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Mössbauer Study of the FeV_2O_4–Fe_3O_4 System

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Mössbauer spectra of the $Fe_{1+x}V_{2-x}O_4$ spinel solid solutions are taken to investigate the cation distribution. Room temperature spectra can be interpreted by assuming that the cation distribution is represented approximately as $Fe^{2+}[Fe_x^{3+}V_{2-x}^{3+}]O_4$ for $0 \leqq x \leqq 0.35$ and $Fe^{3+}[Fe^{2+}Fe_{x-1}^{3+}V_{2-x}^{3+}]O_4$ for $1 \leqq x \leqq 2$ and the ionic valence arrangement changes from the 2-3-3 type ($Fe^{2+}[Fe_x^{3+}V_{2-x}^{3+}]O_4$) to the 3-2-3 one ($Fe^{3+}[Fe^{2+}V^{3+}]O_4$) in the range $0.35 \leqq x \leqq 1$. Fe_2VO_4 is found to be 3-2-3 spinel, $Fe^{3+}[Fe^{2+}V^{3+}]O_4$. Its paramagnetic spectrum at 473°K is, however, composed of a broad single line with isomer shift value of 0.61 mm/sec relative to stainless steel, in which the line splitting due to the ferric and ferrous ions is rendered indistinguishable.

1. Introduction

FeV_2O_4 and Fe_3O_4 are spinels well known of a normal and an inverse type, respectively; the cation distributions are represented as $Fe^{2+}[V_2^{3+}]O_4$ (*1*) and $Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$ (*2*), where the bracket indicates the octahedral site. FeV_2O_4 has been reported by Wold et al. (*3*) to show a spontaneous magnetization (1.9 μ_B/mol at 4.2°K) below 190°K, which is considered to be due to a canted spin structure. However, the precise magnetic structure of the compound has not yet been determined. A detailed Mössbauer study on FeV_2O_4 has been reported by Tanaka et al. (*4*) in connection with the Jahn–Teller distortion which is observed at low temperature due to the tetrahedral ferrous ions of this compound. Fe_3O_4 is a Néel type ferrimagnetic substance with Curie point of 851°K, and a great deal of Mössbauer studies have been done on this compound regarding the phenomenon of the rapid electron exchange between the ferrous and ferric ions on the octahedral sites (*5–8*).

The magnetic properties of the solid solution system FeV_2O_4–Fe_3O_4 ($Fe_{1+x}V_{2-x}O_4$, $0 \leqq x \leqq 2$) were recently studied by Wakihara et al. (*9*). They proposed that a plausible cation distribution of the system would be represented as $Fe_x^{3+}Fe_{1-x}^{2+}[Fe_x^{2+}V_{2-x}^{3+}]O_4$ for $0 \leqq x \leqq 1$ and $Fe^{3+}[Fe^{2+}Fe_{x-1}^{3+}V_{2-x}^{3+}]O_4$ for $1 \leqq x \leqq 2$.

As for the system FeV_2O_4–Fe_2VO_4, various models have been proposed for the cation distribution as follows. Rogers et al. (*10*) studied the electrical, structural and magnetic properties of the system and proposed that the appropriate distribution is represented as $Fe^{2+}[Fe_x^{2+}V_x^{4+}V_{2-2x}^{3+}]O_4$ ($0 \leqq x \leqq 1$), but a small amount of 3-2-3 valence state ($Fe^{3+}[Fe^{2+}V^{3+}]O_4$) should be mixed in Fe_2VO_4. In the Mössbauer study of the system at room temperature, Rossiter (*11*) proposed that the distribution is represented as $Fe^{2+}[Fe_x^{3+}V_{2-x}^{3+}]O_4$ for $0 \leqq x \leqq 0.66$ and $Fe^{2+}[Fe^{2+}V^{4+}]O_4$ for $x = 1$ and the ionic valence state probably changes from the 2-3-3 type to the 2-2-4 one in the range $0.66 < x \leqq 1$. Bernier et al. (*12*) proposed the cation distribution of $Fe^{3+}[Fe^{2+}V^{3+}]O_4$ for Fe_2VO_4 on the basis of their X-ray and magnetic measurements; this model is consistent with what was proposed by Wakihara et al. (*9*).

In this paper, we describe the features of the Mössbauer spectra of the FeV_2O_4–Fe_3O_4 system in the temperature range 92–473°K,

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and propose an interpretation for them, taking the cation distribution into consideration.

