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The Crystal Structure of Synthetic Boehmite

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Crystal structure computations have been made for synthetic boehmite, the α -modification of aluminum oxide monohydrate, using the powder method. The experimental data were found to fit an orthorhombic lattice with constants $a_0 = 2.85_8\text{\AA}$, $b_0 = 12.2_4\text{\AA}$, and $c_0 = 3.69_1\text{\AA}$. The assignment of four $\text{AlO}(\text{OH})$ groups to this unit cell gives a calculated density of 3.06_3 g/cc . The observed density is 2.97_7 g/cc . The general space group extinctions were found to agree with those of D_{2h}^{17} . Generalized atomic coordinates were roughly determined by application of Pauling's coordination theory for ionic crystals and the determinations refined by the usual intensity computations. The parameter values selected were $u_{\text{Al}} = -0.334$, $u_{\text{OI}} = 0.287$, $u_{\text{OII}} = 0.067$. It is suggested that the inconsistencies which exist between the experimental and computed intensity data may be explained by the occurrence of a small quantity of $\gamma\text{-Al}_2\text{O}_3$ in the synthetic samples used. The value of $2.47 \pm 0.07\text{\AA}$ obtained for the hydrogen bridge distance is discussed. This value is less than that observed for any previously determined structure.

I. INTRODUCTION

SINCE the first production and identification of synthetic boehmite by Böhm and Niclassen¹ in 1924, a considerable literature has appeared concerning its production in the laboratory and its relation to the other known hydrates of aluminum. Despite some doubts as to the existence of such a monohydrate,² it has been repeatedly confirmed that such a crystalline modification does exist^{3,4} and the mineralogical counterpart of the synthetic material has been found in many bauxites.⁵ The cumulative result of this work has demonstrated that the hydrated oxides of aluminum are isomorphous with those of iron and has resulted in structural determinations of all the hydrates of alumina except boehmite. The structural determination of boehmite has probably been delayed by the difficulty of obtaining adequate single crystals. Achenbach⁶ and Goldsztaub⁷ have stated, however, that the crystal is orthorhombic and Dana⁸ mentions that the boehmite crystals found in the

French bauxites are microscopic orthorhombic plates.

The structure of lepidocrocite, the hydrated oxide of iron isomorphous with boehmite, has been obtained by Ewing⁹ using oscillation and rotation photographs of a naturally occurring single crystal. Since no single crystal of boehmite, either natural or synthetic, was available or procurable, the work reported here has confined itself to powder techniques. The approach is based on the known similarity of the powder photographs of lepidocrocite and boehmite⁷ and on the previously determined structure of lepidocrocite. The space group assigned to boehmite was that assigned to lepidocrocite by Ewing⁹ and generalized atomic coordinates were determined by application of Pauling's coordination theory for ionic crystals,¹⁰ and refinements in their determination made by appropriate intensity computations.

II. EXPERIMENTAL

A. Manufacture of Boehmite

Two samples of well-crystallized boehmite (designated as *A* and *B*) were used in this work. Sample *A* was obtained by peptizing pure aluminum metal with formic acid. The precipitate which separated during this process was heated under water vapor pressure at 150 to 175 degrees

¹ J. Böhm and H. Niclassen, *Zeits. f. anorg. Chemie* **132**, 5 (1924).

² H. B. Weiser and W. O. Milligan, *J. Phys. Chem.* **36**, 3010 (1933).

³ H. Lehl, *J. Phys. Chem.* **40**, 47 (1936).

⁴ J. D. Edwards and M. Tosterud, *J. Phys. Chem.* **37**, 483 (1933).

⁵ J. Böhm, *Zeits. f. anorg. Chemie* **149**, 203 (1925).

