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and at the boiling point of hydrogen iodide, the value may be estimated from the heat capacity of hydrogen iodide to be 4709 cal. as against 4724 cal. for hydrogen iodide. The effect of this difference upon the vapor pressures is within the limit of accuracy of our measurements. Vapor pressures at the boiling point calculated from a single pressure at the triple point and using, respectively, the two heats of vaporization differing by fifteen calories would be different by 0.7 mm, or the calculated boiling points would differ by 0.05°.

By reference to the summary presented by Claussen and Hildebrand[12] in connection with their vapor pressures of the hydrogen and deuterium fluorides, it is seen that deuterium iodide differs from hydrogen iodide in the same direction as deuterium fluoride from hydrogen fluoride, but to a considerably smaller extent. The greater vapor pressure of the deuterium compounds in these two cases cannot be ascribed to the same cause. The fluoride is known to have properties differing in general from the other halides. This has been supposed to be due to the more ionic nature of the hydrogen fluorine bond. The iodide should according to recent theories be at the other extreme.[13] A possible explanation seems to be that the polarity of the deuterium iodide should be smaller, because of the smaller anharmonicity factor operative in the region of zero point energy.

[12] Claussen and Hildebrand, J. Am. Chem. Soc. 56, 1820 (1934).

[13] Mulliken, J. Chem. Phys. 2, 782 (1934).

The Crystal Structure of Lepidocrocite

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The unit of structure, space group symmetry and detailed atomic arrangement of lepidocrocite are determined from x-ray data, and the existence and location of hydrogen bonds in the structure are established from considerations of interatomic distances. The orthorhombic lattice is end centered on (100), and has the axes $a_0 = 3.87A$, b_0 12.51A, and $c_0 = 3.06A$. The space group is $V_h^{17} - Amam$. The parameters are determined as $u_{Fe} = -0.332$, $u_O = +0.282$, and $u_{OH} = +0.075$. The structure is described as consisting of iron-centered oxygen octahedra joined by the sharing of edges into two-dimensionally infinite layers, with the successive layers held together by hydrogen bonds. The relationship between the diaspore-goethite structure and the böhmite-lepidocrocite structure is discussed from the standpoint of the coordination theory, and found to depend on two alternative ways of satisfying the electrostatic valence rule.

INTRODUCTION

LEPIDOCROCITE, FeO(OH), is described by Posnjak and Merwin[1] as forming orthorhombic crystals with the axial ratios 0.64 : 1 : 0.43. The crystals are red and transparent, and form thin plates tabular on (010), slightly striated in the direction of the c-axis.

The monohydrates of iron and aluminum oxide, with the general formula MHO_2, exist in two modifications. The structure of the modification corresponding to diaspore, $AlHO_2$, and goethite, $FeHO_2$, is known,[2] but no previous investigation of the structure of the second modification corresponding to lepidocrocite,

[1] E. Posnjak and H. E. Merwin, Am. J. Sci. 47, 311 (1919).
[2] M. Deflandre, Bull. Soc. Franc. Mineral. 55, 140 (1932); K. Takane, Proc. Imp. Acad. Tokyo 9, 113 (1933); S. Goldsztaub, Comptes rendus 195, 964 (1932); F. J. Ewing, J. Chem. Phys. 3, 203 (1935).

FeO(OH), and böhmite,[3] AlO(OH), has been made.

In the present investigation the unit of structure, space group symmetry, and detailed atomic arrangement of lepidocrite are determined from x-ray data, and existence and location of hydrogen bonds in the structure are established from considerations of interatomic distances. The lepidocrocite structure and its relation to the diaspore-goethite structure is discussed from the standpoint of the coordination theory.

THE UNIT OF STRUCTURE AND SPACE GROUP SYMMETRY

Oscillation and Laue photographs were prepared with crystals of lepidocrocite from Eiserfeld, Westerfald, Germany. The crystals were tabular on b, forming thin plates about 1 mm² in area. Oscillation photographs of Mo $K\alpha$ radiation reflected from or transmitted through (010) with [001] as the axis gave the value 3.06A for c_0 on the basis of the intervals between side spectra; and gave a_0 as $1.935n_1$, and b_0 as $6.255n_2$ on the basis of the pinacoidal reflections. Calculated values of $n\lambda$ for observed Laue reflections require that $n_1 = n_2 = 2$. The correct unit cell is therefore given by the orthorhombic axes

$$a_0 = 3.87A, \quad b_0 = 12.51A \quad \text{and} \quad c_0 = 3.06A.$$

No first-order Laue reflections were observed in which $(k+l)$ was odd, and the lattice is therefore based on Γ_0', end centered on (100). Assuming holohedral symmetry for the crystal, the possible space groups* are V_h^{17} to V_h^{22}. Observed first order Laue reflections such as (520) and (580) eliminate V_h^{20} and V_h^{22}. Numerous first order prism reflections on the oscillation photographs, such as (011), (031), (051), etc., also eliminate the space groups V_h^{18} and V_h^{21}. Of the two remaining space groups, V_h^{17} and V_h^{19} the former allows only two prism zones to reflect, while the latter permits reflections from all three. No first-order reflections from planes of the type $(h0l)$ were observed in any of the

