Magnetic Properties of $\text{TiFe}_2\text{O}_4\text{--Fe}_3\text{O}_4$ System and Their Change with Oxidation*

By Syun-iti AKIMOTO

Geophysical Institute, Tokyo University,

Takashi KATSURA and Minoru YOSHIDA

*Laboratory of Analytical Chemistry and Geochemistry,
Tokyo Institute of Technology.*

(Read Oct. 9, 1957; Received July 1, 1958)

Abstract

A series of solid solution $x\text{TiFe}_2\text{O}_4 \cdot (1-x)\text{Fe}_3\text{O}_4$ was synthesized by ceramic method over a whole range of the composition, $1 \geq x \geq 0$. Changes of the Curie point, saturation moment and the lattice parameter with the composition were examined. Generalized titanomagnetite having some vacant site in the structure normally occupied in a spinel was also prepared by oxidizing the $\text{TiFe}_2\text{O}_4\text{--Fe}_3\text{O}_4$ solid solution series. The region within which the spinel structure can be in existence as a single phase was settled in a $\text{FeO--Fe}_2\text{O}_3\text{--TiO}_2$ system. An equal lattice parameter line, equal Curie point line and equal saturation moment line for the generalized titanomagnetite were drawn on the $\text{FeO--Fe}_2\text{O}_3\text{--TiO}_2$ system.

1. Introduction

It has been established from recent study on the ferromagnetic minerals contained in rocks that the chemical composition of the natural titanomagnetite with spinel structure does not always accord with $\text{TiFe}_2\text{O}_4\text{--Fe}_3\text{O}_4$ join but in most cases deviates from this join towards $\text{TiFeO}_3\text{--Fe}_2\text{O}_3$ join side and occasionally FeO side in a $\text{FeO--Fe}_2\text{O}_3\text{--TiO}_2$ system. As long as we deal with these natural specimens, it may be very probable that the various magnetic properties are considerably scattered with respect to the calculated TiFe_2O_4 content which was tentatively used in the previous paper as a measure representative of their chemical composition (Akimoto; 1954, 1955).

It is indispensable for interpreting correctly the magnetic properties of these natural titanomagnetites to perform a systematic study on the synthetic titanomagnetites which were prepared under the known physico-chemical condition. Several magneto-chemical studies along this line have already been reported by Ernst (1943), Pouillard (1950), Chevallier and Girard (1950), Kawai, Kume and Sasajima (1954), and Chevallier, Bolfa and Mathieu (1955). The data obtained hitherto by these authors are still unsatisfactory for applying to the interpretation of the magnetic properties of natural titanomagnetites. Pouillard's synthetic titanomagnetites are limited to the solid solution $x\text{TiFe}_2\text{O}_4 \cdot (1-x)\text{Fe}_3\text{O}_4$ of TiFe_2O_4 and Fe_3O_4 over a range of $0.42 > x > 0$. He synthesized

* Contribution from Division of Geomagnetism and Geoelectricity, Geophysical Institute, Tokyo University. Series II. No. 78.

his specimens either by heating mixture of TiO_2 and Fe_3O_4 in an evacuated furnace for one hour at 900°C or by reducing mixture of TiO_2 and Fe_2O_3 with hydrogen gas for two hours at 450°C . In each case other phases were also formed and he estimated the molecular percentages of TiFe_2O_4 by applying the law of Vegard (linear relation between crystal parameter and molecular composition). Therefore, as Nicholls (1955) pointed out in his review on rock-forming ferromagnetic minerals, there remain still some ambiguities upon the chemical composition on his specimens. Although Kawai, Kume and Sasajima have reported that they succeeded in extending the range of synthetic spinels to $x=0.8$ with the aid of usual ceramic method, they do not give any detailed description on the way in which the composition of the synthetic specimen was determined.

On the other hand, very little work has been done with respect to the magnetochemistry on the cubic solid solutions between TiFe_2O_4 - Fe_3O_4 join and TiFeO_3 - Fe_2O_3 join. The only information available is the work carried out on TiFeO_3 - Fe_3O_4 solid solution series by Chevallier and Girard (1950) and Chevallier, Bolfa and Mathieu (1955). They have synthesized cubic solid solutions intermediate between Fe_3O_4 and TiFeO_3 up to 37 molecular percent of TiFeO_3 by means of a borax method.

