Mössbauer Spectra of Titanomagnetite: A Reappraisal

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The Mössbauer spectra of titanomagnetites, $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ ($0 \leq x \leq 1$), synthesized at 1200°C were redetermined to clarify the cation distribution in titanomagnetite. Nine samples from $x=0$ to $x=0.33$ were used in the experiments. The spectra were very distinct for samples between $x=0$ and $x=0.20$, and in that compositional range satisfactory fits were obtained with theoretical curves by nonlinear regression. Uncertainty in the fitting becomes a severe problem for x larger than 0.20, but the trend in the change of spectra can be traced nearly continuously from $x=0$ to $x=0.33$. The variation of the isomer shift with x suggests that the spectra can be divided into three subsets **a**, **b**, and **c** which are attributed to Fe^{3+} in A site, $\text{Fe}^{2.5+}$ in B site (arising from the electron hopping between the Fe^{3+} and Fe^{2+} pair), and other iron ions with locally varying energy states, respectively. The change of the fractional area (f_a) of subset **a** with composition shows that the cation distribution in the present samples follows the Akimoto model (AKIMOTO, 1954). This conclusion is in good agreement with the neutron diffraction study by WECHSLER *et al.* (1984). It was also concluded from the change of the fractional area (f_b) of subset **b** that the proportion of Fe^{3+} – Fe^{2+} pairs which participate in electron hopping is much less than expected from the model.

1. Introduction

Titanomagnetite is one of the most common magnetic minerals contained in rocks over the earth, and many of its properties have been studied. However, one of the long-standing problems about titanomagnetite is the distribution of cations Fe^{3+} and Fe^{2+} between two possible sites. Titanomagnetite is a solid solution of the two end members of Fe_3O_4 (magnetite) and Fe_2TiO_4 (ulvöspinel), and has a spinel structure in which oxygen atoms form a close packed face-centered cubic arrangement. There are two different interstitial positions for metal ions in the spinel structure. A tetrahedral site (A site), in which the cation is surrounded by four oxygen ions forming a tetrahedron, and an octahedral site (B site), in which the cation is surrounded by six oxygen ions forming an octahedron. Magnetite ($x=0$) has an inverse spinel structure with one Fe^{3+} in A site and one each of Fe^{3+} and Fe^{2+} in B site. The B site cations behave as two $\text{Fe}^{2.5+}$ ions because of the electron hopping between them, resulting in a large electrical conductivity above the Verwey transition temperature of 119 K (VERWEY *et al.*, 1947). Ulvöspinel ($x=1$) is an inverse spinel in which Ti^{4+} occurs in B site according to the neutron diffraction study (ISHIKAWA *et al.*, 1971). Recently, WECHSLER *et al.*

(1984) confirmed the confinement of Ti^{4+} to B site as well for the intermediate compositions by the neutron diffraction method.

Three models of cation distribution have been proposed for the intermediate composition in the titanomagnetite series. The simplest model was by AKIMOTO (1954); it assumes that equal numbers of Fe^{3+} ions occupy A and B sites, as given by the following formula where square brackets indicate B site ions.

The second model, proposed by NÉEL (1955) and CHEVALLIER *et al.* (1955), assumes the preference of Fe^{3+} ions for the A site.

O'REILLY and BANERJEE (1965) proposed the third model which is similar to Néel-Chevallier model in the ranges of $x \leq 0.2$ and $x \geq 0.8$.

The last model was proposed mainly to explain the change of saturation magnetization with x at liquid nitrogen temperature and the value of room temperature electric conductivity (determined from sintered polycrystalline samples).