2. Experimental

Samples of the solid solution system FeV_2O_4–Fe_3O_4 were kindly supplied by Wakihara of our Institute. The samples were prepared by heating mixtures of vanadium and iron oxides in controlled atmospheres of CO_2–H_2 mixed gas at 1500°K. For further details of sample preparation, the reader should refer to the papers by Wakihara et al. (*9*, *13*). All the samples were shown to be single phase spinel by X-ray analysis and also to be stoichiometric by thermogravimetric analysis (*9*, *13*).

Mössbauer spectra were taken with a constant acceleration spectrometer (Elron Electronics), using a 256 channel analyzer in the time mode. A 15 mCi of ^{57}Co in a copper matrix was used as a source and the isomer shift values were determined relative to 310 stainless steel absorber. High temperature measurement was carried out using a small furnace and flowing appropriate CO_2–H_2 mixed gas to prevent the sample from oxidizing. The room temperature spectrum was taken for comparison before and after the high temperature measurement. Low temperature measurement was carried out using a styroform-insulated Dewar with liquid nitrogen.

3. Results

3.1. FeV_2O_4–Fe_2VO_4 System

Figure 1 shows the room temperature spectra of the samples FeV_2O_4–$Fe_{1.65}V_{1.35}O_4$ ($0 \leqq x \leqq 0.65$) with the Curie points (9) below room temperature. $FeV_2O_4(Fe^{2+}[V_2^{3+}]O_4)$ provides a sharp Lorentzian line with isomer shift of 1.02 mm/sec relative to stainless steel, which is consistent with the previous reports (*4*, *11*). The absence of the quadrupole splitting in the room temperature spectrum is explained to be in accord with the cubic site symmetry of the tetrahedral sites on which the ferrous ions are located (*4*, *11*). As iron is substituted for vanadium, a shoulder appears in the spectrum ($x = 0.2$ and 0.35), which is rendered indistinguishable with increasing content of iron and it tends to a broad single absorption curve for $Fe_{1.5}V_{1.5}O_4$ ($x = 0.5$) and $Fe_{1.65}V_{1.35}O_4$ ($x = 0.65$).

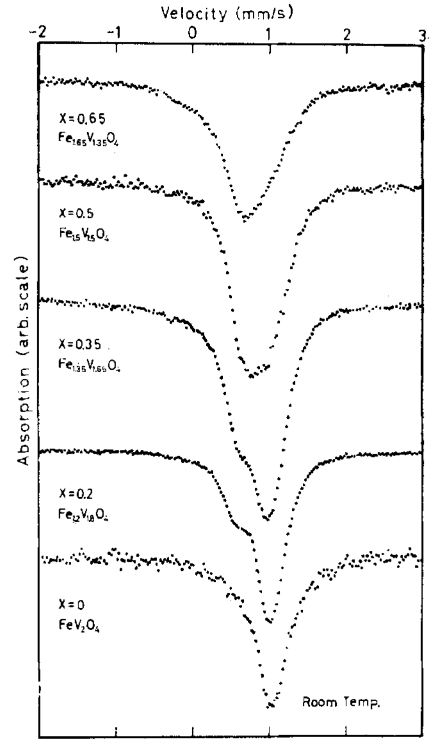

FIG. 1. Mössbauer spectra of the FeV_2O_4–$Fe_{1.65}V_{1.35}O_4$ system ($0 \leqq x \leqq 0.65$) at room temperature.

As illustrated in Fig. 2, the spectrum with the shoulder was computer analyzed by superposing two Lorentzian lines α (main) and β (shoulder) with variable parameters such as isomer shift, peak heights, and half widths. The resultant isomer shift and the intensity ratio β/α are listed in Table I. The isomer shift obtained for the line α (0.99–1.02 mm/sec) and β (0.55–0.61) mm/sec are lying in the range of the typical values reported so far for ferrous and ferric ions, respectively (*14*).

Room temperature spectra of the samples in the composition range $0.65 < x < 1.0$ provide poorly resolvable hyperfine patterns because of the approach of the Curie points to room temperature.

TABLE I

ISOMER SHIFT AMD INTENSITY RATIO FOR THE LINES (α) AND (β) DETERMINED BY COMPUTER ANALYSIS

Compounds		Isomer shift[a] (mm/sec)		Intensity ratio
Formula	x	(α)	(β)	(β)/(α)
FeV_2O_4	0	1.02 + 0.04	—	—
$Fe_{1.2}V_{1.8}O_4$	0.2	1.02 ± 0.04	0.55 ± 0.04	0.23
$Fe_{1.35}V_{1.65}O_4$	0.35	0.99 ± 0.04	0.61 ± 0.04	0.52

[a] Relative to stainless steel.

