

## An X-Ray and Mössbauer Study of the $\text{FeTi}_2\text{O}_5$ - $\text{Ti}_3\text{O}_5$ System

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Mössbauer spectra and X-ray diffraction data have been recorded for compounds in the solid solution series  $\text{Fe}_x\text{Ti}_{3-x}\text{O}_5$ ,  $0 < x < 1$ . Compounds with  $x > 0.35$  have the orthorhombic pseudobrookite structure, and those with  $x < 0.35$  a monoclinic distortion of it. Ferrous ions in the fourfold and eightfold sites give rise to separate quadrupole doublets in the Mössbauer spectra, and thus it has been possible to determine the site occupancy as a function of composition by a least-square analysis of the spectra. The Mössbauer method has also proved to be a sensitive tool for the investigation of the orthorhombic-monoclinic distortion.

### Introduction

In recent years considerable attention has been directed toward compounds with structures related to the pseudobrookite ( $\text{Fe}_2\text{TiO}_5$ ) type (1-11). Åsbrink and Magnéli (1) reported that  $\text{Fe}_2\text{TiO}_5$  forms a continuous solid solution with  $\text{Ti}_3\text{O}_5$ , i.e.,  $\text{Fe}_x\text{Ti}_{3-x}\text{O}_5$ ,  $0 \leq x \leq 2$ . Compounds in this series with  $x > 0.24$  have the orthorhombic pseudobrookite structure (2), and with  $x < 0.24$  a monoclinic, slightly distorted modification of it (3). Åsbrink and Magnéli (1) observed a marked discontinuity in the variation of unit cell parameters with composition for  $\text{Fe}_x\text{Ti}_{3-x}\text{O}_5$  at  $x = 1$ , i.e.,  $\text{FeTi}_2\text{O}_5$ . These results were interpreted by Reid and Ward (4) as evidence for two solid solution series, the first being a solution of  $\text{Fe}_2\text{TiO}_5$  with  $\text{FeTi}_2\text{O}_5$ , containing no  $\text{Ti}^{3+}$ , and the second a solution of  $\text{FeTi}_2\text{O}_5$  with  $\text{Ti}_3\text{O}_5$ , containing no  $\text{Fe}^{3+}$ . This was confirmed by their preliminary Mössbauer studies (4).

The end member ( $x = 0$ ) compound  $\text{Ti}_3\text{O}_5$  has been the subject of numerous investigations (3, 5-7). When prepared at temperatures above  $925^\circ\text{C}$ , the monoclinic pseudobrookite form of  $\text{Ti}_3\text{O}_5$  (high- $\text{Ti}_3\text{O}_5$ ) obtains (3, 5). High- $\text{Ti}_3\text{O}_5$  undergoes a reversible phase transformation at

$190^\circ\text{C}$  to a low temperature form [low- $\text{Ti}_3\text{O}_5$ , (3)] also having a monoclinic structure closely related to that of pseudobrookite. The atom movements involved in the high- $\text{Ti}_3\text{O}_5$  to low- $\text{Ti}_3\text{O}_5$  transformation are indicated by arrows in Fig. 1. High- $\text{Ti}_3\text{O}_5$  may be stabilized at room temperature by replacement of about 1% titanium by iron (3).

The monoclinic pseudobrookite structure for high- $\text{Ti}_3\text{O}_5$  is shown in projection down  $b$  in Fig. 1. There are three independent fourfold octahedral metal atom sites, shown as  $M_1$ ,  $M_2$ , and  $M_3$ . Metals in these three sites share octahedral edges to form a basic trioctahedral unit. These units link together by combined edge and corner sharing to form double chains along  $c$ . Adjacent double chains are displaced by half a unit cell along  $b$  and link by edge sharing into wavy (010) layers. The layers are connected by corner sharing along  $b$  to complete the structure. In the orthorhombic pseudobrookite structure (2), the atoms  $M_1$  and  $M_3$  are symmetry related in an eightfold crystallographic site.

