Dependence of the cation distribution in Manganese ferrite, MnFe_2O_4 , on temperature and oxidation

TAKAMITSU YAMANAKA

Mineralogical Institute, Faculty of Science,
University of Tokyo, Tokyo 113

and

MITSUOKI NAKAHIRA

National Institute for Researches in Inorganic Materials,
Kurakake, Sakura-mura, Niihari-gun, Ibaragi 300-31

ABSTRACT

The cation distribution of manganese ferrite among the tetrahedral and octahedral sites was determined for $(\text{Mn}_x\text{Fe}_{1-x})[\text{Mn}_y\text{Fe}_{2-y-d}\square_d]\text{O}_4$, using the X-ray anomalous dispersion. The specimen had a fixed Mn/Fe ratio and were synthesized under various temperatures and equilibrium oxygen partial pressures. The variation of the lattice constant and the oxygen parameter, and the local distortion of the octahedral sites were found to be strongly dependent on the cation distribution.

With a decreasing oxygen partial pressure, a larger amount of Mn was distributed at the tetrahedral sites, while Fe increased at the octahedral sites. Noticeable temperature dependence of the cation distribution was not confirmed because of the presence of increasing cation vacancy at the octahedral sites with lowering the quenching temperature. This fact may be ascribed to varying oxidation of Mn and Fe with temperature.

The large influence of the cation vacancy on the site occupancy of the ferrite was discussed, based on the valency states of the constituent atoms at each site. The distribution of the charge in the ferrite may be schematically summarized in the form:

Introduction

Crystallographic studies of the solid solution $\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$ as well as other spinel ones have been conducted by various investigators.

Among them, MnFe_2O_4 has been the specific subject of numerous investigations and its cation distribution or site occupancy has often been discussed because of its considerable difference from other ferrites in respect of the magnetic property and electrical conductivity.

Distribution of manganese and iron among the two sites, tetrahedral and octahedral sites of the spinel structure, was determined by the structural analysis using neutron diffraction. MnFe_2O_4 was described to be an intermediate spinel between the inverse and normal ones, $(\text{Mn}_{1-y}\text{Fe}_y)[\text{Mn}_d\text{Fe}_{2-d}]\text{O}_4$, by Hastings (1956), Yamzin (1962) and Kleinstuck (1965).

Moreover, with respect to the valency states of manganese and iron at each site, the disagreement between the experimental value of the magnetization of MnFe_2O_4 and Neel's theory (1948) also attracted attentions of various investigators. Krupicka (1959) and Harrison (1957) proposed the valency states being $(\text{Mn}_{0.8}^{2+}\text{Fe}_{0.2}^{3+})[\text{Mn}_{0.2}^{3+}\text{Fe}_{0.2}^{3+}\text{Fe}_{1.6}^{3+}]\text{O}_{4.0}^{2-}$. Miller (1959) provided a set of octahedral site preference energy for the various cations to support the assumption of the valency formula as described above.

Further, the cation distribution of this ferrite varies with temperature and equilibrium oxygen partial pressure. From the statistical thermodynamics underlying the cation distribution of ferros spinels, Callen (1956) suggested the dependence of the distribution law on temperature. Butler (1962) investigated the variation of the lattice constant and the line width of X-ray reflections from the manganese ferrite as a function of oxygen pressure or temperature or both. He concluded that the lattice constant decreased with increasing oxidation. Wickham (1968) detailed the dependence of the value of d of the spinel compound, $\text{Mn}_x\text{Fe}_{3-x}\text{O}_{4+d}$, upon temperature and composition, showing that d decreased with increasing equilibrium temperature for a given atomic fraction of manganese.

Navrotsky (1969) calculated the oxidation-reduction enthalpies for cations on the octahedral sites in the spinel structure and reported a good agreement of those values with the experimental thermodynamical data obtained from defect equilibria in the spinels based on the diffusion and electrical measurements.

Lotgering (1964) concluded from the electrical conductivity measurements of $\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$ that manganese ferrite presented the following equilibrium between the cations at the octahedral sites:

These investigations indicate that the cation distribution of MnFe_2O_4 is dependent on temperature and oxidation. Rieck (1965) reported the relation between the position and valence of the cations by investigating the site occupancy in the samples of $\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$ prepared under various temperatures and oxygen partial pressures by the method of X-ray anomalous dispersion.

