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Mössbauer Study of Some Barium Orthoferrates

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Mössbauer spectra were taken for the following barium orthoferrates, $BaFeO_X$ ($2.5 \leqq X < 3.0$), at various temperatures between 4.2 K and 300 K: Triclinic-II, cubic-tetragonal and hexagonal phases were prepared by annealing or oxidizing the triclinic-I $BaFeO_{2.5}$ at moderately low temperatures. Four kinds of Fe^{3+} internal field were observed in the spectra of the triclinic-I. Two kinds of Fe^{3+} and one kind of Fe^{4+} were detected in the triclinic-II. The spectrum for cubic-tetragonal had two 6-line splittings corresponding to Fe^{3+} and Fe^{4+} states respectively. The hexagonal sample also had two internal fields corresponding to Fe^{3+} and Fe^{4+} states and it was found that the transition from antiferromagnetic to paramagnetic gradually occurred between 125 K and 171 K.

I. INTRODUCTION

It is well known that tetravalent state of iron, Fe^{4+} ion, is stabilized in alkaline-earth orthoferrates, $RFeO_X$ (R=Ca, Sr or Ba; $2.5 < X \leqq 3.0$).[1~21] In the $SrFeO_X$ system, all of compounds ever reported had perovskite structures.[1~5] On the other hand, the existence of several modifications was reported on the structures of $BaFeO_X$ system.[7~21]

The systematic investigation on $BaFeO_X$ ($2.5 \leqq X < 3.0$) was first made by Van Hook.[9] He studied the phase relations of the system by X-ray powder patterns and by thermogravimetric measurements. He found that the hexagonal phase, which is isomorphous with the high-temperature polymorph of $BaTiO_3$, was stable at low temperature over a wide range of oxygen pressure. At higher temperatures (above 915°C in air), it transformed to a phase of $BaFeO_{2.5}$. Gallagher *et al.*[10] and MacChesney *et al.*[11] prepared the hexagonal compounds with various oxygen contents ranging from $BaFeO_{2.83}$ to $BaFeO_{2.95}$ and susceptibility, resistivity and Mössbauer effect measurements were made at various temperatures. They observed that $BaFeO_{2.95}$ has a ferromagnetization (about 15 CGSemu/g) in the vicinity of the transition temperature. Subsequently, Mori[12] obtained a similar result on $BaFeO_{2.95}$ but the origin of the magnetization has not yet been explained.

Mori found that the powder pattern of $BaFeO_{2.50}$ could be indexed satisfactorily in terms of triclinic symmetry and named this the triclinic-I phase. Besides the hexagonal and triclinic-I phases, he prepared two new ones, triclinic-II and cubic-tetragonal, by annealing the triclinic-I at moderately low temperatures. One of the

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authors (T. I.) has studied the thermal decomposed products of a hexavalent iron compound, $BaFeO_4$, heated under the oxygen pressures from 0.2 to 1500 atm at temperatures below 1200°C.[21] In addition to the hexagonal and triclinic-I phases, two kinds of new $BaFeO_x$ compound were found at low temperatures. The products obtained by annealing the triclinic-I phase of decomposing $BaFeO_4$ at low temperatures were not in accordance with the phase diagram of Van Hook. As the diffusivity of ions is very small at low temperatures, the crystal structure of the product is affected by that of the starting material. Indeed, the thermal equilibrium product should be independent of the starting materials but it is not unusual that metastable phases appear at low temperatures.

The Fe^{57} Mössbauer spectroscopy was applied to the $BaFeO_x$ compounds in order to obtain a structural information and to clarify the magnetic characteristics. Since the examples of Fe^{4+} state so far observed were only a few, of particular interest are the Mössbauer spectroscopic parameters of Fe^{4+} state in those compounds.

II. SAMPLE PREPARATION AND MEASUREMENTS

The triclinic-I phase, $BaFeO_{2.50}$ was prepared from $BaCO_3$ and α-Fe_2O_3 powders by an ordinary ceramic method. These were mixed in the proportion of $2BaCO_3$ and Fe_2O_3 and heated at 1100°C for 24 hr in air. The preheated material was ground to fine powder in a mortar and heated again at 1150°C for 48 hr in a nitrogen atmosphere. Then the sample was rapidly cooled down to room temperature. As barium atoms absorb the gamma ray considerably, the samples have to be enriched with Fe^{57} in order to obtain clear Mössbauer spectra. As the starting material, α-Fe_2O_3 enriched with Fe^{57} up to 15% was used in the present experiment.