As part of a detailed thermodynamic study of the system  $\text{FeO-Ti}_2\text{O}_3\text{-TiO}_2$  we have recently examined the solid solution series  $\text{FeTi}_2\text{O}_5\text{-Ti}_3\text{O}_5$  [ $M_3\text{O}_5$  (ss)] as a function of temperature and

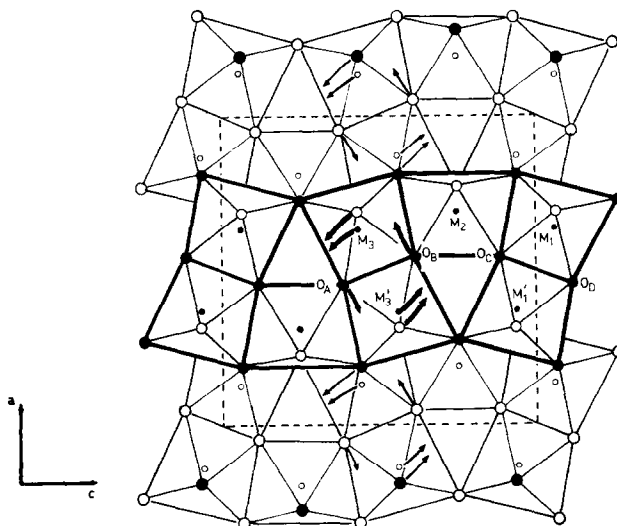


FIG. 1. The structure of pseudobrookite viewed down  $b$ .  $\circ$ , oxygen atoms at  $y = 0$ ;  $\bullet$ , oxygen atoms at  $y = \frac{1}{2}$ ;  $\circ$ , metal atoms at  $y = 0$ ;  $\bullet$ , metal atoms at  $y = \frac{1}{2}$ . Arrows indicate the movement of atoms involved in the high- $\text{Ti}_3\text{O}_5$  to low- $\text{Ti}_3\text{O}_5$  phase transformation. [After Åsbrink and Magnéli (3).]

oxygen pressure  $p\text{O}_2$ . From X-ray diffraction studies on quenched samples we have determined that the solid solution is complete for temperatures above about  $1350^\circ\text{C}$ , and for  $T = 1400^\circ\text{C}$  we have established the  $p\text{O}_2$ -composition diagram shown in Fig. 2. Using the information summarized by Fig. 2 we have prepared a range of single phase compounds  $\text{Fe}_x\text{Ti}_{3-x}\text{O}_5$ ,  $0 \leq x \leq 1$

and report here their structural characteristics as determined by X-ray diffraction and Mössbauer studies.

### Experimental

Compounds in the  $\text{Fe}_x\text{Ti}_{3-x}\text{O}_5$  (ss) series were prepared at  $1400^\circ\text{C}$  by equilibrating mixtures of  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  in  $\text{H}_2/\text{CO}_2$  atm, then quenching to room temperature. The  $\text{H}_2/\text{CO}_2$  ratios were adjusted to give oxygen pressures,  $p\text{O}_2$ , corresponding to single phase  $\text{M}_3\text{O}_5$  (ss) compounds according to Fig. 2. Anatase-form  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$  were both Fisher Certified Reagents. Samples were usually reground and reequilibrated to achieve homogeneity. Equilibration times at  $1400^\circ\text{C}$  were 15–24 hours.

### X-Ray Diffraction Data

X-Ray powder patterns were obtained with a Philips diffractometer fitted with a graphite monochromator, using  $\text{CuK}\alpha$  radiation. Potassium chloride,  $a_0 = 6.2931 \text{ \AA}$ , was used as an internal standard for lattice parameter determination, and slow scan rates ( $0.25^\circ/\text{minute}$ ) ensured high precision in the data.

### Mössbauer Spectra

Mössbauer measurements were made using a Centronic MS100 spectrometer of constant acceleration type. The source was  $10 \text{ mCi } ^{67}\text{Co}$  in a palladium matrix,  $10 \text{ cm}$  away from the

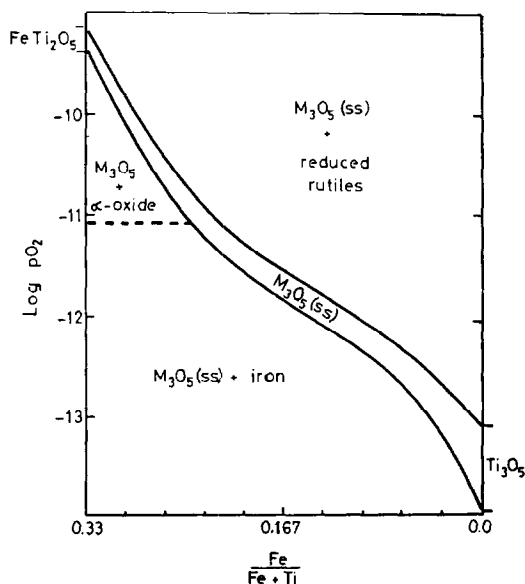


FIG. 2. Fe-Ti-O system at  $1400^\circ\text{C}$  in the composition range  $\text{Fe}/\text{Fe} + \text{Ti} = 0.0\text{-}0.33$ , as a function of oxygen pressure,  $p\text{O}_2$  (atm).

proportional gas counter. Absorbers were made by pressing (at 3.5 tons) circular discs 3.2 cm in diameter, containing 1 g of a mixture of Teflon powder and cellulose powder into which about 100 mg of the sample was finely mixed.

