

The Structure of Manganese-Iron-Oxygen Spinel

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The positions of the metal ions in the spinel-type structures of compounds of the type $Mn_tFe_{3-t}O_4$ in the region $0.25 < t < 1.50$ have been determined by the method of Skolnick, Kondo & Lavine, which employs the diffraction of X-rays of different wavelengths.

After a single-phase spinel has been formed by solid-state reaction of manganese- and iron-oxide mixtures a change in the distribution of cations during heating still occurs. The time needed for reaching the equilibrium state of the distribution of cations depends on the composition. The final structure of samples quenched from 1000°C and from 1400°C, both with the composition $MnFe_2O_4$, is different.

The relation between position and valence of the cations is discussed.

Introduction

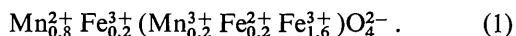
Manganese-iron oxides with spinel structure are used in modern magnetic materials. To improve their properties an oxide of zinc, nickel, cobalt or copper is incorporated. A crystallographic study of the relevant systems can be carried out best by first examining the quasi-binary subsystems.

In the region $0 \leq t < 2$ the compounds of the type $Mn_tFe_{3-t}O_4$ are cubic at room temperature. At $t=1$ the structure is not that of the mineral spinel, $Mg(Al_2)O_4$, nor of the inverse $Fe(MFe)O_4$ of many ferrites, but is intermediate between these two:



(Hastings & Corliss, 1956). Cations in brackets occupy octahedral sites, the others tetrahedral sites.

According to both the crystal field (Dunitz & Orgel, 1957; McClure, 1957) and the ligand field MO-LCAO theory (Goodenough & Loeb, 1955) Mn(III) ions prefer octahedral sites, while Mn(II), Fe(III) and Fe(II) ions have no strong preference. On this ground the valency formula of manganese ferrite might be (Miller, 1960):



According to the theory of Néel (1948) for (1) a magnetic moment of 4.6 Bohr magnetons is expected, which value has been found experimentally (Pauthenet, 1950). If, conversely, the structure of manganese ferrite is calculated from experimental magnetic moments (Krupicka & Zaveta, 1959; Butler & Buessem, 1963), the degree of inversion seems hardly to vary with the temperature and the oxygen content. The same is found with neutron diffraction (Hastings & Corliss, 1956). However, for intermediate spinels one might expect (Callen, Harrison & Kriessman, 1956) a temperature dependence in the distribution of the cations at a certain oxygen content.

From conductivity measurements, Lotgering (1964) concluded that in manganese-iron spinels between -180 and $+300^\circ\text{C}$ the following equilibrium between octahedral ions exists:



The equilibrium (2) lies well to the left, and near to the absolute zero point the valency formula of manganese ferrite may be:

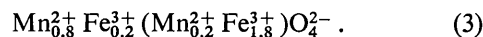


Table 1. Neutron diffraction on manganese-iron spinels $Mn_{t-\varphi}Fe_{1-t+\varphi}(Mn_{\varphi}Fe_{2-\varphi})O_4$

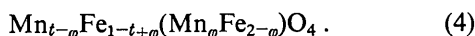
u = oxygen parameter and σ_{φ} standard deviation in φ

