

The Crystal Structure of Potassium Chloroplatinate

The Crystal Structure of Diaspore

The Crystal Structure of Lepidocrocite

THESIS

by

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## ABSTRACT

Crystals of potassium chloroplatinate, studied by means of spectral and Laue photographs, are shown to have the potassium chlorostannate structure with  $d_{100} = 9.73 \text{ \AA}$  and  $u = 0.240 \pm 0.005$ . The reported value of  $u = 0.16$  is shown to be incorrect, and the theoretical treatment of Jones and Dent which supported this latter value is thereby deprived of its supposed agreement with experiment.

The parameters in diaspore are redetermined, and the structure is discussed from the standpoint of the coordination theory. The existence and location of hydrogen bonds in the structure are established, and representative formulas are proposed.

The unit of structure, space group symmetry, and detailed atomic arrangements 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 relationship between the diaspore and lepidocrocite structures is discussed from the standpoint of the coordination theory, and found to depend on two alternative ways of satisfying the electrostatic valence rule.

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## The Crystal Structure of Potassium Chloroplatinate.

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Contribution from Gates Chemical Laboratory, California Institute of Technology,  
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(With 3 figures.)

### Introduction.

It has been reported<sup>1)</sup>, without publication of substantiating experimental information, that crystals of potassium chloroplatinate,  $K_2PtCl_6$ , have the potassium chlorostannate structure, and that the parameter  $u$  determining the position of the chloride ions has a value of about 0,16. On the other hand, the carefully prosecuted study<sup>2)</sup> of ammonium chloroplatinate,  $(NH_4)_2PtCl_6$ , led to a value for  $u$  for this substance lying between 0,22 and 0,24. The discrepancy in results reported for these two related substances has been pointed out by Wyckoff<sup>3)</sup>, who wrote "Inasmuch as  $u$  has the same value for both the potassium and the ammonium chlorostannates<sup>4)</sup> it might be anticipated that  $u = \pm 0,24$  for  $K_2PtCl_6$ . A more detailed investigation is hence to be desired".

Lennard-Jones and Miss Dent have recently<sup>5)</sup> developed a theory designed to predict parameter values for crystals of this type, and have obtained results agreeing with Scherrer and Stoll's work on potassium chloroplatinate and disagreeing with Dickinson's on potassium chlorostannate. This attached still greater interest to the reinvestigation of the structure of this crystal, and especially to the accurate determination of the value of the parameter. The research described in the following pages leads definitely to the conclusion that Scherrer and Stoll's para-

1) P. Scherrer and P. Stoll, Z. anorg. Ch. **121**, 319. 1922.

2) R. W. G. Wyckoff and E. Posnjak, J. Am. Chem. Soc. **43**, 2292. 1921.

3) R. W. G. Wyckoff, "The Structure of Crystals", Chemical Catalog Co., New York, 1924, p. 344.

4) R. G. Dickinson, J. Am. Chem. Soc. **44**, 276. 1922.

5) J. E. Lennard-Jones and B. M. Dent, Phil. Mag. **3**, 4204. 1927.



meter value is incorrect, and hence that Lennard-Jones and Miss Dent's theory disagrees with experiment for potassium chloroplatinate as well as for potassium chlorostannate.

#### Experimental methods.

Potassium chloroplatinate, prepared from chloroplatinic acid and potassium chloride, was recrystallized from distilled water. The crystals obtained were small isotropic octahedra.

The standard method of investigation with X-rays involving the preparation and interpretation of Laue and spectral photographs was used in order to avoid as far as possible any chance of introducing serious error in the structure determination. Spectral photographs were made of the molybdenum *K*-radiation reflected from the face (111) of a crystal about 2 mm. on an edge and simultaneously from (100) of calcite. Laue photographs were then taken with the incident beam of X-rays at various small angles with the normal to (111) of a perfect crystal about 0,7 mm. in its largest dimension. A tungsten anticathode Coolidge tube operated at a peak voltage of about 52 kv. was used. Indices were assigned to the Laue spots with the aid of gnomonic projections.

#### Determination of the structure.

The spectral data of Table I lead to  $d_{100}/n_0 = 9,73 \text{ \AA}$ , in which  $n_0$  is the order of reflection of the first line reflected from (111). Values of  $n\lambda$  calculated on the basis of the unit with  $n_0 = 4$  for over 200 spots arising from planes of over 75 different forms on a Laue photograph were in every case larger than 0,24  $\text{\AA}$ , the short wave-length limit of the incident radiation. There is accordingly no evidence requiring or indicating the existence of a larger unit of structure than that with  $d_{100} = 9,73 \text{ \AA}$ . The density calculated from this unit containing  $4K_2PtCl_6$  is 3,50, in acceptable agreement with the directly measured values, 3,58—3,69.

No odd order reflections were observed from any planes except those with all indices odd, so that the structure may be assumed to be based on a face-centered lattice. A Laue photograph taken with the incident beam normal to (111) showed three planes of symmetry in addition to the three-fold axis; the crystal hence has the symmetry of one of the point-groups  $T_d$ ,  $O$ , or  $O_h$ . The only space-groups<sup>1)</sup> satisfying these requirements and providing atomic positions for 8K, 4Pt and 24Cl are

<sup>1)</sup> R. W. G. Wyckoff, "The Analytical Representation of the Results of the Theory of Space-Groups", Pub. Carnegie Inst., No. 348, 1922.

Table I.  
Spectral data from potassium chloroplatinate.

X-ray line <sup>1)</sup>	Order	Angle of reflection	$\frac{d_{111}}{n_0}$	Intensity	$S$ (for $u=0,240$ )	$S(u=0,46)$
$\beta$	$n_0$	$3^{\circ}44'$	5,59	} strong	0,827	4,300
$\alpha$	$n_0$	3 37	5,63			
$\alpha$	$2n_0$	7 44	5,64	med. weak	0,60 2)	0,034
$\alpha_1$	$3n_0$	10 $52\frac{1}{2}$	5,62	} medium	0,577	0,228
$\alpha_2$	$3n_0$	10 58	5,62			
$\beta$	$4n_0$	12 56	5,65	} strong	2,405	0,499
$\alpha_1$	$4n_0$	14 $35\frac{1}{2}$	5,64			
$\alpha_2$	$4n_0$	14 $42\frac{1}{2}$	5,64	} medium	1,073	4,073
$\alpha_1$	$5n_0$	18 22	5,64			
$\alpha_2$	$5n_0$	18 26	5,62	strong		

