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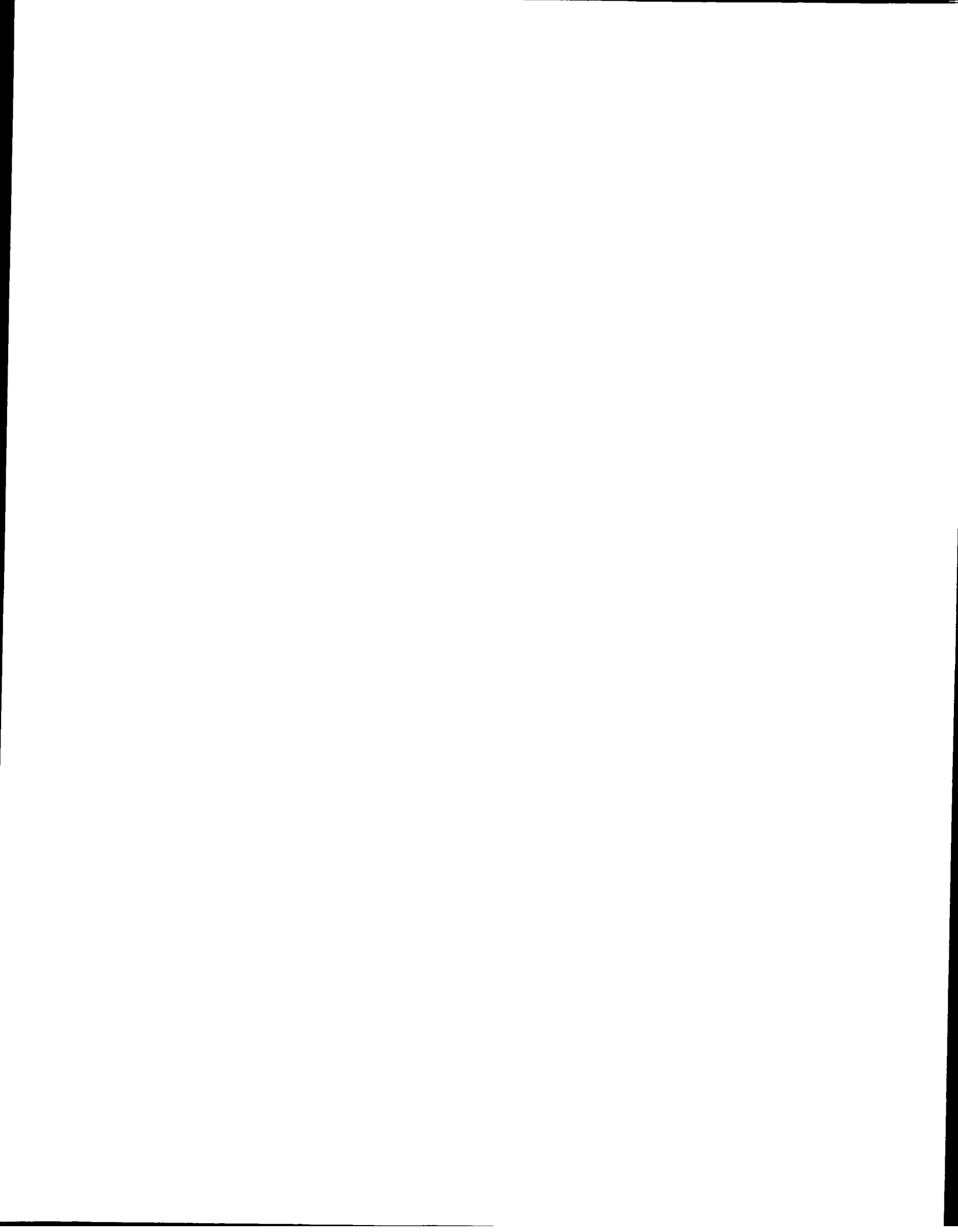
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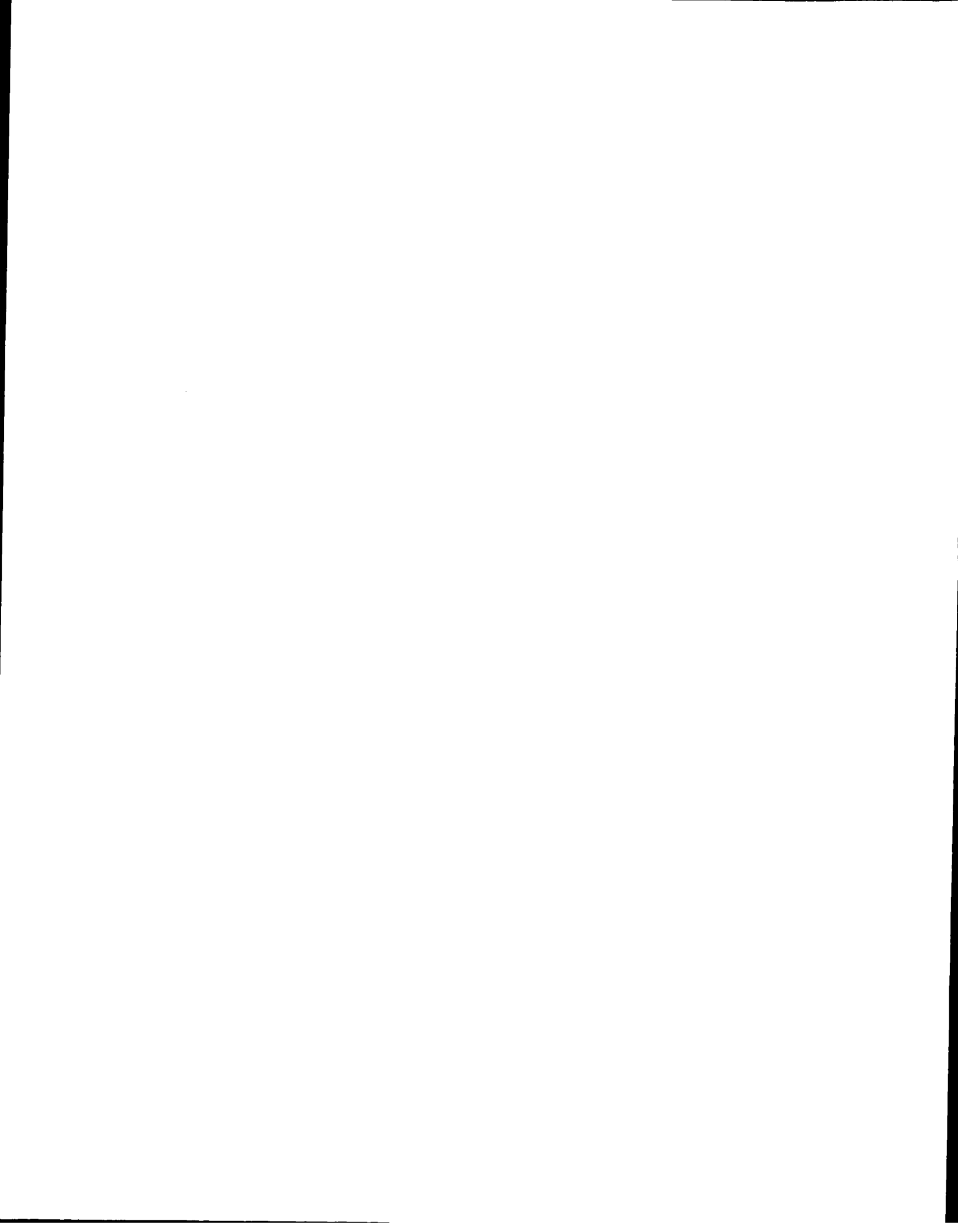
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Crystal Structure of γ -AlOOH and γ -ScOOH

