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Mössbauer Study of the Thermal Decomposition Products of K_2FeO_4

Toshio ICHIDA*
Institute for Chemical Research, Kyoto University, Uji, Kyoto

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The thermal decomposition process of a hexavalent iron compound, K_2FeO_4, was studied by means of the Mössbauer effect. The compound began to decompose in air at about 170°C, and an amorphous product was obtained by the decomposition below 200°C. The product showed a paramagnetic Mössbauer spectrum at 293°K, with an isomer shift and quadrupole splitting of $+0.40 \pm 0.02$ mm/sec and 0.64 ± 0.02 mm/sec respectively; it also showed a magnetically-split six-line spectrum at 4.2°K, with an internal magnetic field of 480 ± 5 kOe. These Mössbauer parameters are characteristic of the Fe^{3+} state. The intermediate valence states, Fe^{5+} or Fe^{4+}, were not observed during the decomposition process, and so it was concluded that the Fe^{6+} ions in K_2FeO_4 were reduced directly to Fe^{3+} ions. $KFeO_2$ was formed in air above 250°C, and the temperature dependence of the internal magnetic field showed the Néel temperature of $KFeO_2$ to be very high, 983 ± 10°K.

Previously, Scholder *et al.*[1,2] reported on the thermal decomposition process of a hexavalent iron compound, K_2FeO_4. According to their reports, the decomposition process below 700°C is represented as the following formula:

$$2K_2Fe^{6+}O_4 \longrightarrow K_3Fe^{5+}O_4 + KFe^{3+}O_2 + O_2,$$

and that above 700°C by:

$$K_3Fe^{5+}O_4 \longrightarrow KFe^{3+}O_2 + K_2O + (1/2)O_2.$$

Although Scholder[2] reported the existence of K_3FeO_4 and Na_3FeO_4 as examples of pentavalent iron compounds, there was no crystallographic justification of them. Indeed, the existence of no pentavalent iron compound has yet been established by physical means.

In recent years, it has been well known that the Mössbauer effect is very useful in the determination of iron valency in the solid state.[3-5] In the present study of the thermal decomposition products of a hexavalent iron compound, K_2FeO_4, the valence state of iron and the magnetic properties of the products were investigated by means of the Mössbauer effect.

Sample Preparation and Measurements

The sample-preparation method of K_2FeO_4 was similar to the procedure of Thompson *et al.*[6]

Into a sodium hypochlorite solution, granular sodium hydroxide was slowly stirred, while we permitted the

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* On leave from Kawasaki Steel Corporation.
Present address: Research Laboratories, Kawasaki Steel Corporation, 1, Kawasaki-cho, Chiba.

[1] V. R. Scholder, H. V. Bunsen, F. Kindervater and W. Zeiss, *Z. Anorg. Allg. Chem.*, **282**, 268 (1955).

[2] V. R. Scholder, Colloque International du C. N. R. S., 1112 (1964).

[3] G. K. Wertheim and R. H. Herber, *J. Chem. Phys.*, **36**, 2497 (1962).

[4] T. Shinjo, T. Ichida, and T. Takada, *J. Phys. Soc. Jap.*, **26**, 154 (1969).

[5] T. Shinjo, T. Ichida, and T. Takada, *ibid.*, **29**, 111 (1970).

[6] G. W. Thopson, L. T. Ockerman, and J. M. Schreyer, *J. Amer. Chem. Soc.*, **73**, 1379 (1951).

temperature to rise as high as 30°C; finally, the mixture was cooled to about 0°C. The precipitated sodium chloride was removed by filtration through a glass filter. To the alkaline hypochlorite solution at about 10°C, fine powder of ferric nitrate was slowly added. The solution was saturated with sodium hydroxide, and the temperature was maintained at about 30°C. The mixture was then filtered with suction through a coarse glass filter. By adding a saturated potassium hydroxide solution with stirring, precipitates of K_2FeO_4 were produced. The following cycle of purification was repeated more than three times: the precipitates of K_2FeO_4 were leached on a glass filter of a fine porosity with a 3M-KOH chilled solution. The liquid was drawn through the filter into a saturated potassium hydroxide solution, whose temperature was also kept at about 0°C. Because the solubility of K_2FeO_4 into a concentrated potassium hydroxide solution is much less than into a dilute solution, recrystallized K_2FeO_4 was thus obtained. The sample was purified by repeating this recrystallization.