Under the circumstances, we intended to extend the studies hitherto made to the more broad region between TiFe_2O_4 - Fe_3O_4 join and TiFeO_3 - Fe_2O_3 join. As the first step of the study we synthesized the solid solution $x\text{TiFe}_2\text{O}_4 \cdot (1-x)\text{Fe}_3\text{O}_4$ over a whole range of the composition. Then we synthesized the cubic solid solution in the concerned region by oxidizing the TiFe_2O_4 - Fe_3O_4 series specimens. The particular interests shown in this paper are related to the following two:

- (1) The one is to settle the region on the FeO - Fe_2O_3 - TiO_2 system, within which the spinel structure can be in existence as a single phase.
- (2) The other is to draw an equal lattice parameter line, equal Curie point line or equal saturation moment line on the FeO - Fe_2O_3 - TiO_2 ternary system.

2. Preparation of TiFe_2O_4 - Fe_3O_4 Solid Solution Series

The specimens dealt with in the present study were prepared by the sintering procedure generally used in the ceramics. A fine powder mixture of pure Fe_2O_3 , TiO_2 and electrolytic iron in the desired proportion, sealed in a silica tube evacuated approximately to 10^{-3} mmHg, was quenched from 1150°C after being maintained at this temperature for six hours.

Twenty specimens were prepared by this method over the whole range of $1 \geq x \geq 0$. The chemical composition of the synthesized specimen is plotted by full circles on the FeO - Fe_2O_3 - TiO_2 diagram in Fig. 1 and is given in Table I.

Analysis by means of the "Norelco" X-ray diffractometer shows that these specimens are generally composed of a single phase having the spinel structure. No trace of the ilmenite-hematite series could be found except the specimen S2-4. Even in this specimen the amounts of the ilmenite-hematite series minerals were estimated to be less than ten percent from the careful examination of the diffraction chart.

Lattice parameters of all synthetic specimens determined from the X-ray analysis are also given in Table I. In Fig. 2 the lattice parameter is plotted against the TiFe_2O_4 content x , which was tentatively determined from the data of chemical analysis as a mean value of the following two values of x derived from different assumptions: the one is based on the assumption that all the titanium oxides are involved into the ulvöspinel (TiFe_2O_4), the other being based on the assumption that all the ferric oxides are attributed to magnetite (Fe_3O_4). As will be seen in Fig. 2 and Table I, it was established that a solid solution $x\text{TiFe}_2\text{O}_4 \cdot (1-x)\text{Fe}_3\text{O}_4$ of spinel structure can be formed continuously throughout the whole range of $1 \geq x \geq 0$. The lattice parameter varies almost linearly with the composition from about 8.39 Å of Fe_3O_4 to 8.53 Å of TiFe_2O_4 .

3. Oxidation of TiFe_2O_4 - Fe_3O_4 Solid Solution Series

Some experimental work on the oxidation of titanomagnetite has been carried out by Nagata and Ozima (1955) in connection with the interpretation of a particular phenomenon of thermoremanent magnetism, i.e. anomalous increase of thermoremanent magnetism. They suggested that a material having spinel structure could be remained

Fig. 1 Chemical composition of synthetic titanomagnetites, represented on a FeO - Fe_2O_3 - TiO_2 ternary diagram in mol. percent.
Broken line: theoretical reduction-oxidation line.

Table I Chemical composition, crystal parameter and magnetic properties of $TiFe_2O_3-Fe_3O_4$ solid solution series.