NISHITANI and KONO (1983) suggested that the differences in cation distribution of original titanomagnetite samples might be one of the causes for the inconsistencies within the results of the low temperature oxidation experiments reported by four groups: OZIMA and SAKAMOTO (1971), READMAN and O'REILLY (1972), KEEFER and SHIVE (1981), and NISHITANI and KONO (1983). These discrepancies cause a severe problem when oxidized oceanic basalts are examined (MOSKOWITZ and BANERJEE, 1981). NISHITANI and KONO (1982) indicated that the main reason for the difference between the data of OZIMA and SAKAMOTO (1971) and those of READMAN and O'REILLY (1972) was in the average size of the ferromagnetic grains, although no significant grain size differences were reported between the samples of other authors. Errors in oxidation parameter (z) will occur if oxidation does not proceed along the constant Fe/Ti ratio line (FURUTA *et al.*, 1985; AKIMOTO *et al.*, 1984), because z is determined by assuming a constant ratio for Fe/Ti in the two methods that were employed—weight change analysis during heating and wet chemical analysis. One possibility is the difference in sample preparation of original titanomagnetite. STEPHENSON (1969) developed a theory that the cation distribution of titanomagnetite is dependent on temperature. The higher the temperature, the more disordered the cation distribution: i.e., the closer the material to the Akimoto model. BLEIL (1971, 1976) supported this theory by comparing the saturation magnetizations

of titanomagnetites which were synthesized at several different temperatures.

Cation distribution in titanomagnetite can also be determined by Mössbauer spectroscopy. In principle, this method is as direct as that by neutron diffraction. Unfortunately, for titanomagnetite, the spectra become vague for larger values of x , as reported by BANERJEE *et al.* (1967a, b) and BHADURI (1982). Titanomagnetite with x less than about 0.2 gives relatively clear spectra (JENSEN and SHIVE, 1973; UMEMURA and IIDA, 1978). JENSEN and SHIVE (1973) concluded that overall cation distribution follows the Akimoto model and a third Mössbauer subspectrum arises from titanium-rich clusters. Their hypothesis of titanium-rich regions seems very arbitrary and is not required to interpret the third spectrum. UMEMURA and IIDA (1978) studied a single-crystal rod of titanomagnetite which composition gradually changes from $x=0$ to 0.05 along the rod. They reappraised the Fe ion state around Ti^{4+} for very small x , but offered no definite conclusion about the cation distribution model. We have repeated the Mössbauer study on titanomagnetite because much progress has been made in both Mössbauer spectroscopy and computer analysis since the previous studies, which gives clearer results.

2. Experimental Procedures

Sample preparation was done in exactly the same way as described by NISHITANI and KONO (1983) who, in turn, followed the method developed by KATSURA *et al.* (1976). The mixture of hematite (Fe_2O_3) and rutile (TiO_2) which gives the required Fe/Ti ratio of titanomagnetite was firstly sintered in air at $900^\circ C$, and then ground into powder. The powder was again sintered in air and reground. This procedure was repeated three times to make the mixture as homogeneous as possible. Lastly, the mixture was heated for several hours at $1200^\circ C$ in a controlled oxygen fugacity (f_{O_2}) atmosphere set at the optimum value reported by KATSURA *et al.* (1976). We prepared 15 kinds of titanomagnetite in this way, from $x=0$ to 1.0. Only nine samples were analyzed for $x \leq 0.33$ in this study because of broad spectral peaks for larger x . Lattice constants (a) of these samples were determined by X-ray diffraction method, extrapolating the a of each peak to $\theta=90^\circ$ against $\cos^2\theta/\sin\theta + \cos^2\theta/\theta$, where θ is the Bragg angle (KLUG and ALEXANDER, 1954). Figure 1 shows a compilation of all the available data of a reported from 1958 to 1984. The new data of the present study are also shown (by open circles) including samples between $x=0.4$ and $x=1.0$ which were not used for Mössbauer measurements. Within the range of scatter, our data agree with the data bank. In particular, our results agree with those of NISHITANI and KONO (1983) whose samples were prepared by the same method employed in this study and were ascertained to be stoichiometric by the wet chemical analysis. It is, therefore, very unlikely that the samples used in this study deviate from the stoichiometry.