By annealing the triclinic-I phase $BaFeO_{2.50}$ in various conditions as reported by Mori,[12] several $BaFeO_x$ compounds were prepared. The triclinic-II phase was obtained by heating the triclinic-I phase in an oxygen atmosphere at 500°C for 24 hr and cooling rapidly to room temperature. The cubic and tetragonal phases were obtained by annealing the triclinic-I $BaFeO_{2.50}$ phase under oxygen pressures of 500 atm for 24 hr at 250°C and 300°C respectively. The hexagonal phase, $BaFeO_{2.95}$, which has the highest oxygen content, was prepared as follows; the triclinic-I phase was preheated at 850°C in an oxygen atmosphere for 48 hr and after crushing, heated

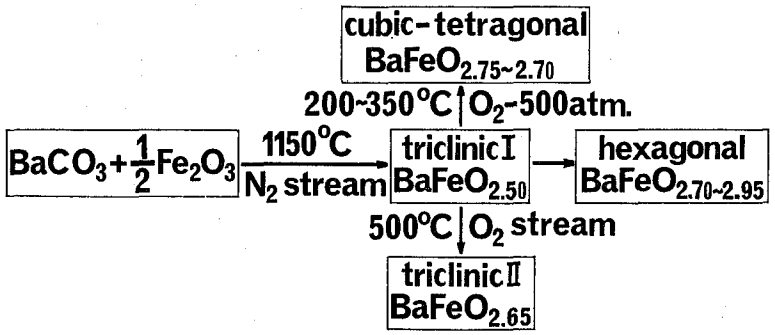

Fig. 1. The sample preparation methods for $BaFeO_x$ phases from the triclinic-I $BaFeO_{2.5}$ phase.

again at 300°C under the oxygen pressure of 500 atm for 48 hr. The sample preparation methods of these $BaFeO_x$ phase are summarized in Fig. 1.

For heat treatments in air, oxygen or nitrogen at 1 atm, the samples were spread thinly on boats of porcelain or platinum. After heating, the samples were rapidly cooled to room temperature in the same atmosphere. For the heating under high oxygen pressure, the sample was placed in a test tube of gold and put in a cone-sealed hydrothermal reaction vessel made of Stellite. The sample under oxygen pressure of 500 atm was kept at temperatures below 300°C and then quenched into cold water with the reaction vessel.

The phase identification of the obtained products was accomplished by X-ray diffraction techniques. Mössbauer effect measurements were carried out using an apparatus consisting of a source driving unit, Elron AME-20, and a multichannel analyzer, Northern Scientific NS-611. The temperature of the absorber was varied between 4.2 K and 293 K. The gamma ray source was Co^{57} embedded in Cu metal, which was always kept at room temperature. The isomer shift is expressed relative to the absorption of pure iron metal. The analysis of the spectra was performed by using a curve analyzer, Du Pont 310.
Measurements of magnetization were made for a part of the samples by using a torsion balance magnetometer.

III. RESULTS AND DISCUSSION

(*A*) *Triclinic-I phase*

Mössbauer absorption spectra of the triclinic-I phase measured at room temperature and 4.2 K are shown in Fig. 2. It is evident that the magnetic ordering temperature is higher than room temperature. According to previously reported data, the values of the internal magnetic field at Fe^{4+} ion lie between 160 and 330 kOe.[3,5,10,21,22] On the other hand, those at Fe^{3+} ion are concentrated in the range between 450 and 550 kOe. Shimony *et al.*[21] have summarized the correlation between the isomer shift and valence state of iron as follows: The isomer shifts of Fe^{6+}, Fe^{4+}, Fe^{3+} and Fe^{2+} are -0.85 ± 0.03, -0.02 ± 0.03, $+0.4\pm0.2$ and $+1.25\pm0.1$ mm/sec, respectively. Judging from the internal magnetic fields and isomer shifts, all the iron ions in the triclinic-I phase are trivalent. This conclusion is consistent with the color of the sample being brown. The composition is therefore concluded to be $BaFeO_{2.5}$. The Mössbauer spectrum of the triclinic-I phase can be divided into two groups of 6-line spectrum. Furthermore, one of the outermost line splits into three. Therefore it is suggested that four kinds of iron site exist in the triclinic-I phase.