Velocity parameters were measured relative to a standard absorber containing 38 mg of "spcc-pure" iron powder, superimposed on the sample absorbed. The iron parameters used for calibration were:  $H_{int} = 333.0$  Oe, quadrupole splitting  $\varepsilon = 0.000$  mm/sec, and isomer shift  $\delta = -0.150$  mm/sec, relative to the source. All Mössbauer measurements were made at  $23 \pm 3^\circ\text{C}$ . Long-term drift in the spectrometer was about 1.5%, but its effect was largely eliminated by the calibration procedure. Counting times were from 20 to 90 hours, and total counts between 5 and  $30 \times 10^6$  per channel were recorded, using 256 channels.

The least-squares curve fitting employed a program written by D. Price of the University of Manitoba. It used the algorithm of Margulies (12). In addition to the usual parameters and constraints, the exponent, normally 2 in the Lorentzian function, could be allowed to vary independently for each spectrum. It was found that values near 2.5 gave the best results, and

quantitative work was done using this value. Estimation of relative peak areas was done by the computer program for separate runs in which the standard absorber was omitted.

## Results and Discussion

### X-Ray Diffraction

High- $\text{Ti}_3\text{O}_5$  has space group  $C2/m$  and lattice parameters  $a = 9.82$ ,  $b = 3.78$ , and  $c = 9.97$  Å and  $\beta = 91.0^\circ$  (3). To maintain the same parameter order throughout the  $\text{Fe}_x\text{Ti}_{3-x}\text{O}_5$  series the compounds with orthorhombic symmetry have been assigned space group  $Cmmm$ . In terms of this space group the parameters for  $\text{FeTi}_2\text{O}_5$ , for example, are then  $a = 9.790$ ,  $b = 3.757$ , and  $c = 10.079$  Å.

Unit cell parameters obtained from least-squares refinement of powder diffraction data for compounds  $\text{Fe}_x\text{Ti}_{3-x}\text{O}_5$  are listed in Table I. For comparison, the parameters for a number of compounds with the pseudobrookite structure are also given. A monoclinic distortion of the orthorhombic cell was first discernible in the X-ray patterns at the composition  $\text{Fe}_{0.25}\text{Ti}_{2.75}\text{O}_5$ . With increasing titanium content the distortion increased, as measured by the deviation of  $\beta$

TABLE I

UNIT CELL DATA FOR  $\text{Fe}_x\text{Ti}_{3-x}\text{O}_5$  (ss),  $0 \leq x \leq 1$ , AND COMPARISON WITH PSEUDOBROOKITE-TYPE COMPOUNDS

Composition	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\beta$	$c/b$	Volume (Å <sup>3</sup> )
$\text{FeTi}_2\text{O}_5$	9.790	3.757	10.079	—	2.683	370.7
$\text{Fe}_{0.90}\text{Ti}_{2.10}\text{O}_5$	9.794	3.763	10.054	—	2.672	370.5
$\text{Fe}_{0.73}\text{Ti}_{2.27}\text{O}_5$	9.792	3.771	10.051	—	2.665	371.1
$\text{Fe}_{0.66}\text{Ti}_{2.34}\text{O}_5$	9.788	3.782	10.041	—	2.656	371.6
$\text{Fe}_{0.50}\text{Ti}_{2.50}\text{O}_5$	9.798	3.781	10.020	—	2.650	371.2
$\text{Fe}_{0.45}\text{Ti}_{2.55}\text{O}_5$	9.798	3.785	10.013	—	2.645	371.3
$\text{Fe}_{0.32}\text{Ti}_{2.68}\text{O}_5$	9.823	3.785	10.000	—	2.640	371.8
$\text{Fe}_{0.25}\text{Ti}_{2.75}\text{O}_5$	9.810	3.786	9.991	90.45	2.639	371.1
$\text{Fe}_{0.20}\text{Ti}_{2.80}\text{O}_5$	9.821	3.785	9.985	90.68	2.638	371.1
$\text{Fe}_{0.16}\text{Ti}_{2.90}\text{O}_5$	9.831	3.785	9.970	91.03	2.634	371.0
High- $\text{Ti}_3\text{O}_5^a$	9.82	3.78	9.97	91.0	2.637	370.1
Low- $\text{Ti}_3\text{O}_5^a$	9.752	3.802	9.442	91.55	2.484	350.1
$\text{Al}_2\text{TiO}_5^b$	9.4237	3.5875	9.6291	—	2.68	325.5
$\text{Fe}_2\text{TiO}_5^b$	9.7954	3.7383	9.9853	—	2.67	365.6
$\text{MgTi}_2\text{O}_5^b$	9.7363	3.7442	9.9870	—	2.67	364.1
$\text{MgTi}_{1.6}\text{Zr}_{0.4}\text{O}_5^b$	9.8159	3.7646	10.0458	—	2.67	371.2

