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# REFINEMENT OF HEMATITE CRYSTAL STRUCTURE

UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

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By R. L. Blake, Tibor Zoltai, R. E. Hessevick,
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# REFINEMENT OF HEMATITE CRYSTAL STRUCTURE

by

R. L. Blake,[1] Tibor Zoltai,[2] R. E. Hessevick,[3]
and Larry W. Finger[4]

## ABSTRACT

The crystal structure of hematite, $\alpha$-$Fe_2O_3$, has been refined as part of a continuing study of the behavior of phases in the Fe-O system during reduction and oxidation. Three-dimensional diffraction intensities were collected on two spherical single crystals of hematite with a semiautomated Buerger single-crystal diffractometer. The first crystal refined was a natural Elba hematite with minor impurities. The other, a synthetic crystal, was refined at the request of Mössbauer spectroscopy investigators concerned with impurities in the natural crystal. The structure has been refined with a least-squares program and the final structure for the natural crystal irradiated with CuK$\alpha$-radiation gave a discrepancy factor (R) of 3.65 percent using 49 unrejected reflections of the 51 measured. For the synthetic crystal, using MoK$\alpha$-radiation, the discrepancy factor converged to 2.8 percent using 95 unrejected reflections and was 3.3 percent for all 109 reflections.

The structure model of Pauling and Hendricks has been confirmed with essentially no change in the iron coordinates and approximately a 5-percent 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 phases in the Fe-O system during reduction and oxidation reactions. Basic understanding of the reduction of hematite to magnetite or oxidation of magnetite to

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hematite must consider the atomic arrangement or crystal structure of each phase and the rearrangement of atoms resulting from the reaction. Also, any change or disruption of existing interatomic bonds, or any formation of new bonds, involves energy changes that would be important in kinetic studies. Examination of the long-accepted crystal structure of hematite indicated that a refinement was needed for reasons outlined below.

The Bureau of Mines refined the hematite structure using a natural crystal from the Island of Elba. The published refinement (2)[5] was of unexpected benefit to investigators in the field of Mössbauer spectroscopy. A. H. Muir, Jr., of North American Rockwell Corporation, principal editor of the Mössbauer Effect Data Index (16), had been seeking a more reliable value for the nuclear quadrupole moment for $Fe^{57}$, a factor used in about one-third of all publications on Mössbauer studies. Determination of this factor based on $\alpha$-$Fe_2O_3$ data makes use of the electric field gradient at the iron site; hence, our refined atom positions were of interest to this study. Dr. Muir requested several of our natural Elba single crystals for Mössbauer Effect (ME) study. These crystals showed somewhat broadened lines and an apparent quadrupole interaction that was about a factor of three times smaller than that of pure synthetic crystals. The impurity content of our natural crystals, the large ME differences, and the sensitivity of electric field gradient calculations to even slight variation in structural parameters (15c), prompted Dr. Muir to ask if we would repeat the structure refinement on a pure synthetic $\alpha$-$Fe_2O_3$ single crystal furnished by G. P. Espinosa of North American Rockwell Corp. This paper presents results of the Bureau's hematite structure refinement using both the natural and the synthetic crystals. The structure parameters resulting were used by Muir and colleagues (1) to determine the nuclear quadrupole moment of $Fe^{57}$.

## Known Structure

The crystal structure of hematite ($\alpha$-$Fe_2O_3$) was determined in 1925 by L. Pauling and S. B. Hendricks (18) from natural crystals using Laue and spectral photographs. At this early date in crystal structure determinations, the absorption and Lorentz-polarization corrections and the atomic scattering factors were not well understood. It is not surprising, therefore, that Pauling and Hendricks determined the hematite structure without using these corrections. Their model (fig. 1) consists of a rhombohedral unit cell containing four iron and six oxygen atoms, or two $Fe_2O_3$ formula units. Each iron atom is surrounded by six oxygen atoms, one at each corner of a distorted octahedron. Three of the oxygen atoms are slightly nearer to the central iron atom than the other three. Each oxygen atom is surrounded by four iron atoms, two of which are nearer than the other two, forming a distorted tetrahedron. In figure 1, the origin of Pauling and Hendricks' rhombohedral cell is shown at (32). This origin was shifted to a center of symmetry at (i) for the hexagonal cell used in the refinement procedure.

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[5] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

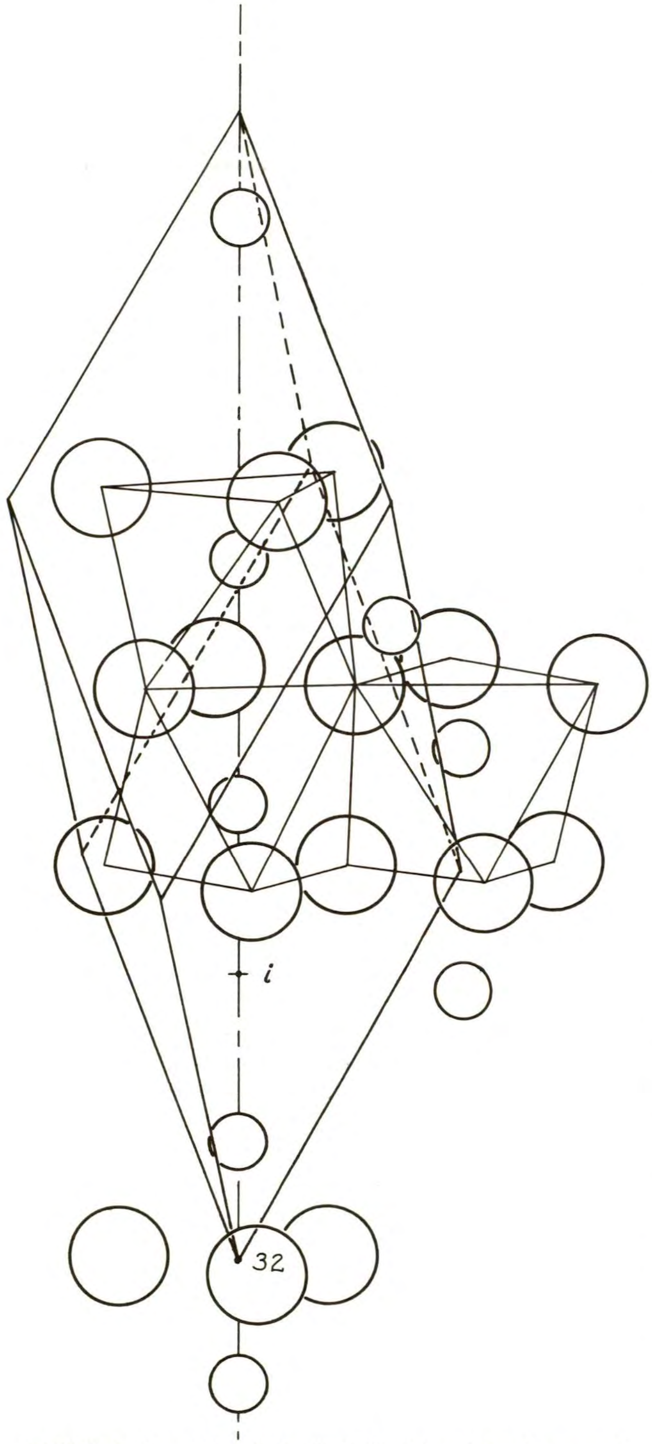

FIGURE 1. - Rhombohedral Model of Pauling and Hendricks (18). Smaller circles represent iron atoms; larger circles, oxygen atoms. Origin of cell at 32 (intersection of threefold and twofold axes) was shifted to *i* (center of symmetry) for the refinement.

## Need for Refinement

The accepted hematite structure postulated by Pauling and Hendricks was reexamined. Initial structure factor calculations for certain reflections, using coordinates of Pauling and Hendricks, showed some deviation from observed intensities. The hematite cell parameters of Pauling and Hendricks were in agreement with several articles (6, 9, 11-12) and the space group ($R\bar{3}c$) reported by them is the same as that determined for isostructural eskolaite (13). This evidence and the rather simple structure of hematite suggested that Pauling and Hendricks' model was essentially correct and needed only refinement, a view later confirmed.

## ACKNOWLEDGMENTS

The following assistance in this study is greatly appreciated. Professor M. J. Buerger, Massachusetts Institute of Technology, suggested several features that were used in modifying the device for preparing small spheres and gave advice on two refinement problems. The following persons cooperated in computer calculations: C. T. Prewitt, Dupont Research Laboratory; I. Jahanbagloo, while a graduate student, University of Minnesota. Special thanks are due to Takaharu Araki, while postdoctoral fellow in the Department of Geology and Geophysics, University of Minnesota, for advice and much assistance in carefully collecting intensity data on the synthetic crystal. The Elba hematite crystals were furnished from the private collection of R. E. Lubker, Minneapolis, Minn. The synthetic crystals were prepared and furnished by G. P. Espinosa of North American Rockwell Corporation, Science Center.