With a fixed cation ratio, the cell constant changes either under varying temperature at a constant oxygen partial pressure or under varying oxygen partial pressure at a constant temperature. Therefore, the present investigation aimed at understanding the mechanism for these changes. Not only site occupancy but also oxygen parameter (*u*-parameter) of the spinel structure, as well as population of cation vacancy were determined in the fixed composition of MnFe_2O_4 .

Preparation of samples

Samples having a fixed composition as MnFe_2O_4 were prepared from a mixture of reagent-grade powders of MnO_2 and Fe_2O_3 . The starting materials with the calculated ratio were mixed in an agate mortar for several hours and pressed into tablets, which were calcinated at 1000°C for 24 hours. To insure the homogeneity of the samples, the tableted mass after firing was ground for 3 hours and again formed into tablets by addition of 5% polyvinyl alcohol

as a binding agent. These tablets were fired again under the various desired conditions of temperature and oxygen partial pressure for at least 24 hours, mostly 48 hours, in order fully to advance their recrystallization. They were then quenched in mercury for the prevention of reoxidation.

Since the spinel phase of MnFe_2O_4 has a large range of stability with respect to oxygen partial pressure, the synthesis has to be carried out under a well controlled oxygen partial pressure. Desired oxygen partial pressure was attained by varying the mixing ratio of $\text{CO}_2\text{-H}_2$ or $\text{O}_2\text{-N}_2$ gases based on the calculation published by Elliot (1960). A homogeneous mixture of the gases bearing a constant ratio was run through the furnace tube, using a gas mixer similar to that devised by Darken (1945).

The homogeneity of the samples was confirmed by a scanning method with an X-ray probe micro-analyzer. Neither lamellar nor zonal structure due to reoxidation or insufficient mixing of the starting materials were observed. The cation ratio of manganese to iron of the samples MnFe_2O_4 was also measured by the analyzer and confirmed to be within a range of $\text{Mn}_{0.99}\text{Fe}_{2.01}\text{O}_4$ to $\text{Mn}_{1.02}\text{Fe}_{1.98}\text{O}_4$.

Determination of the site occupancy and oxygen parameter

Determination of the site occupancy in ferrites mainly composed of transition metal cations is extremely difficult by the X-ray diffraction due to a very small difference between the atomic scattering factors of the constituent cations. Bertaut (1950) evaluated the site occupancy in CuFe_2O_4 and ZnFe_2O_4 from the intensity ratio of $I_{hkl}/I_{h'k'l'}$ using the X-ray anomalous dispersion. Referring to a solid solution of $\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$, Rieck (1966) determined the site occupancy such as $(\text{Mn}_{t-u}\text{Fe}_{1-t+u})(\text{Mn}_u\text{Fe}_{2-u-d}\square_d)\text{O}_4$ from the ratio of intensities $I_{hkl}\text{Fe}K\alpha/I_{hkl}\text{Cr}K\alpha$, diffracted from the same plane (hkl), using two different radiations, $\text{Fe}K\alpha$ and $\text{Cr}K\alpha$, according to the method devised by Skolnick (1958). However, these methods required

the estimation of temperature factor which largely affect the value of structure factors.

In the present experiment, such difficulties were overcome using the ratio of $I_{hkl}\text{FeK}\beta/I_{hkl}\text{FeK}\alpha$ described hereafter.

The intensity ratio widely varied with hkl with no linearity in the Bragg angle θ in the present observations. Since the absorption factor is independent of θ in the usual diffractometer measurements, the variation of the ratio originated from the anomalous dispersion, which is caused by proximity between the wave-lengths of the $\text{FeK}\alpha$ and $\text{FeK}\beta$ radiations and the wave-lengths of K -absorption edges of the constituent atoms Fe and Mn. The anomalous dispersion affects the atomic scattering factors with respect to $\text{FeK}\alpha$ and $\text{FeK}\beta$ to different degree. This results in a non-linear variation of the ratio $I_{hkl}\text{FeK}\beta/I_{hkl}\text{FeK}\alpha$ with θ .