$$\text{Mean } \frac{d_{111}}{n_0} = 5,63 \text{ \AA.}$$

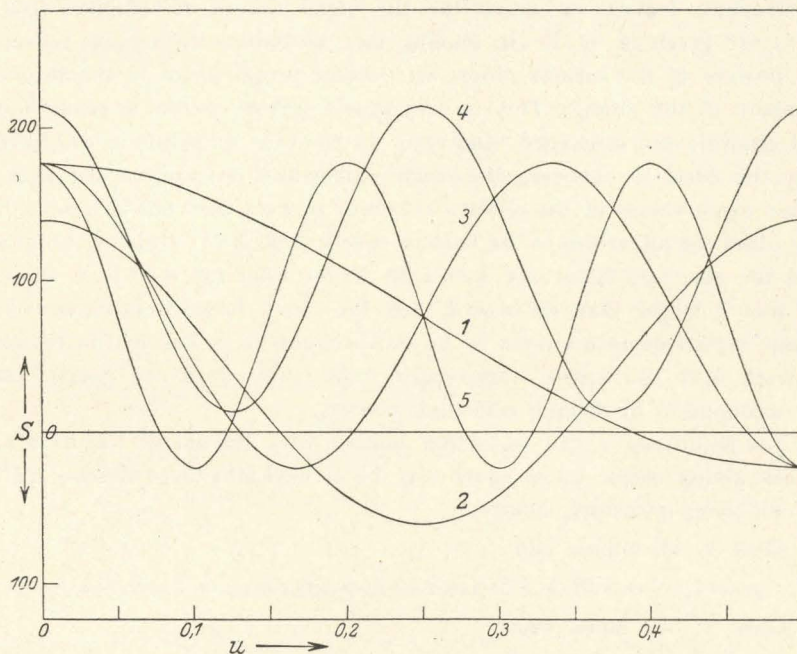


Fig. 4. Structure factor curves for the first five orders of reflection from (111).

1)  $\beta$  signifies  $MoK_{\beta}$ ,  $\lambda = 0,6344 \text{ \AA}$ ;  $\alpha_1$ ,  $MoK_{\alpha_1}$ ,  $\lambda = 0,7078 \text{ \AA}$ ;  $\alpha_2$ ,  $MoK_{\alpha_2}$ ,  $\lambda = 0,7421 \text{ \AA}$ ;  $\alpha$ , mean of  $\alpha_1$  and  $\alpha_2$ ,  $\lambda = 0,7400 \text{ \AA}$ .

2) Increase in the relative reflecting power of platinum would decrease this value of  $S$  further, giving better agreement with the observed intensity.



$T_d^2$ ,  $O^3$  and  $O_h^5$ . Of the several alternative structures provided by these space-groups all but one must be excluded, since they are in pronounced disagreement with the observed relative intensities of reflection from different planes<sup>1</sup>).

The allowed structure, obtainable from all three space-groups, is the following:

$$\begin{aligned} 4Pt & \text{ at } 4b: (0\ 0\ 0); \\ 8K & \text{ at } 8c: \pm (\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4}); \\ 24Cl & \text{ at } 24a: \pm (u\ 0\ 0, 0\ u\ 0, 0\ 0\ u), \end{aligned}$$

in which each indicated position represents one point of a face-centered lattice.

The parameter  $u$  defining the chloride positions can be determined from the relative intensities of reflection with the use of only qualitative assumptions regarding intensity factors other than the structure factor, for if of two planes the one with the smaller value of  $d/n$  reflects more strongly than the other its structure factor must be the larger. Curves of structure factors calculated for the small orders of reflection from (111) are given in fig. 4. In making this calculation the relative reflecting powers of the various atoms were taken proportional to the atomic numbers of the atoms. This is very nearly correct so far as potassium and chlorine are concerned, and error in the case of platinum will have only the effect of changing the origin somewhat; in limiting the parameter exact values of the relative reflecting powers need not be assumed. The observed intensities of the various orders from (111) (Table I) require that the structure-factor for  $n = 4$  be larger than for  $n = 4, 2$ , or 3, for  $n = 3$  larger than for  $n = 2$ , and for  $n = 5$  larger than for  $n = 3$ . These requirements are seen to be satisfied only if  $u$  lies in the region between 0,18 and 0,250. The upper limit 0,250 does not depend on the assumption of definite reflecting powers.

The parameter  $u$  can be further limited with the aid of Laue data. Planes giving useful Laue spots may be divided into three classes, with the following structure factors:

Class 1: all indices odd.

$$n = 4, S = 4\bar{P}t + 8\bar{C}l(\cos 2\pi hu + \cos 2\pi ku + \cos 2\pi lu).$$

Class 2: one index even,

$$n = 4, S = 0; n = 2,$$

$$S = 4\bar{P}t + 8\bar{K} + 8\bar{C}l(\cos 4\pi hu + \cos 4\pi ku + \cos 4\pi lu).$$

<sup>1</sup>) The detailed argument involved has been presented before; see, for example R. G. Dickinson, J. Am. Chem. Soc. 44, 276. 1922; R. W. G. Wyckoff, "The Structure of Crystals", Chemical Catalog Co., New York, 1924, pp. 334—337; etc.

Class 3: two indices even,

$$n = 4, S = 0, n = 2,$$

$$S = 4\bar{P}t - 8\bar{K} + 8\bar{Cl}(\cos 4\pi hu + \cos 4\pi kv + \cos 4\pi lw).$$

Table II.

Selected Laue data for potassium chloroplatinate.

<i>hkl</i>	Class	$d/n$ Å	$\lambda$ Å	Estimated intensity	<i>S</i> $u = 0,240$	<i>S</i> $u = 0,16$
224	3	4,62	0,37	0,9	2,122	0,524
554	4	4,36	0,36	0,9	2,973	3,446
553	4	4,27	0,36	0,6	2,723	0,647
733	4	4,49	0,38	0,4	4,492	4,037
322	3	4,48	0,35	0,4	2,484	0,874
444	2	4,45	0,44	0,5	2,300	2,369
754	4	4,42	0,37	0,4	2,238	3,866
424	3	4,06	0,44	0,5	2,029	0,074
755	4	0,978	0,36	0,3	2,484	3,639
430	3	0,973	0,35	0,3	2,422	2,958
430	3	0,973	0,42	0,3	2,122	2,958
434	2	0,954	0,37	0,3	2,362	3,764
954	4	0,944	0,35	0,3	3,200	2,207
954	4	0,944	0,42	0,3	3,200	2,207
773	4	0,944	0,38	0,4	4,253	2,758
773	4	0,944	0,42	0,2	4,253	2,758
520	3	0,903	0,42	0,2	2,336	0,730
432	3	0,903	0,44	0,2	2,091	2,595
524	2	0,888	0,37	0,2	2,576	4,536
974	4	0,873	0,36	0,2	2,465	2,627
530	2	0,834	0,37	0,4	2,669	4,568
530	2	0,834	0,44	0,2	2,669	4,568
433	2	0,834	0,46	0,25	2,424	5,159
973	4	0,825	0,36	0,2	2,245	4,099
44-3-3	4	0,823	0,38	0,4	4,284	0,374
44-5-4	4	0,802	0,38	0,4	2,027	3,200
44-5-4	4	0,802	0,40	0,4	2,027	3,200
532	2	0,790	0,44	0,2	2,638	2,934
644	2	0,790	0,47	0,2	2,453	3,432
44-5-3	4	0,782	0,36	0,05	4,777	4,672
975	4	0,782	0,38	0,4	2,744	2,400
443	3	0,760	0,40	0,4	4,998	4,774
624	3	0,760	0,37	0,4	4,882	0,989
624	3	0,760	0,44	0,4	4,882	0,989
544	2	0,750	0,44	0,4	2,483	4,986
44-7-4	4	0,744	0,37	0,05	4,292	3,620
44-7-4	4	0,744	0,42	0,05	4,292	3,620
44-7-3	4	0,727	0,39	0,00	4,042	2,092
977	4	0,727	0,44	0,05	4,976	2,820
542	3	0,723	0,43	0,05	2,242	0,457
634	2	0,718	0,44	0,05	2,245	4,827
634	2	0,718	0,38	0,05	2,245	4,827
995	4	0,712	0,39	0,15	3,673	0,744
43-3-3	4	0,712	0,40	0,4	2,647	4,484
43-5-4	4	0,697	0,39	0,4	3,393	4,043
44-7-5	4	0,697	0,38	0,00	4,538	3,393
43-5-3	4	0,683	0,38	0,05	3,443	2,485
644	3	0,668	0,39	0,04	4,789	4,439
724	2	0,662	0,38	0,05	2,748	2,408