Room temperature Mössbauer spectra were obtained by a spectrometer with a ^{57}Co source of about 5 mCi intensity (doped into rhodium) and a proportional counter containing xenon with 5% of carbon dioxide. The source was moved in the constant acceleration mode, the velocity being calibrated by laser interferometry. γ ray spectra were obtained by a 1024-channel pulse height analyzer for both increasing and

Fig. 1. Comparison of lattice constants of titanomagnetite of this study (open circles) with those reported previously. Data are compiled from AKIMOTO *et al.* (1957), AKIMOTO (1962), LINDSLEY (1962), OZIMA and SAKAMOTO (1971), READMAN and O'REILLY (1972), KATSURA *et al.* (1976), OZDEMIR and O'REILLY (1978), KEEFER and SHIVE (1981), NISHITANI and KONO (1983), and WECHSLER *et al.* (1984).

decreasing velocities. The counts in the first and second halves of channels (512 each) were for an approaching and receding source respectively. The two spectra were combined by summing the counts of two channels for each velocity to cancel out the concave shaped background of the first spectrum and the convex shaped background of the second, since an almost horizontal background increases the resolution of spectra. Alpha iron foil of 25 μm thickness was used as the standard to calibrate the velocity scale, and the isomer shifts were measured with respect to this standard.

The Mössbauer spectrum of a ferrimagnetic polycrystalline material is a superposition of two or more magnetic hyperfine spectra, each with six peaks. The center of a magnetic hyperfine spectrum differs from that of the standard iron by the isomer shift. Isomer shift itself depends to some extent on valency of iron ion, as well as various other parameters such as the spin state of iron ions. In the case of titanomagnetite, characteristic values of isomer shift are around 0.3 mm/s for Fe^{3+} and around 1 mm/s for Fe^{2+} ; e.g., 0.266 ± 0.010 mm/s for Fe^{3+} in A site of magnetite (KÜNDIG and HARGROVE, 1969) and 1.08 ± 0.06 mm/s for Fe^{2+} in A and B sites of ulvöspinel (ROSSITER and CLARKE, 1965). From magnetic hyperfine spectra, quadrupole interaction and magnetic hyperfine field can also be obtained. However, these parameters are not very useful for deciding on the cation distribution in titanomagnetite, so we utilized them only for checking consistency with other data. The ratio of spectral peak areas between different sites can be interpreted as the ratio

of iron ions in those sites if it may be assumed that the recoilless fractions of iron ions in different sites are equal. We identified the iron ion valency by isomer shift, and then determined the iron ion distribution among sites from the peak area ratios.

3. Experimental Results

Figure 2 shows the Mössbauer spectrum together with fitted curves for $x=0.12$. Theoretical curves were calculated by nonlinear regression, assuming that three kinds of magnetic hyperfine spectra exist (except magnetite for which there are only two), and that each spectrum is represented by six Lorentzian functions and a quadratic background. Constraints were made for calculation on six peaks area ratio, 3:2:1:1:2:3, and peak positions relations, $P_5 = P_3 + P_4 - P_2$ and $P_6 = P_1 - 4P_2 + 3P_3 + P_4$, ($P_1, P_2, \dots$ are peak positions in ascending order of velocity). The bold-line curve is the total fit and other curves are theoretical spectra for the three components. As typified by Fig. 2, fits of the theoretical curves to the spectrum are excellent, and it is also evident that we obtained much clearer results than those reported formerly. Spectra from the nine samples are all shown in Fig. 3. The isomer shifts, internal fields, and fractional areas determined from the fitted curve are summarized in Table 1.

The magnetite spectrum contains two components, one corresponding to A site Fe^{3+} and, the other to B site $\text{Fe}^{2.5+}$. The latter arises from electron hopping between

Fig. 2. Mössbauer spectra of $\text{Fe}_{2.88}\text{Ti}_{0.12}\text{O}_4$ at room temperature. Bold-line curve is a fit for the total spectra. Three thin-line curves are theoretical spectra for each component, obtained by non-linear least squares analysis. The two main subspectra **a** and **b** correspond to A site Fe^{3+} and B site $\text{Fe}^{2.5+}$ respectively. The first peaks of spectrum **a** lie slightly to the left of the corresponding peaks of spectrum **b**, but sixth peaks are almost coincident. Spectrum **c**, small tails inner side of each peaks of spectrum **b**, arises from energetically distorted iron ions around Ti^{4+} . Excellent agreement is evident between theoretical curve and measured spectra, and the quality of the data is much higher than obtained previously.