Specimen	Chemical composition					Crystal parameter, a (Å)	Curie point, θ (°C)	Saturation moment, σ (e.m.u./gr.) at room temp.	Saturation moment, σ (e.m.u./gr.) at 80°K	Estimated saturation moment at 0°K (μ_B)
	$FeO+Fe_2O_3+TiO_2$ wt%	FeO	Fe_2O_3 mol%	TiO_2 mol%	$TiFe_2O_4$ mol%					
S1-1	97.13*	47.16	52.84	0.00		8.394±0.001	580	93		4.02
S1-2	97.32*	51.30	40.57	8.13	15.4	8.409±0.001				
S1-3	98.62*	55.84	27.77	16.39	37.3	8.438±0.001	330	49		2.17
S1-4	93.97*	64.59	2.18	33.23	95.8	8.527±0.000	-105		4	0.16
S2-1	95.69*	50.46	45.86	3.68	6.4	8.402±0.001	550	85		3.80
S2-2	96.91*	52.16	39.41	8.43	16.8	8.416±0.001	480	76		3.38
S2-3	100.50	53.27	33.99	12.74	26.3	8.427±0.001	420	60		2.63
S2-4	100.03	52.49	30.55	16.96	35.4	8.436±0.001	400	44		2.01
S2-5	100.57	56.65	23.35	20.00	46.6	8.456±0.001	280	48		2.16
S2-6	100.10	59.73	17.55	22.72	56.7	8.473±0.001	160	31	35	1.42
S2-7	100.69	58.93	14.53	26.54	65.4	8.486±0.001	110	19	25	1.05
S2-8	100.45	61.07	9.97	28.96	77.8	8.504±0.001	47		16	0.64
S2-9	100.56	61.54	6.39	32.07	88.1	8.519±0.002	-61		9	0.36
S2-10	98.80*	62.41	3.26	34.33	97.2	8.527±0.002				
S5-1	100.38	55.12	38.02	6.86	16.2	8.416±0.002	490			
S5-2	100.45	55.56	32.22	12.22	27.2	8.428±0.001	420			
S5-3	100.22	55.68	28.12	16.20	36.2	8.442±0.001	350			
S5-4	100.58	58.13	22.66	19.21	46.2	8.456±0.000	265			
S5-5	100.20	59.46	18.29	22.25	55.3	8.474±0.000	190			
S5-6	100.50	61.45	9.19	29.36	79.2	8.507±0.002	15			

* These samples are contaminated by small amount of SiO_2 which is caused by silica tube.

Fig. 2 Relation between lattice parameter and chemical composition in TiFe_2O_4 - Fe_3O_4 solid solution series.

as a single phase in the region between TiFe_2O_4 - Fe_3O_4 join and TiFeO_3 - Fe_2O_3 join. We also obtained the cubic solid solutions in the concerned region by oxidizing the TiFe_2O_4 - Fe_3O_4 series specimen.

The specimens of TiFe_2O_4 - Fe_3O_4 solid solution series, packed in an open air porcelain boat, were inserted into an electric furnace after the temperature in the furnace had settled at the designated temperature, and after being maintained there for a designated length of time, taken out and cooled in air. The length of the heat treatment was two hours in most cases and the temperature of heat treatment was the intermediate between 400°C and 550°C .

Ten specimens from S2-1 to S2-10 and other four specimens S5-1, S5-3, S5-5 and S5-6, described in just preceding section, were used for the present purpose. Chemical compositions of the heat-treated specimens are also plotted by hollow circles in Fig. 1 and given in Table II. The heat-treated specimens are distinguished in the figure or table by a mark ' or ' ' from the original ones. As seen in Fig. 1, the chemical composition of the original specimen was shifted by the heat treatment towards the directions of arrows presented in the figure along the theoretical reduction-oxidation line.

The X-ray analysis by the "Norelco" X-ray diffractometer revealed that the specimens still kept their spinel structure after the heat treatment. As for the greater parts of the specimens (S2-3', S2-5', S2-6', S2-7', S2-8', S2-9', S5-1', S5-3', S5-5', S5-6', S5-1'', S5-3'', S5-5'' and S5-6'') no trace of the ilmenite-hematite series minerals could be detected on the diffraction chart. But as for the specimen S2-1', fairly large amounts of ilmenite-hematite series minerals were found. The amounts were estimated