<sup>a</sup> Reference 3.

<sup>b</sup> Reference 8.

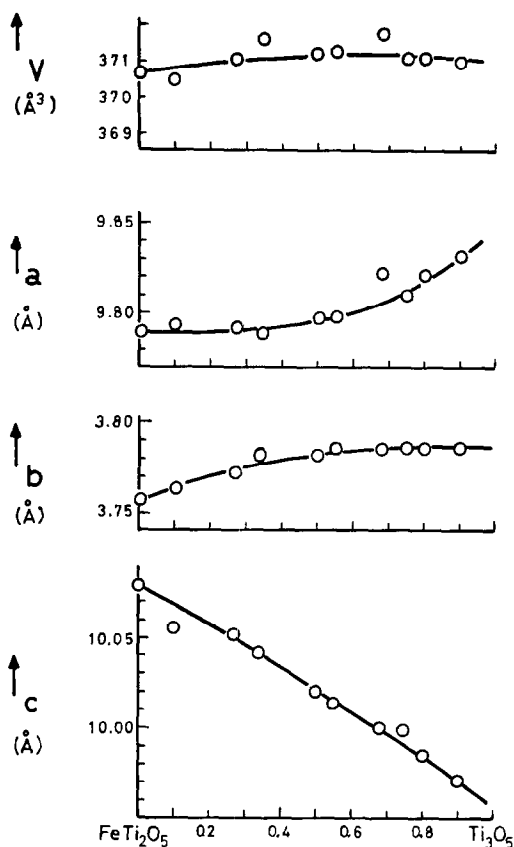


FIG. 3. Variation of lattice parameters and unit cell volume with composition in the series  $\text{Fe}_x\text{Ti}_{3-x}\text{O}_5$ ,  $0 < x < 1$ .

from  $90^\circ$ . Extrapolation of the  $\beta$ -composition relationship gives the composition  $\approx \text{Fe}_{0.35}\text{Ti}_{2.65}\text{O}_5$  as that at which the monoclinic distortion is initiated. The lattice parameters and unit cell volume are plotted as a function of composition in Fig. 3. From  $\text{FeTi}_2\text{O}_5$  to  $\text{Ti}_3\text{O}_5$  there is a very slight increase in unit cell volume, about 0.5%. Although the  $a$  and  $b$  parameters increase toward  $\text{Ti}_3\text{O}_5$ , there is a decrease in the  $c$  parameter. We believe this is due to increased metal-metal bonding between  $\text{Ti}^{3+}$  ions as the amount of  $\text{Ti}_3\text{O}_5$  is increased. This is reflected in the  $c/b$  ratios given in Table I. For a number of pseudobrookites this ratio is quite constant at 2.67–2.68. However, between  $\text{FeTi}_2\text{O}_5$  and  $\text{Ti}_3\text{O}_5$  the value drops markedly to 2.63. In the low-temperature form of  $\text{Ti}_3\text{O}_5$  (3), which has strong homopolar metal bonds,  $c/b$  has the low value of 2.48.