# EXPERIMENTAL WORK

## Refinement Procedure

Refinement of the crystal structure consisted of the following preliminary steps:

1. Checking unit cell parameters.

2. Checking the accepted space group.

3. Preparing a single crystal and collecting reliable diffraction intensities therefrom.

These intensities were then converted to structure factors[6] and used in the refinement procedure which uses the method of least squares to improve coordinates of atomic positions. A measure of agreement between calculated and observed structure factors ($F_c, F_o$) is obtained from the formula:

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

in which the numerator is the sum of all discrepancies between observed and calculated structure factors, and the denominator is the sum of the observed structure factors. In this study, that discrepancy factor, R, for the natural crystal converged to 3.65 percent; for the synthetic crystal, it converged to 2.8 percent.

## Crystal Composition

Tabular crystals of natural hematite from the Island of Elba, and imperfect rhombohedral crystals of synthetic hematite, were used in the present study. Part of the Elba crystal (BMC-283A) used for refinement was analyzed quantitatively with the Bureau's electron probe at its College Park (Md.) Metallurgy Research Center for four elements that could substitute (17) 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 10 different sites. The average concentration of each element in the crystal, expressed in weight-percent, was as follows: Al, 1.0±0.2; Ti, 0.10±0.02; Cr, 0.021±0.005; and V, <0.004. The crystal was also analyzed for manganese, but this element was not detected. It is suggested that the four elements found did substitute for $Fe^{3+}$ in these proportions within the crystal used for refinement, and that in such small quantities their effect on the atomic scattering power of iron was negligible. In calculating atomic scattering factors, both iron and oxygen were assumed half-ionic.

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[6] A structure factor is defined as a complex quantity characterizing the wave scattered by a crystal; its magnitude is the amplitude of the scattered wave, and its direction in the complex plane is determined by the phase of the scattered wave (4, p. 259), and the observed intensity is proportional to the square of the magnitude of the structure factor.

The synthetic crystals were made from Chas. Pfizer & Co., Inc., high-purity iron oxide, EX 1265, lot 9, using as flux $CaMoO_4$ and $Li_2MoO_4$, soaked at 1,200° C, cooled to 850° C at 3° C per hour. The crystals were then annealed in air at 850° C for about 20 hours to remove certain defects (1, p. 339). The sample (designated A-30, or BMC-509B) gave a semiquantitative spectrographic analysis as follows in weight-percent: Fe, 69; Mo, 0.28; Pb, nil; Si, 0.028; Cr, 0.015; Ni, <0.001; and other elements, nil (15a, 15b).

## Cell Parameters and Space Group

Unit cell parameters (dimensions) were determined from powder film data obtained from part of the natural crystal actually used for refinement and from several crystals of the synthetic batch. A program written by J. D. Britton, Chemistry Department, University of Minnesota, for the CD 1604 computer[7] makes a least-squares refinement of cell dimensions by comparing $Q_{calc}$[8] with $Q_{obs}$ and adjusts the approximately known cell dimensions to minimize the mean square error between $Q_{calc}$ and $Q_{obs}$. The refined cell dimensions are shown in table 1 which also lists both rhombohedral and hexagonal unit cell parameters for hematite as follows: Rhombohedral parameters of Pauling and Hendricks and hexagonal parameters calculated therefrom; hexagonal values reported in two other sources; and hexagonal parameters determined for both the natural and synthetic crystals.

TABLE 1. - Unit cell parameters of hematite from the literature and from the Elba and synthetic crystals

| Cell constant | Rhombohedral cell: Pauling and Hendricks (18) | Hexagonal cell (Z = 6), A | | | | |
|---|---|---|---|---|---|---|
| | | Calculated[1] | Aravindakshan and Ali[2] | Newnham and de Haan (17) | Elba crystal powder pattern[3] | Synthetic crystal powder pattern[4] |
| α | 55°17' | - | - | - | - | - |
| a | 5.420±0.010 A | 5.028±0.030 | 5.0317 | 5.0345 | 5.038±0.002 | 5.0346±0.0008 |
| c | - | 13.730± .030 | 13.737 | 13.749 | 13.772± .012 | 13.752 ± .003 |
| c/a | - | 2.731± .06 | 2.730 | 2.731 | 2.733± .015 | 2.731 ± .004 |

[1] Calculated from Pauling and Hendricks' rhombohedral cell values.

[2] ASTM card 13-534.

[3] Part of the Elba crystal used for refinement was pulverized, made into a ball mount, and exposed to FeKα-radiation in a 57.3-mm radius camera using the Straumanis film-loading method.

[4] Same method as footnote 3, on several crystals selected from the batch of synthetic crystals.

The space group proposed by Pauling and Hendricks, R$\bar{3}$c, was confirmed by the $\bar{3}$m diffraction symmetry relations and the absences of $-h+k+l \neq 3n$ and $h0l \neq 2n$ reflections observed in the indexed precession photographs of the natural

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[7] Reference to specific brands and models is made for identification only and does not imply endorsement by the Bureau of Mines.

[8] $Q_{hkl} = 1/d^2_{hkl}$. International Tables for X-Ray Crystallography, v. 2, 1959, Section 3.2.6., p. 106.

crystal used for refinement. The presence of a center of inversion was confirmed from etch pit tests made on adjacent crystals. Crystallographic data for the natural and synthetic crystals are summarized in table 2.

TABLE 2. - Crystallographic data for natural and synthetic hematite

| | Natural crystal | Synthetic crystal |
|---|---|---|
| Space group | $R\bar{3}c$ | Same |
| Lattice constants: | | |
| a | 5.038±0.002 A | 5.0346±0.0008 A |
| c | 13.772± .012 | 13.752 ± .003 |
| Unit cell volume | 302.72 ± .3 $A^3$ | 301.87 ± .13 $A^3$ |
| Unit cell contains | 6 $Fe_2O_3$ | Same |
| Formula weight | 958.20 | Same |
| Calculated density, g/cc | 5.254± .003 | 5.269 ± .001 |
| Measured density, g/cc | 5.27 ± .03 | 5.23 ± .03 |
| Systematic absence | $-h+k+l \neq 3n$ | Same |
| | $h0l \neq 2n$ | Same |

## Crystal Preparation

When measuring intensities from a single crystal, it is desirable to have a crystal less than 0.5 mm diameter and of spherical or cylindrical shape. The small size reduces primary extinction effects and allows the crystal to be bathed in a uniform beam, while the special shapes simplify absorption corrections, thus allowing more accurate intensity determinations. For this study, fragments about 0.5 mm minimum diameter from a selected crystal were placed in a device modified after W. L. Bond (3) and shown in figure 2. An abrasive paper lines the periphery of the 3-inch-diameter chamber, and a strong jet of clean air under pressure enters tangentially through the nozzle to propel the crystals rapidly around the periphery. They become abraded and approach a spherical shape. The air escapes through an opening covered with a fine-mesh screen to retain the crystals. Periodic inspection with a stereomicroscope through the Lucite wall indicates progress and allows measurement of sphere diameter with aid of a calibrated eyepiece. Final polishing is done in a similar, smaller device with a 3/4-inch-diameter chamber and very fine abrasive paper. For this study, spheres of 0.34 mm and 0.19 mm diameter were prepared from the natural and synthetic crystals, respectively.

The spherical crystal was attached by a spear of glue to the end of a glass fiber. It was desired to orient the crystal with its c-axis along the fiber axis so that intensities could be collected in reciprocal lattice levels normal to the c-axis. However, the sphere showed no sheen due to basal cleavage and only a faint indication of being elliptical. Therefore, the first mounting was essentially random. The desired orientation was obtained for each crystal after a series of orientation photographs with a precession camera and several remountings of the sphere. Final orientation of the synthetic crystal was done with a Weissenberg camera.