[3] M. E. Nahmias, Zeits. f. Kryst. **85**, 355 (1933).
* No evidence was found in support of the statement by S. Goldsztaub, Comptes rendus **193**, 533 (1931), that lepidocrocite possesses the space group symmetry V_h^1.

photographs, although a number of such planes were in a position favorable for reflection. The space group of lepidocrocite is thus indicated to be $V_h^{17} - Amam$.

The assignment of four formulas of FeO(OH) to the unit cell gives a calculated density of 3.96 g/cm³, which is in agreement with the observed density of 4.07.

The eight oxygen atoms in the unit cell must be placed on the intersections of the symmetry planes to avoid O−O distances of 1.93A or less. The four iron atoms cannot be at centers of symmetry, because the intensity of the reflection (200) is observed much stronger than that of (400). The general positions of the atoms, referred to a center of symmetry as origin, are therefore;

4Fe at $\frac{1}{4}, u, 0$; $\frac{3}{4}, u, 0$; $\frac{1}{4}, u+\frac{1}{2}, \frac{1}{2}$; $\frac{3}{4}, \frac{1}{2}-u, \frac{1}{2}$:
$4O_I$ at $\frac{1}{4}, u_1, 0$; etc.:
$4O_{II}$ at $\frac{1}{4}, u_2, 0$; etc.

PREDICTION OF THE ATOMIC ARRANGEMENT

A structure may be predicted for lepidocrocite from consideration of the following arguments, which are derived from the rules given in Pauling's[4] coordination theory of the structure of ionic crystals.

1. The elements of the structure are iron-centered oxygen octahedra, in which the Fe−O distances are close to 2.00A, and the O−O distances have values in the neighborhood of 2.70A.

2. The electrostatic valence rule is satisfied, whereby the anions are effectually neutralized by adjacent cations. The two formal ways of distributing the hydrogen ions in $FeHO_2$ are indicated by writing $(OH_{\frac{1}{2}})^{-3/2}$ anions in one instance, and distinct O^- and (OH^-) anions in the other. It has been shown[5] that the assumption that all the anions are of the form $(OH_{\frac{1}{2}})^{-3/2}$ leads to the diaspore-goethite structure. It seems logical to assume, therefore, that lepidocrocite exists as a second modification of $FeHO_2$ by virtue of having the alternative distribution of hydrogens. The O^- and $(OH)^-$ anions corresponding to this second alternative are required by the electrostatic valence rule to be shared between four and two octahedra.

3. Edges shared between octahedra are contracted to about 2.50A, with other edges being compensatorily lengthened.

The length of the a and c axes suggest the probable orientation of the octahedra, since the value 3.87A for a_0 is close to the length 3.82A

[4] Linus Pauling, J. Am. Chem. Soc. **51**, 1010 (1929).
[5] F. J. Ewing, J. Chem. Phys. **3**, 203 (1935).

of the diagonal of an undistorted octahedron, and since the c axis, 3.06A, can readily be associated only with a lengthened edge of an octahedron.

With the character of the sharing and the orientation of the octahedra defined, and with the additional restriction that an identity period of 12.51A be maintained in the direction of the b axis, the layer structure indicated in Fig. 1 immediately suggests itself. The layers are formed by the sharing of edges between octahedra in such a way that the oxygens O_I near the middle of the layers are common to four octahedra and correspond to $O^=$, while the oxygens O_{II} on the outer ridges of the layers are common to two octahedra and correspond to $(OH)^-$. The layers can be regarded as formed by the sharing of edges between "double rutile strings" that were found as characteristic aggregates in diaspore.

The a and c identity distances are contained in the plane of the layer and correspond to a body diagonal and an edge of an octahedron, respectively. The b axis is perpendicular to the layers, and its value of 12.51A suggests that it represents two layer intervals. The most apparent way to satisfy this periodicity is to translate every other layer by $c/2$.

The structure predicted in this manner has the same space group symmetry $V_h{}^{17}$ that is found for lepidocrocite, which is a strong indication that the correct structure has been obtained.

In this structure the parameters for the oxygens are fixed at $u_1 = +0.267$ and $u_2 = +0.067$

FIG. 1. A portion of two layers of lepidocrocite, showing the iron-centered oxygen octahedra joined to form layers, and the layers tied together with hydrogen bonds (drawn as tubes).

by the requirement that shared edges be 2.50A long, while the iron parameter u is calculated as -0.332 on the assumption that the $Fe-O$ distances are as nearly equal as possible. These parameter values differ only by 0.008 to 0.015 from the values to be derived from intensity data in the next section.