#### Mössbauer

Typical Mössbauer spectra for the compounds  $\text{Fe}_x\text{Ti}_{3-x}\text{O}_5$  are shown in Fig. 4. For the ortho-

rhombic compounds the pattern consists of a strong sharp doublet together with a weaker broad doublet of smaller quadrupole splitting. For  $x$  close to 1.0 the inner doublet appears as shoulders on the main peak; for  $x \approx 0.8$  the inner doublet becomes somewhat better resolved. Isomer shifts for both doublets correspond to ferrous iron,  $\text{Fe}^{2+}$ . We have assigned the large outer doublet to  $\text{Fe}^{2+}$  in the fourfold sites ( $M_2$  in Fig. 1) and the inner doublet to  $\text{Fe}^{2+}$  in the eightfold sites ( $M_1 + M_3$  in Fig. 1) for the following two reasons: In  $\text{FeTi}_2\text{O}_5$  the relative areas under the inner and outer doublets are in the approximate ratio 40:100, giving 28% of the  $\text{Fe}^{2+}$  in the eightfold sites and 72%  $\text{Fe}^{2+}$  in the fourfold sites. This corresponds closely to the site occupancy that we have determined from neutron diffraction for this compound,<sup>1</sup> viz. 25%  $\text{Fe}^{2+}$  in eightfold, 75%  $\text{Fe}^{2+}$  in fourfold. Furthermore, for the monoclinic compounds the inner doublet is observed to split into two doublets (for which the combined area is about the same as the area under the unsplit inner doublet), i.e., this would correspond to the eightfold site splitting into two fourfold sites ( $M_1$  and  $M_3$  in Fig. 1) in the lower symmetry monoclinic cell. The Mössbauer parameters from the least-squares fitting procedure are given in Table II, viz. the quadrupole splitting  $\epsilon$ , isomer shift  $\delta$ , and width of the Mössbauer peaks at half-height,  $\Gamma$ . The results are plotted graphically as a function of composition in Fig. 5. Broad trends in the results are an increase in the isomer shift and a decrease in the quadrupole splitting for the quadrupole doublets, with increasing  $\text{Ti}_3\text{O}_5$  content. Abrupt changes in both the isomer shifts and quadrupole splittings were observed near  $\text{Fe}_{0.35}\text{Ti}_{2.65}\text{O}_5$ , associated with the orthorhombic–monoclinic transformation discussed in detail below.

#### Orthorhombic–Monoclinic Transformation

The X-ray powder diffraction results show that the orthorhombic pseudobrookite cell transforms to a monoclinic cell at  $\sim \text{Fe}_{0.35}\text{Ti}_{2.65}\text{O}_5$ . The monoclinic distortion increases with increasing titanium content toward  $\text{Ti}_3\text{O}_5$ . In the lower symmetry unit cell, the eightfold metal-atom site is replaced by two independent fourfold sites containing metals  $M_1$  and  $M_3$  (Fig. 1). This is reflected in the Mössbauer spectra by the splitting of the inner quadrupole doublet into two doublets. Because of the slightly different

<sup>1</sup> Grey, Reid, and Sabine, data to be published.

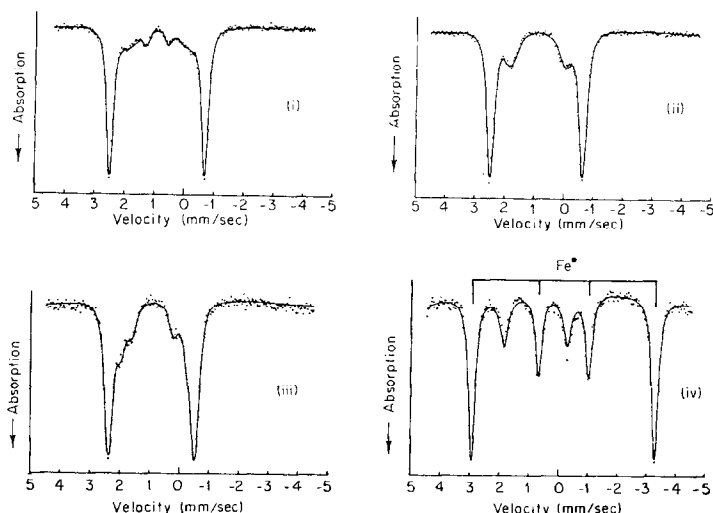


FIG. 4. Typical Mössbauer spectra. The lines are computed least-squares fits. (i)  $\text{FeTi}_2\text{O}_5$ . The central doublet is a trace of ilmenite. Note the poor fit at the left-hand shoulder, which gives rise to a spuriously large linewidth as noted in the text. (ii)  $\text{Fe}_{0.5}\text{Ti}_{2.5}\text{O}_5$ . The fit at the shoulders is better than in (i), but still slightly deficient on the right. (iii)  $\text{Fe}_{0.2}\text{Ti}_{2.8}\text{O}_5$ . The overall upward convexity of the spectrum is an instrumental effect and was corrected for in the computation. (iv) Metallic iron plus ferrous iron in reduced rutile. The outer metallic iron lines are outside the range covered. In this spectrum the Lorentzian exponents of the two spectra were allowed to vary during the fitting process. The values obtained were 1.72 for the reduced rutile iron and 2.12 for the metal ( $\pm 0.05$ ).