Table II *Chemical composition, crystallographic and magnetic properties of the generalized titanomagnetite. The specimens were obtained by oxidizing the $\text{TiFe}_2\text{O}_4\text{-Fe}_3\text{O}_4$ solid solution series. (cf. Table I)*

Specimen	Chemical composition			Crystal parameter, a (Å)	Curie point, θ (°C)	Saturation magnetization at room temperature, σ (e.m.u./gr.)	Heat treatment
	$\text{FeO}+\text{Fe}_2\text{O}_3+\text{TiO}_2$ wt%	FeO	Fe_2O_3				
S2-1'	96.86	36.57	59.39	4.04	575	59	500°C, air, 2hr.
S2-2'	96.92	40.75	50.15	9.10	570	78	"
S2-3'	100.46	33.81	51.18	15.01	565	50	"
S2-4'	100.01	40.80	40.89	18.31	560	58	"
S2-5'	100.56	40.78	35.60	23.62	565	54	"
S2-6'	99.12	40.77	33.58	25.65	560	41	"
S2-7'	100.69	52.95	19.38	27.66	170		420°C, air, 2hr.
S2-8'	100.45	55.18	14.62	30.19	80		"
S2-9'	100.56	58.30	8.89	32.81			440°C, air, 2hr.
S2-10'	98.81	52.86	10.43	36.71			"
S5-1'	100.38	46.52	46.21	7.27	550		400°C, air, 3hr.
S5-3'	100.22	41.13	41.03	17.84	550		"
S5-5'	100.19	44.87	30.57	24.56	540		"
S5-6'	100.49	43.54	22.74	33.72	505 (140)		"
S5-1''	100.38	41.31	51.18	7.51	570		550°C, air, 1hr.
S5-3''	100.20	36.08	45.52	18.40	565		"
S5-5''	100.22	37.17	37.05	25.78	540 (585)		"
S5-6''	100.49	37.71	27.73	34.56	530 (585)		"

from the diffraction chart to be about 30 percent. The specimens S2-2', S2-4' and S2-10' also contained about 10 percent ilmenite-hematite series minerals.

The lattice parameter determined by the X-ray analysis is also listed in Table II, where we can easily find in comparison with Table I that the crystal parameter of all the specimens was decreased considerably by oxidation.

Even though there have been remained some ambiguities with respect to the composition of the spinel phase of the present heat-treated specimens on account of the contamination of a small amount of rhombohedral phase, it may be safely said

from these experimental results that the spinel phase can be in existence as a single phase in fairly broad region between the $\text{TiFe}_2\text{O}_4\text{-Fe}_3\text{O}_4$ join and the $\text{TiFeO}_3\text{-Fe}_2\text{O}_3$ join under an appropriate condition of temperature and oxygen pressure. It may be very probable to expect that the region of the spinel phase can be extended more close to the $\text{TiFeO}_3\text{-Fe}_2\text{O}_3$ join if we find the appropriate heat treatment. The fact that a complete solid solution can be prepared between Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ (Hägg; 1935) may also support the above possibility.

4. Thermomagnetic Curve and Curie Temperature

The variation in magnetic moment of all the synthesized spinel specimens as a function of temperature in a constant magnetic field of a few thousands Oersteds was measured by means of a magnetic balance described in the previous paper (Akimoto; 1954). In the present study the measurement was carried out under the evacuated state of about 10^{-3}mmHg . The Curie temperature determined from the thermomagnetic curve is listed in Table I and Table II. As for the specimens of the $\text{TiFe}_2\text{O}_4\text{-Fe}_3\text{O}_4$ solid solution series, the Curie temperature is plotted against chemical composition in Fig. 3, where it can be found that the Curie temperature changes almost linearly with composition from 580°C of Fe_3O_4 down to about -150°C of TiFe_2O_4 .

As for the specimens with lower Curie temperature the measurement of the thermomagnetic curve down to the liquid nitrogen temperature in a field strength of 8450 Oe was practised by the help of Ishikawa at Institute of Science and Technology, Tokyo University. A few examples of the thermomagnetic curve are shown in Fig. 4, where we can see the peculiar mode of thermomagnetic curve like Néel's *P*-type for

Fig. 3 Relation between Curie temperature and chemical composition in $\text{TiFe}_2\text{O}_4\text{-Fe}_3\text{O}_4$ solid solution series.