In comparing relative intensities of two planes of the same class only qualitative assumptions need be made regarding relative reflecting powers. Values of  $S$  as a function of  $u$  for various planes of Class 4 are shown in Fig. 2. From this figure it is seen that the experimental observation that the form {951} reflects more strongly than {755} at the same wave length limits  $u$  to the region between 0,196 and 0,250. The inequality {975}  $\geq$  {11.5.1} requires similarly that  $u$  lie between 0,244 and 0,250, and several other such inequalities given in the Laue data

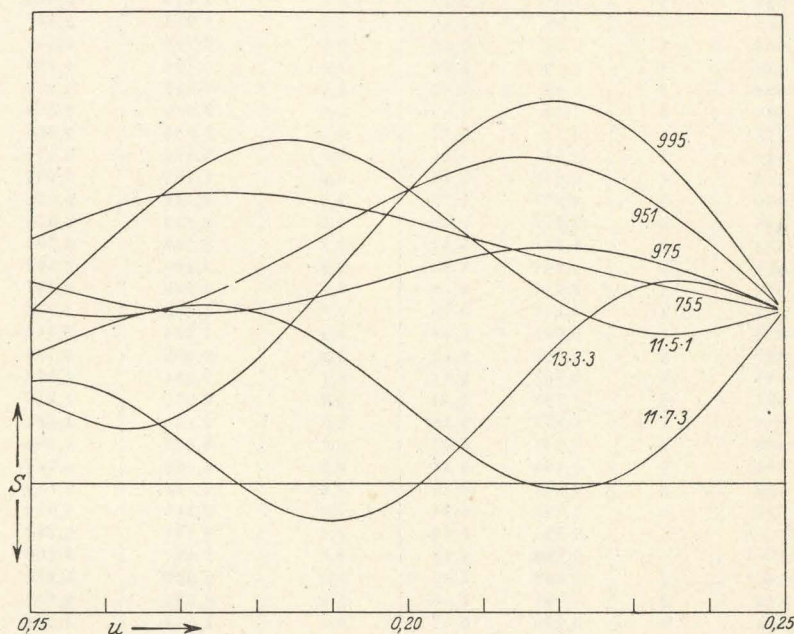


Fig. 2. Structure factor curves for planes of Class 4.

in Table 2 limit  $u$  to about this same range. A closer lower limit is provided by the equality in intensity of {13.3.3} and {975}, which requires that  $u$  be not much less than 0,24. On the other hand the very small intensity of {11.7.3} requires that  $u$  be not much greater than 0,24; so that the parameter value can be safely given as

$$u = 0,240 \pm 0,005.$$

Verification of this value is provided also by planes of Classes 2 and 3. For  $u = 0,25$  their structure-factors are

$$\text{Class 2: } n = 2, S = 4\bar{P}t + 8\bar{K} - 8\bar{C}l;$$

$$\text{Class 3: } n = 2, S = 4\bar{P}t - 8\bar{K} + 8\bar{C}l.$$

These values are only slightly changed (by a maximum of 40% for  $u = 0,24$ ) as  $u$  is changed, for in each case the slope of the curve is zero at  $u = 0,25$ ; i. e.,  $\left(\frac{dS}{du}\right)_{u=0,25} = 0$ . Accordingly the observation that no intensity inequalities are observed between planes of Class 2 or of Class 3 substantiates the conclusion that  $u$  must be close to 0,25. In

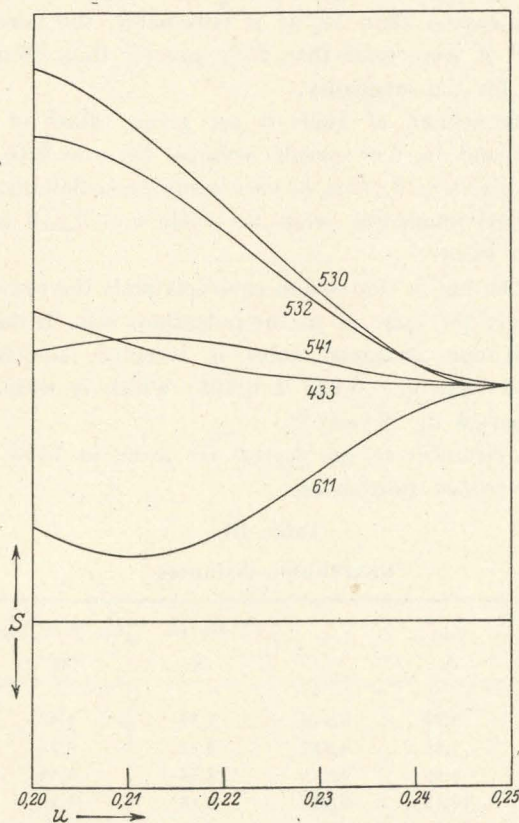


Fig. 3. Structure factor curves for planes of Class 2.

particular the equalities  $\{611\}_{n=2} \cong \{532\}_{n=2}$  and  $\{433\}_{n=2} = \{530\}_{n=2}$  require that  $u$  be considerably greater than 0,23 (see fig. 3).

It was also found that no intensity inequalities between a plane of Class 2 and one of Class 3 exist. This is explicable on the assumption that  $\bar{K} = \bar{Cl}^1$ . The ions  $K^+$  and  $Cl^-$  have the same number of electrons,

<sup>1</sup>) Similar observations and conclusions are reported by Dickinson for potassium chlorostannate.



and may hence be expected to have the same reflecting power for small angles of reflection; at large angles of reflection, however, the reflecting power of  $Cl^-$  should fall off somewhat more rapidly than that of  $K^+$ , on account of its larger size. This effect is not sufficiently great to appear in the visually estimated intensities of Table II.