by

James Lee McAtee, Jr.

A THESIS

SUBMITTED TO THE FACULTY
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

Houston, Texas
May, 1951

Approved
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INTRODUCTION

I. INTRODUCTION

Böhmite, γ -AlOOH, has been found to exist in nature (2,15) and may be prepared in the laboratory in a variety of ways (3,7,16,25). From the close similarity of the powder x-radiograms of böhmite and the mineral lepidocrocite, γ -FeOOH, it has been concluded that the structures are analogous (12,13). The existence of the closely related compound γ -ScOOH has clearly been established by x-ray diffraction and dehydration isobaric studies (10,17,18), but quantitative x-ray studies have not been made.

There are two crystalline modifications of the monohydrate of aluminum oxide with the formula AlOOH. The modification corresponding to diaspore, α -AlOOH, has been found to be isomorphous with goethite, α -FeOOH, of known structure (8). The second modification corresponding to böhmite, γ -AlOOH, is isomorphous with lepidocrocite, γ -FeOOH. The structure of lepidocrocite has been determined by Ewing employing oscillation and rotation photographs of a naturally occurring single crystal (9). Even though böhmite occurs in nature, it has not been possible to obtain individual crystals suitable for single crystal x-ray studies. However, Reichertz and Yost (24) employing powder methods, determined

parameters for the various ions in the crystal structure that lead to a hydrogen bond distance of $2.47 \pm 0.07 \text{ \AA}$, which is considerably less than any similar distance previously reported (22).

Milligan and Weiser (18), from dehydration isobars of scandium trihydroxide and x-ray diffraction studies, reported the existence of scandium oxide monohydrate, $\gamma\text{-ScOOH}$, which they believed to be isomorphous with böhmite. The crystallite size obtained, however, was of such dimensions that the x-radiograms consisted of broad and diffuse bands which could not be employed in a quantitative determination of the structure. The existence of scandium oxide monohydrate was later confirmed by Fricke and Seitz (10).

In the present investigation the unit structure, space group symmetry, and detailed atomic arrangement of $\alpha\text{-AlOOH}$ and $\gamma\text{-ScOOH}$ have been determined. Since numerous attempts to grow single crystals of both of these monohydrates failed, it was necessary to confine the work done here to powder techniques.

EXPERIMENTAL

II. EXPERIMENTAL

A. Preparation of γ -AlOOH:

Several samples of böhmite were employed in the determination of its structure. Two samples of well-crystallized material were obtained from the Aluminum Company of America, while two others were prepared in this laboratory. A fifth sample was not employed in these studies since its x-radiogram indicated the presence of a small amount of γ -Al₂O₃.

The two samples of böhmite prepared here were precipitated from N/10 solutions of aluminum chloride and sulfate with a slight excess of dilute ammonium hydroxide. Both samples were washed in a centrifuge with distilled water until the supernatant liquid was free of the anion. The samples were then placed in a platinum capsule in a special steel bomb capable of operation at temperatures as high as 600°C. and pressures as high as 30,000 lbs./sq. inch. The sample prepared from aluminum chloride was heated in the bomb for one week at 350°C. and 5,000 lbs./sq. inch, while the product precipitated from aluminum sulfate was heated at 400°C. and 6,000 lbs./sq. inch for five days. After removal from the bomb, the crystalline powders were washed five times with distilled water in a

centrifuge, then placed on watch glasses and allowed to dry at room temperature.

All of the samples of böhmite prepared here and those obtained from the Aluminum Company of America gave identical x-ray diffraction patterns whose spacings agreed with published patterns. Several of these x-radiograms are shown in Figures 1 and 3.

B. Preparation of γ -ScOOH:

The method of preparation of γ -ScOOH was that employed by Milligan and Weiser (18). Three separate samples of γ -ScOOH were prepared here, differing in the method of the initial precipitation and the time of heating in the bomb. These were prepared as follows:

1. To a solution of 0.1 M ScCl₃ at room temperature, freshly distilled ammonium hydroxide was added in slight excess. The precipitate was immediately washed in a centrifuge with distilled water until free of chloride ion.

2. Freshly distilled ammonium hydroxide was added to a boiling solution of 0.1 M scandium chloride, the precipitate immediately being washed in a centrifuge with boiling distilled water and finally with cold water. Washing was continued until the wash water no longer gave a positive test for chloride ion when tested with silver nitrate.

3. To a boiling solution of 0.1 M ScCl_3 , freshly distilled ammonium hydroxide was added in slight excess, the precipitate was then allowed to digest for thirty minutes before being washed as described in (2) above.

The washed samples were put separately in a platinum bucket which was then placed in the high temperature bomb. Samples one and two were heated for six days at 350°C . and 6,000 lbs./sq. inch, while sample three was heated for seven days at 350°C . and 5,500 lbs/sq. inch. After heating, the products were washed with distilled water, and then allowed to dry in air at room temperature.