According to the results of the magnetic susceptibility measurements which were made for the triclinic-I sample enclosed in an evacuated quartz tube, the triclinic-I phase is a compensated antiferromagnet. As shown in Fig. 3, the magnetic susceptibility of the triclinic-I phase was fairly small and the susceptibility *vs.* temperature curve showed a broad maximum at about 670 K. Heating and cooling curves did not show a thermal hysteresis. By X-ray diffraction, it was confirmed that the sample was not changed. Mössbauer measurements at higher temperatures are necessary to determine the magnetic transition temperature of this phase.

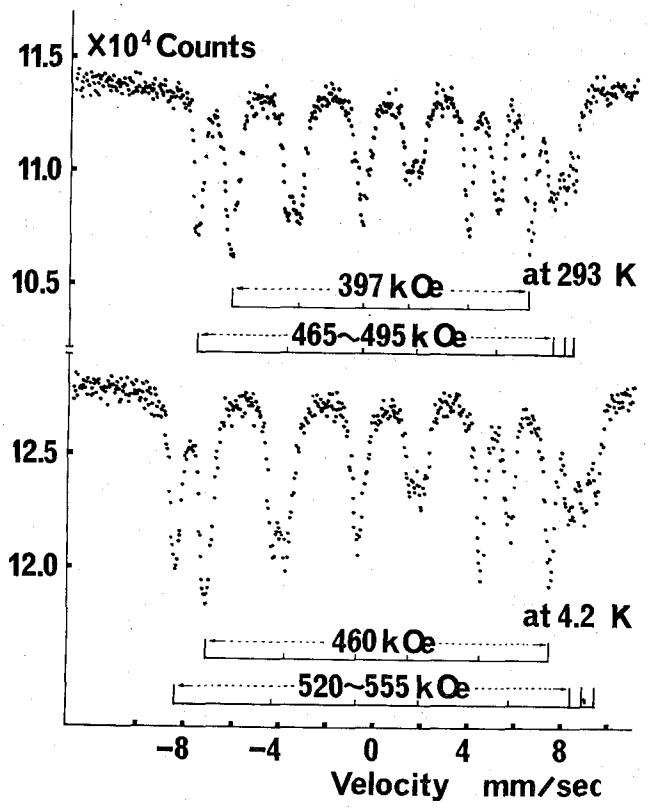

Fig. 2. Mössbauer absorption spectra at 4.2 K and 293 K for $BaFeO_{2.50}$ of the triclinic-I phase.

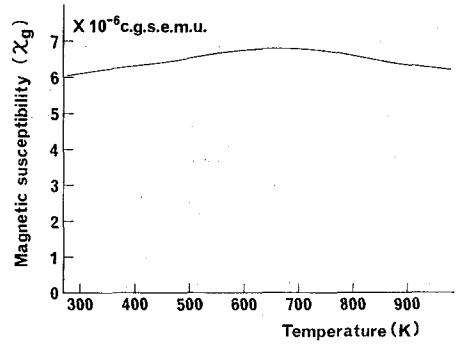

Fig. 3. Magnetic susceptibility of the triclinic-I phase as a function of temperature. (H=14500 Oe)

(*B*) *Triclinic-II phase.*

Mössbauer absorption spectra of the triclinic-II phase measured at room temperature, 78 K, and 4.2 K are shown in Fig. 4. From the spectra at 78 K and 4.2 K, it was evidenced that there are two kinds of Fe^{3+} site and one kind of Fe^{4+} site. The spectrum at room temperature suggested that the magnetic transition temperature is not much higher than room temperature.

