

AD 673299

5

Structural Characterization of Thin Aluminum Oxide -
Hydroxide Layers by the Aluminum and Oxygen X-Ray Emission Bands

G. A. Savanick, P. Gigl and E. W. White

TECHNICAL REPORT NO. 1

Office of Naval Research, Metallurgy Program
Contract No. N00014-67-A-0385-002, NR 032-502

1 AUGUST 1968

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED; REPRODUCTION IN
WHOLE OR IN PART IS PERMITTED FOR ANY PURPOSE OF THE UNITED
STATES GOVERNMENT

Materials Research Laboratory
The Pennsylvania State University
University Park, Pennsylvania

AUG 20 1968

Reproduced by the
CLEARINGHOUSE
for Federal Scientific & Technical
Information, Springfield, Va. 22151

12

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Structural Characterization of Thin Aluminum Oxide-Hydroxide
Layers by the Aluminum and Oxygen X-ray Emission Bands

by

G. A. Savanick, P. Gigl, and E. W. White

ABSTRACT

A new technique is outlined for the characterization of thin films of crystalline and amorphous aluminum oxides, aluminum oxyhydroxides and aluminum hydroxides. Shifts in Al $K\beta$ and $OK\alpha$ X-ray emission lines of known examples of these compounds are presented and are used to identify unknown Al-O-OH compounds.

INTRODUCTION

Characterization of aluminum oxides, aluminum oxyhydroxides and aluminum hydroxides can present serious problems when they are poorly crystallized and especially when they occur as thin layers on metal substrates. This study was undertaken to establish the feasibility of using shifts in the aluminum K-emission band (Al $K\beta$), and the oxygen K-emission band ($OK\alpha$) to determine the short range structure of various corrosion products on aluminum and its alloys. It has been well established that K-emission bands of the second and third period elements undergo significant changes among various compounds but consistent rules governing such changes have not been established. It is the purpose of this investigation to establish the feasibility of developing an empirical technique for identifying Al-O-OH phases.

In the case of anhydrous aluminum oxides and aluminosilicates it has been shown that Al K β shifts depend on the number of oxygens coordinating the Al³⁺ and also on the mean Al-O distance in a given structure.¹ More recently a study was undertaken on some of the compounds in the Al-O-OH system using the Al K α line but the results were not very definitive². The principal result of that study was to establish for the first time the characteristic difference in the Al K β peak from α and γ -Al₂O₃.

The oxygen K-emission band has been studied in considerable detail by at least three investigators but their results have not led to a quantitative interpretation of the shifts^{3,4,5}. The most recent of these studies indicated that bond character may be the most common factor contributing to changes in the OK α ⁵.

EXPERIMENTAL

A set of reference standards for the common Al-O-OH compounds were assembled and carefully characterized to confirm their structure and composition. These compounds included α - and γ -Al₂O₃, boehmite [Al-O(OH)], diasporite [Al-O(OH)], gibbsite [Al(OH)₃] and bayerite [Al(OH)₃]. These standards were studied in the form of thin (two to five micron thick layers) deposited from dilute suspension onto polished beryllium.

An ARL model EMX electron microprobe operated at 20 keV and 0.1 μ A specimen current was used to excite and analyze the x-ray spectra. An electron beam diameter of about 100 μ m was used in order to minimize specimen damage. A four inch radius curved crystal spectrometer, geared to read wavelength directly for an ammonium dihydrogen phosphate (ADP) crystal was used with a thin formvar window flow proportional counter.