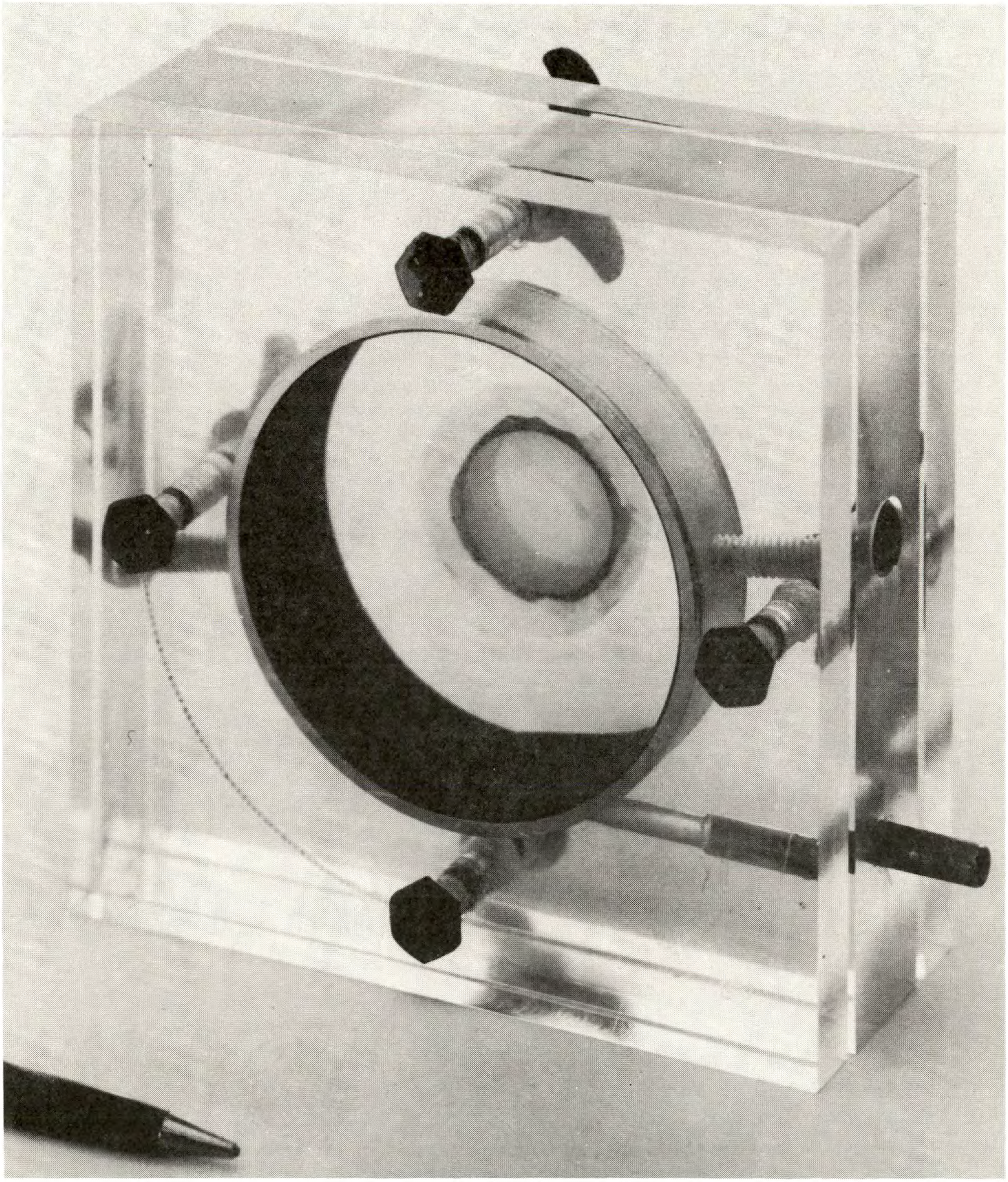

FIGURE 2. - Device for Preparing Small Spheres. Modified after W. L. Bond (3).

## Intensity Measurements

The natural crystal was next mounted at the University of Minnesota on a single-crystal diffractometer of the M. J. Buerger (4) design that had been semiautomated (22). Equi-inclination settings for the instrument were calculated with C. T. Prewitt's program (19) using an IBM 7090 computer. Three-dimensional integrated intensities were collected at room temperature with a proportional counter, using constant-time counting and a digital printer. MoKα-radiation was not available for collecting intensities from the natural crystal. CuKα-radiation (λ = 1.5418 A) was used because FeKα-radiation gave low intensities and would have allowed a smaller number of reflections due to its larger wavelength. The problem of fluorescence was considered to be less important than the advantages of using CuKα-radiation. Most of the fluorescent radiation was discriminated by appropriate setting of the pulse height analyzer.

The synthetic crystal intensity measurements were obtained using techniques similar to those for the natural crystal with the following exceptions: Prewitt's program was used on the University of Minnesota's CD 6600 computer to calculate instrument settings. MoKα-radiation (λ = 0.7107 A) was used along with Zr-Y balanced filters, the diffractometer was manually operated, and the detector was a scintillation counter.

Using CuKα-radiation with the natural crystal there are 60 independent diffracting planes for hematite in reciprocal lattice levels 0 through 15 normal to the c-axis, the rotation axis. Instrument mechanical limitations prevented measurement of intensities from nine such planes. Intensities were collected from all 166 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.

Using MoKα-radiation with the synthetic crystal there are 109 independent diffracting planes for hematite in reciprocal lattice levels 0 through 18 normal to the c-axis, the rotation axis. There were no instrument mechanical limitations. Intensities were collected from all 585 symmetry-equivalent diffractions. Of the 109 measured independent reflections, 14 were judged to be unobserved because their integrated intensities were less than twice the standard deviation of the intensity obtained from counting statistics. These reflections were assigned the most probable intensity using the method of Hamilton (7).

For each of the observed planes from a given crystal, 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 (5).

## REFINEMENT

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, as shown by (i) in figure 1. 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. For both the natural and the synthetic crystals the atomic scattering factors used were those from International Tables for X-Ray Crystallography, volume 3, 1962, table 3.3.1 A, pages 202-207.

For the natural hematite refinement the 51 diffraction amplitude residuals were equally weighted. The least-squares refinement with anomalous dispersion corrections was carried out using the CD 1604 computer at the University of Minnesota and L. W. Finger's program which minimizes the function[9] $r^2 = \frac{\Sigma_w (F_o{}^2 - F_c{}^2)^2}{\Sigma_w F_o{}^4}$. After four cycles of refinement, the discrepancy factor, $R = \frac{\Sigma \left| |F_o| - |F_c| \right|}{\Sigma |F_o|}$, was 7.16 percent. 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 measurements. A weighting scheme similar to that of Hughes (10) was applied. After this refinement, the discrepancy factor converged to 3.65 percent.

For the synthetic hematite refinement, the least-squares refinement was carried out as above except that a CD 6600 computer at the University of Minnesota was used. After three refinement cycles the discrepancy factor, R, was a minimum at 4.8 percent for the 95 observed reflections, but the temperature factors were negative. After unsuccessful experimentation with other weighting schemes, success was achieved by applying secondary extinction correction of the form: $F_{o\ corr} = F_o / \sqrt{1 - S|F_o|^2}$, where S = extinction coefficient; this formula is modified from one suggested by Zachariasen (21). After two additional refinement cycles the anisotropic temperature factors became positive. The discrepancy factor, R, was minimized at 2.8 percent for the 95 unrejected reflections. The value of r was 3.1 percent for the 95 unrejected reflections; and both r and R were 3.3 percent for all 109 reflections. The final structure factors for the synthetic hematite refinement are listed in table 3. Final structure factors for the Elba hematite may be obtained from the authors upon request.

Table 4 lists Pauling and Hendricks' original, Shirane and coworkers' (20) improved, and the refined atomic coordinates of the hematite structure for the hexagonal as well as for the two rhombohedral unit cells most frequently used. In the refined structure, the hexagonal cell coordinates for iron (z = 0.3553) are essentially unchanged from that in the Pauling and Hendricks structure, while the oxygen coordinates are changed about 5 percent, from x = 0.292 to x = 0.306 and 0.3072 for the natural and synthetic crystal refinements, respectively.

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[9] w is a weighting factor; $F_o$ and $F_c$ are observed and calculated structure factors, respectively.