The atomic scattering factors ($f=f_0+\Delta f'+i\Delta f''$) of the constituent atoms Fe and Mn relative to the incident beams, $\text{FeK}\alpha$ and $\text{FeK}\beta$, are obtained from data shown in the following table as calculated by the method described by James (1948):

Radiation		$\text{FeK}\alpha$ (1.9359Å)			$\text{FeK}\beta$ (1.7665Å)		
Element	K -abs. edge	$x=\lambda/\lambda_0$	$\Delta f'$	$\Delta f''$	$x=\lambda/\lambda_0$	$\Delta f'$	$\Delta f''$
25 Mn	1.8964Å	1.0208	-4.24	0	0.9262	-2.14	3.23
26 Fe	1.7433Å	1.1105	-2.01	0	1.0075	-5.35	0

The site occupancy, x and y of $(\text{Mn}_{1-x}\text{Fe}_x)(\text{Mn}_y\text{Fe}_{2-y-d}\square_d)\text{O}_4$, and the oxygen parameter (u -parameter) of the spinel structure were determined by comparison of the observed values with the calculated values of the ratio of structure factors, $|F_{hkl}\text{FeK}\beta|^2/|F_{hkl}\text{FeK}\alpha|^2$.

As apparent from the values of the squared ratio shown in Figs. 1 and 2, the reflections of the following hkl are effective to determine the factors, x and y , and u -parameter:

422, 444, 400, 220.....for x and y 222, 111.....for u .

The intensities of the reflections 220 and 422 depended only

of the reflection, $A(\theta)$ the absorption factor and k a constant of proportionality.

If the thermal vibration is isotropic, C is a constant value independent of reflections and includes the ratio of the constant of proportionality. By the method of least squares, the most reliable value of C in the present experiment was found to be $C=0.176$, which was ascertained using samples of silicon and germanium wherein the effects of $\Delta f'$ and $\Delta f''$ were deemed negligible.

Thereafter the oxygen parameter and site occupancy were determined by collating the observed ratio with the calculated one of $|F_{hkl}\text{FeK}\beta|^2/|F_{hkl}\text{FeK}\alpha|^2$ indicated in Figs. 1 and 2 and using the mean square root method.

The present experiment required the very accurate measurement of reflection intensities. These intensities were measured by step-count with a scintillation counter. The observed reflection intensity was counted for 100 sec at an interval of 0.02° in 2θ , and the step-counting was conducted all over the peak region of reflections and repeated twice.

Measurement of the reflection intensity by the powder diffraction is affected by various factors associated with the preparation such as particle size of powder, preferred orientation, density of powder in a holder and dead angle. Indeed all these factors influence the absorption factor, but the factors did not need to be taken into account in measuring the value of the ratio, $I_{hkl}\text{FeK}\beta/I_{hkl}\text{FeK}\alpha$, because the measurement of the reflection intensity in this experiment was carried out under the same conditions with respect to the factors.

Variation of the cation distribution and oxygen parameter

Samples synthesized at temperatures from 1105°C to 1510°C in an atmosphere of CO_2 and those synthesized under various oxygen pressures ranging from $\text{Po}_2=10^{-0.1}$ to $\text{Po}_2=10^{-3.64}$ atm at a constant

temperature of 1300°C are designated as "T" series and "P" series respectively. These two series were applied to confirm the variation of the cation distribution of $(\text{Mn}_x\text{Fe}_{1-x})(\text{Mn}_y\text{Fe}_{2-y-d}\square_d)\text{O}_4$ in terms of two independent factors of temperature and oxidation.

Table 1 presents the observed intensity ratio of $I_{hkl}\text{FeK}\beta/I_{hkl}\text{FeK}\alpha$ and ratio of structure factors calculated from the above ratio, $|F_{hkl}\text{FeK}\beta|^2/|F_{hkl}\text{FeK}\alpha|^2$, in the case of a sample (designated No. P-6) prepared at 1300°C in an atmosphere of $\text{O}_2/\text{O}_2+9\text{N}_2=1/10$ for 48 hours.

Table 1. Ratio of structure factors calculated from the observed intensity ratio in the case of the sample P-6.

