REFINEMENT OF THE HEMATITE STRUCTURE

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Abstract

Three-dimensional diffraction intensities were collected from a spherical single crystal
of hematite, α-Fe_2O_3, with a Buerger single-crystal diffractometer. The structure has been
refined with a least-squares program, and the final structure gave an R-factor of 3.65
per cent. The structure model of Pauling and Hendricks has been confirmed with essentially
no change in the iron and approximately 5 per cent change in the oxygen coordinates.
Selected interatomic distances and angles were calculated as were anisotropic temperature
factors.

Introduction

The Bureau of Mines is conducting research into the behavior of iron
oxides during reduction and oxidation reactions. Hematite reduction
studies involving atomic positions and vacancies require that the crystal
structure be known more accurately than is the presently accepted struc-
ture.

Pauling and Hendricks (1925) determined the crystal structure of
hematite, α-Fe_2O_3, without using absorption and Lorentz-polarization
corrections and atomic scattering factors, which were not well understood
at that time. The structure postulated by them was re-examined before
proceeding on the current refinement study of hematite. Initial structure
factor calculations for certain reflections, using coordinates of Pauling
and Hendricks, showed some deviation from observed intensities. This
deviation suggested that their structure was essentially correct and
needed only a refinement.

Procedure and Results

A small sphere of approximately 0.3-mm diameter was prepared from a
single crystal of Elba hematite using a modified version of W. L. Bond's
(1951) sphere-grinding device. The spherical crystal was oriented with a
precession camera, several upper-level photographs were taken, and the
space group $R\bar{3}c$ of Pauling and Hendricks was confirmed. The equi-
inclination settings for the M. J. Buerger (1960) single-crystal diffrac-
tometer[1] were calculated with C. T. Prewitt's (1960) program using an
IBM 7090 computer. The three-dimensional integrated intensities were
collected at the University of Minnesota using an automated, equi-

[1] Reference to specific makes or models of equipment is made to facilitate understand-
ing and does not imply endorsement of such makes or models by the Bureau of Mines.

inclination, single-crystal diffractometer with a proportional counter, using constant-time counting and a digital printer. $CuK\alpha$ radiation was used because $FeK\alpha$ radiation gave low intensities and allowed a smaller number of reflections due to instrument mechanical limits. The problem of fluorescence was considered to be less important than the advantages of using $CuK\alpha$ radiation. Most of the fluorescent radiation was discriminated by appropriate setting of the pulse height analyzer.

There are 60 independent diffracting planes for hematite in reciprocal lattice levels zero through fifteen normal to the c^*-axis, the rotation axis. Instrument mechanical limitations prevented measurement of intensities from nine such planes. Intensities were collected from all symmetry-equivalent diffractions of the remaining 51 planes of which 50 were observed. The unobserved plane was assigned an average intensity of one-half the minimum observed value. For each of the 50 observed planes, the symmetry-equivalent diffraction intensities were averaged. These averaged intensities were then corrected for Lorentz-polarization and absorption, using absorption factors calculated for spherical crystals by Evans and Ekstein (1952).

Part of the crystal (BMC-283 A) used for refinement was analyzed quantitatively with the Bureau's electron probe at the College Park Metallurgy Research Center, College Park, Maryland, for four elements that could substitute (Newnham and de Haan, 1962) for Fe^{3+} in the hematite structure. Small amounts of each element were found uniformly distributed across the fragment based on two determinations at each of ten different sites. The average concentration of each element in the crystal, expressed in weight per cent, was: $Al = 1.0 \pm 0.2$, $Ti = 0.10 \pm 0.02$, $Cr = 0.021 \pm 0.005$, and $V < 0.004$. It is suggested that these four elements substitute for Fe^{3+} in these proportions within the crystal used for refinement, but their effect on the atomic scattering power of iron is considered negligible. In calculating atomic scattering factors, both iron and oxygen were assumed half-ionic.