The three samples of $\gamma\text{-ScOOH}$, prepared as described above, gave identical x-ray diffraction patterns, which, except for a slight displacement of the interplanar spacings, closely resembled that of $\gamma\text{-AlOOH}$ (see Figures 1 and 3).

C. X-ray Diffraction Examination:

Two types of x-ray apparatus were employed. A high angle Norelco recording x-ray spectrometer using filtered Cu K_α radiation and General Electric apparatus using Cu K_α and Cr K_α radiation monochromated by means of a sodium chloride crystal monochromator. With the x-ray spectrometer, the reflection method was used, while with the General Electric apparatus both extruded samples of 0.024 cm. radius and wedge

samples were employed.

The observed intensities were obtained from the x-ray spectrometer tracings by computing the area beneath the peaks using Simpson's rule. The x-ray photographs obtained from the General Electric apparatus were run on a modified Kipp and Zonen microphotometer (Figure 4). It was necessary to obtain the areas beneath the peaks because in many cases the half-widths varied considerably from line to line.

STRUCTURE DETERMINATION

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III. STRUCTURE DETERMINATION

A. Unit Cell:

The experimental results from the x-ray diffraction examination of γ -AlOOH and γ -ScOOH lead to an orthorhombic unit cell with values of the axes as shown in Table I. The determination of the lattice constants by any of the precision methods such as those of Bradley and Jay (5), or Cohen (6), require the use of lines with a Bragg angle greater than approximately 60° . The lines obtained in this investigation which obeys this condition were all too broad to justify the use of either of the above mentioned methods to determine the unit cell dimensions. For this reason, the lattice constants reported here were calculated by methods of successive approximation to obtain the best agreement between the experimental and calculated spacings. The lattice values determined here for böhmite were found to agree with those reported by Reichertz and Yost (24). A comparison of the computed and experimental interplanar spacings for γ -AlOOH and γ -ScOOH are shown in Tables III and IV, respectively.

The assignment of four formulas of AlOOH and ScOOH per unit cell gives calculated densities of 3.09 and 3.07 gm./cm.³, respectively, which are to be compared to the measured values of 2.99 and 3.02 gm./cm.³ obtained by use of a pycnometer.

B. Space Group Symmetry:

The general extinctions observed for both the aluminum and scandium oxide monohydrate are the same as those observed by Ewing for lepidocrocite. No first order reflections were found for $(\underline{k+1})$ odd, thus the lattice is based on Γ'_c , end-centered on (100), analogous to lepidocrocite. Assuming holohedral symmetry, the space groups possible are limited to D_{2h}^{17} through D_{2h}^{22} . The existence of prismatic reflections of the type $(\underline{hk}0)$, \underline{h} and \underline{k} odd, eliminates D_{2h}^{18} , D_{2h}^{21} , and D_{2h}^{22} . Reflections of the type $(\underline{0kl})$ with \underline{l} odd are observed, thereby eliminating D_{2h}^{20} . Of the two remaining space groups, D_{2h}^{17} and D_{2h}^{19} , the former permits reflections from $(\underline{h0l})$ only for \underline{h} and \underline{l} even, while the latter permits all reflections from $(\underline{h0l})$. Since for both γ -AlOOH and γ -ScOOH, $(\underline{h0l})$ spacings are observed only for \underline{h} and \underline{l} even, D_{2h}^{19} is improbable. The space group for γ -AlOOH and γ -ScOOH is thus indicated to be D_{2h}^{17} -Amam.

In order to avoid O-O distances less than 1.85 Å in γ -AlOOH and 2.00 Å in γ -ScOOH, the eight oxygen atoms in the unit cell must be placed on the intersection of symmetry planes. Assuming that the four cations in the cell cannot be at centers of symmetry, the generalized coordinates of the atoms referred to a center of symmetry as origin, are as follows:

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

4 O_I in 4(c) at: $1/4, u_I, 0$: etc.

4 O_{II} in 4(c) at: $1/4, u_{II}, 0$: etc.

C. Prediction of the Atomic Arrangement:

The prediction of the atomic arrangement in γ -AlOOH and γ -ScOOH is the same as that presented by Ewing for lepidocrocite (9) which were derived from the rules given in Pauling's coordination theory of the structure of ionic crystals (21).

1. Aluminum or scandium-centered octahedra make up the basic element of structure. In these octahedra, the O-O distance is close to 2.80 Å, and the Al-O and Sc-O distances are in the neighborhood of 1.90 and 2.21 Å, respectively.

2. Ewing points out that there are two formal ways of distributing the hydrogen ions in a compound of general type MOOH. These are indicated by writing $(OH_{1/2})^{-3/2}$ anions in one instance and distinct O^{--} and $(OH)^-$ in the other. It has been found that the anions in the form $(OH_{1/2})^{-3/2}$ leads to the diasporite-goethite structure (8), it seems logical, therefore, that the second alternative with distinct O^{--} and $(OH)^-$ anions would exist in the γ -FeOOH, γ -AlOOH, and γ -ScOOH type structure. The electrostatic valence rule requires that the O^{--} and $(OH)^-$ anions be shared between four and two octahedra, respectively.

3. In γ -AlOOH, the edges shared between octahedra can be expected to be contracted to about 2.50 Å, with the other edges being compensatorily lengthened. On the other

hand, the shared edges in γ -ScOOH will be shortened to approximately 2.60 Å due to the somewhat larger cation present in the octahedra.

The predicted structure for γ -AlOOH and γ -ScOOH is exactly the same as that for γ -FeOOH; i.e., a layer structure formed by the sharing of edges between the 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 edges of the layers are common to two octahedra and correspond to $(OH)^-$.

The orientation of the octahedra is easily predicted from the values of the lattice constants. The values for a_0 , 3.69 and 4.01 Å for γ -AlOOH and γ -ScOOH, respectively, can most easily be associated with the value 3.82 Å, the length of the diagonal for an undistorted octahedron; while the values for c_0 , 2.86 and 3.24 Å, can be closely associated with the shortened edge of the octahedra. The b axes with values of 12.24 and 13.01 Å in γ -AlOOH and γ -ScOOH, respectively, are perpendicular to the octahedra layers and suggests two layer intervals with every other layer translated by $c/2$. A pictorial representation of this structure is given in Figure 2 (after Ewing for lepidocrocite).