<i>h</i>	<i>k</i>	<i>l</i>	$I_{\text{FeK}\alpha}$	$I_{\text{FeK}\beta}$	$I_{\text{FeK}\beta}/I_{\text{FeK}\alpha}$	$ F_{\text{FeK}\beta} ^2/ F_{\text{FeK}\alpha} ^2$
1	1	1	92,880	3,990	4.32	0.495
2	2	0	137,970	15,030	10.92	1.175
3	1	1	468,970	39,400	8.41	0.897
4	0	0	130,170	8,770	6.74	0.712
4	2	2	34,290	4,080	11.91	1.260
5	1	1	174,970	14,830	8.46	0.913
3	3	3				
4	4	4	200,060	16,010	8.00	0.874
5	3	3	42,090	2,920	6.94	0.863
7	3	1	70,960	3,510	4.94	0.818
5	5	3				
8	0	0	50,120	2,180	4.36	0.828

The oxygen parameter (*u*-parameter) and site occupancy (*x*, *y* and *d*) of this sample determined by the least-squares method are $u=0.386\pm0.001$ and $x=0.815\pm0.003$, $y=0.188\pm0.003$, $d=0.00$ respectively. The observed oxygen parameter and site occupancy in these series of samples are summarized in Table 2 and 3.

It was found in the samples of the "T" series that elevation of temperature in synthesizing the samples increased the amount of

Table 2. $(\text{Mn}_x\text{Fe}_{1-x})(\text{Mn}_y\text{Fe}_{2-y-d}\square_d)\text{O}_4$ in the "T" series.

Sample	$a(\text{\AA})$	$x+y$	x	y	d	Oxygen Parameter	Temp.	Preparation Atmosphere	Duration
T-1	8.5108(6)	1.002	0.771	0.231	0.03	0.383(1)	1105°C	CO ₂	48 h
T-2	8.5104(6)	0.996	0.767	0.229	0.03	0.382(1)	1185°C	CO ₂	48 h
T-3	8.5136(8)	1.008	0.792	0.216	0.02	0.385(1)	1215°C	CO ₂	48 h
T-4	8.5143(6)						1248°C	CO ₂	40 h
T-5	8.5152(8)	1.013	0.818	0.195	0.01	0.385(1)	1303°C	CO ₂	44 h
T-6	8.5160(8)	1.006	0.840	0.164	0.00	0.386(1)	1348°C	CO ₂	45 h
T-7	8.5157(6)						1406°C	CO ₂	30 h
T-8	8.5161(6)	1.003	0.842	0.161	0.00	0.387(1)	1452°C	CO ₂	24 h
T-9	8.5155(6)	1.004	0.823	0.181	0.00	0.385(1)	1510°C	CO ₂	24 h

Table 3. $(\text{Mn}_x\text{Fe}_{1-x})(\text{Mn}_y\text{Fe}_{2-y-d}\square_d)\text{O}_4$ in the "P" series.

Sample	$a(\text{\AA})$	$x+y$	x	y	d	Oxygen Parameter	Temp.	Preparation -Log Po ₂	Duration
P-1	8.5100(6)	1.003	0.792	0.211	0.02	0.384(1)	1300°C	0.09	44 h
P-2	8.511(10)	0.998	0.788	0.210	0.03	0.383(1)	1300°C	0.12	40 h
P-3	8.512(10)	1.007	0.792	0.215	0.02	0.384(1)	1300°C	0.18	47 h
P-4	8.5132(6)	1.006	0.801	0.205	0.01	0.384(1)	1300°C	0.48	44 h
P-5	8.514(10)	1.000	0.821	0.179	0.01	0.385(1)	1300°C	0.70	48 h
P-6	8.5165(6)	1.003	0.815	0.188	0.00	0.386(1)	1300°C	1.00	48 h
P-7	8.5166(6)	1.011	0.833	0.178	0.00	0.386(1)	1300°C	2.00	40 h
P-8	8.5165(6)	0.997	0.829	0.168	0.00	0.386(1)	1300°C	3.54	48 h

Standard deviations given in parentheses expressed in units of last digit stated.