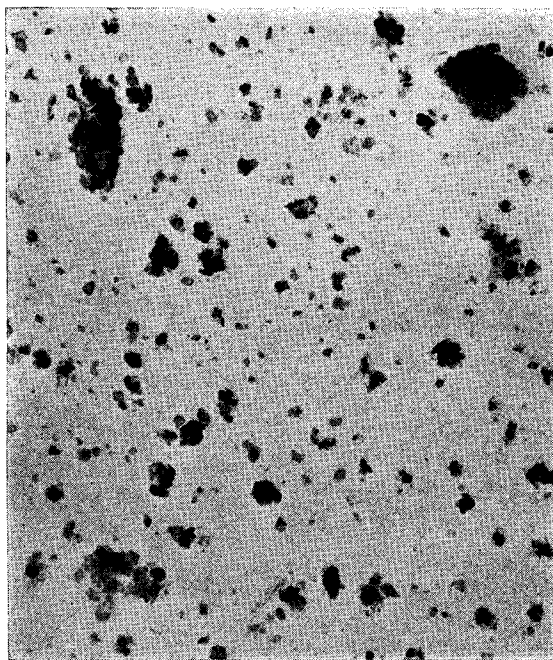
⁶ H. Achenbach, *Chem. Erde* **6**, 307 (1931).

⁷ S. Goldsztaub, *Comptes rendus* **193**, 533 (1931).

⁸ E. S. Dana, *Textbook of Mineralogy* (John Wiley & Sons, 1932) fourth edition, p. 503.

⁹ F. J. Ewing, *J. Chem. Phys.* **3**, 420 (1935).

¹⁰ L. C. Pauling, *J. Am. Chem. Soc.* **51**, 1010 (1929).

FIG. 1. Synthetic $\text{AlO}(\text{OH})$. Sample *A*. ($20,000\times$)FIG. 2. Synthetic $\text{AlO}(\text{OH})$. Sample *B*. ($20,000\times$)

C for four days, then dried at 100°C . Only a small amount of this sample was obtained. Sample *B* was prepared by peptizing pure metallic aluminum in 1 percent nitric acid at room temperature. The alumina trihydrate thus obtained was dried at 100°C . It was then placed in a glass lined bomb together with distilled water and heated for one week at 175°C . The contents were then dried at 105°C for 36 hours.

The two samples gave identical x-ray patterns which checked with published patterns for boehmite. Strong diffraction lines were obtained and no additional lines characteristic of the oxides or other hydrates of aluminum oxide could be observed. Computations from the half-widths of the stronger lines gave crystallite sizes in the neighborhood of 100\AA , for sample *B* and 60\AA for Sample *A*. For both Samples *A* and *B*, the innermost line was appreciably broader than any other on the pattern. Electron micrographs of the two samples indicate an apparent difference in habit despite the identity of the x-ray patterns. Figures 1 and 2 are reproductions of the micrographs of the two samples. The corresponding x-ray diffraction patterns recorded with $\text{Cu } K\alpha$ radiation are shown in Fig. 3. Sample *A* appears

to consist of chains of discrete particles, the elements of the chains being insufficiently resolved to ascertain any characteristic shape or form. Their average diameter is in the neighborhood of 200\AA . Sample *B*, on the other hand, appears to consist of tabular particles, orthorhombic in character. They are apparently extremely thin, since the average particle is almost transparent to the electron beam. Their size varies from less than 100\AA to about 800\AA on a side.

The difference between the physical habits of the two crystallographically identical samples has not been explained. The rough agreement obtained between the values of particle size determined from the electron micrographs and those obtained from computation of x-ray line breadths does indicate that the particles observed are probably single crystallites or, at most, loose groupings of very few single crystals.

The density of Sample *B* was determined with a helium densitometer and found to be 2.977 g/cc . Fricke and Severin¹¹ quote a value of 3.014 g/cc

¹¹ R. Fricke and H. Severin, *Zeits. f. anorg. Chemie* **205**, 287 (1932).

while von Nieuwenburg and Pieters¹² give 3.06 g/cc.