The intensity inequality  $\{13.3.3\} > \{541\}_{n=2}$  again substantiates the value decided on for  $u$ . With  $\bar{K} = \bar{Cl}$  this requires  $u > 0,230$ , and if  $\bar{K}$  is slightly greater than  $\bar{Cl}$ , as is reasonable, the lower limit for  $u$  is increased. If  $\bar{K}$  were more than 25% greater than  $\bar{Cl}$  no value of  $u$  would account for the inequality.

In the sixth column of Table II are given values of  $S$  calculated for  $u = 0,240$ , and in the seventh column for  $u = 0,16$ . It will be seen that the value  $u = 0,16$  is in very many cases definitely at variance with the observed intensities, while the value  $u = 0,240$  is in complete agreement with them.

It is probable that in ammonium chloroplatinate the chlorine-platinum distance is nearly the same as in the potassium salt. If this is assumed to be true, and our parameter value is accepted, ammonium chloroplatinate should have  $u = 0,237 \pm 0,005$ , which is within the region  $0,22-0,24$  reported by Wyckoff.

Interatomic distances in the crystal are given in Table III, together with those for related substances.

Table III.  
Interatomic distances.

Crystal	$d_{100}$ Å	$u$	$M-Cl$ Å	$Cl-K$ or $NH_4$ Å	$M-K$ or $NH_4$ Å
$K_2PtCl_6$	9,73	0,240	2,33	3,45	4,21
$(NH_4)_2PtCl_6$	9,84	0,237	2,33	3,48	4,26
$K_2SnCl_6$	9,96	0,245	2,44	3,52	4,31
$(NH_4)_2SnCl_6$	10,05	0,245	2,46	3,55	4,35

### Summary.

Crystals of potassium chloroplatinate, studied by means of spectral and Laue photographs, are shown to have the potassium chlorostannate structure with  $d_{100} = 9,73$  Å and  $u = 0,240 \pm 0,005$ . The value  $u = 0,16$  reported by Scherrer and Stoll is shown to be incorrect.

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The Crystal Structure of Diaspore.

## The Crystal Structure of Diaspore\*

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The parameters in diaspore are redetermined, and the structure is discussed from the standpoint of the coordination theory. The existence and location of hydrogen bonds in the structure are established, and representative formulas are proposed.

### INTRODUCTION

THE mineral diaspore,  $\text{AlHO}_2$ , is described as forming orthorhombic crystals, with the axial ratios  $a : b : c = 0.9372 : 1 : 0.6039$ , according to Groth. Its composition, symmetry and axial ratios suggest its isomorphism with the goethite modification of  $\text{FeHO}_2$ , and with manganite,  $\text{MnHO}_2$ . A second modification of  $\text{FeHO}_2$ , lepidocrocite, also exists and forms orthorhombic crystals. The existence of a second modification of  $\text{AlHO}_2$  corresponding to lepidocrocite is indicated by the x-ray studies made by Böhm<sup>1</sup> on certain bauxites.

Work begun by the writer in 1929 had disclosed the structure of diaspore and suggested a probable structure for lepidocrocite. The completion of this work was unavoidably delayed until recently, and in the meantime the structure of diaspore was derived by Deflandre<sup>2</sup> and independently by Takané,<sup>3</sup> and Goldsztaub<sup>4</sup> found that the goethite structure was essentially that of diaspore.

In the present paper the diaspore-goethite structure is discussed from the standpoint of the coordination theory, with particular reference to the distribution of the hydrogen atoms and their relation to the existence of a second modification.<sup>5</sup> The results of a more accurate determination of the parameters in diaspore are given, and the interatomic distances thus determined are shown to establish the existence and location of the hydrogen bonds as suggested by the coordination theory.

### THE UNIT OF STRUCTURE, SPACE GROUP SYMMETRY AND THE GENERAL POSITIONS OF THE ATOMS

The unit cell of diaspore was determined from oscillation and Laue photographs to correspond to the axial lengths

$$a = 4.40\text{A}, \quad b = 9.39\text{A}, \quad c = 2.84\text{A}.$$

These values give the axial ratios  $0.469 : 1 : 0.302$ , in good agreement with the crystallographic ratios  $0.4686 : 1 : 0.3020$  obtained by doubling the  $b$ -axis. The observed density of diaspore, 3.4, indicates that a unit of these dimensions contains 4  $\text{AlHO}_2$ .

The space group of diaspore was determined from Laue data to be  $V_h^{16} - Pbnm$ , as found by Deflandre and Takané.

The observed even orders of reflection from (001) were found to decline normally in intensity, indicating that all the atoms are situated in planes perpendicular to  $c$  at a distance  $c/2$  apart. To place the oxygens anywhere except on the reflection plane  $m$  would give O—O distances of 1.42A or less, which is impossible. All the atoms therefore lie on the  $m$  reflection planes, the general positions, referred to a center of symmetry as origin, being as follows:

$$4 \text{ Al at } u, v, -\frac{1}{4}; \frac{1}{2} - u, \frac{1}{2} + v, -\frac{1}{4}; \frac{1}{2} + u, \frac{1}{2} - v, \frac{1}{4}; \bar{u}, \bar{v}, \frac{1}{4}.$$

$$4 \text{ O}_I \text{ at } u_1, v_1, -\frac{1}{4}; \text{ etc.}$$

$$4 \text{ O}_{II} \text{ at } u_2, v_2, -\frac{1}{4}; \text{ etc.}$$

### THE DETERMINATION OF PARAMETERS

Oscillation photographs were taken of  $\text{Mo } K\alpha$  radiation by reflection from (010), ten even orders of reflection being observed. Using the usual methods it was found that the observed intensities of reflections at large angles serve to fix  $v$ , the aluminum parameter, at  $+0.144 \pm 0.003$  irrespective of the oxygen positions. By using

\* No. 456.

<sup>1</sup> J. Böhm, *Zeits. f. anorg. Chemie* **149**, 203 (1925).

<sup>2</sup> M. Deflandre, *Bull. Soc. Franc. Mineral.* **55**, 140 (1932).

<sup>3</sup> Takané, *Proc. Imp. Acad. Tokyo* **9**, 113 (1933).

<sup>4</sup> S. Goldsztaub, *Comptes rendus* **195**, 964 (1932).

<sup>5</sup> The structure of the second modification as typified by lepidocrocite will be described in a future publication.

values of the aluminum parameter within these limits it was then found possible on the basis of observed intensities to fix the oxygen parameters within the ranges  $-0.216 < v_1 < -0.190$  and  $-0.062 < v_2 < -0.042$ . The parameters were then adjusted within these limits to give the best quantitative relation between observed and calculated intensities. The values thus obtained are

$$v = +0.146 \pm 0.001, \quad v_1 = -0.200 \pm 0.002,$$

and  $v_2 = -0.052 \pm 0.002$ ,

in which the probable limits of error as given correspond to the minimum displacement causing disagreement between observed and calculated intensities. The extent of the agreement between observed and calculated intensities of reflection from (010) using these values of the parameters is shown in Table I.