manganese at the tetrahedral sites from $x=0.767\pm0.006$ to 0.840 ± 0.005 in $(\text{Mn}_x\text{Fe}_{1-x})(\text{Mn}_y\text{Fe}_{2-y-d}\square_d)\text{O}_4$, while the amount of manganese (y) and the cation vacancy (d) in the octahedral sites were reduced with a concomitant increase of iron atom in the sites. This temperature rise also raised the oxygen parameter of the samples from $u=0.382\pm0.001$ to $u=0.387\pm0.001$. When temperature was fixed at 1300°C , decrease of the oxygen partial pressure (Po_2) as shown in the "P" series also showed the same tendency as in the "T" series and manganese increased at the tetrahedral sites from $u=0.788\pm0.007$ to 0.833 ± 0.008 with decreasing oxygen partial pressure. The oxygen parameter slightly increased from $u=0.383\pm0.001$ to $u=0.386\pm0.001$.

As observed in Table 3, the oxygen partial pressure affected the cation vacancy of the samples, which was ascertained in the "P" series. Under the condition of higher oxidation ranging from $\text{Po}_2=10^{-0.09}$ to $10^{-0.7}$ atm. nonstoichiometric compounds ($d=0.03$ to 0.01) are formed. The samples prepared at comparatively low temperatures were also found to be nonstoichiometric.

Concerning the distribution of vacancies determined by this study, cation vacancies are assumed to be in the octahedral sites. If tetrahedral cation is absent, repulsion between four oxygen atoms will be too great to keep the frame of tetrahedron.

Such nonstoichiometric samples as T-1, 2 and 3 and P-1, 2 and 3 synthesized at low temperatures or under the condition of high oxidation had a considerably small value of manganese site occupancy in the tetrahedral sites. This may be due to the fact that the creation of iron-ion vacancy at the octahedral sites lowers the manganese fraction at the tetrahedral sites.

With regard to the charge distribution, nothing can be said from the present experiment. However, from the Mössbauer observations, Yamanaka (1972) determined the valence states and coordinations of iron-ions in the same specimens. Furthermore, in view of the crystal field (Dunitz, 1957; Orgel, 1960), divalent manganese (Mn^{2+} ,

$3d^5$) has no particular preference for either site, while trivalent manganese (Mn^{3+} , $3d^4$) has an octahedral preference as evidenced in a normal spinel, Mn_3O_4 . Combined with the present observations regarding the atomic distribution, the distribution of the charge in the ferrite may be schematically summarized in the form presented below.

The variation of the cation distribution in each site in the "P" and "T" series may give a conclusive evidence of the influence of cation vacancies upon the site occupancy in $MnFe_2O_4$ in the consideration of the valency formula described above. Moreover, judging from the larger difference of ionization potential between manganic and manganous ions than that between ferric and ferrous ions, iron has a more eminent tendency to form trivalent cation than manganese. Accordingly, the occurrence of the cation deficiency results in the vacancy of iron-ions at the octahedral sites and in the conversion of ferrous ions into ferric in the sites. This equilibrium reaction corresponding to the above formula can be represented as,

where Po_2 represents the oxygen partial pressure.

At the higher oxidation, the equilibrium proceeds to the right. Compared with the stoichiometric samples, the samples bearing the cation vacancy have the aforementioned small value of manganese site occupancy in the tetrahedral sites. This may be because the site exchange of the cations takes place as follows:

where A and B represent the tetrahedral and the octahedral sites respectively.

Consequently, it can be inferred from the combination of the equilibrium equations (1) and (2) that the reducing octahedral ferrous ion brings about the cation vacancy in the octahedral sites and

simultaneously causes the increase of the tetrahedral and octahedral ferric ion, while the manganous ion decreases in its site occupancy at the tetrahedral sites.

The result of "T" series also proves the temperature dependence of the cation exchange between the two sites to some extent. The process of the cation exchange can be interpreted by the following equilibrium (3) and the above equilibrium (2) as,

From measurement of the enthalpy of formation of MnFe_2O_4 , Navrotsky (1968) determined the reaction (2) to have an enthalpy of $\Delta H_2 = 0$ kcal and the reaction (3) to have an enthalpy of $\Delta H_3 = 6.2$ kcal at 1200°C . Lotgering (1964) also obtained the enthalpy of $\Delta H_3 = 6.9$ kcal from measurement of the electrical conductivity between -180°C and 300°C .

