To estimate the corresponding contribution to C' $= (c_{11}-c_{12})/2$, we consider a strain $\epsilon_z = e$, $\epsilon_x = \epsilon_y(1+e)^{-\frac{1}{2}}$ -1. In this case

$$\tfrac{1}{2}(c_{11}-c_{12})_F = \tfrac{1}{3}(\partial^2 W_F/\partial e^2)_0, \qquad (A13)$$

the differential again being evaluated at $e=0$. For this strain we have

$$(a/\pi)^2 p_n{}^2 = \mathbf{n}^2 + (n_1{}^2 + n_2{}^2 - 2n_3{}^2)e + 3n_3{}^2 e^2, \quad (A14)$$

which equation gives

$$\sum p_n/p = 4 + 2e^2; \quad \sum p_n{}^3/p^3 = 4 + 6e^2;$$
$$\sum p_n{}^5/p^5 = 4 + 10e^2. \qquad (A15)$$

Differentiating as before, we find from (A3) and (A4)

$$(1/K)\tfrac{1}{2}(c_{11}-c_{12})_F = -\tfrac{2}{3}\xi^4 + \tfrac{4}{3}\xi^2 - \tfrac{2}{3}, \qquad (A16)$$

which on substituting (A11) gives

$$(1/K)\tfrac{1}{2}(c_{11}-c_{12})_F = 0. \qquad (A17)$$

Since, to the approximation being considered, we have from (A10) that

$$\nu = \tfrac{2}{3} + 2\delta, \qquad (A18)$$

it follows that δ is proportional to the increase in electron density once overlap has occurred. Hence, from (A12) and (A17) it can be seen that there is an electronic contribution to c_{44} which is linear in solute concentration, but that there is no corresponding contribution to $\tfrac{1}{2}(c_{11}-c_{12})$.

Magnetic Structure and Vacancy Distribution in γ-Fe₂O₃ by Neutron Diffraction

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The neutron diffraction pattern of γ-Fe₂O₃ indicates a cubic defect spinel structure with vacancies located at octahedral lattice sites.

INTRODUCTION

X-RAY studies[1] show that the spinel structure of magnetite is maintained, during oxidation at low temperatures, until γ-Fe₂O₃ is formed. The observed change in the intensities of the x-ray diffraction pattern together with the change in density show that the increase in the oxygen concentration is produced by the appearance of vacant sites in the iron atom lattice of the spinel phase rather than by the addition of oxygen. Thus the suggested structure for this compound is a defect spinel, i.e., cation vacancies in an oxygen framework. If we symbolize magnetite as $Fe_8{}^{2+}Fe_{16}{}^{3+}$-$O_{32}{}^{2-}$ then γ-Fe₂O₃ may be written as $Fe_{21.33}{}^{3+}\square_{2.67}O_{32}{}^{2-}$, where $\square_{2.67}$ denotes 2.67 cation vacancies. Verwey[2] concluded that these vacancies were preferentially located at octahedral sites by a comparison of the x-ray intensities of the (111) reflection in γ-Fe₂O₃ and Fe₃O₄. This model is further supported by measurements of the average magnetic moment for γ-Fe₂O₃ by Henry and Boehm.[3] In this note we shall present additional evidence for the magnetic structure and vacancy distribution obtained by neutron diffraction.

EXPERIMENTAL PROCEDURE

Neutron diffraction patterns (see Fig. 1) of γ-Fe₂O₃ were obtained at room temperature using the N.R.L. "Swimming Pool Type" reactor as a source of neutrons. This reactor has a thermal flux of approximately 8×10^{11} neutrons/cm² sec in the vicinity of the beam port opening. Monochromatization ($\lambda = 1.11$ A) was achieved by (111) reflection from lead. An analysis of the γ-Fe₂O₃ specimen showed a 1.8% concentration of divalent iron and only trace amounts of other impurities.