Fig. 4 A few examples of the thermomagnetic curve of $\text{TiFe}_2\text{O}_4\text{-Fe}_3\text{O}_4$ solid solution series.

the specimens S2-8 and S2-9. This may be a remarkable contrast to the fact that the thermomagnetic curve of the specimens of which TiFe_2O_4 content is less than 60 percent does not show any peculiar mode but is very similar to that of Fe_3O_4 . It must be also noticed from Fig. 4 that the specimen of which chemical composition is determined to be $0.96 \text{TiFe}_2\text{O}_4 \cdot 0.04 \text{Fe}_3\text{O}_4$ (S1-4) becomes ferrimagnetic below 170°K , its intensity of magnetization at 80°K in 8450 Oe being about 4 e.m.u./gr. This suggests that pure TiFe_2O_4 becomes ferrimagnetic below about 120°K . So long as the inverse spinel structure is kept in TiFe_2O_4 ; that is, titanium ions are confined to the octahedral sites in the spinel structure, the intensity of saturation magnetization ought to be zero at 0°K . The present situation that TiFe_2O_4 becomes ferrimagnetic at the lower temperatures may suggest that some titanium ions enter into the tetrahedral sites with the result that the compensation of magnetic moment between tetrahedral and octahedral sites is disturbed. Such disordering of cations from their theoretical distribution is very probable for the present $\text{TiFe}_2\text{O}_4\text{-Fe}_3\text{O}_4$ series specimens, since they were prepared by the quenching method from 1150°C . As for the saturation magnetization of the synthesized titanomagnetite, the detailed discussions will be given in the succeeding section.

Comparing the Curie temperature of both original and heat-treated specimens with each other, the general tendency that the Curie temperature becomes higher according as the oxidation proceeds is found. Similar aspect has already been noticed by Nagata and Ozima (1955) in the iron sand of Niisima on which various kinds of heat treatments were conducted in open air.

5. Saturation magnetization

The magnetization curve of the specimen having the higher Curie temperature was measured at the room temperature by means of the magnetic balance up to a

field strength of about 3000 Oe. The intensity of saturation magnetization was determined by extrapolating the following empirical formula to $H=\infty$

$$\sigma = \sigma_\infty \left(1 - \frac{A}{H}\right),$$

where A is the constant determined experimentally for every specimen. As for the specimens with the lower Curie temperature the magnetization curve was measured at the liquid nitrogen temperature by the help of Ishikawa. The intensity of saturation magnetization of the synthesized titanomagnetite at room temperature or 80°K is given in Table I and Table II. The intensity of saturation magnetization of these specimens at 0°K was estimated by extrapolating their thermomagnetic curve to 0°K . These estimated saturation moments of the $\text{TiFe}_2\text{O}_4\text{-Fe}_3\text{O}_4$ series specimens are also shown in Table I with the Bohr magneton number per one molecule of $x\text{TiFe}_2\text{O}_4 \cdot (1-x)\text{Fe}_3\text{O}_4$.

Fig. 5 Estimated saturation moment at 0°K vs. composition for $\text{TiFe}_2\text{O}_4\text{-Fe}_3\text{O}_4$ solid solution series.

A: theoretical value for Akimoto's model.

B: theoretical value for Néel-Chevallier's model.

Fig. 5 shows the dependence of the estimated value of the saturation moment at 0°K upon the composition of the $\text{TiFe}_2\text{O}_4\text{-Fe}_3\text{O}_4$ series. Although such an estimation as mentioned above includes a considerable error, the general tendency that the magnetization decreases gradually as the content of TiFe_2O_4 increases seems to be true. In the figure, two series of the theoretical values on the saturation moment, based on the different assumptions on the configuration of cations in the crystal lattice sites, are also shown. The one is based on the following configuration of cations,

where the cations inside the bracket indicate the octahedral site and that outside the tetrahedral site of the spinel structure. In this case a saturation moment of $4-4x$ is

calculated (Akimoto; 1954, 1955). The other configuration of cation was postulated by Néel (1955) and Chevallier et al. (1955) by taking the Verwey's empirical law concerning the location of cations in the spinel structure into consideration, that is

for which the saturation moments of $4-6x$ (for $x < \frac{1}{2}$) and $2-2x$ (for $x > \frac{1}{2}$) are calculated.