The water content of Sample *B* was determined in the following manner. A sample was heated for 7 days at 115°C to remove the adsorbed water. A portion of this was then weighed, heated for 2 days at 500°C, and reweighed. Previous tests with numerous hydrated alumina samples indicated that the latter treatment was sufficient to convert the material to γ -Al₂O₃. For Sample *B*, the loss of weight was 15.0 percent, in perfect agreement with the theoretical water content of the monohydrate, Al₂O₃·H₂O. A second portion of the predried sample was ignited at approximately 1100°C and the resulting weight loss was 16.0 percent. The extra 1.0 percent loss may be caused by contaminants which volatilize at the higher temperatures or by water which remains adsorbed at 500°C.

All evidence, therefore, seems to indicate that the samples examined were boehmite.

B. Equipment

Electron micrographs were taken at an electronic magnification of 10,000 diameters and subsequently enlarged optically to a total magnification of 50,000 diameters. A type *B* RCA electron microscope was used for this work.

X-ray diffraction patterns were recorded with cylindrical powder cameras of diameter 14.32 cm. Both Mo $K\alpha$ - and Cu $K\alpha$ -radiations were employed and in all cases the radiation was monochromated by a quartz crystal. In general, the sample was contained in a parlodion capillary of diameter 0.45 mm. It is estimated that the precision of determination of Bragg angle, excluding

TABLE I.

Present work	Goldsztaub
$a_0 = 2.85_a\text{\AA}$	2.85A
$b_0 = 12.2_t\text{\AA}$	11.8A
$c_0 = 3.69_i\text{\AA}$	3.78A

absorption effects, is $\pm 0.01^\circ$. This corresponds to an error of 0.001A at an interplanar spacing of 3.000A and to $\pm 0.0005\text{\AA}$ at a spacing of 2.000A when copper radiation is used. Line densities were determined with a Leeds and Northrup microphotometer and Speedomax pen recorder.

III. STRUCTURAL DETERMINATION

A. Unit Cell

The experimental data from the two samples (*A* and *B*) were found to fit an orthorhombic lattice, as suggested by the isomorphic character of lepidocrocite and boehmite. The lattice constants determined by us as compared with values reported by Goldsztaub¹³ are shown in Table I.

The assignment of four AlO (OH) groups to our unit cell gives a density of 3.063 g/cc which is to be compared to the measured value of 2.97₇ g/cc.

Typical agreement between computed and experimental interplanar spacings is shown in Table II. A method of successive approximations was used to obtain lattice constants which yielded d_{theory} values agreeing most closely with d_{exp} values. The final step in this process consisted of fitting four d_{exp} values to their respective d_{theory} values as a correction for film shrinkage and similar camera errors. The agreement between the theoretical values and the average of measure-

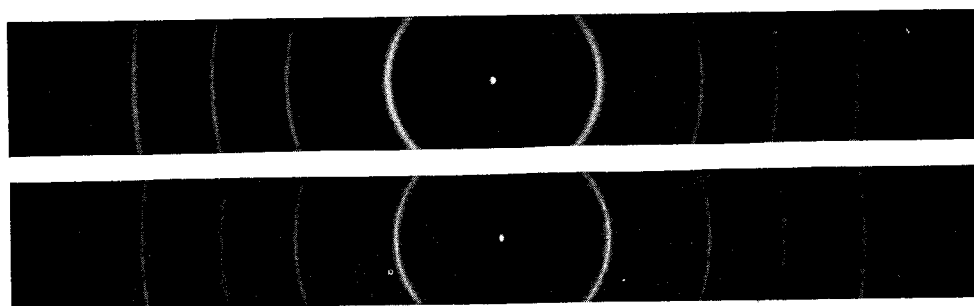


FIG. 3. Powder patterns of synthetic AlO (OH).

¹² C. J. von Nieuwenburg and H. A. J. Pieters, Rec. Trav. Chim. **48**, 27 (1929).