TABLE 3. - Final structure factors for synthetic hematite refinement

| h | k | l | F(OBS) | F(CALC) |
|---|---|---|---|---|
| 3 | 0 | 0 | 258.641 | 249.253 |
| 6 | 0 | 0 | 124.656 | 122.441 |
| 1 | 1 | 0 | 178.816 | 197.689 |
| 2 | 2 | 0 | 147.359 | 146.548 |
| 5 | 2 | 0 | 87.356 | 89.499 |
| 3 | 3 | 0 | 146.299 | 144.286 |
| 1 | 4 | 0 | 122.220 | 118.866 |
| 2 | 1 | 1 | 19.412 | 18.313 |
| 5 | 1 | 1 | 15.634 | 15.598 |
| 3 | 2 | 1 | 12.447 | 12.025 |
| 1 | 3 | 1 | 10.283 | 9.906 |
| 4 | 3 | 1 | 6.459 | 3.300 |
| 2 | 4 | 1 | 7.833 | 13.293 |
| 2 | 0 | 2 | 42.745 | 41.109 |
| 5 | 0 | 2 | 17.826 | 18.470 |
| 0 | 1 | 2 | 77.594 | 79.148 |
| 3 | 1 | 2 | 53.227 | 51.551 |
| 1 | 2 | 2 | 46.837 | 44.517 |
| 4 | 2 | 2 | 28.497 | 28.209 |
| 2 | 3 | 2 | 25.288 | 22.647 |
| 0 | 4 | 2 | 56.885 | 55.457 |
| 3 | 4 | 2 | 40.214 | 39.371 |
| 1 | 5 | 2 | 18.739 | 19.558 |
| 1 | 1 | 3 | 82.521 | 79.510 |
| 4 | 1 | 3 | 26.459 | 26.852 |
| 2 | 2 | 3 | 39.597 | 40.562 |
| 5 | 2 | 3 | 13.987 | 15.248 |
| 3 | 3 | 3 | 5.636 | .527 |
| 1 | 4 | 3 | 26.283 | 26.797 |
| 2 | 5 | 3 | 13.477 | 15.172 |
| 1 | 0 | 4 | 200.403 | 212.017 |
| 4 | 0 | 4 | 108.157 | 110.263 |
| 2 | 1 | 4 | 173.378 | 173.955 |
| 5 | 1 | 4 | 100.310 | 102.507 |
| 0 | 2 | 4 | 205.098 | 205.813 |
| 3 | 2 | 4 | 131.402 | 130.917 |
| 2 | 4 | 4 | 100.366 | 99.819 |
| 1 | 3 | 4 | 129.775 | 128.052 |
| 4 | 3 | 4 | 70.352 | 72.966 |
| 0 | 5 | 4 | 116.212 | 117.342 |
| 3 | 1 | 5 | 5.607 | 8.449 |
| 1 | 2 | 5 | 16.979 | 15.339 |
| 4 | 2 | 5 | 11.643 | 12.237 |
| 2 | 3 | 5 | 11.732 | 11.137 |
| 3 | 4 | 5 | 3.584 | 2.833 |
| 1 | 5 | 5 | 16.012 | 14.795 |
| 3 | 0 | 6 | 67.652 | 64.526 |
| 6 | 0 | 6 | 47.696 | 47.795 |
| 1 | 1 | 6 | 176.552 | 178.014 |
| 4 | 1 | 6 | 99.717 | 98.481 |
| 2 | 2 | 6 | 126,632 | 125.201 |
| 0 | 3 | 6 | 67.974 | 64.587 |
| 3 | 3 | 6 | 51.456 | 51.896 |
| 1 | 4 | 6 | 99.575 | 98.422 |
| 0 | 6 | 6 | 45.530 | 48.030 |
| 2 | 1 | 7 | 8.559 | 14.265 |
| 5 | 1 | 7 | 9.777 | 14.757 |
| 3 | 2 | 7 | 13.585 | 10.635 |
| 1 | 3 | 7 | 9.741 | 8.679 |
| 2 | 4 | 7 | 13.185 | 12.729 |
| 2 | 0 | 8 | 88.849 | 88.953 |
| 5 | 0 | 8 | 50.029 | 50.582 |
| 0 | 1 | 8 | 122.098 | 117.146 |
| 3 | 1 | 8 | 85.613 | 85.121 |
| 1 | 2 | 8 | 88.543 | 86.068 |
| 4 | 2 | 8 | 54.405 | 57.161 |
| 2 | 3 | 8 | 56.604 | 57.537 |
| 0 | 4 | 8 | 87.298 | 86.455 |
| 1 | 5 | 8 | 47.418 | 48.397 |
| 1 | 1 | 9 | 48.064 | 49.061 |
| 4 | 1 | 9 | 23.650 | 22.991 |
| 3 | 3 | 9 | 5.354 | .475 |
| 2 | 2 | 9 | 30.100 | 31.126 |
| 1 | 4 | 9 | 22.492 | 22.850 |
| 1 | 0 | 10 | 171.973 | 172.984 |
| 4 | 0 | 10 | 130.244 | 129.052 |
| 2 | 1 | 10 | 138.933 | 136.815 |
| 0 | 2 | 10 | 149.125 | 142.710 |
| 3 | 2 | 10 | 98.462 | 98.457 |
| 1 | 3 | 10 | 133.302 | 130.263 |
| 2 | 4 | 10 | 93.883 | 95.037 |
| 0 | 5 | 10 | 89.163 | 87.723 |
| 3 | 1 | 11 | 10.612 | 5.980 |
| 1 | 2 | 11 | 12.836 | 9.912 |
| 4 | 2 | 11 | 8.781 | 10.281 |
| 2 | 3 | 11 | 9.765 | 9.034 |
| 3 | 0 | 12 | 24.502 | 23.595 |
| 1 | 1 | 12 | 35.345 | 33.912 |
| 4 | 1 | 12 | 22.301 | 20.492 |
| 2 | 2 | 12 | 27.609 | 25.609 |
| 0 | 3 | 12 | 23.909 | 23.510 |
| 1 | 4 | 12 | 23.606 | 20.394 |
| 2 | 1 | 13 | 13.113 | 9.704 |
| 3 | 2 | 13 | 8.418 | 8.665 |
| 1 | 3 | 13 | 6.451 | 6.834 |
| 2 | 0 | 14 | 136.143 | 130.879 |
| 0 | 1 | 14 | 140.803 | 129.806 |
| 3 | 1 | 14 | 98.007 | 100.217 |
| 1 | 2 | 14 | 125.288 | 120.380 |
| 2 | 3 | 14 | 105.268 | 105.398 |
| 0 | 4 | 14 | 84.751 | 90.384 |
| 1 | 1 | 15 | 29.911 | 30.142 |
| 2 | 2 | 15 | 22.791 | 23.216 |
| 1 | 0 | 16 | 45.364 | 44.165 |
| 2 | 1 | 16 | 45.013 | 45.353 |
| 0 | 2 | 16 | 52.223 | 51.623 |
| 1 | 3 | 16 | 31.654 | 32.890 |
| 1 | 2 | 17 | 7.622 | 6.839 |
| 1 | 1 | 18 | 63.017 | 67.270 |

TABLE 4. - Original, the improved, and the refined atomic coordinates of the hematite structure for three types of unit cells

| Cell type and origin | Atomic coordinates | | | |
|---|---|---|---|---|
| | Original[1] | Improved: Shirane (20) | Refined--$\sigma$[2] | |
| | | | Elba crystal | Synthetic crystal |
| Hexagonal: | | | | |
| Origin at i: | | | | |
| Fe....0,0,z | z 0.355 | - | [3]0.3553-0.0001 | 0.35527-0.00007 |
| O.....x,0,¼ | x .292 | [4]0.300 | [3].306 - .001 | .3072 - .0006 |
| Rhombohedral: | | | | |
| Origin at 32: | | | | |
| Fe....w,w,w | w .105 | - | .1053 | .1053 |
| O.....u,$\bar{u}$,0 | u .292 | .300 | .306 | .3072 |
| Origin at i: | | | | |
| Fe....z,z,z | z .355 | - | .3553 | .3553 |
| O...x,½-x,¼ | x .542 | .549 | .556 | .5572 |

[1] Pauling and Hendricks (18).

[2] ($\sigma$) Standard deviation of refined coordinates calculated by formula 6 of International Tables for X-Ray Crystallography, v. 2, 1959, Section 6.4.3.1., p. 330.

[3] Standard deviations for the Elba crystal were erroneously reported as 0.00001 and 0.0001 for z and x, respectively (2, table 1, p. 125).

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

Thermal motion of the atoms affects the intensities, and it is difficult to make accurate allowance for this motion. A structure that refines well may yield anisotropic temperature factors that partly express this motion. Each new cycle of refinement utilizes the refined temperature factors from the preceding cycle. For hematite, the final anisotropic temperature factors, obtained from the formula: exp $\{-\Sigma_i \Sigma_j h_i h_j \beta_{ij}\}$ (14) are listed in table 5. From these, the synthetic crystal refined equivalent isotropic temperature factor of iron is 0.15 and of oxygen is 0.19, using the method of Hamilton (8). The authors cannot explain the difference in anisotropic temperature factors of table 5 between natural and synthetic hematite on a physical basis, but do offer the following comments. The synthetic crystal has a lower impurity content, as presented earlier; and the intensity data collected from the synthetic crystal are considerably more accurate (especially the background, since the diffractometer was manually operated) than those collected from the natural crystal. This increased accuracy is expected to have more effect on the thermal parameters of table 5 than on the positional parameters of table 4.

