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Vacancy Distribution in $\gamma\text{-Fe}_2\text{O}_3$

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The vacancy distribution in $\gamma\text{-Fe}_2\text{O}_3$ is determined by the X-ray and neutron diffraction. The vacancies do not distribute uniformly through cation sites, but occupy the particular positions of the lattice on the average. We can observe a number of extra lines in the diffraction patterns of both the X-ray and neutron, which do not appear in the magnetite structure.

The intensity calculations were performed by estimating various kinds of vacancy contributions to the diffraction intensities. The existence of the extra lines ruled out the Verwey model in which vacancies distribute in disorder. Among the several models in which vacancies occupy the special positions statistically in cation sites, we could select the most probable one. The agreement between calculated and observed intensities was quite good.

1) Introduction

The ferrimagnetic $\gamma\text{-Fe}_2\text{O}_3$ is formed by the oxydation of the magnetite or dehydration of the lepidocrocite $\gamma\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$. The structure of this crystal was first studied by Hägg¹⁾ and Verwey²⁾ by means of X-ray powder method. They pointed out that it had the same inversed spinel structure as the magnetite and vacancies in the crystal distribute uniformly in the cation sites.

Haul and Schoon³⁾ and Chaudron⁴⁾ found a number of extra lines in X-ray patterns which cannot be assigned to the lines due to magnetite lattice. Braun⁵⁾ and Shinha and Shinha⁶⁾ suggested that light atoms like hydrogen were trapped in the vacancies of the cation sites.

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On the other hand, Néel⁷⁾ pointed out from the calculation of the saturation magnetization for $\gamma\text{-Fe}_2\text{O}_3$ that the vacancies distribute in the 16 (d) cation site of the spinel structure, which was confirmed by magnetic measurements.

Quite recently, Ferguson and Haas⁸⁾ studied this vacancy distribution of $\gamma\text{-Fe}_2\text{O}_3$ by neutron diffraction and supported the Verwey model; i.e. the uniform distribution of the vacancies. In our present studies, the powder data of X-ray and neutron diffraction were taken in detail. From these data, some vacancy distribution in special sites was concluded.

2) Specimen

The extensive studies have been performed to make a stoichiometric $\gamma\text{-Fe}_2\text{O}_3$. However,

the conditions to make a standard specimen is quite difficult to get. In this study we oxidized the magnetite in air at the temperature of about 400°C for a few hours. The chemical analysis showed the nearly stoichiometric composition of Fe_2O_3 .

The temperature change of the lattice constants by X-ray, the magnetic susceptibility by using a magnetic balance, the specific heat by differential calorimetry, and the weight increase in air by the thermo-balance have been measured in our laboratory. All these measurements showed that the transformation from magnetite to $\gamma\text{-Fe}_2\text{O}_3$ began at about 240°C.

When we heated the powder specimen of the magnetite which was synthesized, the Debye lines became broad at about 220°C. In this temperature range, the vacancies, we suppose, will move about in disorder to form the $\gamma\text{-Fe}_2\text{O}_3$, although the extra lines were not observed yet.

When the temperature increased above the 240°C, the extra lines which were typical for the $\gamma\text{-Fe}_2\text{O}_3$ phase appeared. This phase was stable between 240°C and 540°C. Above 540°C, the crystal was oxidized to be $\alpha\text{-Fe}_2\text{O}_3$. The effort to get the single crystal of $\gamma\text{-Fe}_2\text{O}_3$ was made, but it showed unsuccessful except the small needle crystal which is to be used for the electron microdiffraction.

3) X-ray diffraction analysis

The structure of $\gamma\text{-Fe}_2\text{O}_3$ is shown in Table I in which the $2\frac{2}{3}\text{Fe}$ ions are defect in the

Table I.

	8a	16d	32e
Fe_3O_4	$\frac{8\text{Fe}^{3+} + 8\text{Fe}^{2+} + 8\text{Fe}^{3+}}{24 \text{ Fe ions}}$		32O^{2-}
$\gamma\text{-Fe}_2\text{O}_3$	$21\frac{1}{3}\text{Fe}^{3+}$		32O^{2-}

unit lattice of the magnetite. The lattice constants of the magnetite and $\gamma\text{-Fe}_2\text{O}_3$ are 8.374Å and 8.320Å. The atomic coordinates are given in the following equivalent positions: $(0\ 0\ 0; 0\ \frac{1}{2}\ \frac{1}{2}; \frac{1}{2}\ 0\ \frac{1}{2}; \frac{1}{2}\ \frac{1}{2}\ 0) +$

8(a) $0\ 0\ 0; \frac{1}{4}\ \frac{1}{4}\ \frac{1}{4}$

16(d) $\frac{5}{8}\ \frac{5}{8}\ \frac{5}{8}; \frac{5}{8}\ \frac{5}{8}\ \frac{5}{8}; \frac{7}{8}\ \frac{7}{8}\ \frac{7}{8}; \frac{7}{8}\ \frac{7}{8}\ \frac{7}{8}$

32(e) $x\ x\ x; x\ \bar{x}\ \bar{x}; \frac{1}{4}-x, \frac{1}{4}-x, \frac{1}{4}-x; \frac{1}{4}-x, \frac{1}{4}+x, \frac{1}{4}+x;$

$$\bar{x}\ x\ \bar{x}; \bar{x}\ \bar{x}\ x; \frac{1}{4}+x, \frac{1}{4}-x, \frac{1}{4}+x; \frac{1}{4}+x, \frac{1}{4}+x, \frac{1}{4}-x.$$

The parameter x is equal to $\frac{3}{8}$ in the magnetite. We assumed the same value for x in $\gamma\text{-Fe}_2\text{O}_3$.