VERIFICATION OF THE ATOMIC ARRANGEMENT

Spectra up to the twentieth order were photographed by reflecting Mo $K\alpha$ radiation from the pinacoidal plane (010) of a crystal oscillating about [001] as an axis. The observed intensities of reflection were related to the atomic arrangement by means of the formula

$$I = C\frac{1+\cos^2 2\theta}{2\sin 2\theta}\omega F^2 e^{-2B(\sin\theta/\lambda)^2},$$

in which C is a constant, $(1+\cos^2 2\theta)/2\sin 2\theta$ is the polarization factor, ω is the Ott factor for varying time of reflection, $e^{-2B(\sin\theta/\lambda)^2}$ is the temperature factor, and F has the usual form

$$F = \sum_i f_j e^{2\pi i(hx_j+ky_j+lz_j)}.$$

The value of B was estimated as 1.00. Values of f were taken from Pauling and Sherman's[6] calculated f values for Fe and O.

The f values for Fe are so much larger than for O at large angles of reflection that it is possible to evaluate u, the Fe parameter, independently of the oxygen parameters u_1 and u_2. This was done by writing the intensity formulas concerned for a given observed inequality, assigning values to the oxygen parameters most favorable to the observed inequality, and solving graphically for permitted values of the iron parameter. The solution of ten inequalities over the range[7] $-0.50 < u < -0.250$ served to limit u to the region -0.3235 ± 0.004.

The oxygen parameters were varied over the ranges 0.065 to 0.085 and 0.265 to 0.285, which ranges were suggested by the predicted values, while the iron parameter was varied within its above limits; the intensities therewith calculated
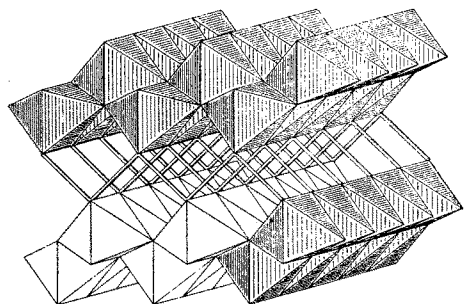
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[6] Linus Pauling and J. Sherman, Zeits. f. Kryst. 81, 1 (1932).
[7] The space group requires one Fe in this interval.

TABLE I. *Observed and calculated intensities of reflection on oscillation photograph from (010) with [001] as axis.*

{hkl} (Equator)	Obs.ᵃ	Calc.	{hkl} (First layer line)	Obs.	Calc.	{hkl} (Second layer line)	Obs.	Calc.
Pinacoid			Prisms			Prisms		
0 2 0	15.	153.	0 1 1	5.	14.4			
0 4 0	1.	1.23	0 3 1	30.	157.	0 4 2	0.8	0.60
0 6 0	10.	9.40	0 5 1	20.	84.	0 6 2	4.	4.68
0 8 0	20.	23.9	0 7 1	0.0	0.02	0 8 2	8.	9.86
0 10 0	0.7	0.81	0 9 1	2.5	2.12	0 10 2	0.2	0.36
0 12 0	2.	2.14	0 11 1	3.	2.62	0 12 2	1.	1.18
0 14 0	1.3	0.91	0 13 1	0.7	0.73	0 14 2	0.5	0.52
0 16 0	0.4	0.27	0 15 1	0.6	0.68	0 16 2	0.1	0.19
0 18 0	0.0	0.09	0 17 1	0.8	0.90	0 18 2	0.0	0.07
0 20 0	0.7	0.86	0 19 1	0.01	0.10	0 20 2	0.6	0.60
Prisms			0 21 1	0.0	0.001	Pyramids		
1 4 0	5.	9.35	Pyramids			1 8 2	1.	2.01
1 6 0	0.7	1.67	1 5 1	20.	35.6	1 10 2	8.	7.35
1 8 0	2.	4.9	1 7 1	10.	19.3	1 12 2	0.8	1.36
1 10 0	4.	16.45	1 9 1	0.2	0.82	1 14 2	0.0	0.005
1 12 0	1.	2.33	1 11 1	0.05	0.16	1 16 2	0.5	0.34
1 14 0	0.0	0.009	1 13 1	3.0	3.33	1 18 2	1.0	0.78
1 16 0	1.0	0.49	1 15 1	1.5	2.20	1 20 2	0.0	0.09
1 18 0	1.4	1.07	1 17 1	0.0	0.02			
1 20 0	0.0	0.12	1 19 1	0.15	0.10			
			1 21 1	0.3	0.23			

ᵃ Estimated visually.

were found to agree with observed intensities for the values

$$u = -0.322 \pm 0.001; \quad u_1 = +0.282 \pm 0.005;$$
$$u_2 = +0.075 \pm 0.005.$$

The probable errors as given correspond to the minimum displacements giving qualitative disagreement between observed and calculated intensities. The extent of the agreement obtained between observed and calculated intensities using these values of the parameters is shown in Table I.