Once the refined unit cell dimensions and the coordinates of the atoms in the cell are known, it is possible to calculate distances and angles between atoms of the structure. The CD 6600 computer was used with L. W. Finger's program to calculate these values. Standard deviations of the 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 6. Identification of the atoms listed in this table can be obtained with the aid of figure 7. Some of the interatomic distances and angles of the unrefined hematite structure given by Newnham and de Haan (17) are also quoted in the footnote of table 6 for comparison.

TABLE 5. - Final anisotropic temperature coefficients (x $10^3$) for natural and synthetic hematite

| Atom | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| Natural:[1] | | | | | | |
| Fe...... | 8.0±0.1 | 8.0±0.1 | 0.29±0.02 | 4.0±0.1 | 0 | 0 |
| O....... | 6.8± .2 | 8.3± .3 | .46± .02 | 4.2± .1 | 0.58±0.04 | 1.2 ±0.1 |
| Synthetic: | | | | | | |
| Fe...... | 2.0± .4 | 2.0± .4 | .2 ± .06 | 1.0± .2 | 0 | 0 |
| O....... | 2.3±1.3 | 4.8±1.7 | .1 ± .2 | 2.4± .8 | .23± .24 | .46± .48 |

[1] Blake (2, table 2, p. 125).

TABLE 6. - Selected interatomic distances and angles in hematite (from synthetic crystal refinement)

| Within one octahedron | | | Within one octahedral layer | | | Between octahedral layers | | |
|---|---|---|---|---|---|---|---|---|
| Atoms | Interatomic distance, A | Std. dev. | Atoms | Interatomic distance, A | Std. dev. | Atoms | Interatomic distance, A | Std. dev. |
| $Fe_1-O_1$ | 1.941 (a)[1] | 0.002 | $Fe_1-Fe_2$ | 2.969 (g) | 0.001 | $Fe_1-Fe_6$ | 3.361 (h) | 0.001 |
| $Fe_1-O_4$ | 2.119 (b) | .002 | $Fe_1-O_7$ | 3.399 | .002 | $Fe_2-Fe_5$ | 2.896 (i) | .002 |
| $O_1-O_2$ | 3.027 (c) | .003 | $Fe_1-O_8$ | 4.398 | .003 | $Fe_2-Fe_6$ | 3.702 (j) | .001 |
| $O_1-O_4$ | 2.882 (d) | .001 | $Fe_1-O_9$ | 4.696 | .001 | $Fe_6-Fe_7$ | 3.980 | .002 |
| $O_1-O_5$ | 2.774 (e) | .001 | $Fe_1-O_{10}$ | 3.776 | .003 | $Fe_1-O_{12}$ | 3.590 | .001 |
| $O_1-O_6$ | 4.180 | .003 | $O_1-O_7$ | 3.027 | .003 | $Fe_2-O_{12}$ | 4.128 | .001 |
| $O_4-O_5$ | 2.679 (f) | .006 | $O_5-O_9$ | 5.703 | .003 | $O_4-O_{12}$ | 4.590 | .001 |
| Atoms | Angle, deg. | Std. dev. | Atoms | Angle, deg. | Std. dev. | Atoms | Angle, deg. | Std. dev. |
| $O_1-Fe_1-O_2$ | 102.49 (k) | 0.03 | $Fe_2-Fe_1-Fe_4$ | 115.98 | 0.02 | $Fe_5-Fe_1-Fe_6$ | 49.42 | 0.01 |
| $O_1-Fe_1-O_4$ | 90.36 | .07 | $Fe_1-O_1-Fe_2$ | 51.05 | .07 | $Fe_6-Fe_1-Fe_7$ | 68.41 | .03 |
| $O_1-Fe_1-O_5$ | 86.11 (l) | .03 | $Fe_1-O_3-Fe_2$ | 93.89 (o) | .02 | $Fe_1-Fe_2-Fe_6$ | 59.32 | .02 |
| $O_1-Fe_1-O_6$ | 162.41 (m) | .10 | $Fe_1-O_6-Fe_2$ | 59.87 | .04 | $Fe_1-Fe_2-Fe_7$ | 71.26 | .01 |
| $O_4-Fe_1-O_5$ | 78.41 (n) | .09 | $O_1-Fe_2-O_6$ | 67.75 | .05 | $Fe_1-O_1-Fe_6$ | 119.99 (p) | .16 |
| $Fe_1-O_1-O_2$ | 38.76 | .02 | $O_3-O_1-O_7$ | 52.53 | .18 | $Fe_1-O_1-Fe_7$ | 77.76 | .05 |
| $Fe_1-O_1-O_4$ | 47.30 | .10 | $O_4-O_1-O_7$ | 58.33 | .02 | $Fe_1-O_3-Fe_6$ | 72.26 | .03 |
| $Fe_1-O_1-O_5$ | 49.63 | .05 | $O_6-O_1-O_7$ | 85.48 | .11 | $Fe_1-O_3-Fe_7$ | 52.51 | .04 |
| $Fe_1-O_1-O_6$ | 9.18 | .04 | $O_1-O_3-O_7$ | 63.74 | .02 | $Fe_6-O_4-Fe_7$ | 86.66 (q) | .06 |
| $Fe_1-O_5-O_6$ | 50.78 | .05 | $O_2-O_3-O_8$ | 176.27 | .09 | $Fe_2-O_7-Fe_6$ | 131.48 (r) | .06 |

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

Distances:

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

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°.

## 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. The structure can be generated by starting with the first octahedral layer shown in figure 3, in which white surfaces represent smaller octahedral faces that will be common with the second layer.

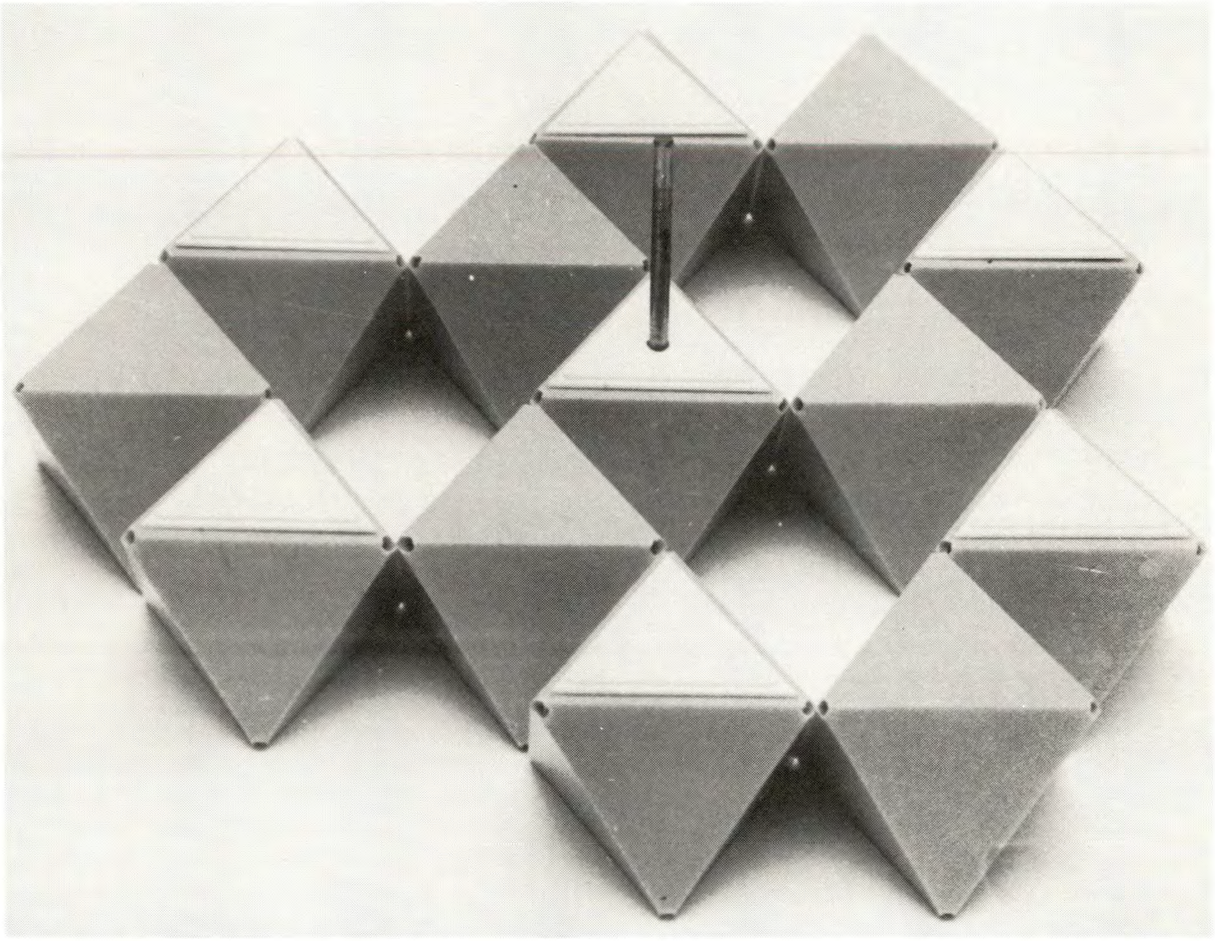

FIGURE 3. - Basal Layer of Octahedra in Hematite. Rod marks rotation axis for generation of next layer.