The powder pattern of X-ray diffraction of $\gamma\text{-Fe}_2\text{O}_3$ is shown in Fig. 1. The extra lines (110), (200), (210), (211), (311) and so on, which are assigned as cubic indices, are clearly shown in the figure in addition to the lines

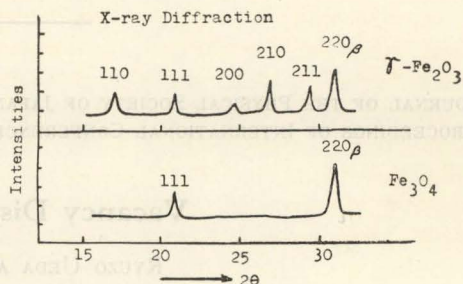


Fig. 1.

due to magnetite structure. The appearance of these forbidden reflections suggests us a kind of superstructure in which vacancies may be arranged in the cation sites regularly like in Fe_7S_8 which was analysed by Bertaut.⁹⁾ It will be quite difficult to determine such a space group of the low symmetry from the powder data. Thus, our plan to solve this structure is to extract $2\frac{2}{3}\text{Fe}$ ions regularly from the cation sites of the magnetite so as to give the observed X-ray intensities.

The structure factor $F_\gamma(hkl)$ of $\gamma\text{-Fe}_2\text{O}_3$ is expressed as follows:

$$F_\gamma(hkl) = F_M(hkl) - \sum_{j(\text{vacancy})} W_j \times f \left(\frac{\sin \theta}{\lambda} \right) e^{2\pi i (hx_j + ky_j + lz_j)}$$

where F_M is the structure factor of the magnetite and W_j is the probability that the vacancy exists in the j -th cation site. The random distribution of the vacancies at 8(a) or 8(a)+16(d) or 16(d) sites respectively is not a case corresponding to these extra lines. We can assume that the vacancies have an equal weight for the equivalent points in the lattice, and then $W_i \neq W_j$, $W_\alpha = W_\beta = \dots = W_\gamma = 0$, and $W_\lambda = W_\eta = W_\tau = \dots = W$.

If we define,

$$S(hkl) = \sum_{j(\text{vacancy})} e^{2\pi i (hx_j + ky_j + lz_j)},$$

the following conditions for the X-ray reflec-

tions are derived:

- (I) $S(100)=0$
- (II) $S(110), S(210), (211)$, and so on are not equal to zero.
- (III) $S(200)\neq 0$

If the vacancies occupy only the 8(a) sites, the conditions (I) and (II) are not satisfied. If both the sites 8(a) and 16(d) are occupied by the vacancies at the same time, the calculated intensities do not correspond to the observed ones. If we take into account various kinds of distributions of vacancies in 16(d) sites, which is not contradicting the general extinction rules above stated, we can select seven models from $2^{16}/4\times 2=2^{13}$ possibilities by the conditions (I) and (II). We carried out the intensity calculations and could see that $2^{\frac{2}{3}}$ vacancies

distributed in four particular sites of the 16(d) sites with an equal weight ($W=\frac{8}{3}\times\frac{1}{4}=\frac{2}{3}$). This is the only one in which the agreement between the observed and calculated intensities is the best (Table II). The coordinates of the four vacancies which distribute in the sites statistically in the cubic unit lattice are as follows in the 16(d) expressions,

$$\begin{matrix} \frac{1}{8} & \frac{1}{8} & \frac{5}{8} \\ \frac{5}{8} & \frac{3}{8} & \frac{3}{8} \end{matrix} \qquad \begin{matrix} \frac{1}{8} & \frac{5}{8} & \frac{1}{8} \\ \frac{5}{8} & \frac{7}{8} & \frac{7}{8} \end{matrix}$$

The space group $O_h^7-F_{d3m}$ of the magnetite lattice becomes T^4-P2_13 in $\gamma\text{-Fe}_2\text{O}_3$. The discrepancy factor $R=0.12$.

4) Neutron diffraction analysis

The neutron diffraction data for the powder specimen of $\gamma\text{-Fe}_2\text{O}_3$ were collected at the Brookhaven National Laboratory by one of the authors (R.U.). The wave length of the monochromatized beam was 1.05Å. The beam came out of the graphite reactor in which the thermal neutron flux was 2.5×10^{13} neutrons/cm².sec.

The powder sample was cased in an aluminium cylinder, the dimension of which was 18 mm in diameter and 75 mm in height. The scanning speed was 0.5/min. and scanning range in 2θ is about 50°.