3.2. Fe_2VO_4–Fe_3O_4 System

Figure 3 shows the room temperature spectra of the samples Fe_2VO_4–Fe_3O_4 ($1 \leq x \leq 2$). $Fe_3O_4(Fe^{3+}[Fe^{2+}Fe^{3+}]O_4)$ shows two distinct hyperfine patterns which are assigned as I and II in the figure; I is due to the tetrahedral ferric ions and II due to the octahedral ferric and ferrous ions rendered indistinguishable by the rapid electron exchange (5, 6). As vanadium is substituted for iron, the spectra become broadened to show poor resolution, but one can distinguish the two patterns I and II as indicated in the figure. The spectrum parameters are determined for both the patterns and summarized in Table II. With the increase of the vanadium content, the internal fields decrease while isomer shift increase in both I and II.

For Fe_2VO_4, the spectrum was taken at 92°

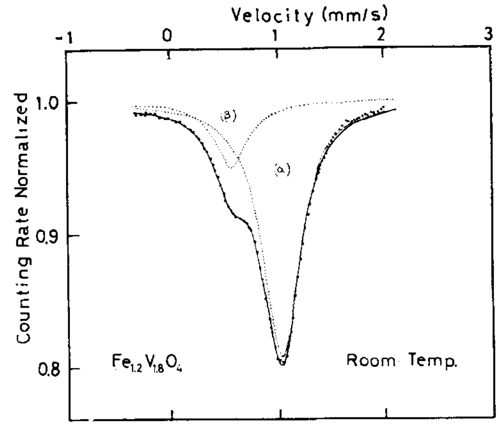

FIG. 2. Mössbauer spectrum of $Fe_{1.2}V_{1.8}O_4$ ($x = 0.2$) at room temperature. Solid line represents the computer fitted line by superposing two Lorentzian lines α and β which are shown by dotted lines.

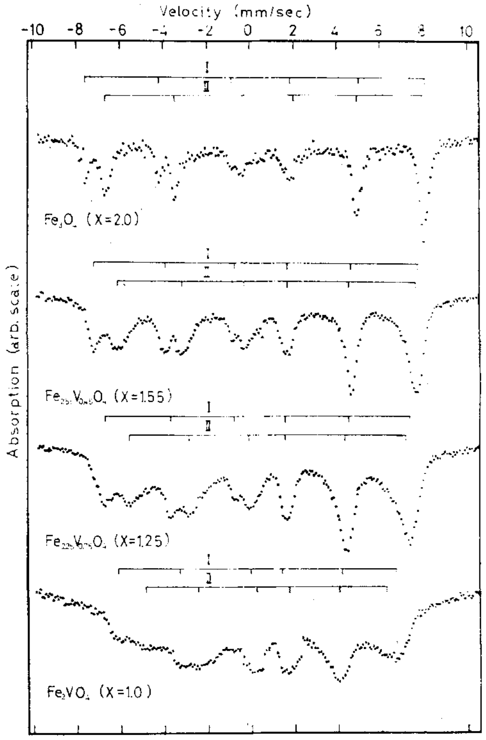

FIG. 3. Mössbauer spectra of the Fe_2VO_4–Fe_3O_4 system ($1 \leq x \leq 2$) at room temperature. Above each spectrum, is shown the assignment of patterns I and II.

TABLE II

THE MÖSSBAUER PARAMETERS FOR THE Fe_2VO_4–Fe_3O_4 SYSTEM AT ROOM TEMPERATURE

Compounds		Internal field (kOe)		Isomer shift[a] (mm/sec)		Quadrupole splitting (mm/sec)	
Formula	x	I	II	I	II	I	II
Fe_3O_4	2.0	-489 ± 5	-455 ± 5	0.33 ± 0.04	0.72 ± 0.04	0.4 ± 0.2	0.1 ± 0.2
$Fe_{2.55}V_{0.45}O_4$	1.55	-466 ± 10	-429 ± 10	0.36 ± 0.05	0.77 ± 0.05	0.2 ± 0.3	0.0 ± 0.3
$Fe_{2.25}V_{0.75}O_4$	1.25	-437 ± 10	-398 ± 10	0.38 ± 0.05	0.77 ± 0.05	0.2 ± 0.3	0.1 ± 0.3
Fe_2VO_4	1.0	-398 ± 15	-346 ± 15	0.44 ± 0.07	0.82 ± 0.07	0.3 ± 0.3	0.3 ± 0.3