The second layer may be formed from the first by an inversion of all octahedra of the first layer, through the centers of their upper faces. This inversion produces an identical layer of octahedra superimposed on the first layer. Then the second layer is rotated 60° about any threefold vertical axis, such as that shown by the rod, to produce the two-layer model shown in figure 4. Note that the threefold axis always passes through the center of a smaller, common face. Since the common faces shift in the basal plane as each layer is added, so does the rotation axis, as shown by the rod shift in figure 4, where the shorter rod is the original rotation axis, and the longer rod is the new axis for rotation of the third layer. Seven such layers are required to complete the octahedral structure of figure 5, in which the hexagonal unit cell is outlined. This cell contains 12 iron atoms and 18 oxygen atoms ($Z = 6$), three times the volume of Pauling and Hendricks' rhombohedral cell. The origin of the hexagonal cell is located at the center of the hexagonal opening of the gibbsite-type layer, so that seven octahedral layers are shown, but the cell is only six layers in height. Note that in the vertical c-direction every third octahedron is missing, showing that only two-thirds of the iron atom positions are occupied. Distortion of octahedra is not shown in the

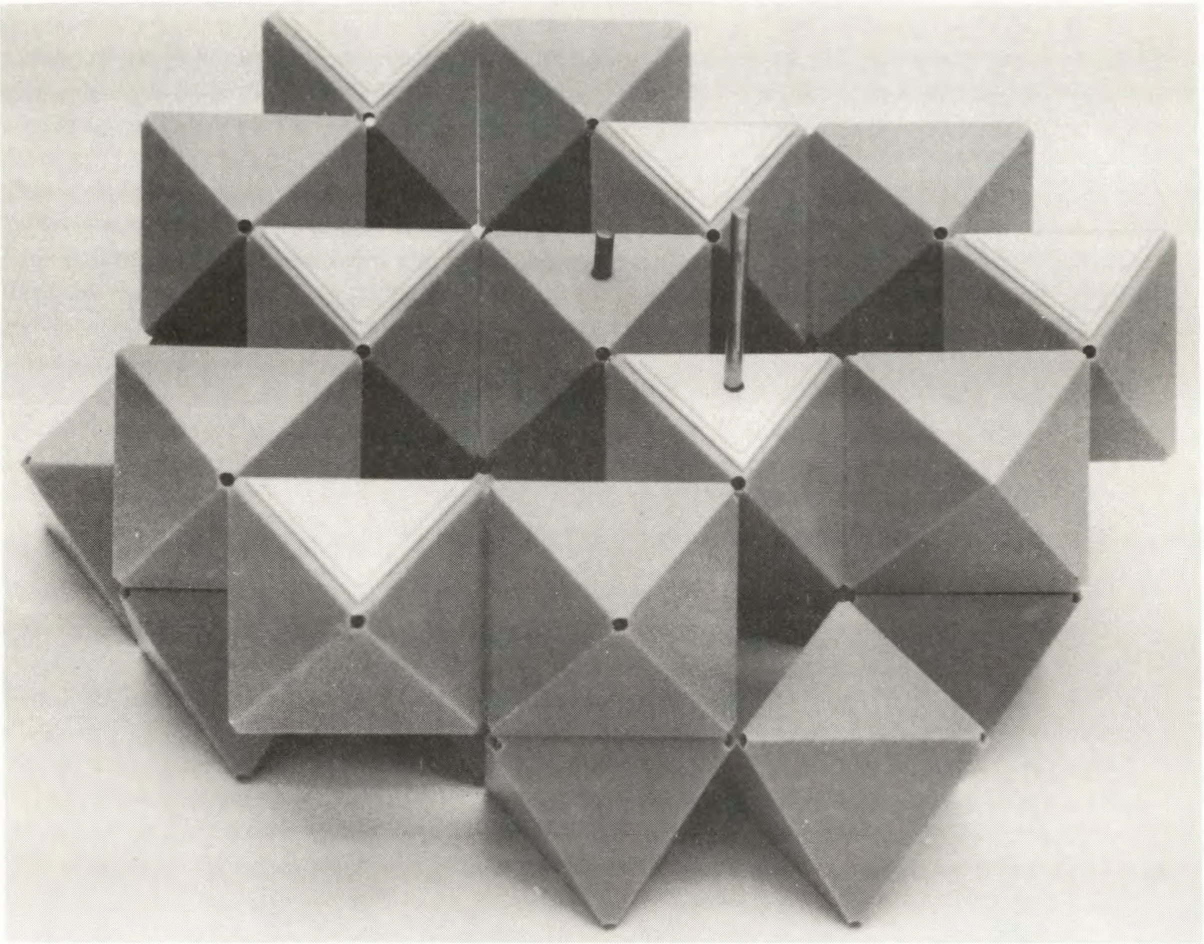

FIGURE 4. - Two Layers of Octahedra in Hematite. Shows the second (top) layer generated from the basal layer of figure 3. Shorter rod represents rotation axis for generating second layer; longer rod, for third layer.

models of figures 3-5. The crystal structure is also shown in figure 6 as a stereoscopic drawing of the octahedral model with the hexagonal unit cell outlined. In this drawing octahedra are distorted to conform to the refined structure.

The refinement confirmed the structure model of hematite proposed by Pauling and Hendricks. As a consequence of the small change in the oxygen atomic coordinates, the $FeO_6$ octahedra are even more distorted than in the original structure model. Figure 7 is a basal (001) view of one layer of octahedra with the hexagonal unit cell outlined in long-dash lines. Iron atoms occupy centers, and oxygen atoms, corners, of octahedra. Due to distortions of octahedra caused by unequal 0-0 distances, alternating faces (outlined with heavy lines) in the basal plane are seen to be larger or smaller than for regular octahedra. Also shown are two octahedra of the next lower layer in short-dash lines ($Fe_5$ and $Fe_6$), and the position of the iron atom ($Fe_7$) in the next higher layer.