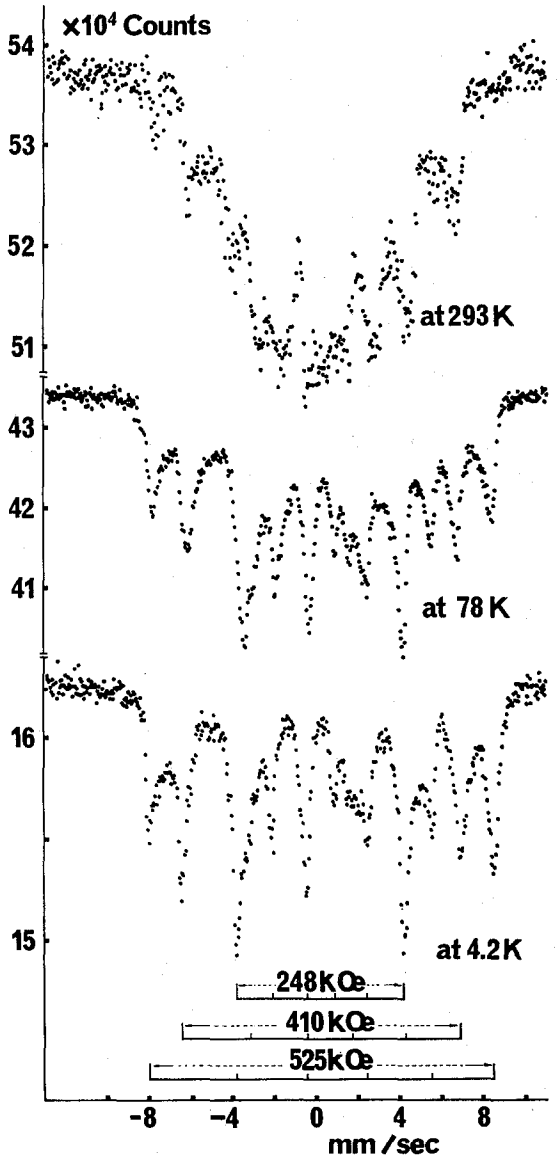

Fig. 4. Mössbauer absorption spectra at 4.2 K, 78 K and 293 K for the triclinic-II phase.

(*C*) *Cubic-tetragonal phase*

Mössbauer absorption spectra of the tetragonal phase measured at room temperature, 78 K and 4.2 K are shown in Fig. 5. The spectrum at 4.2 K consisted of two 6-line spectra. Judging from the internal magnetic fields and isomer shifts, the two spectra correspond to the absorptions of Fe^{3+} and Fe^{4+} ions respectively. The spectra for a sample of cubic phase, obtained by annealing the triclinic-I phase at 250°C in the oxygen pressure of 500 atm, were very similar to those for tetragonal samples.

One of the authors (T. I.) has studied the $SrFeO_x$ system with perovskite structures

which was obtained by the thermal decomposition of a hexavalent iron compound, $SrFeO_4$.[5] The Mössbauer spectrum showed that there are two kinds of Fe^{3+} site and one kind of Fe^{4+} site in the tetragonal perovskite $SrFeO_x$ with high oxygen deficiency. A remarkably large quadrupole interaction was observed in the spectrum for the one of the Fe^{3+} sites. In contrast to the case of $SrFeO_x$, such kind of Fe^{3+} site was not observed in the spectrum of $BaFeO_4$ with perovskite structure.

(*D*) *Hexagonal phase*

Highly oxidized hexagonal samples were prepared according to the method of

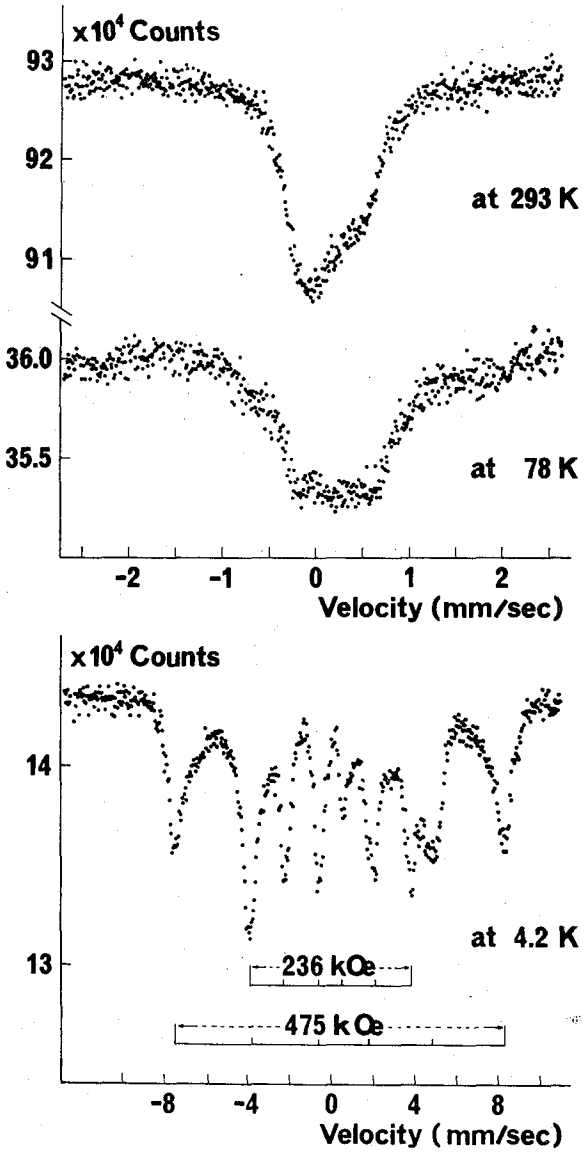

Fig. 5. Mössbauer absorption spectra at 4.2 K, 78 K and 293 K for the tetragonal phase.