| t | u | φ | σ_{φ} | Preparation conditions | Reference |
|------|------------------|-----------|--------------------|-----------------------------------|---------------------------------|
| 0.40 | 0.383 | 0.05 | ± 0.02 | Unknown | Alperin (1962) |
| 0.43 | 0.381 | 0.43 | ± 0.04 | From the melt | Yamzin <i>et al.</i> (1962) |
| 0.53 | 0.383 | 0.53 | ± 0.04 | From the melt | Yamzin <i>et al.</i> (1962) |
| 0.60 | 0.383 | 0.06 | ± 0.02 | Unknown | Alperin (1962) |
| 0.84 | 0.383 | 0.06 | ± 0.04 | From the melt | Yamzin <i>et al.</i> (1962) |
| 0.98 | 0.385 | 0.19 | ± 0.03 | 24 h 1400°C air | Hastings & Corliss (1956) |
| 1.0 | 0.386 | 0.18 | | 6 h 1300°C $N_2 + O_2$ (2000:5) | Hastings & Corliss (1956) |
| 1.0 | 0.385 | 0.21 | | 4 h 1200°C N_2 | Hastings & Corliss (1956) |
| 1.01 | 0.385 | 0.18 | ± 0.04 | 2 h 1100°C $5 \cdot 10^{-2}$ torr | Kleinstück <i>et al.</i> (1965) |
| 1.03 | 0.385 | 0.23 | ± 0.04 | From the melt | Yamzin <i>et al.</i> (1962) |
| 1.06 | 0.385 | 0.25 | ± 0.04 | From the melt | Yamzin <i>et al.</i> (1962) |
| 1.10 | 0.386 | 0.27 | ± 0.04 | From the melt | Yamzin <i>et al.</i> (1962) |
| 1.28 | 0.386 | 0.44 | ± 0.04 | From the melt | Yamzin <i>et al.</i> (1962) |
| 1.50 | 0.387 | 0.61 | ± 0.04 | From the melt | Yamzin <i>et al.</i> (1962) |
| 1.58 | 0.388 | 0.66 | ± 0.04 | From the melt | Yamzin <i>et al.</i> (1962) |
| 2.00 | { 0.400 0.384 | 1.90 | ± 0.03 | Unknown | Murasik & Roul (1964) |

Before these formulae were published, one of us (Driessens, 1964a) made an effort to determine by chemical analysis the valency of cations at 250°C. These experiments seem to show that little Mn(III) and Fe(II) are present in MnFe_2O_4 . Tretjakow (1965) has obtained similar results in an analogous chemical approach.

Different methods for determination of the structure of $\text{Mn}_t\text{Fe}_{3-t}\text{O}_4$

The structure of a number of compounds of the type $\text{Mn}_t\text{Fe}_{3-t}\text{O}_4$ has been determined by neutron diffraction. Polycrystalline specimens have been studied by Hastings & Corliss (1956), Alperin (1962), Murasik & Roullet (1964) and Kleinstück, Wieser, Kleinert & Perthel (1965); single crystals, made by the method of Verneuil, have been investigated by Yamzin, Belov & Nozik (1962). The structure is described by the following formula:



The values found for the oxygen parameter u and the distribution parameter φ at different values of t are shown in Table 1 and in Fig. 1.

At $\text{Mn}_{0.5}\text{Fe}_{2.5}\text{O}_4$ Yamzin *et al.* (1962) have found all manganese ions to be in octahedral sites, whereas Alperin (1962) has found them to be nearly all in tetrahedral sites. It is not impossible that the latter structure is favoured by a 1:1 long-range order of manganese and iron ions in the tetrahedral sites, which order has been found experimentally (Alperin & Pickart, 1960).

Only Kleinstück *et al.* (1965) have referred to the oxygen content of their samples. These may contain an excess of oxygen, while an equivalent number of cation vacancies is present. However, the Bertaut (1950) method of evaluating the neutron diffraction results causes these results to be sensitive to the number and distribution of cation vacancies.

X-ray diffraction was applied in our experiments to compounds with $0.25 < t < 1.50$. The number of cation vacancies was calculated from the chemically determined excess of oxygen (Driessens, 1964a) and we determined the crystallographic place of the vacancies with normally scattered X-rays. After that the distribution of the manganese and iron ions in the tetrahedral sites was determined with anomalously scattered X-rays.

In comparison with neutron diffraction a further advantage of the X-ray method was that smaller samples could be used so that more homogeneous preparation conditions and a more effective quenching to room temperature might be achieved.

Experimental

Mixtures of Fe_2O_3 , spectroscopically pure, and chemically pure MnO were homogenized, pressed in the form of tablets for ten minutes at 10^3 kg.cm^{-2} and fired for three hours in air at 1100°C or higher, if necessary,

to obtain a single phase. After grinding and repressing, the tablets were subjected to a second heating varying from three to about forty hours in various mixtures of CO and CO_2 . The composition of these mixtures, which have a partial oxygen pressure in equilibrium with stoichiometric spinels, was obtained from Smiltenis (1952) for Fe_3O_4 and from Economos (1955) for MnFe_2O_4 . For other Mn/Fe ratios a linear interpolation or extrapolation in the $\log p_{\text{O}_2}$ versus T^{-1} plot was applied. Extrapolation gives satisfactory results up to $t = 1.5$.