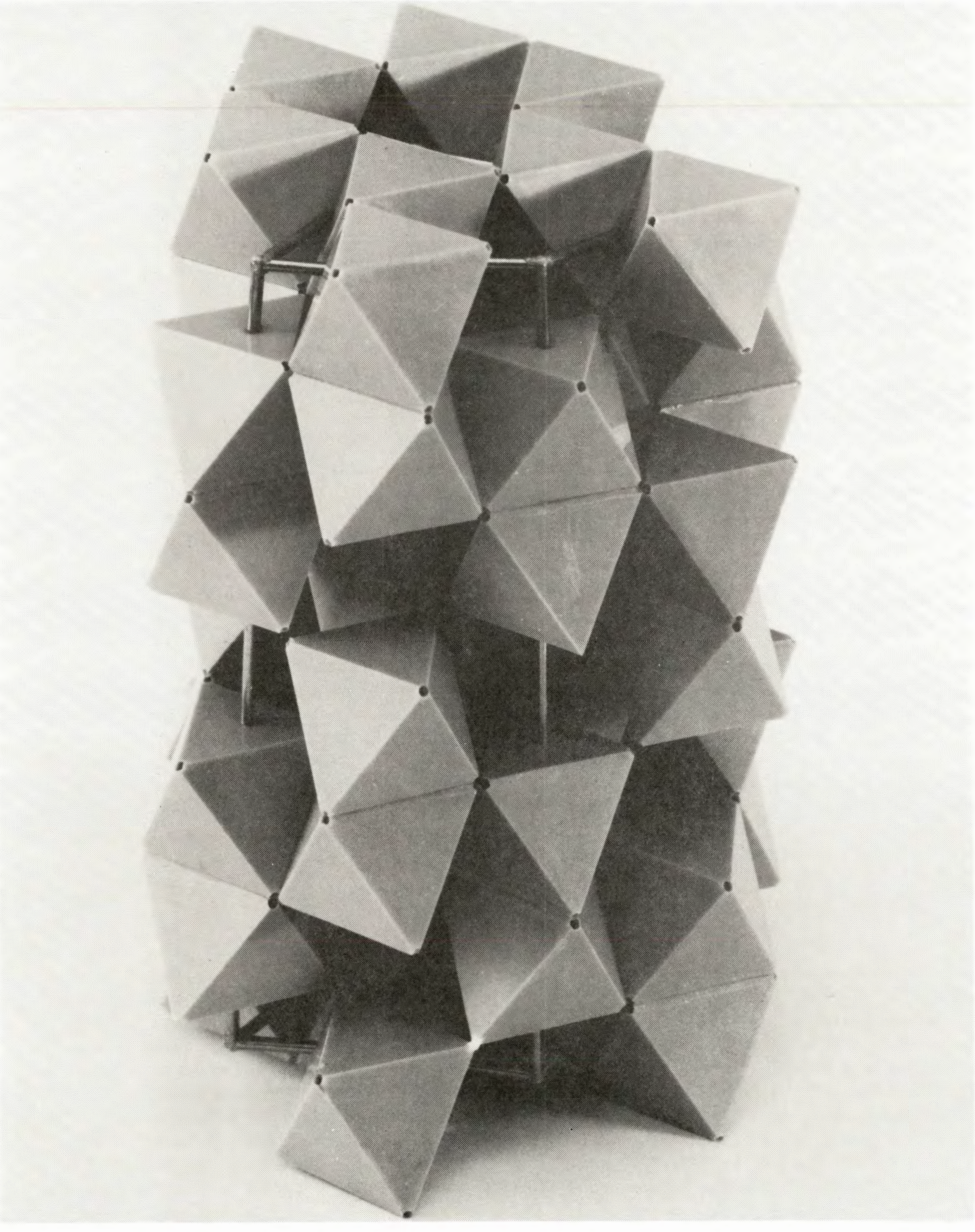

FIGURE 5. - Octahedral Model of Hematite With Hexagonal Unit Cell.

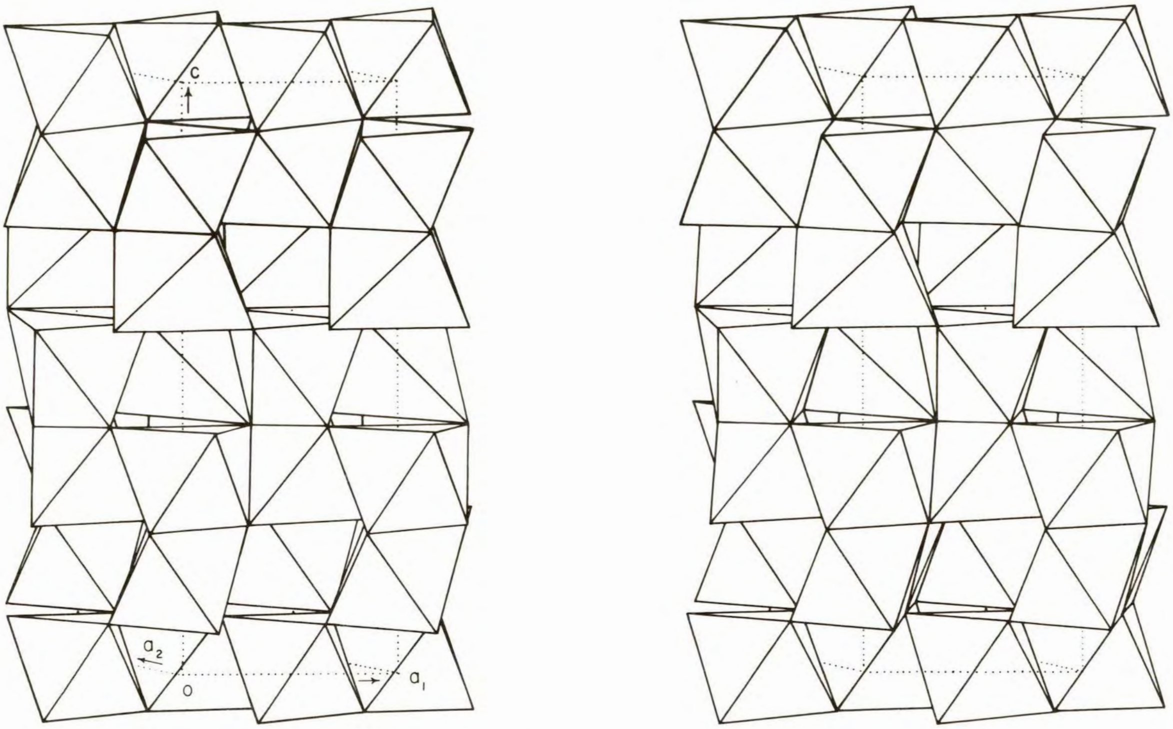

FIGURE 6. - Stereoscopic Drawing of Hematite Octahedral Model.

In figure 7 each octahedron contains three shared and three 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 (for example, figure 7, $O_1$-$O_5$ = 2.774 A) is considerably shorter than that of an unshared edge (for example, $O_1$-$O_4$ = 2.882 A). The oxygen-oxygen distances in the shared basal face are also considerably shorter (for example, $O_4$-$O_5$ = 2.679 A) than the corresponding distance in the unshared basal face (for example, $O_1$-$O_2$ = 3.027 A). Similarly the iron atoms are closer to the oxygens of the unshared faces, 1.941 A, than to the oxygens of the shared faces, 2.119 A. This observation supports the expected nature of distortion caused by local ionic attraction and repulsion.

Thermal motion of an atom in a crystal structure may be expressed as an ellipsoid of vibration which represents the maximum displacement from some average position of the atom. The parameters of the ellipsoid in the principal coordinate system include the lengths of the axes and their angular relationships with the crystallographic axes. Using the anisotropic temperature coefficients of table 5 for synthetic hematite, the thermal ellipsoid parameters for iron and oxygen were calculated and are presented in table 7. The iron ellipsoid has the shape of a sphere. 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 20° from the c-axis. The longest axis is directed toward the vacant octahedral site in the structure. However, the indicated anisotropy of this atom may not be real since the errors in the axis lengths are quite large.