¹³ S. Goldsztaub, Bull. Soc. franc. miner **59**, 348 (1936).

TABLE II. Sample B, Cu $K\alpha$ -radiation.

(hkl)	d_{theory}	d_{exp}	d_1^{**}
020	6.119	6.119*	6.132
021	3.160	3.160	3.153
130	2.341	2.341*	2.337
131	1.977	1.978	
002	1.845	1.845*	1.847
022	1.767	1.766	
151	1.661	1.659	1.654
080	1.530	1.523	
132	1.449	1.447	1.445
200	1.429	1.431	1.427
220	1.392	1.394	
171	1.383	1.379	1.385
152	1.310	1.307	1.304
202	1.130	1.131	

* Values set equal to d_{theory} .

** Average of measurements on 18 films of other synthetic boehmites. No film shrinkage corrections are included.

TABLE III. Atomic coordinate values.

Coordinate	Coordination value	Range studied		Selected
		Upper limit	Lower limit	
u	-0.315	-0.340	-0.315	-0.334
u_1	+0.287	+0.280	+0.294	+0.287
u_2	+0.083	+0.063	+0.083	+0.067

ments on 18 other samples, all recorded and measured in a routine fashion, is gratifying also.

B. Space Group

The general extinctions observed for boehmite were the same as those observed for lepidocrocite by Ewing. No first-order reflections were found for $(k+l)$ odd and hence a lattice end-centered on (100) and based on Γ_0' is to be expected. If holohedral symmetry is assumed for boehmite, the space groups possible are limited to D_{2h}^{17} through D_{2h}^{22} . The existence of first-order prismatic reflections of the type (hko) , h and k odd, eliminates D_{2h}^{18} , D_{2h}^{21} , and D_{2h}^{22} . Since reflections of the type (okl) with l odd are observed, D_{2h}^{20} is eliminated. D_{2h}^{19} permits all (hol) . However, (hol) are observed only for h and l even. Therefore, D_{2h}^{19} is improbable. All of the absences observed are accounted for by D_{2h}^{17} and hence it is the best choice.

In order to avoid O-O distances of 1.85Å or less, it is necessary that the eight oxygen atoms be placed on the intersections of the symmetry planes. Assuming that the aluminum atoms cannot be at the centers of symmetry, the generalized coordinates of the atoms are given by the

following, in which the origin is taken at the center of symmetry:

4Al in 4(c) at 0, $u, \frac{1}{4}; 0, \bar{u}, \frac{3}{4}; \frac{1}{2}, u + \frac{1}{2}, \frac{1}{4}; \frac{1}{2}, \frac{1}{2} - u, \frac{3}{4}$

4O_I in 4(c) at 0, $u_1, \frac{1}{4}$; etc.

4O_{II} in 4(c) at 0, $u_2, \frac{1}{4}$; etc.

The generalized form of the crystal structure factor, F , is expressed by

$$F = \sum_j f_j \exp [2\pi i(hx_j + ky_j + lz_j)], \quad (1)$$

where f_j are the atomic structure factors of the various atoms entering into the composition of the crystal. If the generalized coordinates for boehmite are substituted in (1), one obtains after simplification and reduction the following ex-

TABLE IV. Experimentally observable lines.

d	hkl	Rel. I		Order	
		Exp.	Comp.	Exp.	Comp.
6.119	020	100	100	1	1
3.160	021	48	45	3	3
2.355	041		1.6		
2.341	130	42	41.0	4	4
1.977	131	4.1	0.0	11	17
1.859	150		13.2		
1.845	002	52	36.0	2	2
1.785	061		0.4		
1.766	022	4.1	2.8	10	12
1.660	151	10.6	13.8	7	6
1.538	112		0.0		
1.530	080	*	5.3	14	10
1.449	132		7.9		
1.429	200	21.1	13.3	8	7
1.413	081		5.2	6	5
1.392	220		1.2		
1.383	171		1.7		
1.368	062	9.0	0.9	12	13
1.302	221		2.9		
1.310	152	17.9	3.3	5	8
1.206	023	*	2.0	16	15
1.178	082		1.8		
1.171	260	*	0.6	15	14
1.165	191		0.4		
1.162	0 10 1	*	4.0	17	11
1.160	172		0.5		
1.130	202	*	5.4	9	9