With the compositions $t = 0.5$, $t = 1.0$ and $t = 1.5$ the second heating period was varied at a constant temperature of 1100°C. In the case of $t = 1.0$ different heating temperatures during a very long time were also applied.

All samples were checked metallographically and by means of a Debye—Scherrer photograph to see if they did consist of a single phase. Then they were pulverized to particle size from 2 to 15μ and analysed for chemical composition. For X-ray intensity measurements the powders were packed in a flat specimen holder. The samples with high iron content were used as tablets soon after they were taken from the furnace, because in pulverized form they might be oxidized in air. The tablets were mounted in a rotating specimen holder, as some of their grains were rather large and might disturb the particle statistics.

The intensities were measured with a Philips diffractometer with a proportional counter for both Cr $K\alpha$ and Fe $K\alpha$ radiation. Although the anomalous dispersion of Co $K\alpha$ radiation when scattered by Fe particles is high (Cooper, 1963), only two structure determinations have been performed with the use of Co $K\alpha$ and Fe $K\alpha$ radiation, because the peak/background ratio for Co $K\alpha$ radiation is unfavourable.

Only reflexions with rather strong intensities and undisturbed by other reflexions were selected. For the radiations used, these were: 111, 220, 311, 222, 400, 422, 440, 533 and 622.

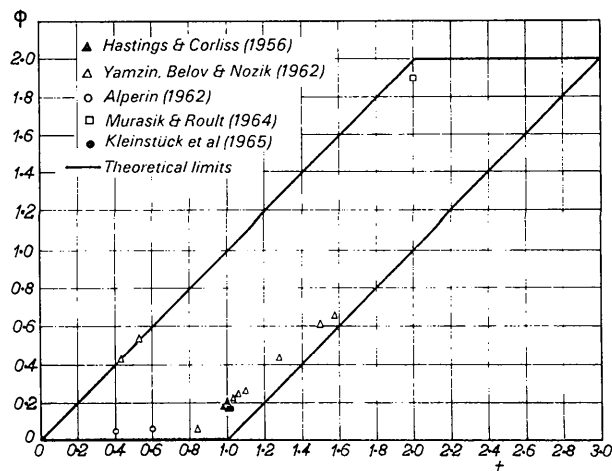


Fig. 1. Neutron diffraction of manganese-iron spinels: $\text{Mn}_{t-\varphi}\text{Fe}_{1-t+\varphi}(\text{Mn}_\varphi\text{Fe}_{2-\varphi})\text{O}_4$.

Distribution of vacancies

Bertaut (1950) pointed out that the intensity of the reflexions 220 and 422 depends only on the scattering power of the ions in tetrahedral sites and that of 400 and 444 mainly on the scattering power of ions in octahedral sites. For the determination of φ in the spinel $A_{1-\varphi}B_{\varphi}(A_{\varphi}B_{2-\varphi})O_4$, intensity ratios such as I_{220}/I_{400} are suitable, on the condition that the specimen is stoichiometric and that there is sufficient difference in the scattering power of A and B ions. This condition, however, is not fulfilled in our case.

But the method of Bertaut (1950) was used here to determine the place of the vacancies. Chemical analysis of the only sample with a non-negligible excess of oxygen resulted in the formula: $Mn_{1.02}Fe_{1.92}\square_{0.06}O_4$. The symbol \square means a cation vacancy. For Cr $K\alpha$ radiation the scattering factors of Mn and Fe ions are

nearly equal and the ratios I_{220}/I_{400} and I_{422}/I_{400} depend strongly on the place of the cation vacancies. Calculated and observed ratios are given in Table 2. Comparison shows that practically all cation vacancies are to be found in the octahedral sites.

The error may be about ± 0.01 in δ . In other samples the total number of vacancies nearly equalled this number, so that their place cannot be determined. It is assumed, however, that these vacancies too are to be found in octahedral sites.

The calculated intensities were obtained with scattering factors derived from SCF orbitals (Ibers, 1962). Corrections for anomalous dispersion were taken from literature in the case of Co $K\alpha$ (Cooper, 1963) and Cr $K\alpha$ (Dauben & Templeton, 1955) and are found by interpolation for Fe $K\alpha$ (Driessens, 1964*b*). The temperature factor is obtained from a $(\log I_{\text{obs}} - \log I_{\text{calc}})$ versus $(\sin \theta/\lambda)^2$ plot (see Table 4).