The sum of the equilibria (2) and (3) leads to the following equilibrium (4) capable of determining the degree of the normality of the spinel structure.

Since the equilibrium (4) represents an endothermic reaction, the equilibrium is shifted to the right at higher temperatures. Thus, the divalent manganese ion in the tetrahedral sites will be converted into trivalent in the octahedral sites.

The cation distribution at various temperatures given in Table 2, however, does not noticeably indicate the above tendency. This fact may be ascribed to the presence of cation vacancy and partly to the variation of oxidation due to the different dissociation constant of CO_2 gas used for the atmosphere through the furnace, which depends on varying temperature.

Variation of the lattice constant of MnFe_2O_4

The lattice constant of the solid solution, $\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$, has been discussed with respect to the molar fraction and temperature

employed in the synthesis of the samples by Finch (1957), Butler (1962) and Bergstein (1963). Yamanaka (1972) interpreted the variation of the lattice constant based on the local distortion and charge distribution as resulted by the Mössbauer experiment of this solid solution.

In the present study, measurements of the lattice constant of all samples of MnFe_2O_4 , synthesized under the consistent condition of temperature or oxygen partial pressure, were conducted at room temperature using high purity germanium metal powder (Ge, 99.999% pure) as an internal reference material by a high angle measurement with an X-ray powder diffractometer under the following conditions: Radiation $\text{FeK}\alpha$, Filter none, Scanning speed $1^\circ/4$ min, Time constant 8, Slit $1/2^\circ$ -0.30 mm- $1/2^\circ$, Detector, Scintillation counter.

Various errors in the measured d_{hkl} -value depending on θ were corrected using the absorption function for powder method (Azaroff, 1958).

$$\frac{1}{2} \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right)$$

The lattice constants obtained from the observed d_{hkl} -values of each sample by the method of least squares were within an accuracy of from $\pm 0.005 \text{ \AA}$ to $\pm 0.001 \text{ \AA}$.

The lattice constant was found to rise with increasing temperature or decreasing oxidation as shown in Figs. 3 and 4. As can be seen in the figures, even though the tested samples might have the same bulk composition, the lattice constant changed. This may be resulted from the variation of cation distribution, or the nonstoichiometry due to cation vacancy, or both.

The tendency of the variation of the lattice constant was in a good agreement with the result reported by Butler (1962). He stated that the variation can be interpreted as the effect of the change in cation distribution between the octahedral and tetrahedral sites at high temperatures. In view of the present measurements in which

Fig. 3. Lattice constant of MnFe_2O_4 with varying quenching temperatures in an atmosphere of CO_2 .

Fig. 4. Lattice constant of MnFe_2O_4 quenched from $1300^\circ\text{C} \pm 5^\circ\text{C}$ as a function of equilibrium oxygen partial pressure.

the dependence of cation distribution in MnFe_2O_4 on temperature and oxidation was confirmed, his interpretations seem to be reasonable.

From the cation and charge distributions as mentioned above, the change in the lattice constant can be interpreted as follows.

The increase of the lattice constant of the manganese ferrite with increase in the quenching temperature or decrease in the oxygen partial pressure was caused by the fact that Mn^{2+} ($0.80\text{\AA}$) replaces Fe^{3+} ($0.64\text{\AA}$) ions at the tetrahedral sites, which increases the volume of the cell. Although the volume decreases to some extent through the replacement of Fe^{2+} ($0.74\text{\AA}$) ions by such smaller ions as Fe^{3+} and partly as Mn^{3+} ($0.65\text{\AA}$) and also by cation vacancies located only at the octahedral sites, the former effect is much larger than the latter.

The change in the cation distribution influences the bond length and the bond angle at the both sites as shown in Table 4. The length of the oxygen-metal bond varies by the replacement of constituent cations having different ionic-radii and eventually changes the lattice constant.

Distortion in the octahedral sublattice

As described in the previous reports on the Mössbauer observation by Yamanaka (1972) and on the infrared experiment by Ishii (1972), the compositional change involving the increase in Mn^{3+} ions at the octahedral site causes a local distortion of the octahedral site due to the Jahn-Teller effect, and eventually leads to the transformation from the cubic to the tetragonal structure. In the present investigation, where the composition was fixed, no change to the tetragonal form took place. Nevertheless, the distortion of the octahedral site was observed based on the changes in the oxygen parameter (u -parameter) and the lattice constant.