Carrying through the appropriate geometrical considerations for the above predicted configurations, the values

for the generalized coordinates obtained are shown in Table II.

D. Intensity Computations:

Relative intensities were calculated to determine the structure of γ -AlOOH and γ -ScOOH. The observed relative intensities are related to the structure through the formula:

$$I_{rel.} = j \cdot (L \cdot p) \cdot F^2 \quad (1)$$

where: j = the multiplicity factor,

$L \cdot p$ = the Lorentz-polarization factor, and

F = the crystal structure factor.

Substituting the values of the generalized coordinates for γ -AlOOH and γ -ScOOH, one obtains for the crystal structure factor:

$$F = \sum_j 4f_j \cos \pi/2(\underline{h} + 4\underline{k}u_j) \cos^2 \pi/2(\underline{k} + \underline{l}) \quad (2)$$

Equation (2) reduces to zero for $(\underline{k} + \underline{l})$ odd, and to the following for $(\underline{k} + \underline{l})$ even:

$$F = \sum_j 4f_j \cos \pi/2(\underline{h} + 4\underline{k}u_j) \quad (3)$$

The term f_j , in the above equation, is the atomic structure factor. The values of f_j used here were those computed by James and Brindley (14).

The Lorentz-polarization factor employed was dependent on the experimental procedure used to obtain the x-ray

diffraction pattern. For those cases where a crystal monochromator was employed to obtain Cu K_{α} and Cr K_{α} monochromatic x-radiation, the following factor was used (11,12):

$$L \cdot p = \frac{1 + \cos^2 2\psi \cos^2 2\theta}{\sin^2 \theta \cos \theta} \quad (4)$$

where ψ is the angle which the primary x-ray beam makes with the crystal monochromator, and θ is the Bragg angle associated with the diffraction lines obtained.

For comparison of the calculated intensities with the experimental intensities obtained by use of the x-ray spectrometer, the usual Lorentz-polarization factor was used:

$$L \cdot p = \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \quad (5)$$

Computations were also made to determine the effect of absorption of the x-rays in the powder samples (4). However, since the absorption coefficient and the sample radius (0.024 cm.) are small for both γ -AlOOH and γ -ScOOH, the effect of absorption was found to be negligible in all cases.

The calculated intensities were determined by varying the predicted values of the atomic parameters over small ranges consistent with the structure described above. The parameters which gave the best agreement of the observed with the calculated intensities, are shown in Table II. A compar-

ison of the calculated and observed relative intensities using the above parameters are presented in Table III for γ -AlOOH and in Table IV for γ -ScOOH.

It is difficult to determine the error involved in the parameters given in Table II; however, changes of ± 0.002 in the aluminum or scandium parameter, and changes of ± 0.005 for the oxygen parameters causes the calculated intensities to be in general disagreement with the observed intensities.

DISCUSSION OF THE RESULTS

IV. DISCUSSION OF THE RESULTS

The structures of aluminum and scandium oxide monohydrate as obtained here are in good agreement with the predicted atomic arrangement. The calculated and predicted parameters for the various atoms differ by only 0.006, 0.004, and 0.003 in γ -AlOOH, and by 0.005 and 0.016 in γ -ScOOH. The interatomic distances have been computed and are presented in Tables V and VI for γ -AlOOH and γ -ScOOH, respectively.

There is considerable distortion of the octahedral units in the layers from the shape of a regular octahedron as evidenced by the interatomic distances. This distortion has the effect of flattening out the portion of the octahedra which are in the interior of the double layer, and a corresponding stretching of the edges away from the layer. The Al-O distances of 1.87, 1.99, and 1.88 Å can be compared with the similar distances of 1.99 and 1.85 Å found in corundum (20); both böhmite and corundum exhibiting the effect of Al-Al repulsion. The Sc-O distances of 2.17, 2.08, and 2.06 Å are found to be quite similar to the corresponding distance of 2.10 Å in Sc₂O₃ (23). The lengths 2.54 and 2.58 Å for the shared O-O edge in böhmite is in good correspondence with the value 2.50 Å found in corundum, while the corresponding lengths in γ -ScOOH of 2.71 and 2.74 Å are in agreement with the interpolated

value of 2.61 Å found in Sc_2O_3 .

In the discussion of the "ideal" structures of $\gamma\text{-AlOOH}$ and $\gamma\text{-ScOOH}$, it was mentioned that the $(\text{OH})^-$ anions are on the outer surfaces of the layers. It is now possible to show that these anions give rise to hydrogen bonds holding the layers of octahedra together. As in lepidocrocite and diasporite, the hydrogen bonds are postulated to explain certain O-O distances. The hydrogen bonds, or OHO groups, which hold the layers together are taken to be the shortest unshared O-O distances in the structure. These distances of 2.70 and 2.72 Å for $\gamma\text{-AlOOH}$ and $\gamma\text{-ScOOH}$, respectively, must be regarded as a hydrogen bond since the repulsive forces between the oxygens would otherwise be effective in raising the distance above 2.72 Å. This indicates that the only forces holding the layers together would be the relatively weak ones arising from dipole interactions. The values of 2.70 and 2.72 Å are likewise in good agreement with the hydrogen bridge distance found in other compounds; e.g., 2.70 Å in $\gamma\text{-FeOOH}$, 2.71 Å in $\alpha\text{-AlOOH}$ and $\alpha\text{-FeOOH}$, and in many organic compounds (22). The stoichiometric composition of the crystals is explained by the association of one hydrogen with each 2.70 or 2.72 Å distance. The hydrogens may then be placed between the bonded oxygens at centers of symmetry with coordinates 000; 1/2,0,0; 0,1/2,1/2; 1/2,1/2,1/2. In the pictorial representation of $\gamma\text{-AlOOH}$

and γ -ScOOH (Figure 2) the OH bonds are drawn as small tubes between the layers.

The structure determined here for γ -AlOOH easily explains its tabular habit. Since the OH bonds are relatively weak, there is excellent cleavage on (010) corresponding to the breaking of these weak OH bonds, hence its existence as orthorhombic plates (15,19). This property would also account for the increased breadth and relative intensity of the (020) reflection found for some samples of γ -AlOOH. For an example of this phenomena see Figure 3, b. This picture is a reproduction of the high angle x-ray spectrometer tracing of a sample of γ -AlOOH which has a very "soapy" feel to the touch, which is an indication of its extreme plate-like structure.