The filtered precipitates of K_2FeO_4 were washed with benzene, 95% alcohol, and ether successively. The sample thus obtained was rapidly dried up and stored in a dry atmosphere. Particles of K_2FeO_4 showed a dark purple color and a needle shape (the longest axis was a few mm long).

By the X-ray diffraction technique, the sample was confirmed to be a single phase of K_2FeO_4. The measurements of the magnetization and the Mössbauer effect were carried out on the obtained samples at 80°K in order to confirm the absence of a ferromagnetic impurity and all iron ions except the hexavalent ones.[5]

Using the pure sample thus obtained, the thermal decomposition process of K_2FeO_4 was investigated. In the case of heating under high oxygen pressures, the K_2FeO_4 was held in a test tube of silica or gold. This test tube was placed in a cone-seal hydrothermal reaction vessel made of Stellite.

The decomposition products obtained were identified by using an X-ray diffractometer. Mössbauer effect measurements were carried out using an apparatus consisting of Elron's driving unit, AME-20, and Northern Scientific Co.'s 1024-channel pulse-height analyzer, NS-600. The temperature of the absorber was varied between 4.2 and 1023°K. The gamma ray source, ^{57}Co embedded in Cu metal, was always kept at room temperature. The calibration of the velocity scale was done by using pure Fe and α-Fe_2O_3 as the standard absorbers. The isomer shift is expressed relative to pure Fe.

Results and Discussion

Potassium ferrate, K_2FeO_4, gradually began to decompose in air at about 170°C. The X-ray diffraction pattern of the sample obtained by keeping K_2FeO_4 at 170°C in air for 10 days (Sample A) showed a slight trace of K_2FeO_4, but the sample kept for 90 days (Sample B) showed no diffraction peak. The Mössbauer spectra of the two samples measured at room temperature are shown in Fig. 1. As for Sample B, the Mössbauer spectrum measured at the temperature of liquid helium is shown in Fig. 2.

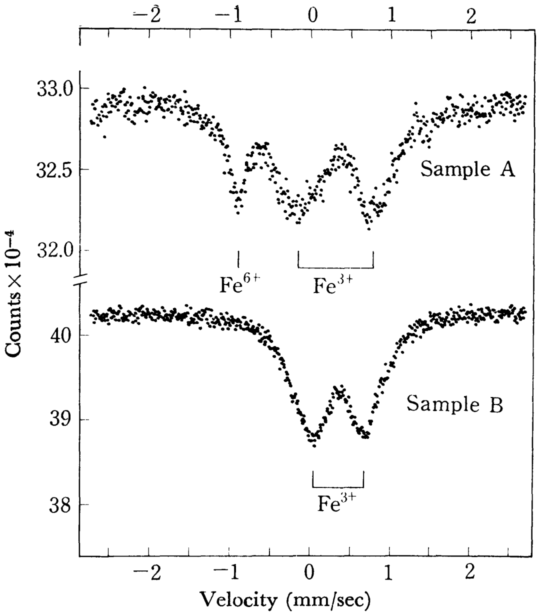

Fig. 1. Mössbauer absorption spectra at room temperature of ^{57}Fe in thermal decomposed products of K_2FeO_4 obtained at 170°C for 10 days (Sample A) and for 90 days (Sample B).