isomer shifts involved, these appear as shoulders on the inside of the left-hand peak of the main doublet (from metal  $\text{M}_2$ ) as shown in Fig. 4

(iii) for  $\text{Fe}_{0.2}\text{Ti}_{2.8}\text{O}_5$ . There is a wide divergence in both isomer shift and quadrupole splitting for the two inner doublets, as given in Table II.

TABLE II  
MÖSSBAUER PARAMETERS FOR  $\text{Fe}_x\text{Ti}_{3-x}\text{O}_5$ ,  $0 \leq x < 1$

Composition	$\text{Fe}^{2+}$ in fourfold site			$\text{Fe}^{2+}$ in eightfold site			Fe% in fourfold site
	Isomer shift (mm/sec)	Quadrupole splitting (mm/sec)	Half-width (mm/sec)	Isomer shift (mm/sec)	Quadrupole splitting (mm/sec)	Half-width (mm/sec)	
$\text{FeTi}_2\text{O}_5$	0.923	1.622	0.292	0.888	1.096	0.936 <sup>a</sup>	72.0 <sup>b</sup>
$\text{Fe}_{0.73}\text{Ti}_{2.27}\text{O}_5$	0.924	1.589	0.299	0.902	0.961	0.643	73.2 <sup>b</sup>
$\text{Fe}_{0.66}\text{Ti}_{2.34}\text{O}_5$	0.926	1.568	0.314	0.896	0.943	0.661	76.3
$\text{Fe}_{0.60}\text{Ti}_{2.40}\text{O}_5$	0.926	1.563	0.318	0.894	0.933	0.574	75.5
$\text{Fe}_{0.50}\text{Ti}_{2.50}\text{O}_5$	0.929	1.535	0.330	0.899	0.920	0.570	72.2
$\text{Fe}_{0.32}\text{Ti}_{2.68}\text{O}_5$	0.935	1.461	0.362	0.898	0.898	0.566	62.7
$\text{Fe}_{0.25}\text{Ti}_{2.75}\text{O}_5$	0.931	1.445	0.349	0.873	1.073	0.378	68.1
				0.911	0.725	0.421	
$\text{Fe}_{0.20}\text{Ti}_{2.80}\text{O}_5$	0.934	1.426	0.349	0.859	1.094	0.374	65.8
				0.908	0.681	0.353	
$\text{Fe}_{0.10}\text{Ti}_{2.90}\text{O}_5$	0.926	1.385	0.310	0.856	1.126	0.358	60.9
				0.900	0.639	0.296	

<sup>a</sup> Probably overestimated; see text.

<sup>b</sup> Probably underestimated; see text.