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

{hkl}	Intensity		{hkl}	Intensity	
	Obs. <sup>a</sup>	Calc. <sup>b</sup>		Obs. <sup>a</sup>	Calc. <sup>b</sup>
(020)	4.0	5.4	(021)	2.0	1.7
(040)	10	7.3	(041)	4.5	4.0
(060)	6.0	4.7	(061)	25	17.5
(080)	0.25	1.2	(081)	4.0	3.0
(0.10.0)	3.0	2.1	(0.10.1)	0.7	0.15
(0.12.0)	0.7	0.15	(0.12.1)	1.4	0.79
(0.14.0)	1.1	0.48	(0.14.1)	0.85	0.22
(0.16.0)	0.0	0.03	(0.16.1)	0.5	0.16
(0.18.0)	0.25	0.07	(0.18.1)	0.0	0.04
(0.20.0)	0.7	0.15	(0.20.1)	0.0	0.03

<sup>a</sup> Estimated visually, and corrected in the case of side spectra for varying time of reflection.

<sup>b</sup> Based on Bragg and West's *f* values.

The relative shortness of the *a*-axis limits the amount of diffraction data obtainable by reflection from (100), so that an exact determination of the parameters along *a* by rigorous methods is difficult. By assumptions which will be discussed in the next section it is possible to predict values of these parameters, the predicted values being

$$u = -0.036, \quad u_1 = +0.27, \quad u_2 = -0.21.$$

These values give excellent quantitative agreement between the calculated and observed intensities of reflection, as is shown in Table II. A shift of 0.01 in any of these parameters somewhat impairs the quantitative nature of the agreement.

TABLE II. Observed and calculated intensities of reflection on oscillation photograph from (100) with [001] vertical.

{hkl}	Intensity		{hkl}	Intensity	
	Obs. <sup>a</sup>	Calc. <sup>b</sup>		Obs. <sup>a</sup>	Calc. <sup>b</sup>
(200)	0.2	0.13	(101)	0.8	0.81
(400)	5.0	3.4	(301)	1.7	2.2
(600)	0.0	0.00	(501)	0.5	0.57
(500)	0.0	0.08	(701)	0.3	0.28

<sup>a</sup> Estimated visually, and corrected in the case of side spectra for varying time of reflection.

<sup>b</sup> Based on Bragg and West's *f* values.

The parameter values determined by Deflandre are, restated in our convention,  $u = -0.042$ ,  $u_1 = +0.25$ ,  $u_2 = -0.25$ ,  $v = +0.144$ ,  $v_1 = -0.20$ ,  $v_2 = -0.05$ . His values for *v*,  $v_1$  and  $v_2$  are in close accord with ours, but his values for *u*,  $u_1$  and  $u_2$  do not account quantitatively for reflections from (100) as well as do ours. This is illustrated, for instance, by the reflection (701), which is observed 0.6 as strong as (501); the calculated ratio is 0.5 using our parameters values and 0.2 using Deflandre's values. Takané's parameter values differ more widely from ours, and lead in some instances to calculated intensities that are in qualitative disagreement with our data.

#### DISCUSSION OF THE STRUCTURE

The diaspore-goethite structure can be regarded as built of aluminum or iron centered octahedra arranged in the manner shown in Fig. 1. The octahedra share edges in such a way as to form one-dimensionally infinite aggregates which may be called "double rutile strings" running parallel to the *c* axis. These strings are joined by sharing corners, as shown in the figure. Each anion is common to three octahedra.

This type of structure is readily predictable on the basis of the coordination theory<sup>6</sup> if a distribution of the hydrogens is assumed giving all the anions the form  $(\text{OH}_3)^{-\frac{1}{3}}$ , such anions being required by the electrostatic valence rule to be shared between three octahedra.<sup>7</sup> The only alternative distribution of the hydrogens gives the anions  $\text{O}^-$  and  $\text{OH}^-$ , and the electrostatic

<sup>6</sup> Linus Pauling, J. Am. Chem. Soc. 51, 1010 (1929).

<sup>7</sup> With the character of the polyhedra and their method of sharing defined, the number of structures fitting the unit cell is greatly limited, and the structure shown in Fig. 1 is the only one that is immediately apparent under the conditions given.



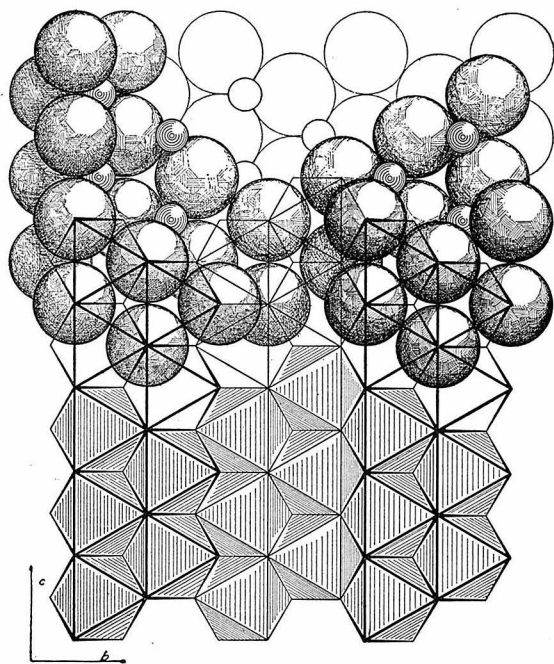


FIG. 1. The ideal structure of diaspore, showing the "double rutile strings" formed by the aluminum-centered oxygen octahedra. The relationship between the octahedra and the close packed arrangement of the oxygens is also shown. The aluminums are represented by the small spheres.

valence rule requires that  $O^{=}$  and  $OH^{-}$  anions be shared between four and two octahedra, respectively. This latter type of sharing is actually that found in the structure of the second modification of  $FeHO_2$ , lepidocrocite.<sup>5</sup>

The coordination theory not only gives the ideal structure successfully, but also indicates the degree of distortion to be expected. Edges shared between octahedra, according to the rule for distortion, should be reduced to 2.50Å, with other edges being compensatorily lengthened. The lengthened edge is given in the case of diaspore by the  $c$  identity distance, 2.84Å. By fitting the distorted octahedra to the unit cell values for the entire set of parameters can be obtained, and  $v$ ,  $v_1$  and  $v_2$  thus obtained are within 0.02 of the values derived rigorously from intensity measurements.

Starting with the rigorously determined values of  $v_1$  and  $v_2$  the requirement that shared edges be 2.50Å long leads directly to the values of +0.27 and -0.21 for  $u_1$  and  $u_2$ , respectively. As previously shown arguments based on quantitative

agreement with intensities serve to confirm these values, but equally important is the fact that they introduce into the structure the 2.50Å shared edge which appears in many accurately known structures such as rutile, anatase, brookite, and corundum, and which has been shown to correspond to a minimum of crystal energy in the case of rutile and anatase.<sup>8</sup>

The value of -0.036 for the aluminum parameter  $u$  is calculated by making the reasonable assumption that structurally similar Al-O distances inside the octahedron are equal, i.e. that the aluminum is equidistant from the three oxygens in the center of the double rutile string, and likewise equidistant from the three oxygens at the corner of the string. These two conditions lead to slightly different values for  $u$ , the average of which is given by -0.036.