From x-ray and electron diffraction examinations, Milligan and Weiser (19), recently reported that transparent films of γ -AlOOH exhibit orientation. The formation of these thin films and the orientation effects noted are easily accounted for by the layer structure found for γ -AlOOH. No microscopic crystals of γ -ScOOH have been observed, but electron micrograph studies have shown that it also exists as orthorhombic plates.

SUMMARY

SUMMARY

1. The unit structure, space group symmetry, and detailed atomic arrangement of γ -AlOOH, böhmite, and the isomorphous compound γ -ScOOH have been determined. Both were found to be isomorphous with lepidocrocite, γ -FeOOH.
2. The unit of structure of γ -AlOOH and γ -ScOOH is orthorhombic end-centered on (100) and has the axes $a_0=3.69$, $b_0=13.24$, and $c_0=2.86$ for γ -AlOOH; and $a_0=4.01$, $b_0=13.01$, and $c_0=3.24$ for γ -ScOOH.
3. The space group is D_{2h}^{17} -Amam, with all atoms in 4(c). The parameters were determined to be: $u_{Al} = -0.322$, $u_O = 0.291$, and $u_{OH} = 0.080$ in γ -AlOOH, while the values $u_{Sc} = -0.318$, $u_O = 0.282$, and $u_{OH} = 0.071$ are the parameters in γ -ScOOH.
4. The elements of the structure are aluminum or scandium-centered oxygen octahedra. The octahedra are joined together by sharing edges to form a "double" layer, and the successive layers held together by hydrogen bonds.
5. The hydrogen bonds are postulated to account for short, unshared O-O distances of 2.70 and 2.72 Å in γ -AlOOH and γ -ScOOH, respectively. These values are in good agreement with those found for many other compounds containing hydrogen bonds.

ACKNOWLEDGMENTS

ACKNOWLEDGMENT

The author wishes to express his grateful appreciation to Dr. W. O. Milligan, under whose direction these experiments were conducted. Professor Milligan's encouragement and guidance during the past four years have proved invaluable. The author is further indebted to the Exploration and Production Research Laboratories of the Shell Oil Company for the use of their high angle x-ray spectrometer.

Thanks are also due the members of the Faculty and Staff of the Rice Institute for the many helpful services which they have rendered. Acknowledgement is also due Mrs. James L. McAtee for the typing of this manuscript.

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TABLES AND FIGURES

TABLE I

VALUES OF THE LATTICE CONSTANTS

	7-ALOOH	8COOH
a_0	3.69 Å	4.01 Å
b_0	12.24 Å	13.01 Å
c_0	2.86 Å	3.24 Å

TABLE II

ATOMIC PARAMETERS

	γ -AlOOH		ScOOH	
	Predicted	Calculated	Predicted	Calculated
u	-0.315	-0.322	-0.334	-0.318
u _I	+0.287	+0.291	+0.266	+0.282
u _{II}	+0.083	+0.080	+0.066	+0.071

TABLE III

COMPARISON OF CALCULATED AND OBSERVED INTENSITIES FOR γ -AlOOH

Relative Intensities								
hkl	Interplanar Spacings		X-ray Spectrometer Cu K α		Crystal Monochromator Cu K α Cr K α			
	d _{calc.}	d _{obs.}	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
020	6.119	6.108	10.00	10.00	10.00	10.00	10.00	10.0
120	3.160	3.160	6.13	6.06	6.19	6.10	5.77	5.7
040	3.061	3.066	0.09	wk.	0.09		0.08	
011	2.799		0.00		0.00		0.00	
140	2.356		0.03		0.02		0.02	
031	2.342	2.340	5.47	5.29	5.81	5.55	5.20	5.2
111	2.222		0.01		0.01		0.01	
060	2.040		0.10	wk.	0.11		0.10	
131	1.982	1.966	0.43	0.55	0.48	0.58	0.42	0.4
051	1.859	1.851	3.87	3.53	4.31	5.66	4.00	4.0
200	1.845	1.841	2.64	3.08	2.97		2.59	2.7
160	1.785		0.00		0.00		0.00	
220	1.767	1.761	0.70	0.66	0.79	0.70	0.71	1.1
151	1.661	1.663	1.00	1.28	1.17	1.46	1.07	1.9
240	1.580		0.02		0.04		0.03	
211	1.538		0.02		0.04		0.03	
080	1.530	1.530	0.69	0.67	0.83	0.59	0.82	0.9
071	1.491		0.00		0.00		0.00	
231	1.483	1.455	2.00	1.41	2.44	1.89	2.62	3.0
002	1.429	1.425	0.99	0.89	1.23	1.32	1.49	2.1
180	1.413		0.13		0.16		0.21	
022	1.392	1.394	0.28	0.29	0.36	0.41	0.48	0.7
171	1.383	1.384	1.11	0.80	1.39	1.03	1.89	1.9
260	1.368	1.364	0.10	wk.	0.13	0.15	0.18	wk.
251	1.310	1.310	1.87	1.47	2.35	2.49	4.08	4.4
122	1.302	1.301	0.69	0.70	0.87	0.90	1.54	1.9
042	1.295		0.01		0.02		0.04	
091	1.228		0.07		0.10		0.20	
0100	1.224	1.221	0.06	0.12	0.09	0.28	0.24	**
142	1.222		0.04		0.05		0.14	
320	1.206	1.201	0.29	0.17	0.38	0.26	1.22	**
280	1.177		0.49		0.64		3.05	**
062	1.170	1.171	0.07	0.33	0.09	0.56	0.48	**

TABLE III (Continued)

