ELECTRON-DIFFRACTION STUDY OF Fe$_{3}$O$_{4}$

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ELECTRON-DIFFRACTION STUDY OF Fe_3O_4

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As magnetic ([1]) and electrical ([2,3]) measurements, as well as neutron-diffraction studies ([4,5]), have shown, magnetite Fe_3O_4 has the structure of an "inverse" spinel ([6,2,3]). In this structure, 8 tetrahedral voids in the cubic close packing of oxygen ions are occupied by 8 trivalent iron ions, and in 16 octahedral voids 8 divalent iron ions and the remaining 8 Fe^{3+} ions are distributed in a disordered manner.

On the basis of such a structural model, the remarkable electrical ([2,3,7–9]) and magnetic ([1,10]) properties of magnetite are well explained, owing to which it is a valuable technical material.

The position of oxygen in the spinel structure is fixed by one parameter u, which in the case of an ideal spinel is equal to 0.375. In real spinel structures usually $u > 0.375$. For example, for magnesium ferrite $MgFe_2O_4$, $u = 0.381$ was found ([11,12]).

No special studies to determine the parameter u in the structure of Fe_3O_4 had been carried out. In an x-ray study ([13]) devoted to determining the scattering powers of oxygen and iron for x-rays, in which the author proceeded from the structure of a "normal" spinel for Fe_3O_4, the value of the parameter $u = 0.379 \pm 0.001$ was incidentally established. However, for a number of reasons this determination cannot be considered reliable. In work ([7]), the value 0.379 was obtained for the parameter u by calculation using a very approximate method of the minimum of the total lattice potential.

In the present work we set ourselves the task of refining the structure of Fe_3O_4 by an electron-diffraction study of thin layers.

The Fe_3O_4 specimens were prepared from iron films, obtained by evaporation of the metal in vacuum and deposition on a NaCl cleavage, by annealing these films in high vacuum for 4 hours at a temperature of 300–350° and cooling to room temperature in air.

The electron diffraction patterns obtained by us from three specimens corresponded to diffraction from a polycrystal. Calculation made it possible to interpret the resulting pattern as diffraction from Fe_3O_4. The lattice period, determined by us using NaCl lines as a standard, was 8.40 ± 0.01 Å. The intensities of the first 46 lines were measured by microphotometry of electron diffraction patterns with multiple exposures, followed by construction of blackening curves. The intensities of 28 more distant lines were measured from one electron diffraction pattern by photometry of it and application of the formula

$$I \sim \log \frac{I_{\text{background}}}{I_{\max}}.$$

Thus intensities were obtained for 74 lines, corresponding to 153 reflections, owing to the regular merging on electron diffraction patterns from a polycrystal of reflections with one and the same interplanar···

distance d_{hkl}. To determine the intensities of such reflections, their total experimental intensity was divided in proportion to the theoretical intensities. The latter, as well as Φ_{theor}, were calculated for the space group O_h^7—$Fd3m$ with the origin at the center of symmetry, for the following atomic positions: 8FeI$b(a)$; 16FeII$b(d)$ and 32O$b(e)$. In this case the oxygen parameter $u = 0.25$, which corresponds to $u = 0.375$ when the origin is chosen at FeI. The atomic factors for Fe and O were taken from the new tables f_{el} (^{14}). At $u = 0.25$, oxygen contributes to the structural amplitudes of those reflections for which $h + k = 4n$; $k + l = 4n$; $l + h = 4n$. The remaining reflections are formed only by scattering from iron atoms*.

Φ_{theor}, multiplied by the temperature factor ($B_{\text{Fe}} = 0.3$ Å^2, $B_{\text{O}} = 0.5$ Å^2), was compared with $\Phi_{\exp}$ for each of the three specimens separately. It turned out that for the intensities of two specimens it was necessary to introduce a dynamical correction, while for one specimen the scattering could be considered purely kinematical. Comparison of Φ_{theor} with the values of $\Phi_{\exp}$ averaged after introducing the dynamical correction (^{16}) gave a discrepancy factor $R = 18.5\%$.

For further study a specimen with kinematical scattering was selected, which ensured a more objective determination of the parameter u than for specimens in which a dynamical correction was introduced.

To refine the oxygen parameter by minimizing the discrepancy factor from reflections whose intensities were determined by the microphotometric method using multiple exposures, 16 reflections with $h + k = 4n$, $k + l = 4n$; $l + h = 4n$ were selected. The minimum factor $R = 11.7\%$ was obtained for $u = 0.263$. At this position oxygen already contributes to all *hkl* reflections. Using this parameter, we determined the distribution of cations in the Fe_3O_4 lattice by comparing $\Phi_{\exp}$ with Φ_{theor} for two models, normal and "inverse" spinel.