* Lines too weak for accurate integrated intensity measurements to be made.

pression:

$$F = 16 \cos^2 (\pi/2)(k+l) \times [\sum_j f_j \cos (\pi/2)(h-4u_jk)]^2. \quad (2)$$

Before applying this formula to intensity calculations, it was necessary to determine approximate values for the generalized coordinates. This was done by application of Pauling's coordination theory for ionic crystals and involved the following assumptions:

a. The structure is built up from Al-centered oxygen octahedra. Al-O distances are approximately 1.9Å and O-O distances about 2.70Å.

b. O²⁻ and (OH)⁻ anions are shared between four and two octahedra, respectively. The cations are thus effectively neutralized by neighboring anions.

c. Shared edges between octahedra are contracted to 2.50Å. Other edges are correspondingly lengthened. The octahedra are therefore distorted from a regular shape.

The orientation of the octahedra in the unit cell is suggested by the fact that the c_0 value of 3.691Å is close to the value of 3.82Å which is the length of the body diagonal of an undistorted octahedron. Correspondingly, the a_0 value of 2.859Å can be most easily linked with the lengthened edge of an octahedron. This picture suggests a layer structure similar to that found for lepidocrocite. The a and c identity distances would be in the plane of the layer and correspond to the body diagonal and edge of an octahedron, respectively. The b identity distance would then be perpendicular to the layers with each layer very probably translated through a distance of $b/2$.

Carrying through the appropriate geometrical considerations given above, the following values were obtained for the generalized coordinates:

$$\begin{aligned} u &= -0.315, \\ u_1 &= 0.287, \\ u_2 &= 0.083. \end{aligned} \quad (3)$$

Intensity computations were made by application of the usual formula

$$I = N_p |F|^2 F_p,$$

where

$$\begin{aligned} N_p &\text{—Number of planes in a given family,} \\ |F| &\text{—Crystal structure factor (see Eq. (2)),} \\ F_p &\text{—}(1 + \cos^2 2\theta) / \sin \theta \sin 2\theta. \end{aligned}$$

The atomic structure factors chosen were those

TABLE V. Computed lines not observed experimentally.

d	hkl	Computed rel. intensity 6.119Å line = 100
3.060	040	1.7
2.784	110	0.0
2.222	111	0.0
2.040	060	2.3
1.580	042	0.5
1.492	170	1.1
1.295	240	0.2
1.228	190	0.2
1.224	0 10 0	0.4
1.222	241	0.0
1.125	113	0.0

for the Hartree ion which have been published by James and Brindley.¹⁴

During the progress of the computations, an attempt was made to include a correction due to sample absorption and also to apply the Debye-Waller temperature correction. Application of each of these corrections involves assumptions difficult to justify. However, each individual correction failed to improve the agreement between theoretical and experimental intensity values. In addition, it is easily demonstrated that the two corrections tend to nullify one another. Hence, they were not included in the final computations.

In the process of the computations, the generalized atomic coordinates were varied over a range sufficient to produce wide variations in the computed relative intensities. The ranges covered are given in Table III together with the values selected on the basis of best over-all agreement between experimental and computed intensities.

The limits of error on the final selection of generalized coordinates are difficult to estimate. However, the intensity values obtained would be in significant disagreement with experimental values if either upper or lower limit values or any combination of them given in Table III were used in the computations.

Computed and experimental results are presented in Table IV for the lines which were experimentally observed, while computed relative intensities for lines which were not experimentally observed are presented in Table V. The experimental relative intensities are those com-

¹⁴ R. W. James and G. W. Brindley, *Phil. Mag.* **12**, 81 (1931).