<u>hkl</u>	<u>d_{calc.}</u>	<u>d_{obs.}</u>	<u>Calc.</u>	<u>Obs.</u>	<u>Calc.</u>	<u>Obs.</u>	<u>Calc.</u>	<u>Obs.</u>
191	1.165		0.00		0.00		0.00	
1100	1.161	1.160	0.66	0.33	0.85	0.50	5.86	**
271	1.160		0.00		0.00		0.00	
340	1.141		0.02					
202	1.130		0.79					
311	1.125	1.127	0.01	0.59*				
162	1.116		0.00					
222	1.111	1.108	0.26	0.19*				
331	1.089	1.080	0.04	0.03*				
242	1.060		0.02					
360	1.053		0.00					
082	1.044		0.35					
0111	1.037	1.043	0.13	0.21*				
351	1.026	1.028	0.36	0.14*				
291	1.022		0.07					
2100	1.020	1.021	0.08	0.09*				
0120	1.020		0.04					
182	1.005		0.09					
1111	0.995	0.998	0.05	0.03*				
262	0.989		0.10					
1120	0.983	0.986	0.08	0.06*				
380	0.958		0.04					
013	0.949		0.01					
371	0.948	0.945	0.38	0.20*				
0102	0.930		0.07					
033	0.927	0.925	0.13	0.20*				
400	0.922		0.27					
322	0.922	0.920	0.29	0.22*				
113	0.919		0.04					
420	0.912		0.10	0.07*				
282	0.909	0.909	0.59	0.29*				
2111	0.904		0.11					
1102	0.901	0.905	0.83	0.31*				
133	0.900		0.03					
0131	0.894	0.897	0.13	0.11*				
2120	0.892		0.07					
342	0.892	0.885	0.03	0.23*				
053	0.888		0.37					
440	0.884		0.01					
411	0.875		0.01					
391	0.869		0.00					
1131	0.868	0.870	0.54	0.27*				

TABLE III (Continued)

<u>hkl</u>	<u>d_{calc.}</u>	<u>d_{obs.}</u>	<u>Calc.</u>	<u>Obs.</u>	<u>Calc.</u>	<u>Obs.</u>	<u>Calc.</u>	<u>Obs.</u>
3100	0.867	0.866	0.45	0.25*				
153	0.863	0.863	0.35	0.19*				
431	0.858		0.02					
362	0.848		0.00					
213	0.844		0.02					
460	0.841	0.838	0.05	wk.				
073	0.836		0.00					
2102	0.830		0.18					
0122	0.830	0.830	0.09	0.31*				
233	0.829		0.22					
451	0.826	0.826	0.95	0.33*				
173	0.816	0.819	0.54	0.13*				
1122	0.810	0.807	0.23	0.06*				
2131	0.805	0.804	0.39	0.14*				
253	0.800	0.800	0.46	0.34*				
382	0.796		0.16					
3111	0.793	0.798	0.09	0.15*				
480	0.790		0.62					
3120	0.786		0.18					
471	0.784		0.00					

* Obs. intensities for $K\alpha_1$ only.

** Lines too broad to determine the intensities.

TABLE IV

COMPARISON OF CALCULATED AND OBSERVED INTENSITIES FOR
T-SOOH

hkl	Relative Intensities					
	Interplanar Spacings		X-ray Spectrometer Cu K α		Crystal Monochromator Cu K α	
	d _{calc.}	d _{obs.}	Calc.	Obs.	Calc.	Obs.
020	6.506	6.510	10.00	10.00	10.00	10.00
120	3.412	3.414	5.59	5.57	5.69	5.70
040	3.253		0.02		0.02	
011	3.146		0.07		0.06	
031	2.596	2.595	5.10	5.02	5.27	4.99
140	2.525	2.525	0.29	0.26	0.30	wk.
111	2.474	2.473	0.67	0.84	0.70	1.14
131	2.179	2.185	0.26	0.34	0.27	0.39
060	2.168	2.170	0.12	0.12	0.13	
051	2.028	2.026	2.69	2.88	2.97	1.73
200	2.004	2.009	1.97	2.44	2.19	3.42
220	1.914	1.916	0.67	0.52	0.75	0.93
160	1.906	1.907	0.16	0.14	0.18	
151	1.809	1.805	1.87	1.96	2.10	1.50
240	1.706		0.00		0.00	
211	1.690		0.05		0.05	
071	1.686		0.02		0.01	
080	1.626		0.52		0.61	
002	1.620	1.620	0.87	0.90	1.12	1.71
231	1.586		0.84		1.03	
022	1.572	1.588	0.32	1.56	0.38	2.28
180	1.506		0.10		0.12	
171	1.495	1.494	1.00	1.10	1.22	1.55
260	1.471	1.471	0.09	0.10	0.11	
122	1.463	1.462	0.66	0.64	0.82	1.34
042	1.450		0.00		0.00	
251	1.425	1.427	1.32	0.81	1.64	1.14
142	1.363	1.364	0.15	0.06	0.14	
091	1.324		0.01		0.01	
320	1.308		0.21		0.27	
0100	1.301	1.311	0.03	0.17	0.04	0.98

TABLE IV (Continued)

<u>hkl</u>	<u>d_{calc.}</u>	<u>d_{obs.}</u>	<u>Calc.</u>	<u>Obs.</u>	<u>Calc.</u>	<u>Obs.</u>
062	1.298		0.06		0.08	
202	1.267		0.63		0.81	
280	1.262	1.262	0.38	0.72	0.37	1.87
271	1.256		0.01		0.01	
191	1.254	1.250	0.11	0.12	0.14	
1100	1.237		0.49		0.62	
222	1.237		0.25		0.26	
340	1.235	1.236	0.06	0.68	0.07	1.30
162	1.234		0.08		0.08	
311	1.225	1.226	0.12	0.12		
331	1.187		0.04			
242	1.174		0.00			
082	1.147	1.145	0.27	0.11*		
360	1.137		0.03			
351	1.115		0.27			
0111	1.110	1.116	0.09	0.10*		
182	1.103		0.06			
291	1.102	1.102	0.02	0.08*		
2100	1.091		0.04			
262	1.089	1.087	0.08	0.07*		
0120	1.084		0.01			
013	1.076		0.01			
1111	1.070		0.00			
033	1.048		0.21			
1120	1.046	1.045	0.12	0.07*		
113	1.039		0.09			
380	1.032		0.03			
371	1.028	1.030	0.31	0.11*		
322	1.018		0.21			
0102	1.014	1.019	0.03	0.10*		
133	1.008		0.03			
400	1.002	1.004	0.66	0.3*		
053	0.997		0.21			
282	0.996	0.994	0.41	0.2*		

* Obs. intensities for K_{α_1} only.