The bond distances between oxygen (O) and metal atoms (Me)

Table 4. Variation of the bond length and bond angle in the samples of the "T" and "P" series.

Sample	a (Å)	Oxygen Parameter	Me-O _{tet.} (Å)	Me-O _{oct.} (Å)	$\angle$ O-Me-O _{oct.}
T-2	8.5104(6)	0.382(1)	1.931(3)	2.069(4)	86°40'(30)
T-5	8.5152(8)	0.385(1)	1.990(4)	2.047(5)	85°10'(30)
T-8	8.5160(8)	0.387(1)	2.020(4)	2.031(6)	84°00'(30)
P-2	8.5111(10)	0.383(1)	1.960(4)	2.062(6)	86°10'(30)
P-5	8.5141(10)	0.385(1)	1.990(4)	2.046(5)	85°10'(30)
P-8	8.5165(6)	0.386(1)	2.006(3)	2.040(4)	84°40'(30)

Standard deviations given in parentheses expressed in units of the last digit stated.

Fig. 5. Local distortion of the octahedral site by increasing the oxygen parameter of the spinel structure.
(This figure represents the local distortion at $u=0.385$).

and the bond angles $\angle(\text{O-Me-O})$ at the two sites in the manganese ferrite were calculated from its oxygen parameter and lattice constant as presented in Table 4. Since the bond angle at the tetrahedral sites, $\angle(\text{O-Me-O})_{\text{tetr.}}$, had a constant value of $109^{\circ}27'$, independent of the oxygen parameter, these sites were not subject to any distortion, despite the expansion or contraction of the sites. On the other hand, that of the octahedral sites, $\angle(\text{O-Me-O})_{\text{oct.}}$, changes with varying the parameter. The angle between equatorial Me-O bonds changes from $87^{\circ}05'$ to $84^{\circ}06'$. The increasing oxygen parameter leads to a greater distortion at the octahedral sites as shown in Fig. 5.

From the fact that the elevation of temperature or the reduction of the oxygen partial pressure employed at the synthesis of samples causes the increase in the oxygen parameter as shown in Tables 2 and 3, it may be concluded that the bond distances at the octahedral sites are gradually reduced, while those at the tetrahedral sites extremely increases as shown in Table 4. This is quite consistent with the experimental results of the cation distribution: the increasing amount of the larger ion of Mn^{2+} replacing the smaller ion of Fe^{3+} at the tetrahedral sites gives rise to the expansion of these sites, whereas the substitution of such smaller ion as Fe^{3+} and Mn^{3+} for the larger ion of Fe^{2+} at the octahedral sites brings about the contraction of these sites.

At the same time, X-ray precession photographs of $h0l$ and hhl reflections of a synthetic single crystal of $\text{Mn}_{1.01}\text{Fe}_{1.99}\text{O}_{4.0}$ did not show any extra spots indicating a super structure, and indicated the random distribution and orientation of the distortions of octahedral sites. No cooperative interaction between the distortions occurred and the overall symmetry was still cubic. The evidence of a long range order was not found in this ferrite.

Discussion

Numerous investigations have been conducted on the temperature dependence of the cation distribution in spinels. As to the dependence of MnFe_2O_4 samples, Hasting (1956) and Krupicka (1959) did not find the above fact. On the other hand, Rieck (1965) reported that the temperature dependence could be proved by the different site occupancies in the samples quenched from 1000°C and 1400°C , namely, manganese ions had a tendency to shift towards the octahedral sites at higher temperatures.

From the equilibrium (4), the temperature dependence does not contradict thermodynamical consideration. The present experiment did not apparently confirm the noticeable dependency. The reason is assumed to be that the presence of cation vacancy largely affects the site occupancy due to the samples being overoxidized at low temperatures.