The formal existence of  $(OH_4)^{-3}$  anions is most readily explained by postulating hydrogen bonds between pairs of oxygens. Hydrogen bonds, forming collinear OHO groups, have been found in certain crystals containing oxygen and acidic hydrogen, namely  $H_3BO_3$ ,<sup>9</sup>  $NaHCO_3$ ,<sup>10</sup> and  $K_2HPO_4$ ,<sup>11</sup> and in ice<sup>12</sup> and the crystalline hydrates  $H_2C_2O_4 \cdot 2H_2O$ <sup>13</sup> and  $Li_2SO_4 \cdot H_2O$ .<sup>14</sup> The hydrogen bond has also been shown to exist in gaseous  $(HCOOH)_2$  by means of electron diffraction methods.<sup>15</sup>

In diaspore the location of the hydrogen bonds can be expected to be between oxygens in different octahedra because of the effect of Al-H repulsion; their exact location is finally determined by a comparison of the interatomic distances concerned.

Interatomic distances calculated from our values of the parameters are shown in Table III. With the exception of the shared edges (which are 2.50Å long), the O-O distances within each octahedron lie in the range from 2.73 to 2.84Å, or somewhat in excess of 2.70Å, the sum of the ionic radii. Between different octahedra the O-O distances are 3.10Å or greater with the important

<sup>8</sup> Linus Pauling, *Zeits. f. Krist.* **67**, 377 (1928).

<sup>9</sup> W. H. Zachariasen, *Zeits. f. Krist.* **88**, 150 (1934).

<sup>10</sup> W. H. Zachariasen, *J. Chem. Phys.* **1**, 634 (1933).

<sup>11</sup> J. West, *Zeits. f. Krist.* **74**, 306 (1930).

<sup>12</sup> W. H. Barnes, *Proc. Roy. Soc. (London)* **125**, 670 (1929).

<sup>13</sup> W. H. Zachariasen, *Zeits. f. Krist.* **89**, 442 (1934).

<sup>14</sup> G. E. Ziegler, *Zeits. f. Krist.* **89**, 456 (1934).

<sup>15</sup> L. Pauling and L. O. Brockway, *Proc. Nat. Acad. Sci.* **20**, 336 (1934).

TABLE III. *Interatomic distances in diaspore.*

Atom	Neighbors in same octahedron	Neighbors in other octahedra
O <sub>I</sub>	2 O <sub>I</sub> at 2.84A 4 O <sub>I</sub> at 2.78 2 O <sub>II</sub> at 2.78 2 O <sub>II</sub> at 2.73 1 O <sub>II</sub> at 2.50	2 O <sub>II</sub> at 4.11A 2 O <sub>II</sub> at 3.92 1 O <sub>II</sub> at 2.71
O <sub>II</sub>	2 O <sub>II</sub> at 2.84A 2 O <sub>I</sub> at 2.78 2 O <sub>I</sub> at 2.73 2 O <sub>II</sub> at 2.50 1 O <sub>I</sub> at 2.50	2 O <sub>I</sub> at 4.11A 2 O <sub>I</sub> at 3.92 2 O <sub>II</sub> at 3.10 1 O <sub>I</sub> at 2.71
Al	1 O <sub>II</sub> at 2.01A 2 O <sub>II</sub> at 1.98 1 O <sub>I</sub> at 1.86 2 O <sub>I</sub> at 1.82	2 Al at 3.10A

exception of the 2.71A distance. This distance of 2.71A is not only characterized by the fact that it is much the shortest of similar distances, but also by the fact that it is inexplicably so unless it is assumed to correspond with a hydrogen bond.

The location of the 2.71A distances in the diaspore structure is shown by the small tubes in Fig. 2. This figure perhaps makes it clear that by slightly twisting the double strings about their points of contact the distances corresponding to the tubes can be lengthened and brought into equality with other O—O distances between octahedra. The only apparent explanation for the structure having a twist which differentiates

these distances is that the tubes correspond to hydrogen bonds.<sup>16</sup>

The allocation of one hydrogen to each tube gives the correct stoichiometric composition to the crystal, and hence accounts for all of the hydrogens.

The value of 2.71A found for the OHO distance in diaspore is in agreement with the values 2.71 and 2.67A found in H<sub>3</sub>BO<sub>3</sub> and (HCOOH)<sub>2</sub>, respectively, and lies somewhat above the values 2.54 and 2.55A found in K<sub>2</sub>HPO<sub>4</sub> and NaHCO<sub>3</sub>, and below the values 2.77 and 2.96A found in H<sub>2</sub>O and Li<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O. This indicates that the strength of the hydrogen bond in diaspore is considerably greater than that in ice or in the hydrate Li<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O, and is approximately the same as in H<sub>3</sub>BO<sub>3</sub> and (HCOOH)<sub>2</sub>.

The Al—O distances in diaspore correspond closely to the Al—O distances of 1.99 and 1.85A found in corundum, since in diaspore the Al—O<sub>II</sub> distances average 1.99A and the Al—O<sub>I</sub> distances average 1.84A. The slight deviations of 0.01 to 0.02A from these average Al—O distances shown in Table III are within the error of the parameter determinations, but on the other hand they are in the proper direction to be related to a distortion produced by the hydrogen bond. In

<sup>16</sup> This differentiation of distances is not seriously affected by variation of the parameter values over ranges considerably greater than their probable error. Deflandre's values of the parameters might have been used to deduce the hydrogen bond, obtaining an OHO distance of 2.60A in comparison with a next smallest distance of 2.80A.

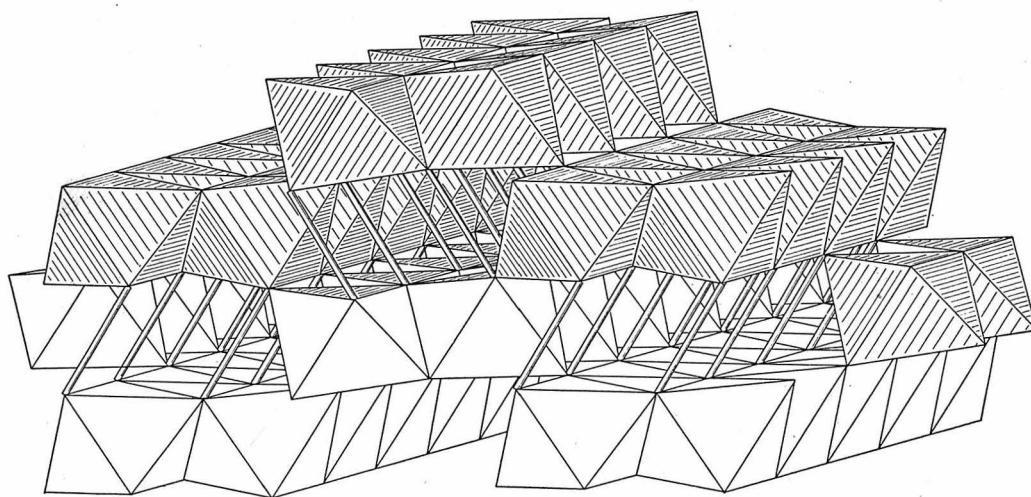


FIG. 2. A pictorial representation of the diaspore structure, with the hydrogen bonds shown as tubes.



both corundum and diaspoire the shift of the Al—O distances from 1.90A, the sum of the radii concerned, is evidence of the effect of Al—Al repulsion.