TABLE V
INTERATOMIC DISTANCES IN γ -ALOOH

Atom	Neighbors in same octahedron		Neighbors in other octahedron		Neighbors in next layer	
Al	20 _{II}	1.87 Å	2A1	2.86 Å		
	20 _I	1.99 Å	2A1	2.92 Å		
	20 _I	1.88 Å				
O _I	20 _I	2.86 Å			20 _{II}	3.82 Å
	40 _{II}	2.82 Å				
	40 _I	2.54 Å				
	10 _{II}	2.58 Å				
O _{II}	20 _{II}	2.86 Å			20 _I	3.82 Å
	40 _I	2.82 Å			40 _{II}	3.05 Å
	10 _I	2.58 Å			20 _{II}	2.70 Å

TABLE VI

INTERATOMIC DISTANCES IN ScOOH

Atom	Neighbors in same octahedron		Neighbors in other octahedron		Neighbors in next layer	
Sc	20 _{II}	2.17 Å	2Sc	3.24 Å		
	20 _I	2.08 Å	2Sc	3.12 Å		
	20 _I	2.06 Å				
O _I	20 _I	3.24 Å			20 _{II}	4.10 Å
	40 _{II}	3.21 Å				
	40 _I	2.71 Å				
	10 _{II}	2.74 Å				
O _{II}	20 _{II}	3.24 Å			20 _I	4.10 Å
	40 _I	3.21 Å			40 _{II}	3.17 Å
	10 _I	2.74 Å			20 _{II}	2.72 Å



Figure 1. X-radiograms

- (a) γ -FeOOH, Cr K_{α} radiation
- (b) γ -AlOOH, Cr K_{α} radiation
- (c) α -AlOOH, Cu K_{α} radiation
- (d) γ -ScOOH, Cu K_{α} radiation

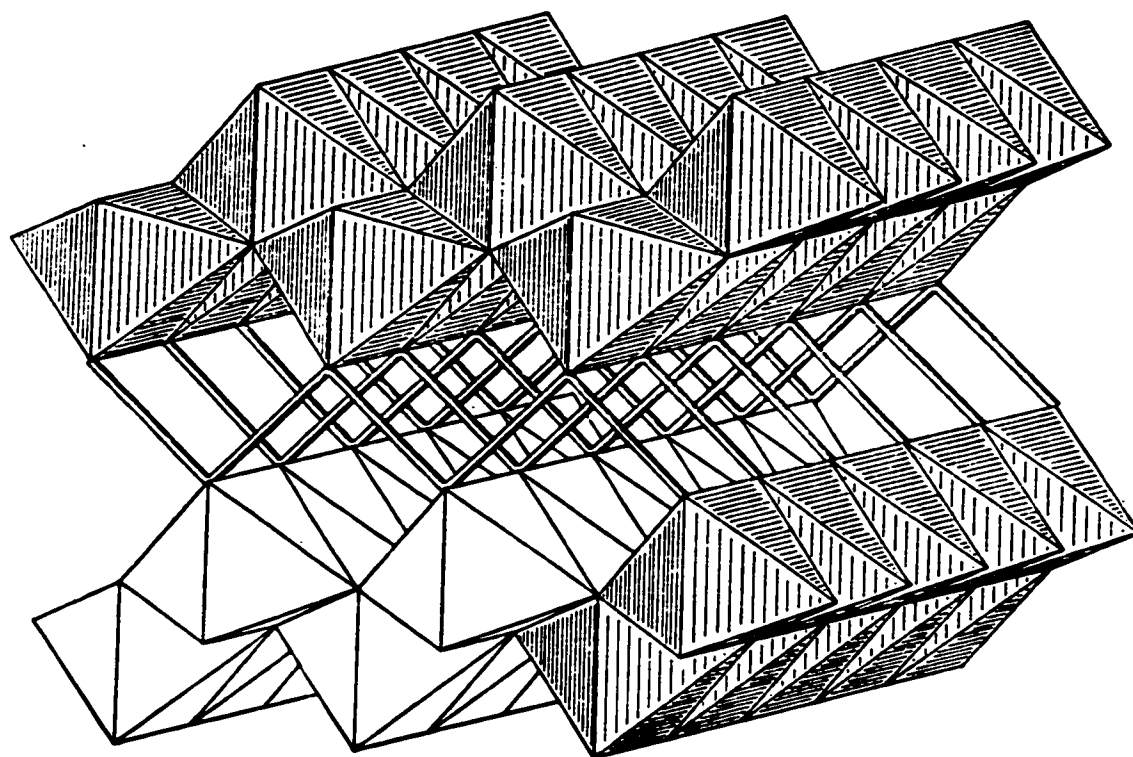


Figure 2. Structure of γ -AlOOH and γ -ScOOH
(after Ewing for γ -FeOOH)