Fig. 3. Room temperature Mössbauer spectra for all samples ($0 \leq x \leq 0.33$) used in this study. For $x=0$, two subspectra **a** and **b** are identified. For $x>0$, the third spectrum **c** appears, whose fractional area relative to the total spectra rapidly increases with x .

Table 1. Mössbauer parameters for $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ at 300 K.

x	a (Å)	Spectra	I.S. (mm/s)	Q.S. (mm/s)	Hi (KOe)	Area fractions
0.00	8.398	a	0.272 ± 0.003	0.001 ± 0.005	492 ± 0	0.333 ± 0.004
	± 0.002	b	0.669 ± 0.002	0.022 ± 0.004	462 ± 0	0.667 ± 0.004
0.04	8.399	a	0.273 ± 0.003	-0.011 ± 0.005	492 ± 0	0.327 ± 0.004
	± 0.001	b	0.665 ± 0.003	0.001 ± 0.004	461 ± 0	0.610 ± 0.006
		c	0.717 ± 0.016	0.062 ± 0.033	416 ± 2	0.064 ± 0.007
0.077	8.404	a	0.281 ± 0.004	0.002 ± 0.007	489 ± 0	0.307 ± 0.007
	± 0.001	b	0.670 ± 0.004	-0.000 ± 0.007	458 ± 0	0.529 ± 0.011
		c	0.766 ± 0.023	0.049 ± 0.046	418 ± 3	0.165 ± 0.014
0.12	8.409	a	0.285 ± 0.007	-0.012 ± 0.013	486 ± 1	0.284 ± 0.012
	± 0.000	b	0.647 ± 0.010	-0.021 ± 0.017	455 ± 1	0.467 ± 0.018
		c	0.745 ± 0.015	0.034 ± 0.034	415 ± 2	0.249 ± 0.022
0.16	8.411	a	0.315 ± 0.011	-0.045 ± 0.019	483 ± 1	0.267 ± 0.013
	± 0.001	b	0.612 ± 0.018	-0.009 ± 0.030	452 ± 2	0.436 ± 0.021
		c	0.754 ± 0.012	0.042 ± 0.028	414 ± 2	0.297 ± 0.025
0.20	8.414	a	0.284 ± 0.008	-0.005 ± 0.014	481 ± 1	0.279 ± 0.015
	± 0.001	b	0.644 ± 0.015	-0.069 ± 0.025	450 ± 1	0.353 ± 0.023
		c	0.767 ± 0.018	-0.008 ± 0.031	414 ± 2	0.368 ± 0.026
0.24	8.425	a	0.300 ± 0.011	-0.021 ± 0.019	476 ± 1	0.272 ± 0.018
	± 0.001	b	0.644 ± 0.019	-0.078 ± 0.034	446 ± 2	0.298 ± 0.028
		c	0.752 ± 0.017	0.013 ± 0.035	410 ± 2	0.431 ± 0.030
0.28	8.430	a	0.332 ± 0.013	-0.061 ± 0.023	471 ± 1	0.236 ± 0.018
	± 0.001	b	0.614 ± 0.029	-0.020 ± 0.048	436 ± 2	0.345 ± 0.031
		c	0.796 ± 0.020	0.073 ± 0.048	390 ± 3	0.419 ± 0.035
0.333	8.439	a	0.302 ± 0.012	-0.003 ± 0.021	463 ± 1	0.170 ± 0.014
	± 0.001	b	0.718 ± 0.013	-0.029 ± 0.023	418 ± 1	0.353 ± 0.030
		c	0.846 ± 0.046	0.047 ± 0.091	322 ± 5	0.477 ± 0.037
0.40	8.448					
	± 0.001					
0.50	8.466					
	± 0.001					
0.56	8.476					
	± 0.001					
0.665	8.490					
	± 0.001					
0.774	8.510					
	± 0.002					
1.00	8.537					
	± 0.001					

x : ulvöspinel content, a : lattice constant, I.S.: isomer shift, Q.S.: quadrupole splitting, Hi: internal field.