Bergstein (1963) reported the dependence of oxygen nonstoichiometry (d) of the spinels $\text{Mn}_x\text{Fe}_{3-x}\text{O}_{4+d}$ on the fraction (x), using the samples quenched from various temperatures, also showing that the value of d in $\text{MnFe}_2\text{O}_{4+d}$ was more reduced with increasing temperatures. This indicates the oxidation of MnFe_2O_4 changes with temperature. Butler (1962) stated that the oxygen nonstoichiometry which varies with the degree of oxidation has a large effect on the lattice constant of MnFe_2O_4 . The present experiment also indicated the influence of the cation vacancy on the site occupancy, which was caused by varying the oxygen partial pressure based on the equilibrium (2) and (3).

Since oxidation changes with temperature, it will be difficult to detect the temperature dependence itself of the cation distribution, unless the atmosphere is so well controlled as to obtained a consistent oxygen partial pressure in each run at various temperatures. Therefore, in order to speak of the temperature dependence of cation

distribution in manganese ferrite with any certainty, it is indispensable to have a strict control on the degree of oxidation of specimens.

Acknowledgements—The work reported here is a part of a thesis for the degree of a Doctor submitted by T. Yamanaka. The authors wish to express their sincere gratitude to Prof. R. Sadanaga of the Mineralogical Institute of the University of Tokyo for his helpful suggestions during the present work as well as for his critical reading of the manuscript. The authors are also indebted to Dr. S. Takasu of the Central Research Lab., Toshiba Electric Co., Ltd., for his fruitful technical suggestions.

REFERENCES

- AZAROFF, L.V. & BUEGER, M.J. (1958) *The powder method in X-ray crystallography*. New York: McGraw-Hill.
- BERGSTEIN, A. (1963) *Czechoslov. Chem. Comm.*, **28**, 2381.
- BERTAUT, F. (1948) *C.R. Acad. Sci. Paris*, **228**, 187.
- BERTAUT, F. (1950) *C.R. Acad. Sci. Paris*, **230**, 215.
- BUESSEM, W.R. & BUTLER, S.R. (1963) *J. Amer. Ceram. Soc.*, **46**, 444.
- BUTLER, S.R. & BUESSEM, W.R. (1963) *J. Appl. Phys.*, **34**, 1754.
- CALLEN, H.B., HARRISON, S.E. & KRISMAN, C.J. (1956) *Phys. Rev.*, **103**, 851.
- DARKEN, L.S. & GURRY, R.W. (1945) *J. Amer. Chem. Soc.*, **67**, 1398.
- DUNITZ, J.D. & ORGEL, L.E. (1957) *J. Phys. Chem. Solids*, **3**, 20.
- HASTING, J.M. & CORLISS, L.M. (1956) *Phys. Rev.*, **104**, 328.
- HARRISON, F.W., OSMOND, W.P. & TEALE, R.W. (1957) *Phys. Rev.*, **106**, 865.
- ISHII, M., NAKAHIRA, M. & YAMANAKA, T. (1972) *Solid State Comm.*, **11**, 209.
- KLEINSTUCK, K., WIESER, E., KLEINNERT, P. & PERTHEL, R. (1965) *Phys. Stat. Sol.*, **8**, 271.
- KRUPICKA, S. & ZAVETA, K. (1959) *Czech. J. Phys.*, **9**, 324.
- LOTGERING, F.K. (1964) *Phys. Chem. Solids*, **25**, 95.
- MILLER, A. (1959) *J. Appl. Phys.*, **30**, 245.
- NAVROTSKY, A. & KLEPPA, O.J. (1968) *J. Inorg. Nucl. Chem.*, **30**, 479.
- NAVROTSKY, A. (1969) *J. Inorg. Nucl. Chem.*, **31**, 59.
- RIECK, G.D. & DRIESSENS, F.C.M. (1966) *Acta Cryst.*, **20**, 521.
- SKOLNICK, L.P., KONDO, S. & LAVINE, L.R. (1958) *J. Appl. Phys.*, **29**, 198.
- WICKHAM, D.G. (1969) *J. Inorg. Nucl. Chem.*, **31**, 313.
- YAMANAKA, T. (1972) *Acta Cryst.*, **A28**, 237.
- YAMZIN, J.J., BELOV, N.V. & NOZIK, Y.Z. (1962) *J. Phys. Soc. Japan*, **17**, B-III, 55.

Received February 27, 1973