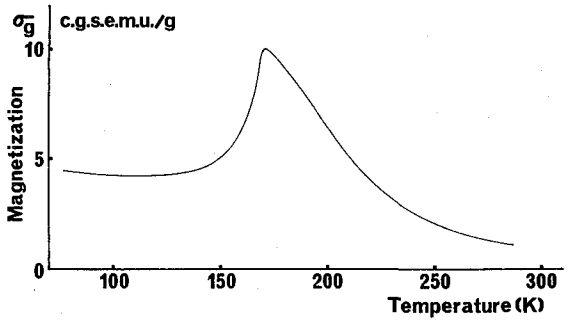

Fig. 6. Magnetization *vs.* temperature curve for $BaFeO_{2.94}$ of the hexagonal phase. (H=14500 Oe)

Mori.[12] Described below are the results on a sample with the highest oxygen content. The oxygen content could be estimated as $BaFeO_{2.94}$, in comparison with the data reported by MacChesney *et al.*[11] The magnetization *vs.* temperature curve is shown in Fig. 6. A weak ferromagnetization has appeared gradually below 250 K but it decreased rather steeply below 171 K. This curious magnetic behavior is in accordance with the previously reported data by MacChesney *et al.*[11] and Mori.[12] MacChesney *et al.* proposed that $BaFeO_{2.95}$ is ferromagnetic and the sudden decrease of the magnetization is due to an exchange inversion mechanism, similar to the case of Cr-modified Mn_2Sb. However, Mori has measured the lattice parameters as a function of temperature and found no discontinuous change of the lattice parameters at the transition temperature. He therefore concluded that the exchange inversion mechanism is not the origin of the decrease of the ferromagnetization.

In order to make clear the magnetic properties of the hexagonal phase, the temperature dependence of the Mössbauer spectra was measured, especially in the vicinity of the transition temperature. The results are shown in Figs. 7, 8 and 9. At 4.2 K, the lines of the spectrum were very sharp and two internal fields were observed, corresponding to Fe^{3+} and Fe^{4+} states, respectively. The spectra above 125 K showed the coexistence of paramagnetic fraction and the fraction increased with an increase of temperature. Above 174 K, the spectrum has turned to be completely paramagnetic. This result suggests a distribution of the magnetic transition temperature in a considerably wide range. By X-ray diffraction measurements, the samples were identified to be homogeneous and of a single phase. However, it seems inevitable that the sample prepared at such a low temperature is not homogeneous from a microscopic point of view. The present results could not give us any useful information to explain the unusual magnetic behavior of the hexagonal phase. The ferromagnetization may have a correlation with the microscopic imhomogeneity.

The present sample of hexagonal phase was prepared in the same condition that Mori had prepared $BaFeO_{2.95}$. In comparison with the magnetic data of MacChesney *et al.*, the composition of the present sample could be presumed as $BaFeO_{2.94}$. The spectrum at 4.2 K is very similar to that for hexagonal $BaFeO_{2.95}$ previously reported by Gallagher *et al.*[10] Thus it is supposed that the ratio of Fe^{3+} to the total Fe is about 10%. However, the Mössbauer result is in remarkable disagreement. The observed amount of Fe^{3+} was comparable to that of Fe^{4+}. The spectrum at 4.2 K was fairly