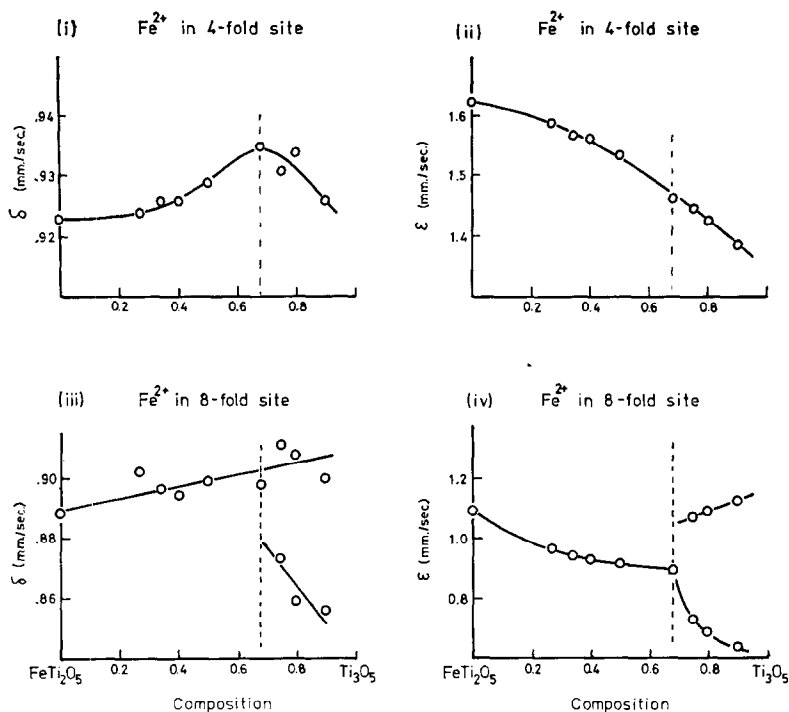


FIG. 5. Room-temperature Mössbauer parameters for the  $\text{Fe}_x\text{Ti}_{3-x}\text{O}_5$  solid solution. The vertical lines at  $[\text{Ti}_3\text{O}_5] = 0.68$  indicate approximately the onset of monoclinic distortion. (i) Isomer shift  $\delta$  (fourfold site); (ii) quadrupole splitting  $\epsilon$  (fourfold site); (iii) isomer shift (eightfold site); and (iv) quadrupole splitting (eightfold site).

This indicates that the environment of the atoms  $M_1$  and  $M_3$  (which were symmetry related in the orthorhombic structures) becomes quite different in the monoclinically distorted structures. Thus, the isomer shift  $\delta$  and quadrupole splitting  $\epsilon$  for one of the sites continues the broad trends observed for the orthorhombic compounds, i.e., increasing  $\delta$  and decreasing  $\epsilon$  with increase of Ti in  $\text{Fe}_x\text{Ti}_{3-x}\text{O}_5$ , whereas  $\delta$  and  $\epsilon$  for the other site reverse these trends. One can make a tentative assignment of the inner two quadrupole doublets to specific metal-atom sites  $M_1$  and  $M_3$  if it is assumed that the monoclinic distortion in  $\text{Fe}_x\text{Ti}_{3-x}\text{O}_5$ ,  $x < 0.35$ , is a result of atom movements, on a small scale, similar to those that occur in the high  $\rightarrow$  low temperature transformation of monoclinic  $\text{Ti}_3\text{O}_5$ . As shown in Fig. 1, metal  $M_1$  and its environment is little affected by the phase transition, whereas metal  $M_3$  moves a considerable distance and there is a large change in the local environment around  $M_3$ . We thus assign the inner quadrupole doublet with the largest isomer shift and smallest quadrupole splitting to site  $M_1$  of Fig. 1.

Across the orthorhombic-monoclinic transition the isomer shift for the main outer doublet, corresponding to site  $M_2$ , also shows a discontinuity although not as marked as those for sites  $M_1$  and  $M_3$ . Thus, with increasing monoclinic distortion,  $\delta$  for the  $M_2$  site reverses its composition dependence and decreases with increasing  $\text{Ti}_3\text{O}_5$  content. As a result the quadrupole doublets for sites  $M_2$  and  $M_3$  would be expected to merge together at compositions close to  $\text{Ti}_3\text{O}_5$ . The Mössbauer spectrum of  $\text{Ti}_3\text{O}_5$  doped with 1.8% Fe has recently been reported by Rao et al. (6).  $\text{Ti}_3\text{O}_5$  containing such a small amount of iron has the low-temperature monoclinic structure. It is interesting that the pattern consists of two asymmetric quadrupole doublets of about equal intensity, with Mössbauer parameters very similar to those for our two inner doublets. We tentatively assign the outer doublet of Rao et al. to the combined  $M_2$  and  $M_3$  sites and the inner doublet to  $M_1$ . We are then led to the conclusion that no more than half the iron is on site  $M_2$ , which is quite consistent with the extrapolation of Fig. 6 (see below).

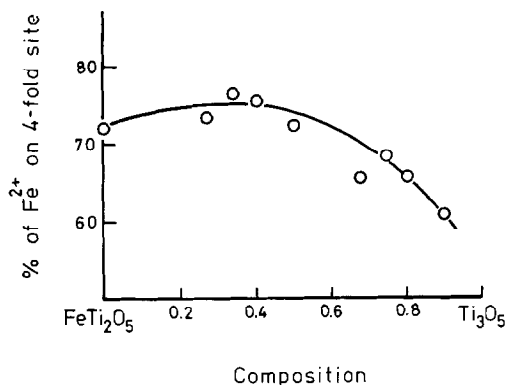


FIG. 6. Percent total iron in fourfold site as a function of composition.