We found the same kind of extra lines in the powder pattern of the neutron diffraction which was not detected by Ferguson and Haas (Fig. 2). These differences between F. and H.'s and ours are supposed to be due to the resolution power of the spectrometer used. In the case of the neutron scattering, the structure amplitude is expressed as

$$F^2=F_{\text{nuel}}^2+\frac{2}{3}F_{\text{mag}}^2,$$

where

Table II.

<i>hkl</i>	X-ray Diffraction		Neutron Diffraction	
	(<i>I</i> / <i>I</i> ₃₃₁) _{ob.}	(<i>I</i> / <i>I</i> ₃₃₁) _{cal.}	(<i>I</i> / <i>I</i> ₄₄₀) _{ob.}	(<i>I</i> / <i>I</i> ₄₄₀) _{cal.}
(110)	3	3.9	3	2.1
(111)	4	3.7	53	53.2
(200)	1.5	1.7	1	0.9
(210)	5	2.2	5	3.0
(211)	3	1.4	3	1.3
(220)	36	36.3	23	23.8
(311)	100	100	52	52.3
(222)	v.w.	0.3	12	12.3
(400)	22	17.2	45	46.2
(331)	—	0.8	8	10.9
(422)	12	11.7	12	13.4
(511)	30	29.7	33	29.3
(333)				
(440)	44	45.4	100	100

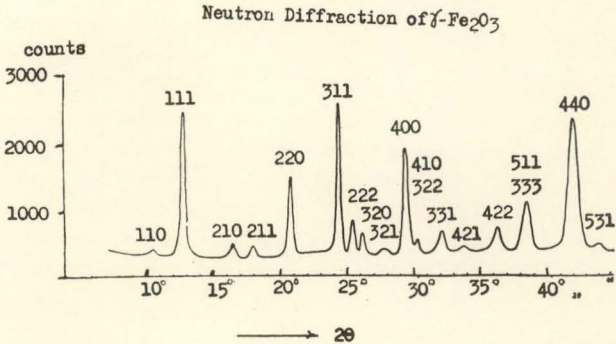


Fig. 2.

$$\begin{aligned}
 F_{\text{nuel}} &= \sum_{j(8a)} b_{\text{Fe}^{3+}} e^{2\pi i h r_j} + \sum_{j(16d)} b_{\text{Fe}^{3+}} e^{2\pi i h r_j} \\
 &= \sum_{j(32e)} b_{\text{O}^{2-}} e^{2\pi i h r_j} - \frac{2}{3} \sum_{j(\text{vacancy})} b_{\text{Fe}^{3+}} e^{2\pi i h r_j} \\
 F_{\text{mag}} &= - \sum_{j(8d)} p_{\text{Fe}^{3+}} e^{2\pi i h r_j} + \sum_{j(16)} p_{\text{Fe}^{3+}} e^{2\pi i h r_j} \\
 &\quad - \frac{2}{3} \sum_{j(\text{vacancy})} p_{\text{Fe}^{3+}} e^{2\pi i h r_j} .
 \end{aligned}$$

In the nuclear scattering, $b_{\text{Fe}^{3+}} = 0.95 \times 10^{-12}$ cm, $b_{\text{O}^{2-}} = 0.575 \times 10^{-12}$ cm. We used p values, magnetic scattering factors, which were given in the papers by Corliss *et al.* and Brockhouse *et al.* If we assume the Néel model for $\gamma\text{-Fe}_2\text{O}_3$ where the spins couple in the antiparallel way as shown in the table 3, the calculated intensities are expressed as follows:

$$I_{\text{cal}} \propto PL(\theta) |F(hkl)|^2 ,$$

where

P =multiplicity

$L(\theta)$ =Lorentz factor

$F(hkl)$ =structure factor.

The results are shown in Table III, which are calculated by using the same model obtained from the X-ray analysis. $R=0.10$. We carried

Table III.

	8a	16d
Fe_3O_4	8Fe^{3+} ↓	$8\text{Fe}^{3+} + 8\text{Fe}^{2+}$ ↑ ↑
$\gamma\text{-Fe}_2\text{O}_3$	8Fe^{3+} ↓	$8\text{Fe}^{3+} + 5\frac{1}{3}\text{Fe}^{3+}$ ↑ ↑
$\text{P}_{\text{Fe}^{3+}}$	—	+

ried out further calculations of the intensities, assuming that the hydrogens were trapped in the vacancy sites. The results became worse.

5) Conclusion

If we assume that the unit cell of $\gamma\text{-Fe}_2\text{O}_3$ has $2\frac{2}{3}$ vacancies, we can obtain the statistical distribution of vacancies in the particular four cation sites. This distribution gives a good agreement between the calculated and observed intensities. Both the uniform distribution of the vacancies proposed by Verwey and the model in which hydrogens are trapped in the vacancies have been ruled out.

Finally, the authors express their sincere thanks to Dr. B. C. Frazer of the Brookhaven National Laboratory for his kindness in giving one of them (R.U.) an opportunity to collect the neutron diffraction data.

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