The rhombohedral atomic coordinates of the hematite structure model proposed by Pauling and Hendricks were converted to hexagonal coordinates and their unit-cell origin was shifted to a center of symmetry. The hexagonal coordinates were used as initial parameters in the refinement in which two positional factors, six anisotropic temperature factors, and a scale factor were allowed to vary. The 51 diffraction amplitudes were equally weighted. The least-squares refinement with anomalous dispersion corrections was carried out using the Control Data (C. D.) 1604 computer at the University of Minnesota and L. W. Finger's program which minimizes the function

TABLE I. ATOMIC COORDINATES OF THE HEMATITE STRUCTURE

Hexagonal unit cell:	$a=5.038\pm0.002$ A[1] $c=13.772\pm.012$ A[1]		$c/a=2.733\pm0.015$ Z=6	

Space Group = $R\bar{3}c$; origin at i: iron- 0, 0, z; oxygen- x, 0, $\frac{1}{4}$

Original (Pauling and Hendricks, 1925)	Improved (Shirane *et al.*, 1959)	Refined (this study)	
		Coordinates	Std. dev.[2]
z=0.355 x= .292	— x=0.300[3]	z=0.3553 x= .3059	0.00001 .0001

[1] Cell dimensions from this study (powder films XF-23B and XF-106).

[2] (σ) Standard deviation calculated by formula (6) of *Inter. Tables for X-ray Crystallography*, Vol. II, page 330, Section 6.4.3.1.

[3] Oxygen parameter adjusted to give best agreement for neutron diffraction intensities.

$$r = \frac{\Sigma w(F_0{}^2 - F_c{}^2)^2}{\Sigma w F_o{}^4}.$$

After four cycles of refinement, the discrepancy factor,

$$R = \frac{\Sigma\|F_o| - |F_c\|}{\Sigma|F_o|},$$

was 7.16 per cent. An additional three refinement cycles were run by L. W. Finger using only 49 reflections; 300 and $1\bar{1}2$ were omitted because of the low precision of their intensity measurement. A weighting scheme similar to that of Hughes (1941) was applied. After this refinement, the discrepancy factor converged to 3.65 per cent. The atomic coordinates of hematite are listed in Table I for the hexagonal unit cell as follows: Pauling and Hendricks' (1925) original parameters; Shirane *et al.*'s (1959) improved oxygen parameter; and the refined parameters from this study. Table II lists the anisotropic temperature factors which were obtained from the formula: exp $\{-\Sigma_i\Sigma_j h_i h_j \beta_{ij}\}$. From these, the refined equivalent isotropic temperature factor of iron is 0.48 and of oxygen is 0.49, using the method of Hamilton (1959). A list of structure factors,

TABLE II. FINAL ANISOTROPIC TEMPERATURE COEFFICIENTS ($\times 10^3$)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	8.0 ± 0.1	8.0 ± 0.1	0.29 ± 0.02	4.0 ± 0.1	0	0
O	6.8 ± 0.2	8.3 ± 0.3	0.46 ± 0.02	4.2 ± 0.1	0.58 ± 0.04	1.2 ± 0.1

calculated from the final parameters and observed, is available from the authors on request.

Unit-cell dimensions (Table I) were determined from powder-pattern data using a program written by Dr. J. D. Britton, Chemistry Department, University of Minnesota, for the C. D. 1604 computer. This program makes a least-squares refinement of cell dimensions by comparing

TABLE III. SELECTED INTERATOMIC DISTANCES AND ANGLES IN HEMATITE

Within one octahedron			Within one octahedral layer			Between octahedral layers		
Atoms	Interatomic distance, Å	Std. dev.	Atoms	Interatomic distance, Å	Std. dev.	Atoms	Interatomic distance, Å	Std. dev.
Fe_1-O_1	1.945 (a)[1]	0.0010	Fe_1-Fe_2	2.971 (g)	0.0015	Fe_1-Fe_5	3.364 (h)	0.0017
Fe_1-O_4	2.116 (b)	.0012	Fe_1-O_7	3.398	.0017	Fe_2-Fe_5	2.900 (i)	.0026
O_1 O_2	3.035 (c)	.0016	Fe_1-O_8	4.394	.0022	Fe_2-Fe_6	3.706 (j)	.0020
O_1-O_4	2.888 (d)	.0019	Fe_1-O_9	4.701	.0023	Fe_6-Fe_7	3.986	.0035
O_1-O_5	2.775 (e)	.0019	Fe_1-O_{10}	3.798	.0018	Fe_1-O_{12}	3.596	.0026
O_1-O_6	4.013	.0021	O_1-O_7	3.035	.0016	Fe_2-O_{11}	4.136	.0032
O_4-O_5	2.669 (f)	.0014	O_5-O_9	5.701	.0029	O_4-O_{12}	4.596	.0041