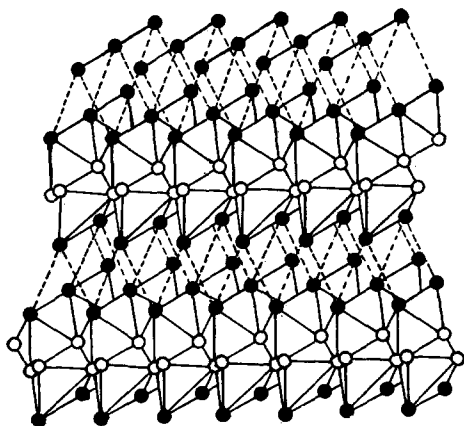


FIG. 4. Schematic diagram of boehmite structure. Dotted lines indicate ($\text{--OH}\cdots\text{O--}$) bonds. $\circ = \text{O}_T$ positions; $\bullet = \text{H}$ positions.

puted from the microphotometer trace of Sample *B*. Peak intensities were not used because of the wide differences in half-width from line to line. Rather, the traces of each line were replotted on a linear density scale using values obtained from the microphotometer trace. The areas under these replotted curves were then determined using a planimeter and were assumed to be a measure of the integrated intensity of each diffraction line. Since this procedure was valid only for relatively intense reflections, the experimental order of intensity was determined by an average of visual estimates of films of both Samples *A* and *B*.

IV. DISCUSSION

Considering the limitations and difficulties of the powder method of approach to problems of this nature, the agreement is gratifying. In particular, those reflections not experimentally observed should all have very weak intensities on the basis of these computations. However, particular features of the results as presented in Table IV seem to be in rather serious disagreement with experimental data. The (131) (221) and (152), and (171) and (220) reflections are much stronger in the experimental data than can be accounted for on the basis of the assigned structure. It is suggested that the interplanar spacings corresponding to these reflections are, within experimental error, the same as those of the stronger lines of $\gamma\text{-Al}_2\text{O}_3$. Since experimental intensities for these reflections are consistently

higher than computed values, the discrepancy may be explained by postulating the occurrence of some $\gamma\text{-Al}_2\text{O}_3$ in the original boehmite. The other strong line of $\gamma\text{-Al}_2\text{O}_3$ which occurs at an interplanar spacing of 2.34 Å coincides in position with the fourth strongest line of boehmite as computed here and, hence, can have only very minor influence on the intensity of this line. This line of reasoning could be most easily justified by the usual single crystal type of analysis in which the crystalline purity of the sample would be beyond question.

A schematic diagram of the structure as calculated here is shown in Fig. 4. It is entirely similar in character to that found for lepidocrocite by Ewing⁹ and hence need not be discussed here. The interatomic distances for this structure have been computed and are presented in Table VI. The marked distortion of the octahedra is to be noted. Also, the Al–O distances of 1.87, 2.06, and 1.93 Å exhibit an effect of Al–Al repulsion. Such an effect is not exhibited by lepidocrocite. These are to be compared with the corresponding distances of 1.99 and 1.85 Å found for corundum.¹⁵ The smallest shared O–O distance of 2.50 Å is also to be compared with the value of 2.50 Å for corundum.

The hydrogen bonds which link the separate layers of oxygen octahedra are indicated by dotted lines. Such bonds are postulated on the basis of the short, unshared O–O distance between layers. This OHO distance of 2.47 Å is smaller than any similar distance previously known.¹⁶ In particular, it is smaller than the corresponding hydrogen bridge distances for lepidocrocite (2.71 Å) and for diaspore (2.70 Å). This fact, corresponding as it does to increased bond energy, should result in a greater temperature stability of the boehmite crystallites over those of lepidocrocite and diaspore. Experimentally Sample *B* loses its water at approximately 450°C, while lepidocrocite undergoes a similar transition at 250°C¹⁷ and diaspore at from 300 to 350°C.¹⁸ The error in the determination of the hydrogen bridge distance in boehmite is

¹⁵ L. C. Pauling, J. Am. Chem. Soc. **47**, 281 (1925).