Fe^{3+} and Fe^{2+} on B site (KÜNDIG and HARGROVE, 1969). We designate the former as spectrum **a** and the latter as spectrum **b**. Both the isomer shifts and internal fields for the two spectra obtained in this study coincide with the values reported previously for magnetite. It is noted that our area ratio of spectra **a** and **b**, $1:(2.00 \pm 0.04)$, is in very good agreement with the theoretical value of 1:2. This is in contrast with the result of JENSEN and SHIVE (1973) who obtained a ratio of 1:1.88 and made corrections by using the recoilless fraction ratio of 0.94 for iron ions in A and B sites reported by SAWATZKY *et al.* (1969). However, this recoilless fraction ratio is not generally accepted because the sample used by Sawatzky *et al.* is for natural magnetite rather than synthetic material, even though they reported that the stoichiometry is better than 1%. We consider that the purer the magnetite, the closer to 1:2 would be the area ratio. As the difference of recoilless fraction ratio between A and B sites is not known for titanomagnetite, we assumed the ratio to be unity for the following calculation.

An extra spectrum **c** appears and the total spectrum becomes broader as titanium substitutes iron in B site. It should be noted that the spectrum **c** does not arise from any one site but is a superposition of various spectra arising from iron ions of locally varying energy states caused by the substitution of Ti^{4+} (BANERJEE *et al.*, 1967a, b; UMEMURA and IIDA, 1978). The distortion of energy states of Fe ions extends well beyond the nearest neighbors of Ti^{4+} , and all those ions contribute to the spectrum **c**. Although not valid in general, it is almost correct to assume that the effect of the substitution of Ti^{4+} on the Mössbauer spectra is represented by the spectrum **c** when x is small.

4. Discussion

The change of isomer shift with composition is shown in Fig. 4. For $x=0$, isomer shift for the spectrum **b** is 0.67 mm/s. This is typical for $\text{Fe}^{2.5+}$, and is close to the mean of 0.3 mm/s for Fe^{3+} and 1 mm/s for Fe^{2+} . The isomer shift of spectrum **a** decreases slightly and that of **b** increases slightly as x increases. We do not think that those changes represent a change of valency of the iron ion because such small deviation of isomer shift can be attributed to changes in the surroundings of the iron ion. If a valency change of iron ions does really take place because of a change in the ratio of Fe^{3+} and Fe^{2+} in the same site, isomer shift should show a much greater change with x . Consequently, for small x , we assign the spectra **a**, **b**, and **c** respectively to the Fe^{3+} in A site, the $\text{Fe}^{2.5+}$ in B site, and all other Fe^{3+} and Fe^{2+} ions in A and B sites. There is a possibility that extra Fe^{3+} ions on B site which are not taking part in electron hopping also contribute to the spectrum **a**. However, it is reasonable for this extra Fe^{3+} to contribute instead to spectrum **c** because the isomer shift of the B site Fe^{3+} is usually much different from that of A site Fe^{3+} , as shown for magnetite at 82 K (HARGROVE and KÜNDIG, 1970), iron-chromium oxide (ROBBINS *et al.*, 1971) and iron-vanadium oxide (ABE *et al.*, 1974). With this assignment there is no need to make the ad hoc assumption of Ti^{4+} clustering that was proposed by JENSEN and SHIVE (1973).

Cation distribution can be assessed from the fractional areas of the two spectra **a** and **b**, which we denote by f_a and f_b respectively. Figure 5 shows that the change of f_a ,

Fig. 4. Change of isomer shifts of the three spectra with x . Only small changes of isomer shift of spectra **a** and **b** occur for small values of x . This supports the interpretation that spectra **a**, **b**, and **c** arise from the A site Fe^{3+} , B site $\text{Fe}^{2.5+}$, and all other Fe^{3+} and Fe^{2+} ions on both A and B sites, respectively.

