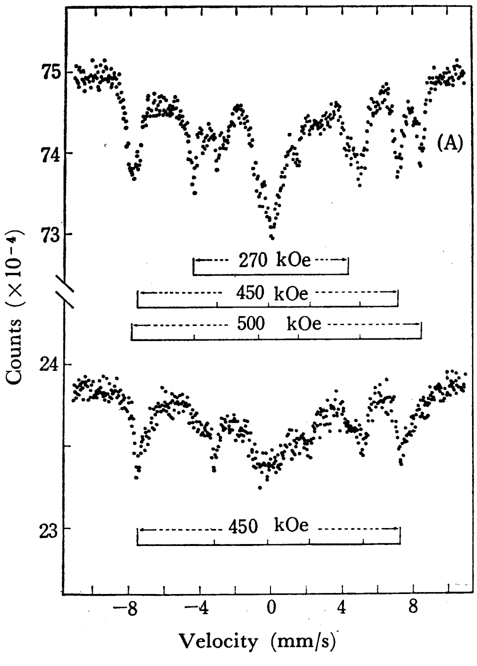

Fig. 6. ^{57}Fe Mössbauer absorption spectra at 4.2 K of tetragonal perovskite SrFeO$_x$ compounds obtained by heating SrFeO$_4$ in air at 800 °C(A) and 1200 °C(B).

The Mössbauer spectra of the products with a tetragonally distorted perovskite structure, obtained by heating at 800 °C and 1200 °C in air, are shown in Fig. 5 (spectra measured at room temperature) and in Fig. 6 (at 4.2 K). In contrast to the cubic samples (Fig. 3), two extra absorptions appeared at about $+1.0$ mm/s and -0.3 mm/s in the spectrum of a tetragonal sample obtained by heating at 800 °C in air. The relative intensities of these two outer-most absorptions increased with the increase in the heating temperature. This spectrum should be interpreted as having two kinds of Fe^{3+} sites in the tetragonal phase. This interpretation is supported by the results in a magnetically-ordered state. In Fig. 5, the results of the curve resolutions are represented by broken lines. The paramagnetic Mössbauer spectra of tetragonal SrFeO$_x$ samples were composed of three kinds of absorptions: (1) a singlet of Fe^{4+} with an isomer shift of $+0.07\pm0.02$ mm/s, (2) an Fe^{3+}-I doublet of Fe^{3+} with an isomer shift and a quadrupole splitting of $+0.19\pm0.02$ mm/s and 0.63 ± 0.02 mm/s respectively, and (3) an Fe^{3+}-II doublet of Fe^{3+} with an isomer shift and a quadrupole splitting of $+0.38\pm0.02$ mm/s and 1.25 ± 0.02 mm/s respectively. Fe^{3+}-I is similar to those in the cubic perovskite phase (Fig. 3).

The Mössbauer spectra of tetragonally-distorted samples measured at 4.2 K (Fig. 6) were very complex. In the spectrum of the tetragonal perovskite sample obtained at 800 °C in air (Fig. 6), two kinds of magnetically-split Fe^{3+} absorptions were observed; one had an internal magnetic field of 500 kOe and a negligibly small quadrupole interaction, and the other, an internal magnetic field of 450 kOe and a large quadrupole interaction (S_1—S_2; -2.30 ± 0.05 mm/s). The absorption due to Fe^{4+} ions showed an internal magnetic field of 270 kOe, which was consistent with the data on Fe^{4+} ions in the cubic perovskite phase with a large oxygen deficiency (Fig. 4). The spectra of the tetragonally-distorted SrFeO$_x$ samples showed that a considerable part of both the Fe^{3+} and Fe^{4+} ions was in a paramagnetic state even at 4.2 K (see Fig. 6). It was obvious that the relative intensity of the Fe^{3+}-II increased with the increase in the heating temperature from 800 to 1200 °C. The Mössbauer spectrum measured at 4.2 K on the tetragonal $SrFeO_x$ sample obtained at 1200 °C in air consisted mainly of magnetically-ordered Fe^{3+}-II absorptions and a paramagnetic absorption. The relative intensities of the Fe^{4+} absorptions and Fe^{3+}-I was small.

The X-ray results show that a sample has a cubic structure if the heating temperature is lower than 700 °C. In the Mössbauer results, however, the Fe^{3+}-II doublet appeared in a sample heated at 650 °C as a result of local distortion.

As is shown in Fig. 1, the perovskite-type products obtained by heating $SrFeO_4$ below 900 °C and at oxygen pressures from 50 to 500 atm showed no tetragonal distortion. The lattice constants of the products obtained under the oxygen pressures of 500 atm were near 3.850 Å, which had previously been reported as the value for the non-defective cubic perovskite, $SrFeO_3$.[10] The product obtained at 700 °C and at oxygen pressures of 500 atm showed the smallest lattice constant, therefore; it was supposed that it had the largest Fe^{4+} concentration among the samples obtained in this work. The Mössbauer spectra of the sample are shown in Fig. 7. The results of the curve resolutions on the paramagnetic spectrum are represented there by broken lines.