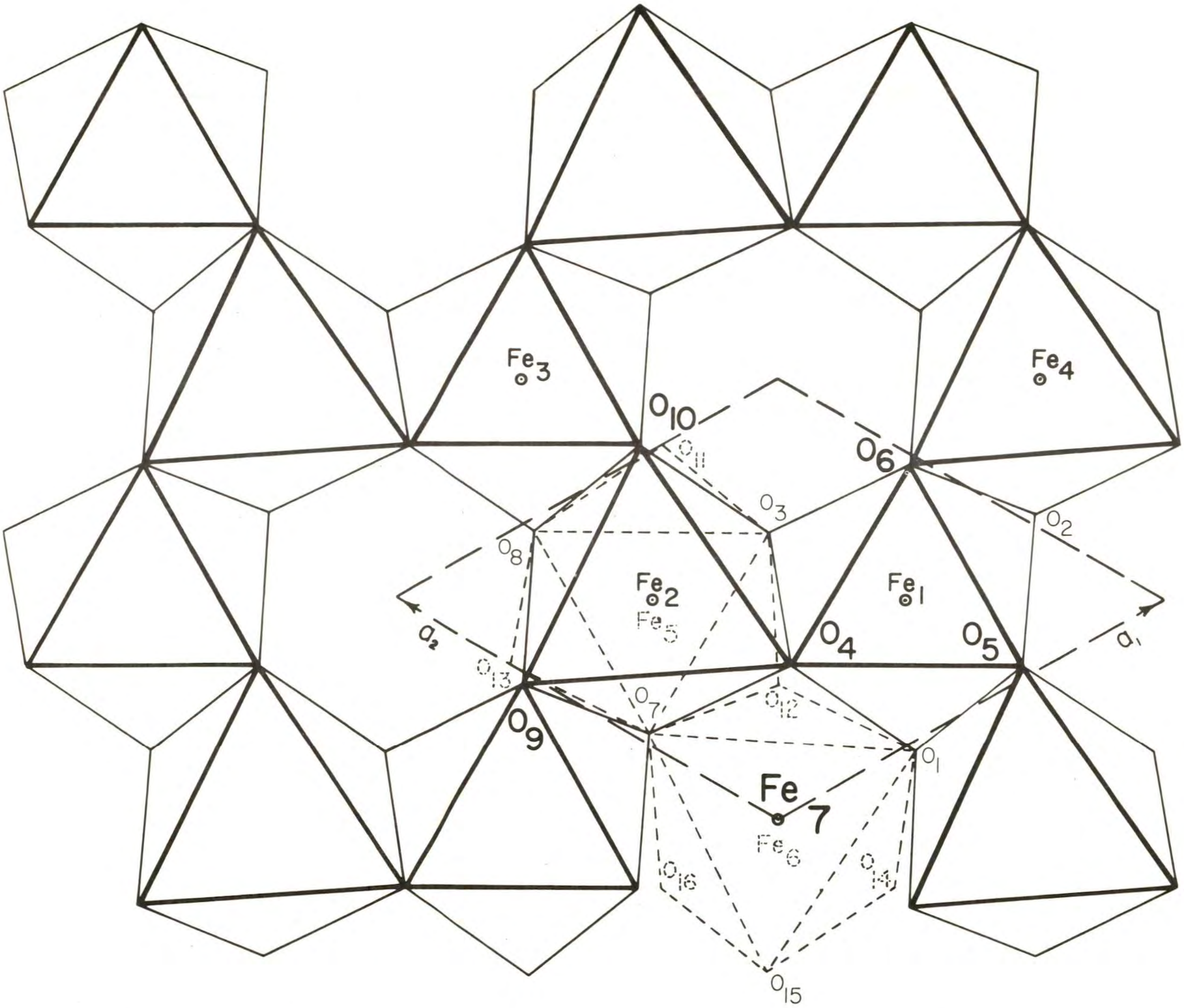

FIGURE 7. - Octahedral Layers in Hematite Structure With Hexagonal Unit Cell Outlined. Note, in bold outline, and all in one basal plane, the alternating larger and smaller octahedral faces resulting from varying 0-0 distances. Dashed octahedra are in next lower layer; Fe$_7$, in next higher layer. Size of atomic symbol denotes its relative elevation along the c-direction (normal to the page); the largest symbol is the highest.

TABLE 7. - Thermal ellipsoids for synthetic hematite: r.m.s. displacements and orientations[1]

| Atom | r | $\mu(r)$, A | $\varphi(a_1)$ | $\varphi(a_2)$ | $\varphi(c)$ |
|---|---|---|---|---|---|
| Fe......... | 1 | 0.043±0.007 | 0° | 120° | 90° |
|  | 2 | .043± .006 | 90° | 30° | 90° |
|  | 3 | .043± .006 | 90° | 90° | 0° |
| O.......... | 1 | .023± .041 | 90° | 106°±16° | 19°±19° |
|  | 2 | .038± .025 | 0° | 120° | 90° |
|  | 3 | .072± .011 | 90° | 35°± 9° | 17°±19° |

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

## SUMMARY AND CONCLUSIONS

The crystal structure of hematite has been refined using both a natural and a synthetic crystal shaped into small spheres. Three-dimensional intensities were collected with an equi-inclination, semiautomated single-crystal diffractometer using CuK$\alpha$- and MoK$\alpha$-radiation. Using a least-squares refinement program the final structure for the natural crystal irradiated with CuK$\alpha$-radiation gave a discrepancy factor (R) of 3.65 percent using 49 unrejected reflections of the 51 measured. For the synthetic crystal, using MoK$\alpha$-radiation, the discrepancy factor converged to 2.8 percent for 95 unrejected reflections and was 3.3 percent for all 109 reflections. Anisotropic temperature factors and thermal ellipsoid parameters were calculated for iron and oxygen atoms.

The space group ($R\bar{3}c$) of Pauling and Hendricks has been confirmed. Refinement of their structure model has resulted in essentially no change in the iron coordinates and approximately a 5-percent change in the oxygen coordinates. The refined hexagonal cell coordinate for iron is $z = 0.35527 \pm 0.00007$ and for oxygen is $x = 0.3072 \pm 0.0006$. The cell parameters were determined by least-squares refinement of powder film data, and are $a = 5.0346 \pm 0.0008$ A, $c = 13.752 \pm 0.003$ A, $c/a = 2.731 \pm 0.004$.

The O-O distances on the shared face of the coordination polyhedron (2.679 A) are shorter than those of the unshared face (3.027 A), resulting in even greater distortion in the refined structure than in the original model. Selected interatomic distances and angles in the structure have been tabulated, and the structure details have been discussed.

## REFERENCES[10]

1. Artman, J. O., A. H. Muir, Jr., and H. Wiedersich. Determination of the Nuclear Quadrupole Moment of $Fe^{57m}$ from $\alpha$-$Fe_2O_3$ Data. Phys. Rev., v. 173, No. 2, 1968, pp. 337-343.

2. Blake, R. L., R. E. Hessevick, T. Zoltai, and L. W. Finger. Refinement of the Hematite Structure. Am. Miner., v. 51, 1966, pp. 123-129.

3. Bond, W. L. Making Small Spheres. Rev. Sci. Instr., v. 22, 1951, pp. 344-345.

4. Buerger, M. J. Crystal Structure Analysis. John Wiley & Sons, Inc., New York, 1960, 668 pp.

5. Evans, H. T., Jr., and Miriam G. Ekstein. Tables of Absorption Factors for Spherical Crystals. Acta Cryst., v. 5, 1952, pp. 540-542.

6. Goldsztaub, S. Deshydratation des hydrates ferriques naturels (Dehydration of Natural Ferric Hydrates). Compt. rend., des seances, Acad. Sci., Paris, v. 193, 1931, pp. 533-535.

7. Hamilton, W. C. On the Treatment of Unobserved Reflections in the Least-Squares Adjustment of Crystal Structures. Acta Cryst., v. 8, 1955, pp. 185-186.

8. _____. On the Isotropic Temperature Factor Equivalent to a Given Anisotropic Temperature Factor. Acta Cryst., v. 12, 1959, pp. 609-610.

9. Harrington, E. A. X-Ray Diffraction Measurements on Some of the Pure Compounds Concerned in the Study of Portland Cement. Am. J. Sci., v. 213, 1927, pp. 467-479.

10. Hughes, E. W. Crystal Structure of Melamine. J. Am. Chem. Soc., v. 63, 1941, pp. 1737-1752.

11. Jansen, W. Röntgenographische Untersuchungen über die Kristall orientierung in Parallelfasrigen Aggregaten (X-Ray Investigation on Crystal Orientation in Parallel-Filament Aggregates). Z. Krist., v. 86, 1933, pp. 171-185.

12. Katzoff, S., and E. Ott. On the Lattice Constants of Ferric Oxide. Z. Krist., v. 86, 1933, pp. 311-312.

13. Kouvo, O., and Y. Vuorelainen. Eskolaite, A New Chromium Mineral. Am. Miner., v. 43, 1958, pp. 1098-1106.

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[10] Titles enclosed in parentheses are translations from the language in which the item was originally published.

14. Levy, H. A. Symmetry Relations Among Coefficients of the Anisotropic Temperature Factor. Acta Cryst., v. 9, part 8, 1956, p. 679.

15. Muir, A. H., Jr. Personal Communications: (a) March 28, 1967; (b) April 6, 1967; (c) June 20, 1967. Available for consultation at the Bureau of Mines Twin Cities Metallurgy Research Center, Minneapolis, Minn.

16. Muir, A. H., Jr., K. J. Ando, and Helen M. Coogan. Mössbauer Effect Data Index 1958-1965. Interscience Publishers, New York, 1966, 351 pp.

17. Newnham, R. E., and Y. M. de Haan. Refinement of the $\alpha$-$Al_2O_3$, $Ti_2O_3$, $V_2O_3$, and $Cr_2O_3$ Structures. Z. Krist., v. 117, 1962, pp. 235-237.

18. Pauling, L., and S. B. Hendricks. The Crystal Structures of Hematite and Corundum. J. Am. Chem. Soc., v. 47, 1925, pp. 781-790.

19. Prewitt, C. T. The Parameters $\tau$ and $\varphi$ for Equi-Inclination, With Application to the Single-Crystal Counter Diffractometer. Z. Krist., v. 114, Nos. 5-6, 1960, pp. 355-360.

20. Shirane, G., S. J. Pickart, R. Nathans, and Y. Ishikawa. Neutron-Diffraction Study of Antiferromagnetic $FeTiO_3$ and Its Solid Solutions With $\alpha$-$Fe_2O_3$. J. Phys. Chem. Solids, v. 10, 1959, pp. 35-43.

21. Zachariasen, W. H. The Crystal Structure of Cubic Metaboric Acid. Acta Cryst., v. 16, 1963, pp. 380-384.

22. Zoltai, T. Z. Inexpensive Automation of Buerger's Single-Crystal Diffractometer. Pres. at Annual Meeting, American Crystallographic Assoc., Cambridge, Mass., Mar. 28-30, 1963; available for consultation from the Bureau of Mines Twin Cities Metallurgy Research Center, Minneapolis, Minn.