### Cation Distribution in $\text{Fe}_x\text{Ti}_{3-x}\text{O}_5$

From the statistical analysis of the Mössbauer spectra the relative amounts of  $\text{Fe}^{2+}$  in each of the metal-atom sites was derived. These are given in Table II and represented in Fig. 6 as a plot of percentage of the total iron that is in the fourfold site,  $M_2$  of Fig. 1, versus composition. In the series  $\text{FeTi}_2\text{O}_5$ – $\text{Ti}_3\text{O}_5$  there is a strong preference of the large ferrous ions for site  $M_2$ . For compositions close to  $\text{Ti}_3\text{O}_5$  about 60% of the total iron is in the  $M_2$  site, compared with expected 33% for a completely random distribution. With increasing iron content in  $\text{Fe}_x\text{Ti}_{3-x}\text{O}_5$  the preferred occupation of the  $M_2$  site increases, and at  $\text{Fe}_{0.75}\text{Ti}_{2.25}\text{O}_5$  over 75% of the iron is in this site. At about this composition the plot of percent iron in  $M_2$  passes through a maximum—compositions close to  $\text{FeTi}_2\text{O}_5$  have about 72% of  $\text{Fe}^{2+}$  in site  $M_2$ . This maximum in the plot is hard to explain and may be tied up with the poor computer fitting of the Mössbauer spectra for compositions near  $\text{FeTi}_2\text{O}_5$ , where there is the greatest overlap of the quadrupole doublets. In particular, the calculated half-widths for the inner doublet [ $\text{Fe}^{2+}$  in eightfold site ( $M_1$ ,  $M_3$ )] are unreasonably large (see Table II).

We have conducted preliminary investigations on the related solid solution series  $\text{MgTi}_2\text{O}_5$ – $\text{FeTi}_2\text{O}_5$ , which indicate that the site occupation in the pseudobrookite structure is markedly dependent on the temperature and conditions of preparation, i.e., on whether the sample is annealed or quenched. In the  $\text{FeTi}_2\text{O}_5$ – $\text{Ti}_3\text{O}_5$  system reported here, care was taken to ensure that all the samples were subjected to the same

preparative conditions. Slow cooling of samples is not possible in this series (see below).

### Ferrous Iron in Reduced Rutile

As shown in Fig. 2 the  $\text{FeTi}_2\text{O}_5$ – $\text{Ti}_3\text{O}_5$  solid solution series is complete at  $1400^\circ\text{C}$ . However, at lower temperatures there exists a miscibility gap in which the  $\text{Fe}_x\text{Ti}_{3-x}\text{O}_5$  (ss) is unstable relative to a phase assemblage of reduced rutiles and metallic iron. We were interested to know whether or not iron was incorporated into the reduced rutile lattice. A sample corresponding to the composition  $\text{Fe}_{0.4}\text{Ti}_{2.6}\text{O}_5$  was equilibrated at  $1200^\circ\text{C}$  at an oxygen pressure of  $10^{-14}$  atm then quenched. The product contained reduced rutile of composition  $\text{M}_8\text{O}_{15}$  and metallic iron. The Mössbauer pattern for this sample shown in Fig. 4(iv) shows a single symmetrical doublet with isomer shift corresponding to ferrous iron, and quadrupole splitting comparable with that for  $\text{Fe}^{2+}$  in the eightfold site of  $\text{FeTi}_2\text{O}_5$  (see Table II), i.e., the Magnéli phases  $\text{Ti}_n\text{O}_{2n-1} \equiv \text{Ti}_2\text{O}_3 \cdot (n-2)\text{TiO}_2$  extend toward their ferrous counterparts  $(\text{FeTi}_{n-1})\text{O}_{2n-1} \equiv \text{FeTiO}_3 \cdot (n-2)\text{TiO}_2$  in the Fe–Ti–O phase diagram. In the reduced rutile phases there are two distinct metal-atom sites; those in face-shared octahedra in the “shear” sections and those associated with the unaltered parent structure, rutile. The Mössbauer results suggest that the large  $\text{Fe}^{2+}$  ions prefer to go into the rutile slabs, which contain edge-shared octahedra as in the pseudobrookite structure.

In studies now in progress we are using enriched  $^{57}\text{Fe}$  to investigate the incorporation of iron into other reduced rutile phases and also to study the high/low-temperature phase transition in  $\text{Ti}_3\text{O}_5$ .

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