Atoms	Angle, deg.-min.	Atoms	Angle, deg.-min.	Atoms	Angle, deg.-min.
O_1-Fe_1-O_2	102-34 (k)	Fe_2-Fe_1-Fe_4	115-58	Fe_5-Fe_1-Fe_6	49-13
O_1-Fe_1-O_4	90-33	Fe_1-O_1-Fe_2	50-35	Fe_6-Fe_1-Fe_7	68-26
O_1-Fe_1-O_5	86-06 (l)	Fe_1-O_3-Fe_2	93-57 (o)	Fe_1-Fe_2-Fe_6	59-18
O_1-Fe_1-O_6	162-21 (m)	Fe_1-O_6-Fe_2	59-58	Fe_1-Fe_2-Fe_7	71-18
O_4-Fe_1-O_5	78-12 (n)	O_1-Fe_2-O_6	67-31	Fe_1-O_1-Fe_6	119-43 (p)
Fe_1-O_1-O_2	38-43	O_3-O_1-O_7	52-10	Fe_1-O_1-Fe_7	77-42
Fe_1-O_1-O_4	47-07	O_4-O_1-O_7	58-18	Fe_1-O_3-Fe_6	72-20
Fe_1-O_1-O_5	49-32	O_6-O_1-O_7	85-06	Fe_1-O_3-Fe_7	52-37
Fe_1-O_1-O_6	9-12	O_1-O_5-O_7	63-55	Fe_6-O_4-Fe_7	86-37 (q)
Fe_1-O_5-O_6	50-54	O_2-O_5-O_8	176-17	Fe_2-O_7-Fe_6	131-41 (r)

[1] The corresponding unrefined interatomic distances and bond angles given by Newnham and de Haan (1962) are:

Distances:

(a) 1.96, (b) 2.09, (c) 3.06, (d) 2.89, (e) 2.76, (f) 2.62, (g) 2.97, (h) 3.37, (i) 2.89, (j) 3.70, all in Angströms.

Bond Angles:

(k) 102.7, (l) 85.9, (m) 161.5, (n) 77.5, (o) 94.1, (p) 118.2, (q) 87.4, (r) 132.1, all in degrees.

$Q_{calc.}$ with $Q_{obs.}$ and adjusting the approximately known cell dimensions to minimize the mean square error between $Q_{calc.}$ and $Q_{obs.}$.

Refined unit cell dimensions were used to calculate interatomic distances and angles for the refined structure. Standard deviations of interatomic distances were calculated using the full matrices from the least-squares refinements of both the atomic and the unit-cell parameters. Selected interatomic distances and angles are given in Table III. Identification of the atoms listed in this table can be obtained with the aid of

Fig. 2. Some of the interatomic distances and angles of the unrefined hematite structure given by Newnham and de Haan (1962) are also quoted in the footnotes of Table III for comparison.

DISCUSSION OF THE STRUCTURE

The hematite structure can be described in mineralogical terms as being composed of gibbsite-type octahedral layers stacked six-high normal to the c-axis. Subsequent octahedral layers are related to each other by a combination of (1) inversion of all octahedra through the centers of their horizontal faces and (2) by a 60° rotation of the layer about any 3-
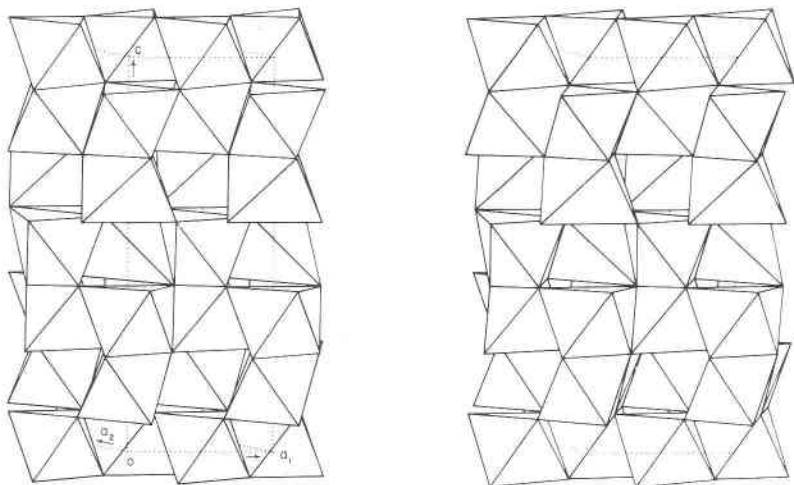
FIG. 1. Stereoscopic drawing of the hematite structure with hexagonal unit cell outlined.

fold vertical axis. The crystal structure of hematite is shown in a stereoscopic drawing in Fig. 1, with the hexagonal unit cell outlined.