$$
\begin{aligned}
&1)\qquad h+k=4n, \qquad k+l=4n, \qquad l+h=4n+2;\\
&A = 32\{\cos 2\pi lz \cos \pi(h+k)(x+y) \cos \pi(h-k)(x-y)+\\
&\quad + \sin 2\pi lz \sin \pi(h-k)(x+y) \cos \pi(h+k)(x-y)+\\
&\quad + \cos 2\pi lx \cos \pi(h+k)(y+z) \cos \pi(h-k)(y-z)+\\
&\quad + \sin 2\pi lx \sin \pi(h-k)(y+z) \cos \pi(h+k)(y-z)+\\
&\quad + \cos 2\pi ly \cos \pi(h+k)(z+x) \cos \pi(h-k)(z-x)+\\
&\quad + \sin 2\pi ly \sin \pi(h-k)(z+x) \cos \pi(h+x)(z-x)\};\\
&B = 0; \qquad F_{hkl} = F_{\bar{h}\bar{k}\bar{l}} = F_{\bar{h}kl} = -F_{h\bar{k}l} = F_{hk\bar{l}}.
\end{aligned}
$$

$$
\begin{aligned}
&2)\qquad h+k=4n+2, \qquad k+l=4n, \qquad l+h=4n;\\
&\qquad h \to k \to l \to h \text{ in } 1).
\end{aligned}
$$

$$
\begin{aligned}
&3)\qquad h+k=4n, \qquad k+l=4n+2, \qquad l+h=4n;\\
&\qquad h \to l \to k \to h \text{ in } 1).
\end{aligned}
$$

To simplify the calculations, not all reflections were taken, but only the first 20 reflections; the scattering factors f_{el} for the ions Fe^{2+}, Fe^{3+}, and O^{2-} were calculated by interpolation from X-ray data. Allowance for the ionic state affected only Φ_{theor} of the first two reflections: (111) and (220), with $\sin\theta/\lambda$ equal to 0.103 and 0.169 Å^{-1}. For the normal spinel structure a factor $R = 12.6\%$ was obtained, and for the "inverse" one $R = 11.2\%$. Compar— of Φ_{theor}, calculated for all 153 reflections ($\sin\theta/\lambda$ from 0.103 to 1.136 Å^{-1}) using the model of an "inverse" spinel and the parameter $u = 0.263$, with Φ_{exp} gave $R = 15.7\%$, while the coinciding experimental reflections were separated in accordance with the new Φ_{theor}. From Φ_{exp} a one-dimensional section of the three-dimensional potential series along the direction [111] was constructed. In the section of the Φ-series, oxygen shifted from the position $u = 0.263$ to the position $u = 0.258$.

Using this value of u, new Φ_{theor} were calculated, and the experimental ones were separated with respect to these theoretical values. The discrepancy factor was $R = 15.4\%$.

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* In calculating the structural amplitudes for three groups of reflections: 1) $h+k=4n$, $k+l=4n$, $l+h=4n+2$; 2) $h+k=4n+2$, $k+l=4n$, $l+h=4n$; 3) $h+k=4n$, $k+l=4n+2$, $l+h=4n$, we found that the structure factors and the relations between them (connections) for these groups of reflections in the new edition of the International Tables (15) are given incorrectly. We have derived the correct formulas for the structure factors and the connections for these groups of reflections from the general formula for the structure factor.

Fig. 1. One-dimensional section of the Φ-series along the direction [111] in the structure of Fe_3O_4

Figure 1: Fig. 1. One-dimensional section of the Φ-series along the direction [111] in the structure of Fe_3O_4

In the section of the Φ-series along [111] (Fig. 1), constructed from these Φ_{exp}, the position of oxygen did not change. Thus, we obtained the oxygen parameter $u = 0.258 \pm 0.002$.

Fig. 1. One-dimensional section of the Φ-series along the direction [111] in the structure of Fe_3O_4

The peak heights in the synthesis were normalized to volts. The small difference in the heights of the maxima of the potentials of oxygen and iron at $^1/_8\,^1/_8\,^1/_8$ (tetrahedron) 1120 V and at $^1/_2\,^1/_2\,^1/_2$ (octahedron) 1062 V once again confirms the "inverse" spinel structure of magnetite.

The ratio of the heights of the maxima of the potentials of oxygen and iron (taking into account $\varphi(000)$), equal here to 452 V/1150 V = 0.393, may be compared (17) with the ratio $(Z_{\text{O}}/Z_{\text{Fe}})\,0.75 = 0.414$. Thus, a slight decrease is observed in the scattering power of oxygen relative to iron, which confirms the ionic state of oxygen and iron in Fe_3O_4.

It was further of interest to calculate the distance between O^{2-} and the nearest iron ions in the tetrahedral and octahedral positions and to compare them with the sums of the ionic radii. The ionic radii according to Goldschmidt (18) for coordination number 6: $r_{\text{Fe}^{2+}} = 0.83$ Å; $r_{\text{Fe}^{3+}} = 0.67$ Å, $r_{\text{O}^{2-}} = 1.32$ Å give the distances

$$r_{\text{Fe}^{2+}} + r_{\text{O}^{2-}} = 2.15\ \text{Å}, \qquad r_{\text{Fe}^{3+}} + r_{\text{O}^{2-}} = 1.99\ \text{Å}, \qquad {}^1/_2(r_{\text{Fe}^{2+}} + r_{\text{Fe}^{3+}}) = 2.07\ \text{Å}.$$

A reduction of the ionic radii for coordination number 4 by approximately 4% leads to the distances:

$$r'_{\text{Fe}^{2+}} + r'_{\text{O}^{2-}} = 2.06\ \text{Å}, \qquad r'_{\text{Fe}^{3+}} + r'_{\text{O}^{2-}} = 1.91\ \text{Å}.$$

The experimental distances calculated for the parameter $u = 0.258$ are as follows: oxygen—center of octahedron 2.03 Å, oxygen—center of tetrahedron 1.935 Å, i.e., in good agreement with the indicated sums.

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Note: Figure translations are in progress. See original paper for figures.