The formula for diaspoire we have written  $\text{AlHO}_2$ , the  $\text{HO}_2$  group so indicated being taken as representing hydrogen-bonded oxygens. The formula  $\text{HAlO}_2$  would be equally correct as indicating that both H and Al cations formed coordinated structures with the oxygen cations, and the chemical inference in this latter formula that diaspoire is meta-aluminic acid is borne out

by the existence of meta-aluminate salts such as the spinels. Either formula would be more correctly written in the polymerized form  $(\text{AlHO}_2)_n$  or  $(\text{HAlO}_2)_n$  to admit the known coordination number of 6 for Al. The usual formulas for diaspoire,  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ,  $\text{Al}_2\text{O}_2(\text{OH})_2$ , or  $\text{AlO}(\text{OH})$  are wrong in indicating a distinct existence of water or  $\text{OH}^-$  ions.

I am gratefully indebted to Professor Linus Pauling for his original suggestion as to the probable structure of diaspoire and for his interest and advice during the work.

The Crystal Structure of Lepidocrocite.

## The Crystal Structure of Lepidocrocite.

### Summary

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  $\underline{a}_0 = 3.87 \text{ \AA}$ ,  $\underline{b}_0 = 12.51 \text{ \AA}$ , and  $\underline{c}_0 = 3.06 \text{ \AA}$ . The space group is  $\underline{V}_h^{17} = \underline{Amam}$ . The parameters are determined as  $\underline{u}_{Fe} = -0.332$ ,  $\underline{u}_O = +0.282$ , and  $\underline{u}_{OH} = +0.075$ . 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 diaspor-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

1

Lepidocrocite,  $\text{FeO(OH)}$ , is described by Posnjak and Merwin 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  $\text{MHO}_2$ , exist in two modifications. The structure of the modification corresponding to diaspor,  $\text{AlHO}_2$ , and goethite,  $\text{FeHO}_2$ , is known<sup>2</sup>,

but no previous investigation of the structure of the second modification corresponding to lepidocrocite,  $\text{FeO}(\text{OH})$ , and bohmite<sup>3</sup>,  $\text{AlO}(\text{OH})$ , has been made.

In the present investigation the unit of structure, space group symmetry, and detailed atomic arrangement of lepidocrocite 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, Westerfeld, Germany. The crystals were tabular on  $\underline{b}$ , forming thin plates about  $1 \text{ mm}^2$  in area. Oscillation photographs of  $\text{Mc K}$   $\alpha$  radiation reflected from or transmitted through (010) with (001) as the axis gave the value  $3.06 \text{ \AA}$  for  $\underline{c}_0$  on the basis of the intervals between side spectra; and gave  $\underline{a}_0$  as  $1.935 \frac{\underline{n}_1}{\underline{n}_2}$ , and  $\underline{b}_0$  as  $6.255 \frac{\underline{n}_1}{\underline{n}_2}$  on the basis of the pinacoidal reflections. Calculated values of  $\underline{n}\lambda$  for observed Laue reflections require that  $\underline{n}_1 = \underline{n}_2 = 2$ . The correct unit cell is therefore given by the orthorhombic axes,

$$\underline{a}_0 = 3.87 \text{ \AA}, \quad \underline{b}_0 = 12.51 \text{ \AA}, \quad \text{and} \quad \underline{c}_0 = 3.06 \text{ \AA}.$$

No first order Laue reflections were observed in which  $(k + \ell)$  was odd, and the lattice is therefore based on  $\sqrt{\quad}$ , and centered on (100). Assuming holohedral symmetry for the crystal, the possible space groups are  $\frac{17}{h}$  to  $\frac{22}{h}$ . No evidence was found in support of

4

the statement by Goldsztaub that lepidocrocite possesses the space group symmetry  $V_h^1$ . 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 (hol) were observed in any of the 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 gms/ccm., 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 1.93 Å 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:

4 Fe at  $1/4, \underline{u}, 0$ ;  $3/4, \underline{u}, 0$ ;  $1/4, \underline{u}-\frac{1}{2}, \frac{1}{2}$ ;  $3/4, \frac{1}{2}-\underline{u}, \frac{1}{2}$  :

4 O at  $1/4, \underline{u}, 0$ ; etc.:

I 1

4 O at  $1/4, \underline{u}, 0$ ; etc.

II 2

The four hydrogen atoms are located subsequently from consideration of interatomic distances.

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<sup>5</sup> 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 2.00 Å, and the O-O distances have values in the neighborhood of 2.70 Å.

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  $\text{FeHO}_2$  are indicated by writing  $(\text{OH})^{-3/2}$  anions in one instance, and distinct  $\text{O}^-$  and  $(\text{OH})^-$  anions in the other. It has been shown<sup>6</sup> that the assumption that all the anions are of the form  $(\text{OH})^{-3/2}$  leads to the diasporo-goethite structure. It seems logical to assume, therefore, that lepidocrocite exists as a second modification of  $\text{FeHO}_2$  by virtue of having the alternative distribution of hydrogens. The  $\text{O}^-$  and  $(\text{OH})^-$  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 2.50 Å, with other edges being compensatorily lengthened.

The length of the a and c axes suggest the probable orientation of the octahedra, since the value 3.87 Å for a is close to the length 3.82 Å of the diagonal of an undistorted octahedron, and since the c axis, 3.06 Å, 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 12.51 Å be maintained in the direction of the  $\underline{b}$  axis, the layer structure indicated in Figure 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  $O^{\bar{2}}$ , while the oxygens  $O_{II}$  on the outer ridges of the layers are common to two octahedra and correspond to  $(OH)^{\bar{1}}$ . The layers can be regarded as formed by the sharing of edges between "double rutile strings" that were found as characteristic aggregates in diasporite.