The actual values of the saturation moments of the synthetic TiFe_2O_4 – Fe_3O_4 solid solution series are the intermediate between these two. It may also be worthwhile to note that the actual values in our synthetic specimens were always larger than the Néel-Chevallier's theoretical value over the whole range of the composition. This seems to suggest that some titanium ions enter into the tetrahedral sites apart from the normal octahedral sites of $\text{Fe}^{3+}(\text{Fe}_{1+x}^{2+}\text{Fe}_{1-2x}^{3+}\text{Ti}_x^{4+})\text{O}_4^{2-}$ or $\text{Fe}_{2-2x}^{3+}\text{Fe}_{2x-1}^{2+}(\text{Fe}_{2-x}^{2+}\text{Ti}_x^{4+})\text{O}_4^{2-}$. In these cases, as suggested by Gorter (1957), the cation distribution should be considered as

or

the saturation moment being $4-6x+10a$ and $2-2x+8a$ respectively. Then, the saturation moment should be increased with the increase of Ti ions in the tetrahedral sites. As for the present synthetic specimens prepared by the quenching method from high temperature, such disordering of cations may be very probable. Similar effect of the disordering of cations from the ideal inverse spinel structure has already been demonstrated for MgFe_2O_4 by Bertaut (1952) and for NiFeAlO_4 by Gorter (1954). The implications of such a behaviour for rock magnetism are discussed by Néel (1955) and Verhoogen (1956) in connection with the mechanism causing self-reversal of the remanent magnetization of ferromagnetic minerals. The effect of annealing on the saturation moment of the synthetic specimens is now under investigation.

The variation of saturation moment of the TiFe_2O_4 – Fe_3O_4 solid solution series with oxidation was also investigated. Comparing the saturation moment of the original specimen (Table I) with the oxidized one (Table II), we may notice the following remarkable situations. That is, the saturation moment at the room temperature of the specimen with the lower content of TiFe_2O_4 decreases considerably according as the degree of oxidation proceeds, but that of the specimen with higher content of TiFe_2O_4 is increased by oxidation. These experimental results would be explained fairly satisfactorily if we regard the specimen in the intermediate between TiFe_2O_4 – Fe_3O_4 join and TiFeO_3 – Fe_2O_3 join as a generalized titanomagnetite having some vacant sites in the structure normally occupied by metallic ions in a spinel and if we assume that the solid solution can be in existence between any composition on the TiFe_2O_4 – Fe_3O_4 join and the corresponding oxidation product on the TiFeO_3 – Fe_2O_3 join. It is needless

to say that we must assume here the cubic crystal form on the $\text{TiFeO}_3\text{--Fe}_2\text{O}_3$ join. As for Fe_2O_3 , $\gamma\text{Fe}_2\text{O}_3$ is well known and its magnetic structure is considered to be $\text{Fe}^{3+}(\text{Fe}_{\frac{8}{3}}^{3+}\square_{\frac{8}{3}})\text{O}_4^{2-}$, where $\square$ denotes the vacant site in the structure normally occupied in a spinel. On the other hand as for the cubic form of TiFeO_3 magnetic structures of $\text{Fe}_{\frac{8}{3}}^{2+}\square_{\frac{8}{3}}(\text{Fe}_{\frac{8}{3}}^{3+}\text{Ti}_{\frac{4}{3}}^{4+})\text{O}_4^{2-}$ and $\text{Fe}^{2+}(\text{Ti}_{\frac{4}{3}}^{4+}\text{Fe}_{\frac{8}{3}}^{3+}\square_{\frac{8}{3}})\text{O}_4^{2-}$ have already been postulated by Chevallier et al. (1955) and Nicholls (1955) respectively for interpreting the saturation moment of the $\text{TiFeO}_3\text{--Fe}_3\text{O}_4$ solid solution series. In the present paper hypothetical cubic form of the $\text{TiFeO}_3\text{--Fe}_2\text{O}_3$ system, $y\text{TiFeO}_3\cdot(1-y)\text{Fe}_2\text{O}_3$ is taken to be