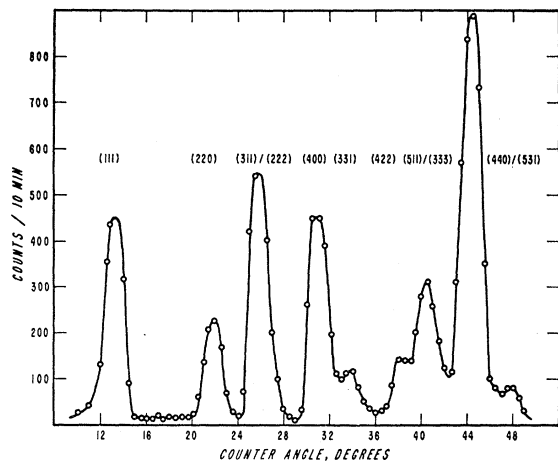FIG. 1. Neutron diffraction pattern of powdered γ-Fe₂O₃: cylindrical specimen, $\lambda = 1.111$ A.

[1] G. Hagg, Z. Krist. **B29**, 95 (1953).
[2] E. J. W. Verwey, Z. Krist. **91**, 65 (1935).
[3] W. E. Henry and M. J. Boehm, Phys. Rev. **101**, 1253 (1955).

TABLE I. Comparison between observed intensities for γ-Fe_2O_3 and those calculated for several models.[a]

Reflection	Tetrahedral vacancies			Calculated intensities Random vacancies			Octahedral vacancies			Observed intensity
	Nuclear	Magnetic	Total	Nuclear	Magnetic	Total	Nuclear	Magnetic	Total	
(111)	6.8	40.8	47.6	1.7	45.9	47.6	0.4	47.2	47.6	47.6
(220)	6.1	3.4	9.5	11.2	6.4	17.6	14.2	8.1	22.3	22.9
(311)	44.4	2.5	58.4	48.2	0.1	59.6	50.0	0.2	61.4	60.4
(222)	1.0	10.4		2.5	8.7		3.5	7.7		
(400)	49.6	8.4	58.0	39.1	9.1	48.2	34.2	9.1	43.3	44.3
(331)	3.4	7.6	11.0	0.8	8.6	9.4	0.2	8.9	9.1	10.2
(422)	4.3	1.0		7.8	1.9		10.0	2.3		
(333)	6.3	0.1	30.9	6.8	0.05	36.8	7.0	0.1	40.7	41.9
(511)	18.7	0.5		20.2	0.1		21.0	0.3		
(440)	95.0	0.7	100	97.0	0.5	100	97.4	0.1	100	100
(531)	1.9	2.4		0.4	2.1		0.1	2.4		

[a] All intensities relative to (440)+(531).

RESULTS

A comparison between the observed and calculated intensities is given in Table I where we have used an oxygen parameter, u, equal to $\frac{3}{8}$. For the reflections measured a change in the oxygen parameter from 0.375 to 0.380 resulted in a change of less than one percent in the calculated intensities. In the calculations the magnetic form factor for Fe^{3+} as determined by Brockhouse et al.[4] has been used. Corrections due to the Debye-Waller factor and absorption were found to be negligible. It has been assumed in the calculations that the magnetic moments are 85% oriented at room temperature. This assumption is based on measurements of the (111) reflection.

A similar analysis was carried out for magnetite and the relative intensities of the experimentally observed values and those calculated assuming a Néel model agree to within 2%.

DISCUSSION

The experimental data obtained by neutron diffraction support the Néel structural model for γ-Fe_2O_3 in which the Fe^{3+} ions, located at tetrahedral and octahedral positions in a defect spinel structure, are coupled antiferromagnetically. In addition, the data indicate that the vacant sites are largely restricted to octahedral

lattice points. This is best illustrated by noting the ratio of the intensities of the (400) to the (440) reflection. The assumption of a random distribution of vacancies gives for this ratio the value of 0.482. For a preferential distribution of vacancies over tetrahedral and octahedral sites we get 0.580 and 0.433, respectively. The experimentally observed ratio is 0.443.

The preferential distribution of vacancies at octahedral sites indicates that Fe^{3+} ions in γ-Fe_2O_3 are more strongly bound at the tetrahedral lattice points. This view is in agreement with that suggested by Verwey and Heilmann[5] for spinel structures. This ionic arrangement is most easily explained by the formation of tetrahedral covalent bonds as described by Goodenough and Loeb.[6]

ACKNOWLEDGMENTS

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[5] E. J. W. Verwey and E. L. Heilmann, J. Chem. Phys. 15, 174 (1948).

[6] J. B. Goodenough and A. L. Loeb, Phys. Rev. 98, 391 (1955).