¹⁶ L. C. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, New York, 1940), p. 311.

¹⁷ W. H. Albrecht and O. Bandisch, J. Am. Chem. Soc. **54**, 943 (1932).

¹⁸ W. H. Albrecht, Ber. **62B**, 1475 (1929).

difficult to estimate. It resides wholly in the error in determination of the parameter u_2 . The best estimate (on the basis of intensity computations for various values of u_2) is that the OHO distance in boehmite is $2.47 \pm 0.07\text{\AA}$. Therefore even assuming maximum error, the hydrogen bridge distance for boehmite is only equal to the shortest previously known; namely, 2.54\AA for the tetragonal crystal KH_2PO_4 .¹⁶

The OHO bonds are relatively weak in character and hence are easily sheared. This accounts for the apparent cleavage of boehmite and its existence in orthorhombic plates, such as are shown in the electron micrograph of Sample *B* (see Fig. 2). This factor may also account for the greater half-width of the (020) reflection which was consistently observed on a large number of preparations of synthetic boehmite. The weak hydrogen bonds would permit distortion of the "b" axis direction and this crystalline distortion could account for the varying values of line breadth observed from sample to sample and from diffraction line to diffraction line. Aside from the factor of distortion, the tendency for the crystal

TABLE VI. Interatomic distances in boehmite.

Atom	In the same octahedron	In other octahedra In same layer	In other octahedra In next layer
Al	2O _{II} at 1.87\AA 2O _I at 2.06\AA 2O _I at 1.93\AA	2Al at 2.86\AA 2Al at 3.69\AA	
O _I	2O _I at 2.86\AA 4O _{II} at 2.94\AA 4O _I at 2.50\AA 1O _{II} at 2.69\AA		
O _{II}	2O _{II} at 2.86\AA 1O _I at 2.69\AA 4O _I at 2.94\AA		2O _I at 4.66\AA 4O _{II} at 3.78\AA 2O _{II} at 2.47\AA

to occur in the form of thin crystalline plates would also account for the increased breadth of the (020) reflection.

The authors wish to express their appreciation to Mr. J. M. Waite for assistance in the experimental x-ray work and to Mr. W. C. Skinner for the electron micrographs. We also wish to thank Dr. A. G. Oblad, Dr. H. T. Brown, and Mr. J. U. Messenger for the preparation of the boehmite and measurement of its density.

Liquid Association and the Critical Temperature

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A THEORETICAL basis for a critical region instead of a critical point is furnished by Mayer who has calculated on a statistical mechanical basis¹ the general form of the pressure volume curve for a number of temperatures in the region of the critical temperature. The type of P - V diagram obtained for a pure liquid-saturated vapor system is such that two critical or characteristic temperatures, T_m and T_c , may exist. T_m is interpreted to correspond to the temperature at which the meniscus disappears and the surface tension becomes zero. This temperature is lower than the true critical temperature, T_c , the temperature at which the

P - V curve has an inflection point for only one volume. At and above T_c , no differences exist between gas and liquid. Below T_m , a definite meniscus exists and the condensed phase has a surface tension. Between T_m and T_c , the P - V curve is horizontal over a finite volume and no surface tension exists. The magnitude of the temperature interval between T_m and T_c has not been theoretically calculated. This interval according to the Van der Waals equation is, of course, zero.

Since a liquid possesses a more definite structure (order) than a gas,² this structure may be regarded as persistent beyond T_m and not com-

¹ Mayer and Harrison, *J. Chem. Phys.* **6**, 87 (1938); Harrison and Mayer, *ibid.*, 101.

² Stewart, *Chem. Rev.* **6**, 483 (1929); *Rev. Mod. Phys.*, **2** 116 (1930).