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

The structure predicted in this manner has the same space group symmetry  $V_{17}^h$  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  $\underline{u}_1 = +0.267$  and  $\underline{u}_2 = +0.067$  by the requirement that shared edges be 2.50 Å long, while the iron parameter  $\underline{u}$  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,

$\frac{1 + \cos^2 2\theta}{2 \sin^2 \theta}$  is the polarization factor,  $\omega$  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

$$F = \sum_j \frac{f_j}{j} e^{2\pi i(hx_j + ky_j + lz_j)}$$

The value of B was estimated as 1.00. Values of  $f$  were taken from Pauling and Sherman's<sup>7</sup> 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  $\underline{u}$ , the Fe parameter, independently of the oxygen parameters  $\underline{u}_1$  and  $\underline{u}_2$ . 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  $-0.50 < \underline{u} < -0.250$  served to limit  $\underline{u}$  to the region  $-0.3235 \pm 0.004$ .

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 were found to agree with observed intensities for the values

$$\underline{u} = -0.322 \pm 0.001;$$

$$\underline{u}_1 = 0.282 \pm 0.005;$$

$$\frac{u}{2} = +0.075 \pm 0.005.$$

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 OH<sub>2</sub> groups, or hydrogen bonds, holding the layers together.

Hydrogen bonds are postulated in lepidocrocite, as in diaspor<sup>6</sup>, for the explanation of certain O-O distances. In Table II are given the interatomic distances in lepidocrocite. In each layer the O-O distances along shared edges are 2.59 Å, and the other O-O distances, along the lengthened octahedral edges, are 3.05 Å and 3.06 Å. Between the layers the O-O distances are 2.70 Å, 3.10 Å, and greater. The O-O distance of 2.70 Å 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

Table I. Observed and Calculated Intensities of Reflection on Oscillation Photograph from (010) with [001] as axis.

(hkl) (Equator) <u>Pinacoid</u>	<sup>a</sup> Observed Intensity	Calculated Intensity	(hkl) { First (layer line) Prisms	Observed Intensity	Calculated Intensity	(hkl) { Second (layer line) Prisms	Observed Intensity	Calculated Intensity
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
<u>Prisms</u>			0 21 1	0.0	0.001	<u>Pyramids</u>		
1 4 0	5.	9.35	<u>Pyramids</u>			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			

<sup>a</sup> Estimated visually.

oxygen would be effective in raising the distance above 2.70 Å. The value of 2.70 Å for the OH distance in lepidocrocite is, moreover, equal within experimental error to the value 2.71 Å found in diaspore.

The association of one hydrogen with each 2.70 Å distance gives the correct stoichiometric composition to the crystal. If the hydrogens are placed exactly halfway between the bonded oxygens they lie at centers of symmetry, with the coordinates  $000$ ;  $\frac{1}{2} 0$ ;  $0\frac{1}{2} \frac{1}{2}$ ;  $\frac{3}{2} \frac{1}{2}$ . Figure 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.

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

The four Fe-O bonds around O have directions differing by  $5^\circ$  to  $20^\circ$  from regular tetrahedral directions; the directions of the four bonds around O, two to Fe and two to H, differ by only  $3.5^\circ$  to  $9^\circ$  from tetrahedral directions. While this approximate orientation of the hydrogen bond along a tetrahedral direction is probably dependent on

Table II. Interatomic Distances in Lepidocrocite

Atom	Neighbors in the same octahedron	Neighbors in other octa- hedra of the same layer	Neighbors in the next layer
Fe	2 O at 2.00 Å <sup>o</sup> II	3 Fe at 3.06 Å <sup>o</sup>	
	2 O at 2.00 Å <sup>o</sup> I		
	2 O at 2.01 Å <sup>o</sup> I		
O I	2 O at 3.06 Å <sup>o</sup> I		2 O at 3.97 Å <sup>o</sup> II
	4 O at 3.05 Å <sup>o</sup> II		
	4 O at 2.59 Å <sup>o</sup> I		
	1 O at 2.59 Å <sup>o</sup> II		
O II	2 O at 3.06 Å <sup>o</sup> II		2 O at 3.97 Å <sup>o</sup> I
	4 O at 3.05 Å <sup>o</sup> I		4 O at 3.10 Å <sup>o</sup> II
	1 O at 2.59 Å <sup>o</sup> I		2 O at 2.70 Å <sup>o</sup> II



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 relative 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  $\text{FeO}(\text{OH})$  has been chosen for lepidocrocite as reflecting in some degree the character of the structure, although the  $(\text{OH})$  anions do not actually exist as such, but rather as strings of ( -- HOHOHOH -- ).

I wish to express my indebtedness to Professor Linus Pauling for the interest and helpful advice that he has extended to this work.

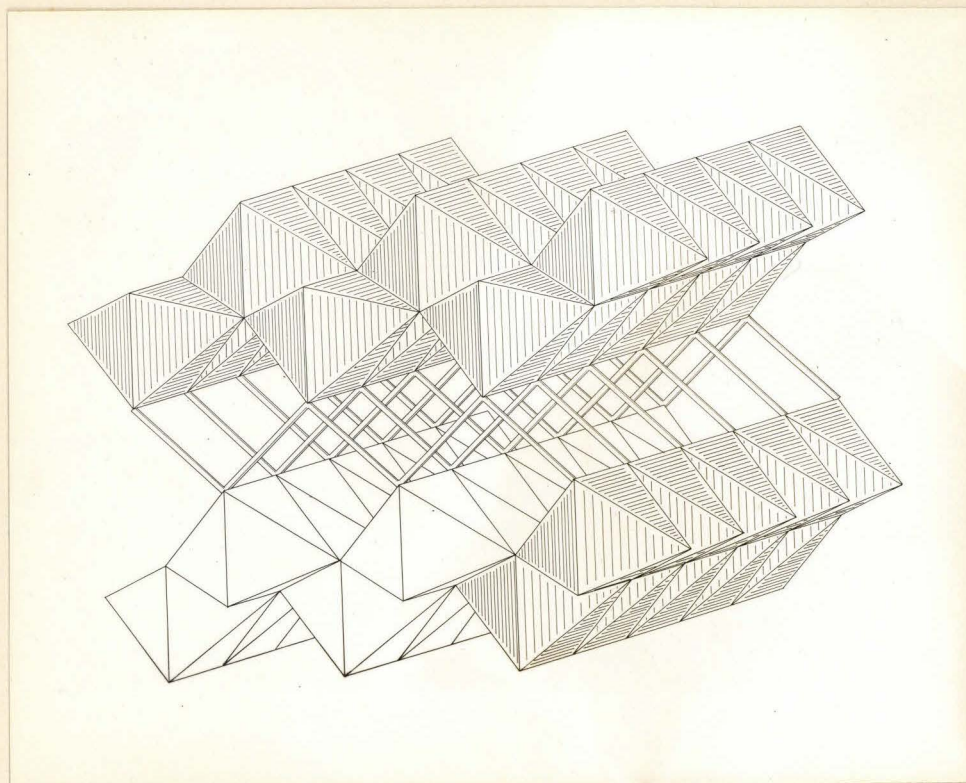


Figure 1. A portion of two layers of lepidocrocite, showing the iron-centered oxygen octahedra joined to form layers, and the layers tied together with hydrogen bonds (drawn as tubes.)

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