DISCUSSION OF THE STRUCTURE

The atomic arrangement as calculated from intensities differs from the predicted arrangement only by shifts of 0.008 to 0.012 in the parameter values, and the predicted structure for lepidocrocite is thereby verified. As was mentioned previously the layers in this structure have the $(OH)^-$ anions on their outer surfaces, and it is now possible to show that these anions give rise to OHO groups, or hydrogen bonds, holding the layers together.

Hydrogen bonds are postulated in lepidocrocite, as in diaspore,[5] for the explanation of certain O−O distances. In Table II are given the inter-atomic distances in lepidocrocite. In each layer the O−O distances along shared edges are 2.59A, and the other O−O distances, along the lengthened octahedral edges, are 3.05A and 3.06A. Between the layers the O−O distances are 2.70A, 3.10A, and greater. The O−O distance of 2.70A between the layers is not only the shortest unshared O−O distance in the structure, but is inexplicably so unless it is regarded as a hydrogen bond. Alternatively the only forces holding the layers together would be the relatively weak ones arising from dipole interactions, against which the repulsive force between the oxygens would be effective in raising the distance above 2.70A. The value of 2.70A for the OHO distance in

TABLE II. *Interatomic distances in lepidocrocite.*

Atom	Neighbors in same octahedron	Neighbors in other octahedra of same layer	Neighbors in next layer
Fe	2 O_{II} at 2.00A 2 O_I at 2.00A 2 O_I at 2.01A	3 Fe at 3.06A	
O_I	2 O_I at 3.06A 4 O_{II} at 3.05A 4 O_I at 2.59A 1 O_{II} at 2.59A		2 O_{II} at 3.97A
O_{II}	2 O_{II} at 3.06A 4 O_I at 3.05A 1 O_I at 2.59A		2 O_I at 3.97A 4 O_{II} at 3.10A 2 O_{II} at 2.70A

lepidocrocite is, moreover, equal within experimental error to the value 2.71A found in diaspore.

The association of one hydrogen with each 2.70A distance gives the correct stoichiometric composition to the crystal. If the hydrogens are placed exactly half-way between the bonded oxygens they lie at centers of symmetry, with the coordinates 000; $\frac{1}{2}00$; $0\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. Fig. 1 is a pictorial representation of the lepidocrocite structure, with the hydrogen bonds drawn as small tubes between the layers.

The octahedral units in the layers are considerably distorted from the shape of a regular octahedron, this distortion expressing itself in a flattening of that portion of the octahedron that is in the interior of the layer, and in a projection of the edge formed by the two $(OH)^-$ anions away from the layer. The distortion is not as marked, however, as in certain other structures, notably those of bixbyite and the C modification of the sesquioxides.[8]

The $O-Fe$ distances of 2.00 to 2.01A are equal to the sum of the radii concerned and do not exhibit the effect of $Fe-Fe$ repulsion shown in hematite.[9] The value of 2.59A for the length of the shared edges in lepidocrocite is in good correspondence with the value 2.55A found in hematite.

[8] Linus Pauling and M. D. Shappell, Zeits. f. Kryst. **75**, 128 (1930).
[9] Linus Pauling and S. B. Hendricks, J. Am. Chem. Soc. **47**, 781 (1925).

The four $Fe-O$ bonds around O_I have directions differing by 5° to 20° from regular tetrahedral directions; the directions of the four bonds around O_{II}, two to Fe and two to H, differ by only 3.5° to 9° from tetrahedral directions. While this approximate orientation of the hydrogen bond along a tetrahedral direction is probably dependent on the specific structure of the crystal, it nevertheless admits the possibility that the hydrogen bond is in part covalent.

In connection with the problem of correlation between the microscopic structure and macroscopic properties of crystals it may be pointed out that the tabular habit of lepidocrocite is such that the structural layers run parallel to the tabular face, that the excellent cleavage on (010) corresponds to the breaking only of the relatively weak hydrogen bonds, and that the striations on the tabular face run parallel to the "double rutile strings" in the layers. The parallel relation between the double rutile string and striations on developed faces is likewise noted in diaspore, and in rutile the striations run parallel to the single rutile strings.

The structural formula FeO(OH) has been chosen for lepidocrocite as reflecting in some degree the character of the structure, although the OH^- anions do not actually exist as such, but rather as strings of $(-HOHOHOH-)$.