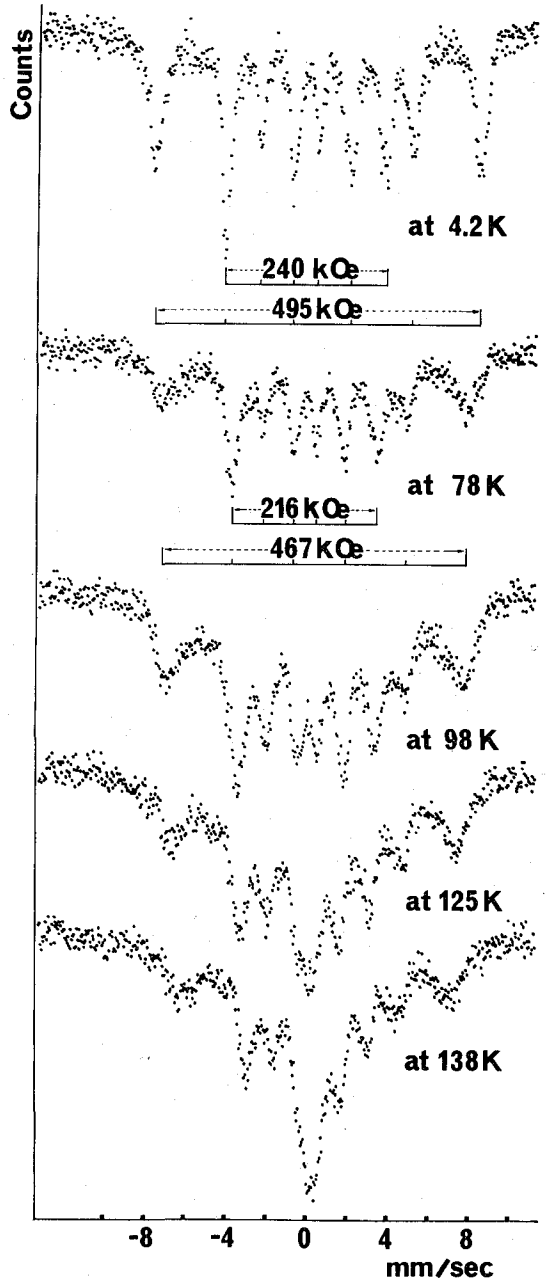

Fig. 7. Mössbauer absorption spectra for $BaFeO_{2.94}$ of the hexagonal phase at various temperatures.

clear and the absorptions by Fe^{3+} and Fe^{4+} ions could be unambiguously distinguished. At 4.2 K, it is generally a good assumption that the Mössbauer absorption area is proportional to the amount of iron. The relative amount of Fe^{3+} to the total iron was estimated to be 39%. As shown in Fig. 9, the ratio derived from the spectrum at room temperature was very similar to this value. At the present stage, no plausible ex-

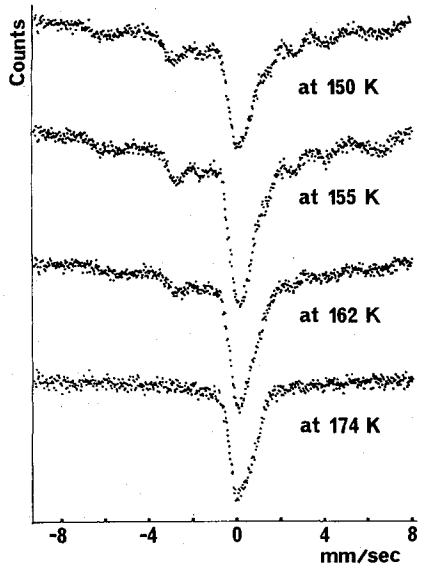

Fig. 8. Mössbauer absorption spectra for $BaFeO_{2.94}$ of the hexagonal phase in the vicinity of the transition temperature.

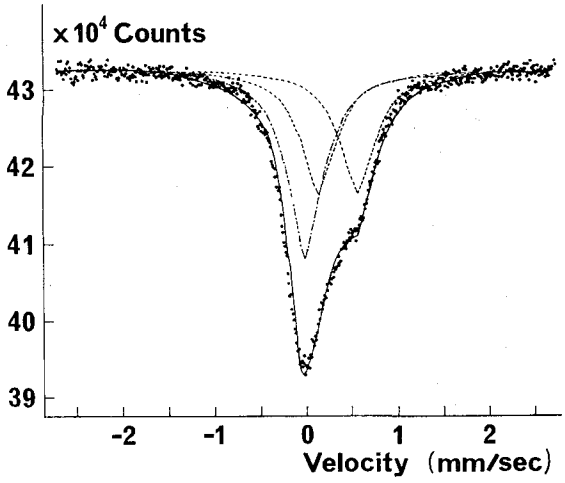

Fig. 9. Mössbauer absorption spectrum for $BaFeO_{2.94}$ of the hexagonal phase at room temperature.

planation can be proposed concerning the inconsistency between the Mössbauer data and the chemical analysis.

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