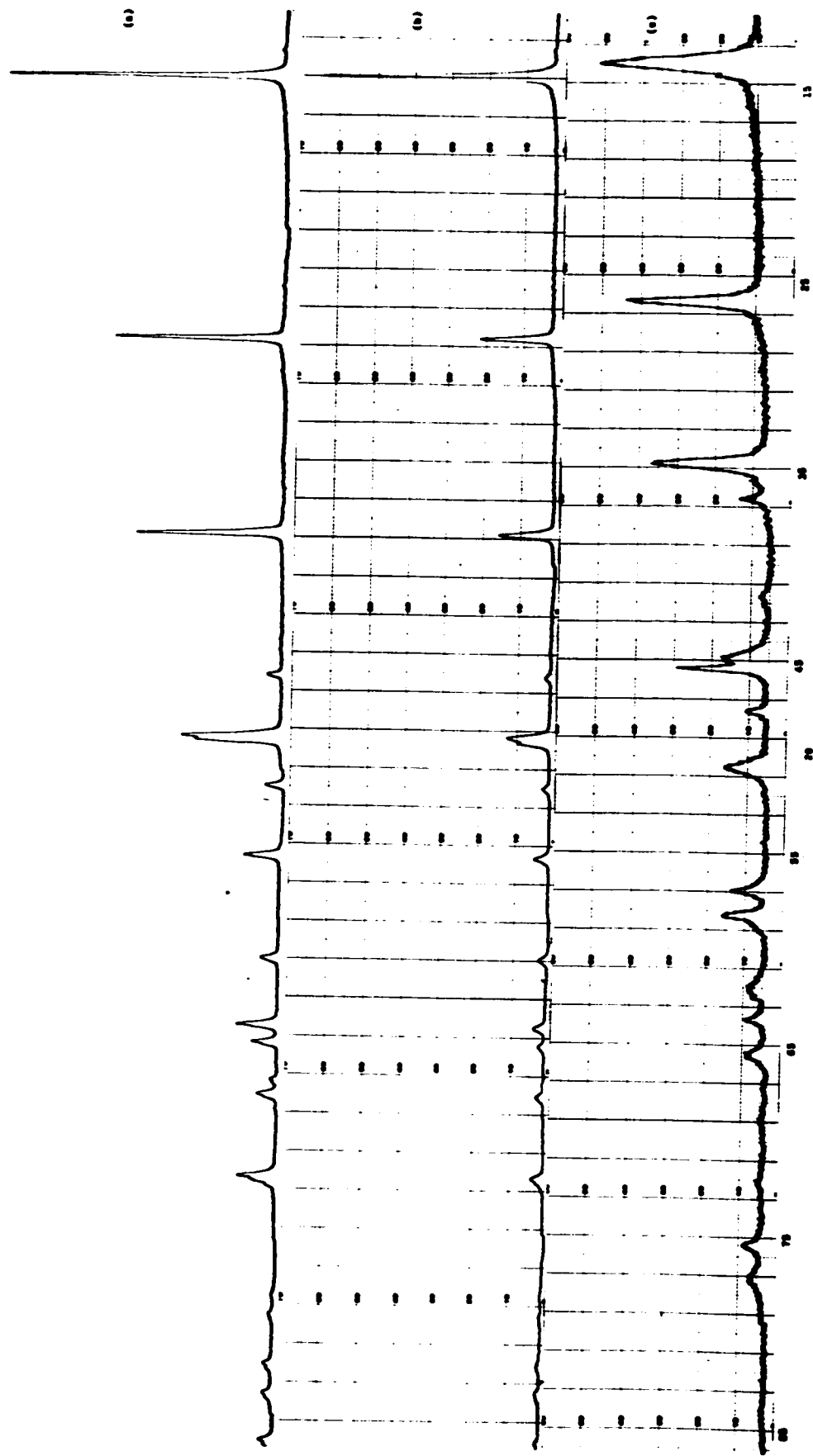


Figure 3. High Angle X-ray Spectrometer Treatings
 (a) $\text{Pb}(\text{C}_2\text{H}_5)_2$ (b) $\text{Pb}(\text{C}_2\text{H}_5)_2$ (c) $\text{Pb}(\text{C}_2\text{H}_5)_2$

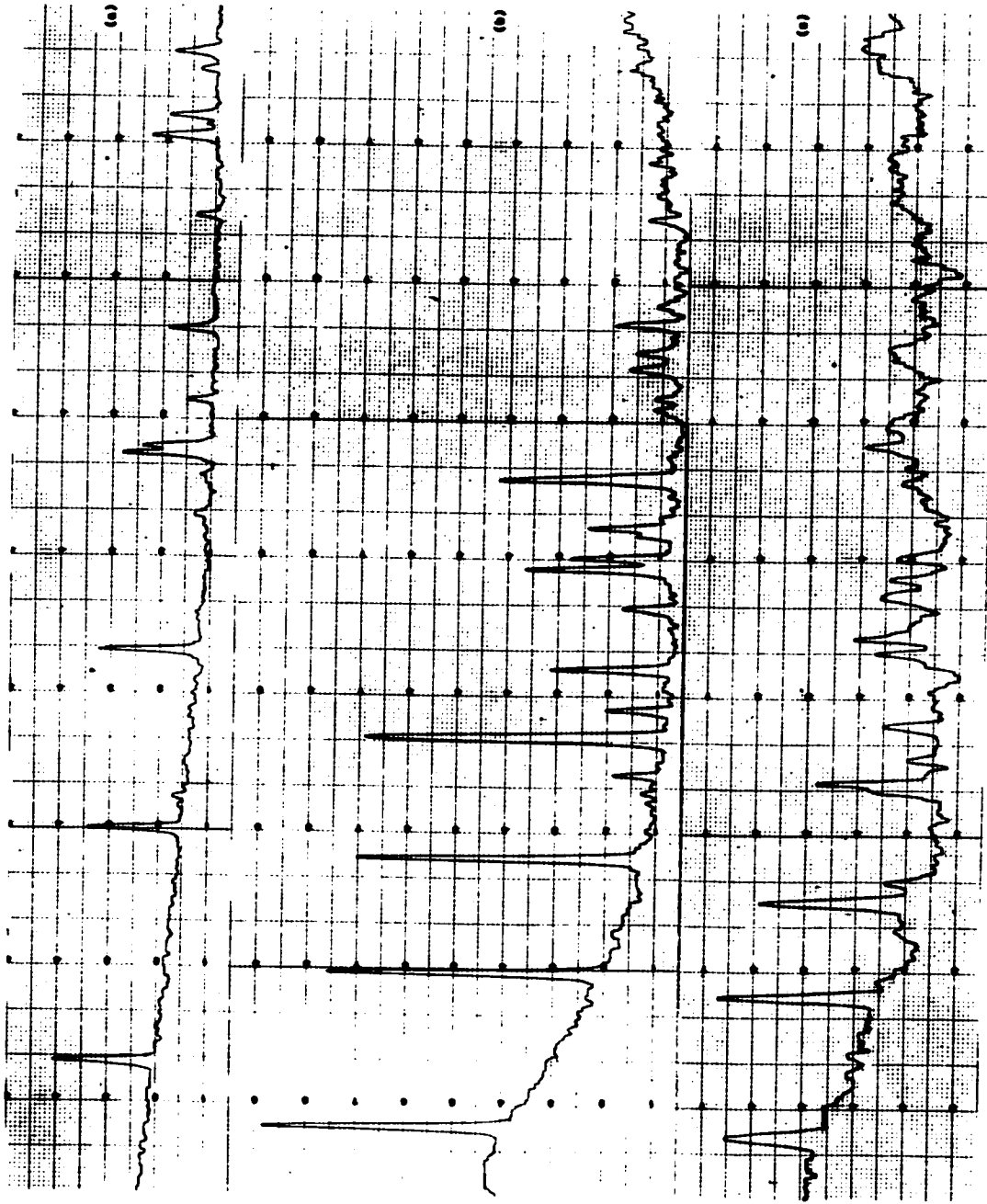


Figure 4. Spectrometer curves
 (a) 2000 eV resolution
 (b) 1000 eV resolution
 (c) 500 eV resolution