in making use of the Chevallier's γTiFeO_3 . This implies that the saturation moment of the cubic $\text{TiFeO}_3\text{--Fe}_2\text{O}_3$ system changes linearly with the composition according to equation

$$M = \frac{10}{3}(1-y)\mu_B.$$

We showed the variation of saturation moment along the reduction-oxidation line in Table III, where the original value of saturation moment of $\text{TiFe}_2\text{O}_4\text{--Fe}_3\text{O}_4$ join and the final value of $\text{TiFeO}_3\text{--Fe}_2\text{O}_3$ join are given for different values of $\text{Fe}/\text{Fe}+\text{Ti}$ in the unit of Bohr magneton number per molecule. As for the saturation moment of

Table III *Change in saturation moment of $\text{TiFe}_2\text{O}_4\text{--Fe}_3\text{O}_4$ solid solution series with oxidation.*

Fe/Fe+Ti	Original spinel, $x\text{TiFe}_2\text{O}_4\cdot(1-x)\text{Fe}_3\text{O}_4$		Oxidation product, $y\text{TiFeO}_3\cdot(1-y)\text{Fe}_2\text{O}_3$	
	x	saturation moment(μ_B)	y	saturation moment(μ_B)
1.000	0	4.0*	0	3.33
0.966	0.1	3.4 (3.6)**	0.067	3.11
0.933	0.2	2.8 (3.2)	0.133	2.89
0.900	0.3	2.2 (2.8)	0.200	2.67
0.866	0.4	1.6 (2.4)	0.267	2.44
0.833	0.5	1.0 (2.0)	0.333	2.22
0.800	0.6	0.8 (1.6)	0.400	2.00
0.766	0.7	0.6 (1.2)	0.467	1.78
0.733	0.8	0.4 (0.8)	0.533	1.56
0.700	0.9	0.2 (0.4)	0.600	1.33
0.666	1.0	0	0.667	1.11

* after Néel-Chevallier's model.

** after Akimoto's model.

$\text{TiFe}_2\text{O}_4\text{--Fe}_3\text{O}_4$ join, two sets of values are listed in the table; i.e. Néel-Chevallier's value (Néel; 1955, Chevallier et al.; 1955) and the value postulated previously by one of the authors (Akimoto; 1954). From the table it is clearly seen that the saturation moment of the specimen with lower content of TiFe_2O_4 decreases according as the oxidation proceeds, while that of the higher content of TiFe_2O_4 increases. This situation accords well at least qualitatively with the above-mentioned experimental results.

6. Conclusive Remarks

The accumulation of the reliable data on the chemical, crystallographic and magnetic properties of the spinel specimens enables us to draw an equal lattice constant line, equal Curie point line or equal saturation moment line on the spinel region in the

Fig. 6 Lines of equal lattice parameter of the generalized titanomagnetite in a $\text{FeO-Fe}_2\text{O}_3\text{-TiO}_2$ system.

Fig. 7 Lines of equal Curie temperature of the generalized titanomagnetite in a $\text{FeO-Fe}_2\text{O}_3\text{-TiO}_2$ system.

Fig. 8 Lines of equal saturation moment at the room temperature of the generalized titanomagnetite in a $\text{FeO-Fe}_2\text{O}_3\text{-TiO}_2$ system.

$\text{FeO-Fe}_2\text{O}_3\text{-TiO}_2$ system. Figs. 6, 7 and 8 are the equal lattice parameter diagram, equal Curie point diagram and equal saturation moment diagram respectively. The results of Chevallier and Girard's study (1950) are also taken into account in drawing these diagrams.