Table 2. Observed and calculated intensity ratios with Cr $K\alpha$ radiation for the substance $Mn_{1.02}Fe_{1.92}\square_{0.06}O_4$: (a) calculated for all vacancies in tetrahedral sites, (b) calculated for all vacancies in octahedral sites

| | Calculated | | Observed |
|-------------------|------------|-------|----------|
| | a | b | |
| I_{220}/I_{400} | 0.240 | 0.296 | 0.294 |
| I_{422}/I_{400} | 0.131 | 0.161 | 0.155 |

Distribution of the cations

The method used here to evaluate the distribution of cations was first applied by Skolnick, Kondo & Lavine (1958) in a slightly different form and is analogous to the method of isomorphous replacement. In the usual formula for the integrated intensity of a diffraction peak

Table 3. Results of X-ray diffraction on the structure of manganese iron spinels

$Mn_{1-\varphi}Fe_{1-t+\varphi}(Mn_{\varphi}Fe_{2-\varphi-\delta}\square_{\delta})O_4$; φ_1 and φ_2 were obtained by two independent determinations, $\bar{\varphi}$ is the mean value.

| No. | t | φ_1 | φ_2 | $\bar{\varphi}$ | $\sigma_{\bar{\varphi}}$ | δ | Preparation conditions |
|-----|------|-------------|-------------|-----------------|--------------------------|----------|-------------------------------|
| 1 | 0.25 | 0.12 | | 0.12 | ± 0.07 | 0.01 | 6h 1100°C CO/CO ₂ |
| 2 | 0.50 | 0.26 | 0.28 | 0.27 | ± 0.04 | 0.01 | 6h 1100°C CO/CO ₂ |
| 3 | 0.50 | 0.17 | 0.21 | 0.19 | ± 0.04 | 0.01 | 10h 1100°C CO/CO ₂ |
| 4 | 0.50 | 0.06 | 0.06 | 0.06 | ± 0.04 | 0.00 | 42h 1150°C CO/CO ₂ |
| 5 | 0.74 | 0.23 | | 0.23 | ± 0.06 | 0.01 | 6h 1100°C CO/CO ₂ |
| 6 | 1.02 | 0.44 | 0.39 | 0.42 | ± 0.04 | 0.06 | 3h 1100°C air |
| 7 | 1.04 | 0.33 | 0.34 | 0.33 | ± 0.04 | 0.00 | 6h 800°C CO/CO ₂ |
| 8 | 1.03 | 0.15 | 0.18 | 0.17 | ± 0.04 | 0.02 | 6h 1100°C CO/CO ₂ |
| 9 | 1.00 | 0.14 | 0.14 | 0.14 | ± 0.04 | 0.00 | 6h 1100°C CO/CO ₂ |
| 10* | 0.97 | 0.11 | 0.12 | 0.12 | ± 0.03 † | 0.01 | 30h 1400°C CO ₂ |
| 11* | 0.97 | 0.08 | 0.05 | 0.07 | ± 0.03 † | 0.01 | 46h 1000°C own pressure |
| 12 | 1.22 | 0.34 | | 0.34 | ± 0.06 | 0.02 | 6h 1100°C CO/CO ₂ |
| 13 | 1.47 | 0.66 | 0.60 | 0.63 | ± 0.04 | 0.02 | 6h 1100°C CO/CO ₂ |
| 14 | 1.48 | 0.52 | 0.51 | 0.52 | ± 0.04 | 0.01 | 16h 1300°C CO/CO ₂ |

* These samples were kindly submitted by Dr F. K. Lotgering.

† The structure was determined by using Fe $K\alpha$ and Co $K\alpha$ instead of Fe $K\alpha$ and Cr $K\alpha$.

Table 4. Data on structure and chemical constitution of $MnFe_2O_4$

a = cell dimension (Å).

B = Debye temperature coefficient (Å²).

β is defined by the formula $Mn_{1-\beta}Mn_{\beta}Fe_{2-\beta}O_4$.