Fig. 5. Changes of fractional areas of the three subspectra **a**, **b**, and **c** (f_a , f_b , and f_c , respectively) with x . The ordinate indicates f_a ; f_b should be measured from the top of y -axis; and f_c equals the interval between the two lines for f_a and f_b . The lines $(1-x)/(3-x)$ and $1/(3-x)$ give f_a according to the Akimoto and the Néel-Chevallier models, respectively. The change of f_b seems to follow the curve $(2-4x)/(3-x)$.

f_b , and f_c with x is smooth up to $x=0.20$. The expected change of fractional area f_a, f_b , and f_c for each model is determined by simple arithmetic. The f_a changes with x as $(1-x)/(3-x)$ according to the Akimoto model and as $1/(3-x)$ according to the Néel-Chevallier model. The trend of f_a in Fig. 5 clearly follows the Akimoto model. On the other hand, the trend of f_b largely deviates from the line of $(2-2x)/(3-x)$ expected from the Akimoto model, and it seems instead to follow the line of $(2-4x)/(3-x)$. We propose that the proportion of $\text{Fe}^{3+}\text{-Fe}^{2+}$ pairs which behave as $\text{Fe}^{2.5+}$ is much less than the expected from the model when titanium ions occur in B site. Taking these iron ion pairs into consideration, we propose to rewrite the Akimoto model as

where the $\text{Fe}^{3+}\text{-Fe}^{2+}$ pair in the first parenthesis participates in electron hopping.

WECHSLER *et al.* (1984), using a neutron diffraction method, found Akimoto type cation distribution in titanomagnetites for the samples with three different x values: 0.00, 0.25, and 0.50. They also reported the independency of cation distribution on annealing of sample at 800°C. The present study yielded an independent evidence from Mössbauer study for Akimoto type cation distribution. Our results not only strengthen the conclusion of Wechsler *et al.*, but provide almost continuous data for the range of $0 \leq x \leq 0.20$. The confirmation of the Akimoto model automatically excludes the O'Reilly and Banerjee model as an alternative. Although BANERJEE *et al.* (1967a) found evidence in favor of the O'Reilly and Banerjee model from the x dependency of saturation magnetization and electrical resistivity, WECHSLER *et al.* (1984) showed that the saturation magnetization agrees also with the value predicted by Akimoto model for two samples of $x=0$ and 0.5 if the effect of thermal disorder above 0 K is corrected. The electrical conductivities of titanomagnetites measured on polycrystalline sintered bars are not sufficiently accurate for discrimination between the various cation distribution models.

O'DONOVAN and O'REILLY (1980) compared the lattice constants (a), Curie temperatures (T_c), and room temperature saturation magnetizations (J_s) of two suites of titanomagnetite samples (including small amount of Mg^{2+}) synthesized at 1350°C and 1425°C and annealed for different time intervals of up to five hours at 600°C and 1000°C. They found no temperature dependency. WECHSLER *et al.* (1984) also examined the effect on the cation distribution of synthesis temperature at 1350°C and 930°C followed by annealing for up to 95 days at 800°C, but found no significant differences on crystallographic and magnetic parameters. These similar results on the temperature dependency, together with the same conclusion on the cation distribution by WECHSLER *et al.* (1984) and this study, suggest that there is no temperature dependency of cation distribution in titanomagnetite.

5. Conclusions

Mössbauer spectroscopy was applied to improve our knowledge of cation

distribution in titanomagnetites. The samples were synthesized at 1200°C in f_0 , controlled furnace. From the change of the fractional area of A site Fe^{3+} spectrum with titanium content, it was concluded that the cation distribution of these samples follow the Akimoto model. From much faster decrease with x of the fractional area of B site $\text{Fe}^{2.5+}$ than the expected change from the model, we propose that the proportion of Fe^{3+} - Fe^{2+} pairs sharing hopping electrons decreases with the substitution of Ti^{4+} much more rapidly than the formula predicts.

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