It can be easily found from these diagrams that the general view of the equal lattice parameter diagram and the equal Curie point diagram resembles very much with each other; that is, the parallelism of the equal lattice parameter line and the equal Curie point line is generally found. Another remarkable character found in these diagrams is that the equal Curie point line representing the temperature higher than about 500°C has a marked curvature in contrast to the straight line of the lower temperatures.

It must also be mentioned here that such an attempt to draw an equal Curie point line on the $\text{FeO-Fe}_2\text{O}_3\text{-TiO}_2$ system has already been done by Chevallier and Girard (1950). They suggested the Curie point variation may be expressed by

$$\theta^\circ\text{K (Curie point)} = 1245s$$

where

$$s = \frac{\text{wt}\%\text{Fe}_2\text{O}_3}{\text{wt}\%\text{Fe}_2\text{O}_3 + \text{FeO}}.$$

The present diagram shown in Fig. 7 accords well with that postulated by them within the $\text{Fe}_3\text{O}_4\text{-TiFeO}_3\text{-TiFe}_2\text{O}_4$ system except higher temperature side.

The general view of the equal saturation moment diagram differs greatly from other two diagrams, that is, the equal saturation moment line intersects the equal lattice parameter line or the equal Curie point line in the $\text{FeO-Fe}_2\text{O}_3\text{-TiO}_2$ diagram.

These diagrams seem to have a deep significance especially in the field of

geological application of rock magnetism. It has already been shown that the magnetic analysis, together with chemical and X-ray analyses, is sometimes useful for determining the constitution of the ferromagnetic minerals contained in rocks. As the present diagrams show, however, the chemical composition having a definite lattice parameter or Curie point is not represented by a point but form a line on the $\text{FeO-Fe}_2\text{O}_3\text{-TiO}_2$ system. Hence, even if the lattice parameter or Curie point of the ferromagnetic minerals were determined with sufficient accuracy by X-ray or magnetic analysis, it is impossible to fix their chemical composition to a point on the $\text{FeO-Fe}_2\text{O}_3\text{-TiO}_2$ system. The determination of the chemical composition by these method is always accompanied with some uncertainties. When we measure the saturation moment of the specimen at the same time, this uncertainty will vanish, the chemical composition of the specimen being able to be fixed to a single point. It is also expected that the reliable data on the specific gravity of the specimen is useful for the determination of the chemical compositions.

In concluding the present paper, the authors wish to express their sincere thanks to Prof. T. Nagata for his constant guidance throughout the study. They also wish to thank Prof. I. Iwasaki for his kind encouragement and interest. The authors are also indebted to Dr. Y. Ishikawa for his magnetic measurement at lower temperatures.

References

- Akimoto, S., 1954, *Journ. Geomag. Geoelect.*, **6**, 1.
1955, *Jap. Journ. Geophysics*, **1**, No. 2, 1.
Bertaut, F., 1952, *C. R. Acad. Sci. Paris*, **234**, 1295.
Chevallier, R., and Girard, J., 1950, *Bull. Soc. Chem. France*, **5**, 17, 576.
Chevallier, R., Bolfa, J. and Mathieu, S., 1955, *Bull. Soc. Franc. Miner. Crist.*, **78**, 307, 365.
Ernst, T., 1943, *Zeits. angew. Min.*, **4**, 394.
Gorter, E.W., 1954, *Philips Res. Rep.*, **9**, 295, 321, 403.
1957, *Advanc. Phys.*, **6**, 336.
Hägg, G., 1935, *Zeits. Phys. Chem.*, **29**, 95.
Kawai, N., Kume, S., and Sasajima, S., 1954, *Proc. Japan Acad.*, **30**, 588.
Nagata, T. and Ozima, M., 1955, *Journ. Geomag. Geoelect.*, **7**, 105.
Néel, L., 1955, *Advanc. Phys.*, **4**, 191.
Nicholls, G.D., 1955, *Advanc. Phys.*, **4**, 113.
Pouillard, E., 1950, *Ann. Chimie*, **5**, 164.
Verhoogen, J., 1956, *Journ. Geophys. Res.*, **61**, 201.