φ is defined by the formula $Mn_{1-\varphi}Fe_{\varphi}(Mn_{\varphi}Fe_{2-\varphi})O_4$.

| No. | a | B | β | φ | Preparation conditions | | |
|-----|-------|-----|---------|-----------|------------------------|--------|--------------------|
| 6 | 8.505 | 1.2 | 0.18 | 0.42 | 3h | 1100°C | air |
| 7 | 8.508 | 0.9 | 0.15 | 0.33 | 6h | 800°C | CO/CO ₂ |
| 8 | 8.515 | 0.5 | 0.05 | 0.17 | 6h | 1100°C | CO/CO ₂ |
| 9 | 8.519 | 0.5 | 0.03 | 0.14 | 6h | 1100°C | CO/CO ₂ |
| 10 | 8.520 | — | < 0.025 | 0.12 | 30h | 1400°C | CO ₂ |
| 11 | 8.521 | — | < 0.025 | 0.07 | 46h | 1000°C | own pressure |

$$I_{hkl} = sFF^*p \exp[-2B(\sin \theta/\lambda)^2]A(\theta)Lp. \quad (5)$$

s is a constant of proportionality and Lp is the Lorentz and polarization factor. The ratio of diffracted intensity for the same reflexion using the wavelengths Fe $K\alpha$ and Cr $K\alpha$ is simply:

$$\frac{(I_{hkl})_{\text{Fe } K\alpha}}{(I_{hkl})_{\text{Cr } K\alpha}} = K \frac{(FF^* \cdot Lp)_{\text{Fe } K\alpha}}{(FF^* \cdot Lp)_{\text{Cr } K\alpha}}, \quad (6)$$

since the multiplicity factor and the temperature factor are the same for both wavelengths. A flat specimen was used so that the absorption path is independent of the Bragg angle; the thickness of the specimens was such that the transmitted part of the radiation was at most one per thousand. K is a constant having the same value for all reflexions, and includes the ratio of the absorption corrections and that of the constants of proportionality. The two FF^* factors are different for the two wavelengths.

The left hand side of equation (6) is an experimentally obtained quantity, while the value of the theoretical right hand side depends on the value of K and that of φ from formula (4). The X-ray intensities are relatively insensitive to the value of the oxygen parameter u , which therefore was taken from Table 1. By the method of least squares for the whole series of intensities the theoretical part of (6) was adjusted to the experimental part to obtain the most reliable values for K and φ . For details and numerical evaluation see Driessens (1964b).

K was about 1.2, nearly equal for all samples. The calculation of least squares was started with that value of K and with a value of φ taken from Table 1. Then, only two iterative calculations were necessary to obtain shifts ΔK and $\Delta\varphi$, corresponding to less than 25% of their respective standard deviations. Further calculations did not improve the result. For the usually low vacancy concentrations the value of φ did not depend on the place of the vacancies within the limits of error.

The values of φ obtained are shown in Table 3. The standard deviation by least squares σ_φ varied from ± 0.04 to ± 0.06 in agreement with the differences in two results φ_1 and φ_2 obtained for the same sample. The mean value $\bar{\varphi}$ may have an error of ± 0.04 , comparable to that of neutron diffraction data.

Nearly all products were fired at 1100°C. Fig. 2 gives the change in φ during firing. At $t=1.0$ and $t=1.5$ no change of φ occurred after 10 hours; at $t=0.5$ this was the case after about forty hours within the limits of error.

Products Nos. 7 and 8 were made from No. 6 by heating for three hours at 800 and 1100°C respectively. It follows that at higher temperature the decrease of φ is more rapid.

Samples MnFe_2O_4 quenched from 1400°C (No. 10) or annealed at about 1000°C (No. 11) have a difference in cation distribution.

Discussion

Single crystals made with the Verneuil method in a flame with high H_2/O_2 ratio to avoid over-oxidation (as applied by Yamzin *et al.*, 1962) were studied by us and contained an excess of oxygen. This may partly explain the deviating results obtained by Yamzin *et al.* for φ at $t=0.5$.

Our findings with respect to the Debye temperature coefficient of 0.5 \AA^2 are in agreement with those arrived at by Murasik & Roullet (1964) and by Nozik & Yamzin (1961). The high values found by Cervinka (1961, 1962) could not be reproduced.