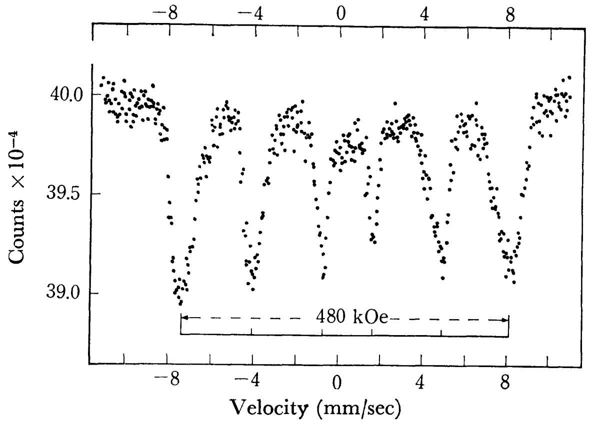

Fig. 2. Mössbauer absorption spectrum of ^{57}Fe in Sample B measured at 4.2°K.

As has previously been reported,[3–5] the Mössbauer absorption of K_2FeO_4 at room temperature is a sharp single line whose isomer shift is -0.89 ± 0.03 mm/sec; this is characteristic of the Fe^{6+} state. Below 5°K, magnetic hyperfine splitting appears. The internal magnetic field extrapolated to 0°K was 140 ± 7 kOe. The narrow single-line absorption at -0.90 mm/sec in Fig. 1 (Sample A) was due to the remaining Fe^{6+} ions. A broad quadrupole doublet was observed in the spectrum of Sample A; a similar broad symmetric absorption spectrum was also found in Sample B. As is shown in Fig. 2, the Mössbauer spectrum of Sample B measured at 4.2°K consisted of six broad absorption lines. The values of the internal magnetic field, 480 ± 5 kOe and the isomer shift, $+0.44\pm0.05$ mm/sec, show that the state of the iron was not Fe^{4+} or Fe^{5+} ions, but Fe^{3+} ions. The broad symmetric doublet in Fig. 1 was ascribed to the paramagnetic absorption of Fe^{3+}

ions. It was evident that, when K_2FeO_4 was kept at about 170°C in air, Fe^{6+} ions were reduced to Fe^{3+} ions directly, without passing through the intermediate valence states, Fe^{5+} or Fe^{4+} ions. These results disagree with the hypothesis reported by Scholder *et al.*[1,2]

As is shown in Fig. 1, the symmetric doublet of Sample B has a narrower line-width and a smaller quadrupole splitting (0.64 mm/sec) than that of Sample A, whose quadrupole splitting is 0.93 mm/sec. The main origin of the electric-field gradient is possibly the crystallographic imperfections; therefore, the quadrupole splitting decreased with the increase in the heating period. Judging from the Mössbauer spectra and the fact that no X-ray diffraction peak was observed, it seems that Sample B consists of ultra-fine particles of a ferric compound which show superparamagnetism at room temperature. The broad line-width of the magnetically-split spectrum (Fig. 2) shows that a distribution of the internal magnetic field exists; it is caused by the lack of homogeneity of the crystallographic circumstances of the iron ions.

By heating K_2FeO_4 at temperatures between 250 and 1000°C in air, light green compounds were produced. All of the X-ray diffraction peaks of these samples were those of the $KFeO_2$ phase; no other compound containing the extra potassium was detected. It seemed that the yellow substance which was found on the surface of the decomposition products was a compound of the extra potassium (oxide?).

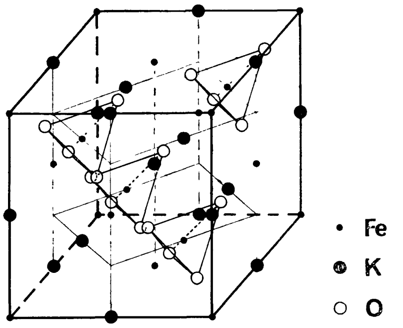

Fig. 3. The crystal structure of $KFeO_2$.