[a] Relative to stainless steel.

and 195°K as shown in Fig. 4, where the room temperature spectrum is also shown for comparison. It is noticed that at low temperatures, well resolved lines are observed for pattern I, but weak and broad lines are observed for II. Paramagnetic spectrum of Fe_2VO_4 (its Curie point is 454°K (9)) taken at 473°K is illustrated in Fig. 5. The spectrum is composed of a broad single line with a symmetric shape having isomer shift of 0.61 mm/sec. This value is considered to lie on the border line between those expected for ferrous and ferric ions, when the effect of second-order Doppler shift is taken into account.

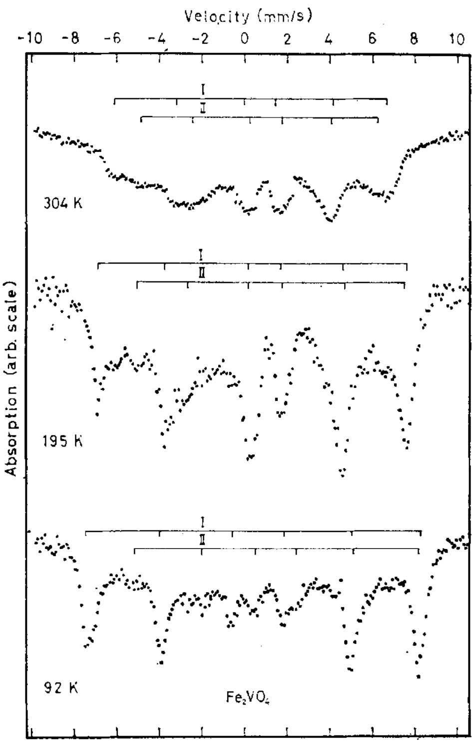

FIG. 4. Mössbauer spectrum of Fe_2VO_4 ($x = 1$) at and below room temperature.

4. Discussion

From the features of the Mössbauer spectra described in the preceding chapter, the following cation distributions of the $Fe_{1+x}V_{2-x}O_4$ system can be proposed.

(1) The fact that the spectrum in the composition range $0 < x \leqq 0.35$ is composed of

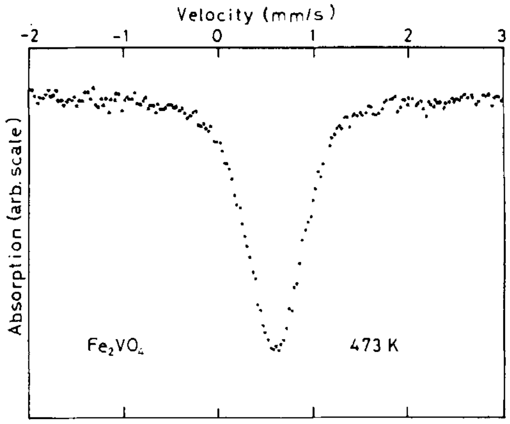

FIG. 5. Paramagnetic spectrum of Fe_2VO_4 at 473°K.

two Lorentzian lines α (main) and β (shoulder) having isomer shift appropriate for ferrous and ferric ions respectively suggests the cation distribution of $Fe^{2+}[Fe_x^{3+}V_{2-x}^{3+}]O_4$ for $0 \leqq x \leqq 0.35$. Other possible arrangements such as $Fe^{2+}[Fe_x^{2+}V_x^{4+}V_{2-2x}^{3+}]O_4$ or $Fe_{1-x}^{2+}Fe_x^{3+}$-$[Fe_x^{2+}V_{2-x}^{3+}]O_4$ should be rejected, because in these arrangements, ferrous ions which are required to occupy the octahedral sites cause strong quadrupole splitting due to the trigonal site symmetry of the octahedral sites.