In order to ascertain the mechanism accompanying the prolonged decrease of φ at a constant firing temperature (Fig. 2) we determined, at the composition MnFe_2O_4 , not only φ but also the cell dimension a and the Debye temperature coefficient B .

The combined phenomena given in Table 4, *i.e.* the decrease of φ , the increase of a , and the decrease of the Debye temperature coefficient, accompanied by a re-

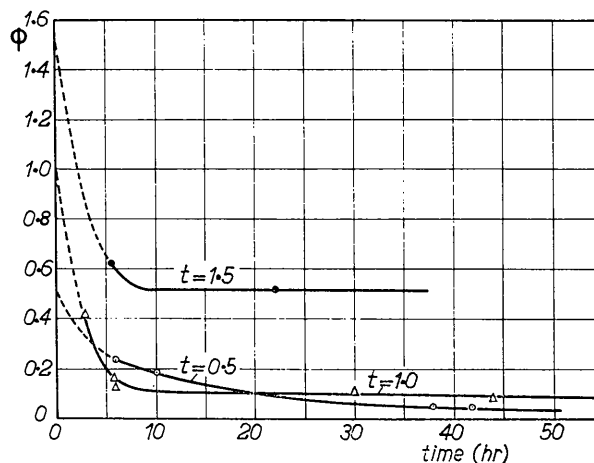


Fig. 2. The structure of manganese-iron spinels by X-rays: φ as a function of heating time (hours) at 1100°C for different values of t .

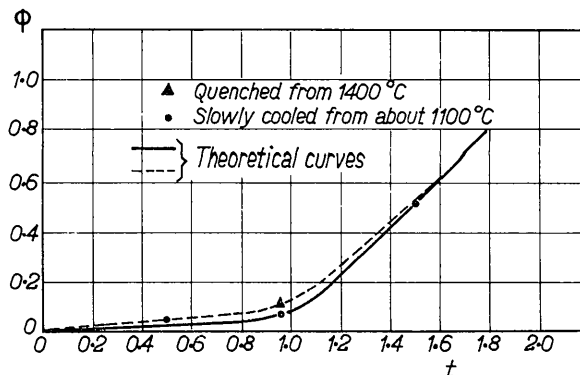
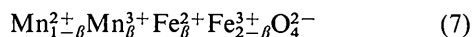


Fig. 3. The structure of manganese-iron spinels by X-rays: φ as a function of t for samples quenched from different temperatures after long heating periods.

markable decrease of line broadening. all suggest that in the reacting mixture of oxides the freshly formed particles with spinel structure have not attained the equilibrium distribution of cations. The formation of one oxygen matrix as a first step may, on prolonged heating, be followed by a process of continued counter diffusion of iron and manganese ions, perhaps accompanied by a transport of oxygen in the gas phase.

In a foregoing paper (Driessens, 1964a) a chemical method was described to determine the parameter β . With this number the overall composition of a product with formula MnFe_2O_4 can be more precisely described by the formula



The values of β found for the six samples are given in Table 4.

When there is any inhomogeneity in the sample with relation to the distribution of manganese and iron, then in regions with less manganese than in MnFe_2O_4 the presence of Fe(II) ions is all but certain (Lotgering, 1964), and in regions with more manganese, a number of Mn(III) ions is necessary for the sake of electro-neutrality. Both defects would, therefore, result in a non-zero value of β , increasing with the inhomogeneity. In accordance with this assumption the higher values of β in Table 4 were found for samples which were fired for the shortest times or at the lowest temperatures.

The equilibrium cation distribution is given in Fig. 3 as a function of composition at different temperatures. The values of φ for $t=1$ are somewhat smaller than is found in the case of neutron diffraction. This fact may be partly ascribed to our use of a controlled oxygen pressure and perhaps also to a more homogeneous temperature during heating. The apparent temperature independence of the structure of MnFe_2O_4 found by Hastings & Corliss (1956) may be the result of the opposing effects of overoxidation (increasing φ) and of cation counter diffusion (decreasing φ).

Hitherto the structure of intermediate spinels has always been determined on quenched samples. Since from these structures and their temperature dependence one can derive an empirical check on the theoretically calculated preference energies of the cations for the

different sites (McClure, 1957; Dunitz & Orgel, 1957) it seems worth while to determine the structures at high temperatures.

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