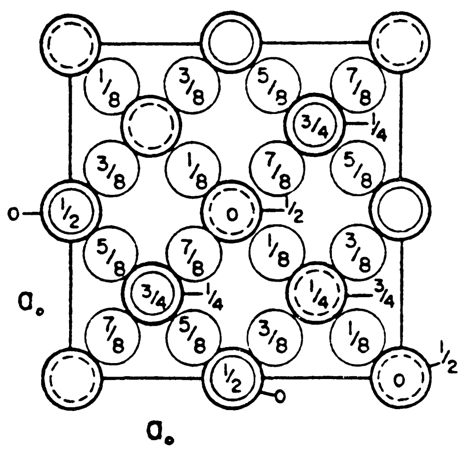

Fig. 4. The projection of $KFeO_2$ crystal along the cubic axis. The heavy circles are potassium, the larger, light circles are oxygen and the small circles are iron.
The lattice constant $a_0 = 7.958$ Å.

Potassium orthoferrite, $KFeO_2$, is isomorphous with $KAlO_2$[7,8] and has a cubic structure ($a_0 = 7.96$ Å) related to the high-cristobalite structure of silica. A perspective drawing of the cubic unit cell is shown in Fig. 3, while a projection along the cubic axis is shown

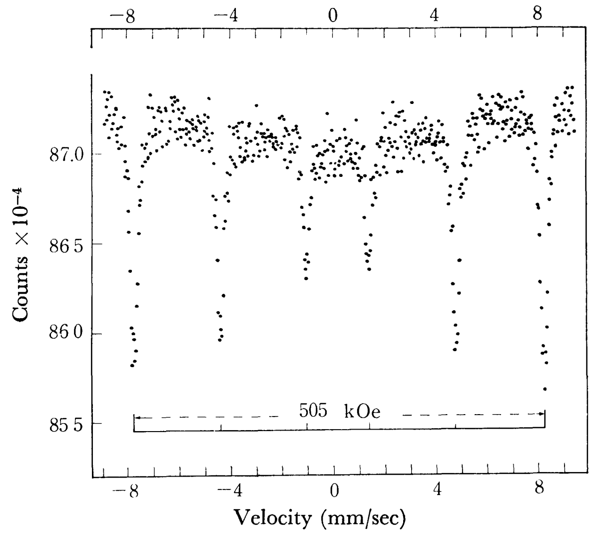

Fig. 5. Mössbauer absorption spectrum of ^{57}Fe in $KFeO_2$ measured at 293°K.

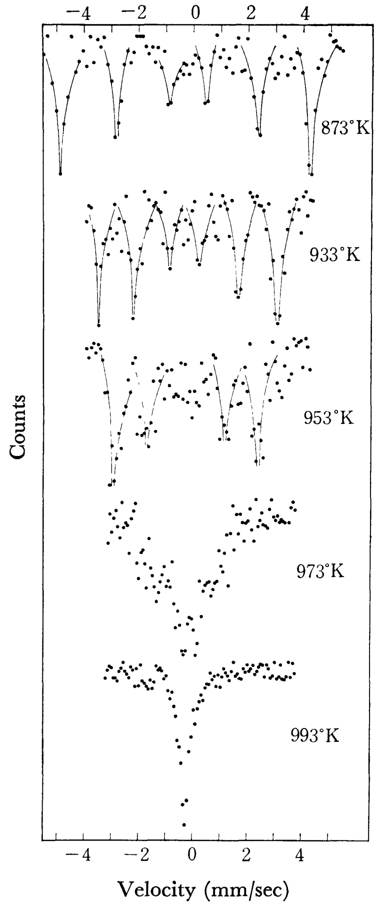

Fig. 6. Mössbauer absorption spectra of ^{57}Fe in $KFeO_2$ measured at temperatures above 873°K.

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[7] T. F. W. Barth, *J. Chem. Phys.*, **3**, 323 (1935).

[8] R. G. Wyckoff, "Crystal Structures," 2nd ed., Vol. 2, Interscience Publishers, Inc., New York (1964), p. 326.

in Fig. 4. Every iron atom occupies a crystallographically-equivalent site, tetrahedrally-surrounded by four oxygen atoms. The adjacent tetrahedrons of the oxygen atoms hold an apex in common, and the angle of Fe–O–Fe is 180°. The closest atomic approaches are O–O=2.72 Å, Fe–O=1.73 Å, and K–O=3.32 Å.