(2) The isomer shift of the patterns I and II for Fe_2VO_4 are estimated as 0.44 and 0.82 mm/sec respectively at room temperature (cf. Table II); the former is close to the typical values reported so far for ferric ions and the latter is a little smaller than the typical values for ferrous ions. This fact suggests that Fe_2VO_4 is not a 2-2-4 spinel but a 3-2-3 spinel. Since patterns I and II for Fe_3O_4 are attributed to the tetrahedral and octahedral irons, respectively, it may be natural to consider that the patterns I and II for Fe_2VO_4 would be attributed mostly to the tetrahedral ferric and the octahedral ferrous ions, respectively. The cation arrangement of Fe_2VO_4 is therefore like $Fe^{3+}[Fe^{2+}V^{3+}]O_4$ and the arrangement can be approximately represented as Fe^{3+}-$[Fe^{2+}Fe_{x-1}^{3+}V_{2-x}^{3+}]O_4$ for the Fe_2VO_4–Fe_3O_4 system ($1 \leqq x \leqq 2$).

(3) There is a possibility that a change in the cation arrangement from the 2-3-3 type ($Fe^{2+}[Fe_x^{3+}V_{2-x}^{3+}]O_4$) to the 3-2-3 one ($Fe^{3+}$-$[Fe^{2+}V^{3+}]O_4$) may occur in the range $0.35 \leqq x \leqq 1$. The broad line observed for $Fe_{1.5}V_{1.5}O_4$ and $Fe_{1.65}V_{1.35}O_4$ (cf. Fig. 1) is perhaps due to the coexistence of the ferrous and ferric ions on both the tetrahedral and octahedral sites.

The description in (2) is consistent with the model of the cation arrangement for the Fe_2VO_4–Fe_3O_4 system proposed by Wakihara et al. (*9*) and that of Fe_2VO_4 proposed by Bernier et al. (*12*) on the basis of their magnetic measurements. The models mentioned in (1) and (3) are slightly different from those used in the Rossiter's Mössbauer study (*11*); he chose the 2-3-3 type arrangement over the wider range $0 \leqq x < 0.66$. He also observed a single broad line for all the samples FeV_2O_4–$Fe_{1.66}V_{1.34}O_4$ ($0 \leqq x \leqq 0.66$) and suggested that the two lines corresponding to the tetrahedral ferric and the octahedral ferrous ions are superimposed to present a broad single line. He could not find any shoulder in the spectrum; it might be partly due to poorer resolving power of his equipment.

The intensity ratio β/α of the two patterns should correspond to the composition parameter x according to the above interpretation based on the arrangement $Fe^{2+}[Fe_x^{3+}V_{2-x}^{3+}]O_4$. As can be seen in Table II, the agreement is fairly good for $x = 0.2$ ($\beta/\alpha = 0.23$), but not for $x = 0.35$ ($\beta/\alpha = 0.52$). This fact suggests that the cation arrangement deviates considerably from the 2-3-3 type to the 3-2-3 one even at $x = 0.35$.

The speculations in (1) and (3) are plausible also from the stand point of the crystallographic property of the system: As is pointed out by Rogers et al. (*10*), the Jahn–Teller distortion due to the tetrahedral ferrous ions observed for FeV_2O_4 at low temperature does not occur in the composition range $x > 0.5$. The same situation seems to be realized in Fe_2VO_4 with the 3-2-3 type arrangement.

We are confronted with a difficulty to interpret the marked temperature dependence of the spectrum of Fe_2VO_4. At low temperatures (Fig. 4), the relative intensity ratio of pattern II becomes weak in comparison with that observed at room temperature, and the paramagnetic spectrum (Fig. 5) is composed of a broad single line with isomer shift lying on the border line between the values expected for ferrous and ferric ions.

5. Conclusion

The room temperature Mössbauer spectra of the $Fe_{1+x}V_{2-x}O_4$ system can be interpreted by assuming that the cation arrangement is represented approximately as $Fe^{2+}[Fe_x^{3+}$-$V_{2-x}^{3+}]O_4$ for $0 \leqq x \leqq 0.35$ and $Fe^{3+}[Fe^{2+}$-$Fe_{x-1}^{3+}V_{2-x}^{3+}]O_4$ for $1 \leqq x \leqq 2$, and the arrangement changes from the 2-3-3 type (Fe^{2+}-$[Fe_x^{3+}V_{2-x}^{3+}]O_4$) to the 3-2-3 one ($Fe^{3+}[Fe^{2+}$-$V^{3+}]O_4$) in the range $0.35 \leqq x \leqq 1$. A spectrum of Fe_2VO_4 shows a marked temperature dependence, which can not be interpreted consistently. Further study of the ionic states in Fe–V spinels is required.

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