The refinement confirms the structure model of hematite proposed by Pauling and Hendricks with essentially no change in the iron and approximately a 5% change in the oxygen atomic coordinates. As a consequence of this change in the atomic coordinates, the FeO_6 octahedra are even more distorted than in the original structure model. In Fig. 2 each octahedron contains 3 shared and 3 unshared edges not in the basal plane; and one shared plus one unshared face in the basal and top planes. The oxygen-oxygen distance of a shared edge (*e.g.*, Fig. 2, $O_1-O_5 = 2.775$ Å) is considerably shorter than that of an unshared edge (*e.g.*, $O_1-O_4 = 2.888$ Å). The oxygen-oxygen distances in the shared basal face are also considerably shorter (*e.g.*, $O_4-O_5 = 2.669$ Å) than the corresponding distance in the unshared basal face (*e.g.*, $O_1-O_2 = 3.035$ Å). Similarly the iron atoms
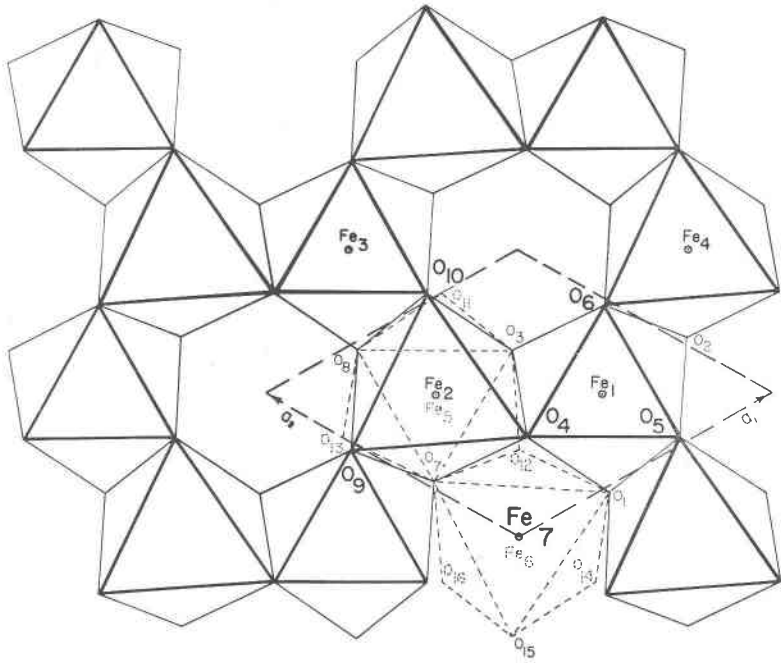
FIG. 2. Illustration of the octahedral layers in the hematite structure with hexagonal unit cell outlined. Note, in bold outline, and all in one basal plane, the alternating larger and smaller octahedral faces resulting from varying O–O distances. Dashed octahedra are in next lower layer; Fe_7, in next higher layer. Size of atomic symbol denotes its relative elevation along the c-direction (normal to the page); the largest symbol is the highest.

are closer to the oxygens of the unshared faces, 1.945 Å, than to the oxygens of the shared faces, 2.116 Å. This observation supports the expected nature of distortion caused by local ionic attraction and repulsion.

The thermal ellipsoid parameters for iron and oxygen are presented in

TABLE IV. THERMAL ELLIPSOIDS: r.m.s. DISPLACEMENTS AND ORIENTATIONS[1]

Atom	r	$\mu(r)$	$\varphi(a_1)$	$\varphi(a_2)$	$\varphi(c)$
Fe	1	0.088 ± 0.001 Å	0°	120°	90°
	2	.088 ± .001	90	30	90
	3	.053 ± .001	90	90	0
O	1	.047 ± .002	90	117 ± 1°	31 ± 1°
	2	.078 ± .002	0	120	90
	3	.101 ± .002	90	42 ± 1°	59 ± 1°

[1] $\mu(r)$ is the displacement along principal axis r; the φ's are the angles between r and the crystallographic axes.

Table IV. The iron ellipsoid has the shape of an oblate spheroid with its unique, shorter axis along the crystallographic c-axis. The oxygen ellipsoid is triaxial with its intermediate axis fixed along the crystallographic a_1-axis. The shortest vibrational axis is directed toward an adjacent oxygen approximately along an octahedral edge at an angle close to 30° from the c-axis. The longest axis is directed toward the vacant octahedral site in the structure.

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