The Mössbauer spectrum of $KFeO_2$ at 293°K is shown in Fig. 5. The spectrum shows that iron is in trivalent state in $KFeO_2$ and that there is a magnetic ordering, even at room temperature, with an internal magnetic field of 505 ± 5 kOe. The Mössbauer spectra obtained above 873°K are shown in Fig. 6. The internal magnetic field disappeared at 983 ± 10°K. Therefore, the Néel temperature of $KFeO_2$ was estimated to be 983 ± 10°K from the temperature variation in the internal magnetic field. Figure 7 shows the temperature dependence of the internal field. The Brillouin function for $S=5/2$ is also represented there for the sake of comparison. Previously, Kerler *et al.*[9,10] also measured the Mössbauer effect of $KFeO_2$ below 348°K. As is shown in Fig. 7, their data show a good agreement with the present data.

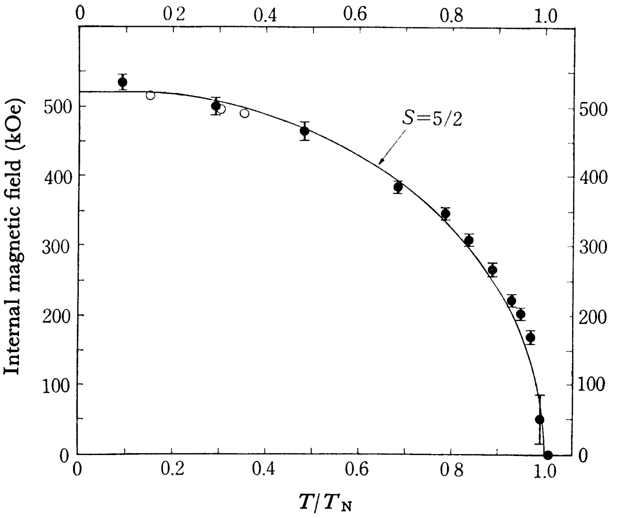

Fig. 7. The temperature dependence of the internal magnetic field in $KFeO_2$. Open circles are after Ref. 10. T_N is 983°K. Solid line represents the Brillouin function for $S=5/2$.

According to the results of the magnetic susceptibility measurements, $KFeO_2$ is a compensated antiferromagnet, but no anomaly was observed around the T_N value in the susceptibility-temperature curve. The present value, 983 ± 10°K, is the highest among all the Néel temperatures of iron compounds thus far reported. Since the angle of Fe–O–Fe is 180° and the distance is very short (3.46 Å), the superexchange interaction must be very strong. Assuming that the spin directions of all the neighboring Fe^{3+} ions are antiparallel with each other, a completely compensated antiferromagnetic spin arrangement can be composed. This structure seems reasonable, although no experimental confirmation has yet been presented.

The decomposition temperature of K_2FeO_4 changed slightly with the oxygen pressure. Under the oxygen pressure of 500 atm, K_2FeO_4 began to decompose at about 250°C, while it began to decompose at 170°C in air. Independently of the oxygen pressure, it was confirmed by the Mössbauer-effect measurements that the Fe^{6+} ions in K_2FeO_4 were reduced directly to Fe^{3+} ions. There was no difference in the crystal structure and magnetic properties of the $KFeO_2$ samples obtained under various conditions. It was concluded that, in the low-temperature range, ultra-fine particles of a trivalent iron compound were formed and that, in the high-temperature range, K_2FeO_4 decomposed as follows:

$$K_2FeO_4 \longrightarrow KFeO_2 + KO_x + (2-x/2)O_2$$

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9) U. E. Fluck, W. Kerler, and W. Neuwirth, *Z. Anorg. Allg. Chem.*, **333**, 235 (1964).

10) W. Kerler, W. Neuwirth, E. Fluck, P. Kuhn, and B. Zimmerman, *Z. Phys.*, **173**, 321 (1963).