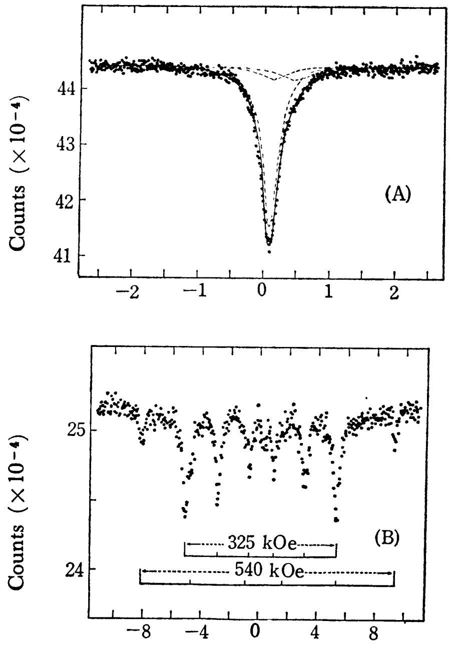

Fig. 7. ^{57}Fe Mössbauer absorption spectra at 293 K(A) and 4.2 K(B) of a cubic perovskite $SrFeO_x$ compound obtained by heating $SrFeO_4$ at 700 °C and the oxygen pressures of 500 atm.

The relative intensity of Fe^{3+}/Fe^{4+} was estimated by measuring the areas of the Mössbauer absorption spectra. Consequently, it was confirmed that the relative intensity does not change with the temperature. The oxygen contents in the $SrFeO_x$ products formed under various conditions were determined by using the ratio of the Fe^{3+} and Fe^{4+} ions thus obtained. The results are shown in Fig. 8. Isobaric curves for 0.2, 50, and 500 atm oxygen pressures are drawn to show the variation in the total composition with the temperature and the pressure.

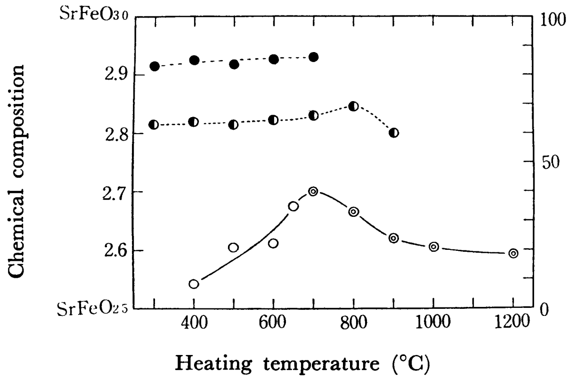

Fig. 8. Relation among the oxygen concentrations and heating conditions in the perovskite-type $SrFeO_x$ $(2.5<x<3.0)$ compounds obtained by heating $SrFeO_4$. The abscissa shows the heating temperature.

○: a cubic $SrFeO_x$ phase obtained in air.
◎: a tetragonal $SrFeO_x$ phase obtained in air.
◐: a cubic $SrFeO_x$ phase obtained under the oxygen pressures of 50 atm.
●: a cubic $SrFeO_x$ phase obtained under the oxygen pressures of 500 atm.

Comparison with Previously-reported Results. It has been reported, for the $SrFeO_x$ $(2.5<x\leqq3.0)$ system, that the cubic perovskite structure was no longer stable when the concentration of Fe^{3+} ion exceeded 30%.[10] Then a tetragonal distortion occurred. When the concentration of Fe^{3+} was more than 70%, the other phase, $SrFeO_{2.50}$, with a dicalcium ferrite structure, became more stable than the perovskite. On the other hand, in the present work, a cubic perovskite $SrFeO_x$ product with a Fe^{3+}-ion concentration of about 90% was obtained when $SrFeO_4$ was heated in air below 650 °C. The tetragonal perovskites obtained above 700 °C in air included Fe^{3+} ions in a concentration of 60—80%. Such a disagreement with the previous data may be due to the difference in the starting material.

In the case of $BaTiO_3$, which has the same perovskite structure, it has been reported that the crystal system of the compound is affected by the particle size.[21,22] Barium titanate, $BaTiO_3$, is transformed from a cubic to a tetragonal system below the Néel temperature (393 K). Ern[21] reported that fine particles (200 Å) of barium titanate obtained by a wet method show a cubic perovskite structure with $a_0=$ 4.035 Å even at room temperature. Nishimoto *et al.*[22] also prepared fine particles ($\geqq$500 Å) of barium titanate by the thermal decomposition of barium titanyl oxalate tetrahydrate, $BaTiO(C_2O_4)_2\cdot4H_2O$, at temperatures from 600 to 1100 °C; they found that the tetragonality decreased with a decrease in the particle size. In the present case of $SrFeO_x$ compounds obtained by heating $SrFeO_4$ at low temperatures, the cubic structure with a high oxygen deficiency

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21) V. Ern, *J. Amer. Ceram. Soc.*, **46**, 295 (1963).

22) K. Nishimoto, Y. Goto, N. Nakanishi, and S. Kachi, *Funtai oyobi Funmatsu Yakin*, (Kyoto), **14**, 221 (1967).

seems to be stabilized when the particle size is small.

Another characteristic of the Mössbauer spectra observed on the tetragonal $SrFeO_x$ (Fig. 6) was the existence of a paramagnetic component even at 4.2 K. Gallagher *et al.*[9] have also observed very similar spectra on oxygen-deficient $SrFeO_x$. Since the linewidth of their X-ray peaks was very narrow, it is not possible that these samples consist of ultra-fine particles which show superparamagnetism even at 4.2 K. At the present stage, no likely interpretation can be proposed, but the oxygen vacancies with high concentrations should play an important role in determining the magnetic properties. There remain some unsolved problems with regard to the complicated magnetic structure of $SrFeO_x$ ($2.5<x<3.0$) compounds.

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