An ADP crystal ($2d=10.64\text{\AA}$) was scanned at $0.01\text{\AA}/\text{min}$ to diffract the first order Al $K\beta$ line. A clinochlore crystal ($2d=28.36\text{\AA}$) was scanned at $0.0267\text{\AA}/\text{min}$ to diffract the oxygen $K\alpha$ line. The resolution of the ADP crystal is approximately $1000 \left(\frac{\lambda}{\Delta\lambda}\right)$ at 8\AA and the clinochlore crystal has a resolution of about 500 at 28\AA . Al $K\beta$ peak count rates were in the range of 50 to 150 counts per second while the O $K\alpha$ peak count rate varied from 100 to 250 counts per second. The peak positions were measured at two-thirds height and could be reproduced within $\pm 0.0003\text{\AA}$ for Al $K\beta$ and $\pm 0.001\text{\AA}$ for O $K\alpha$.

RESULTS AND DISCUSSION

The spectra recorded in this study are reproduced in Figures 1 and 2. Data on changes in peak position and line widths are tabulated in Table 1. The values are tabulated as changes in peak position measured at $2/3$ height. Each value in the table is average for five separate measurements. Figure 1 is a composite of the Al $K\beta$ lines for the pure compounds. This figure shows that a broad doublet (6eV) at half-height is characteristic of $\alpha\text{-Al}_2\text{O}_3$ (corundum) while all other peaks are observed as singlets at this level of resolution. The peak positions and profiles of the two Al O(OH) compounds boehmite and diaspor—are significantly different. Likewise, the peak positions and profiles of gibbsite and bayerite, the two $\text{Al}(\text{OH})_3$ compounds, are distinctly different. The peak from $\gamma\text{-Al}_2\text{O}_3$ occurs at the longest wavelength of the singlet peaks.

Figure 2 is a composite of the oxygen K-emission bands obtained from the same standards. This figure shows that each emission band appears as a fairly sharp peak with a well resolved long wavelength tail. Boehmite, diaspor—and $\alpha\text{-Al}_2\text{O}_3$, are not significantly different at this level of resolution. The peaks from gibbsite and bayerite resemble each other but occur at a distinctly higher energy than those from the other materials. In addition, the long wavelength tails from

Table I
 Summary of Peak Shifts ($\Delta\lambda$) Measured at 2/3 Peak Height

Standard	Formula	$\Delta\text{AlK}\beta$ ($\text{\AA} \times 10^4$)	$\Delta\text{OK}\alpha$ ($\text{\AA} \times 10^4$)
Corundum	$\alpha\text{-Al}_2\text{O}_3$	0	0
	$\gamma\text{-Al}_2\text{O}_3$	-1	-32
Diaspore	Al O (OH)	-16	0
Böhmite	Al O (OH)	-8	+3
Gibbsite	Al (OH)_3	-15	-88
Bayerite	Al (OH)_3	-12	-77

gibbsite and bayerite are shifted toward higher energies.

The oxygen spectra in Figure 2 are not as well resolved as those reported recently by Chun and Hendel⁵. However, it is advantageous to use the electron microprobe to study oxygen peak shifts because they can be recorded quickly (15 minutes per scan) on a linear intensity scale and only a very small sample is required.

Figures 1 and 2 can be used to positively identify unknown aluminum oxide-hydroxide compounds provided the unknown is a single phase of one of the six dealt with in this study.

A broad doublet Al K β peak is characteristic of α -Al₂O₃. The Al(OH)₃ compounds can be distinguished from the other compounds by their short wavelength oxygen peak and once this distinction is made they can be distinguished from each other on the basis of the position of the Al K β peak. The Al K β peak of γ -Al₂O₃ is distinctive in that it occurs at the longest wavelength side of the single Al K β peaks. The Al K β peak from diasporite is significantly narrower than that from boehmite.

The Al K β and OK α result from electronic transitions from the valence band to the ionized K-shell. Since the electronic configuration of Al⁺³ and O⁻² is identical it seems reasonable to expect that the Al K β and OK α would have the same form if the Al⁺³ and O⁻² valence electrons were populating the same energy level. However, there is a great disparity in the width of the Al K β band (up to 6eV) as compared with that of the OK α band (ca 1.5eV). This suggests that the oxygen valence electrons and the aluminum valence electrons form independent valence bands and are not homogenized into one valence band characteristic of the entire solid.

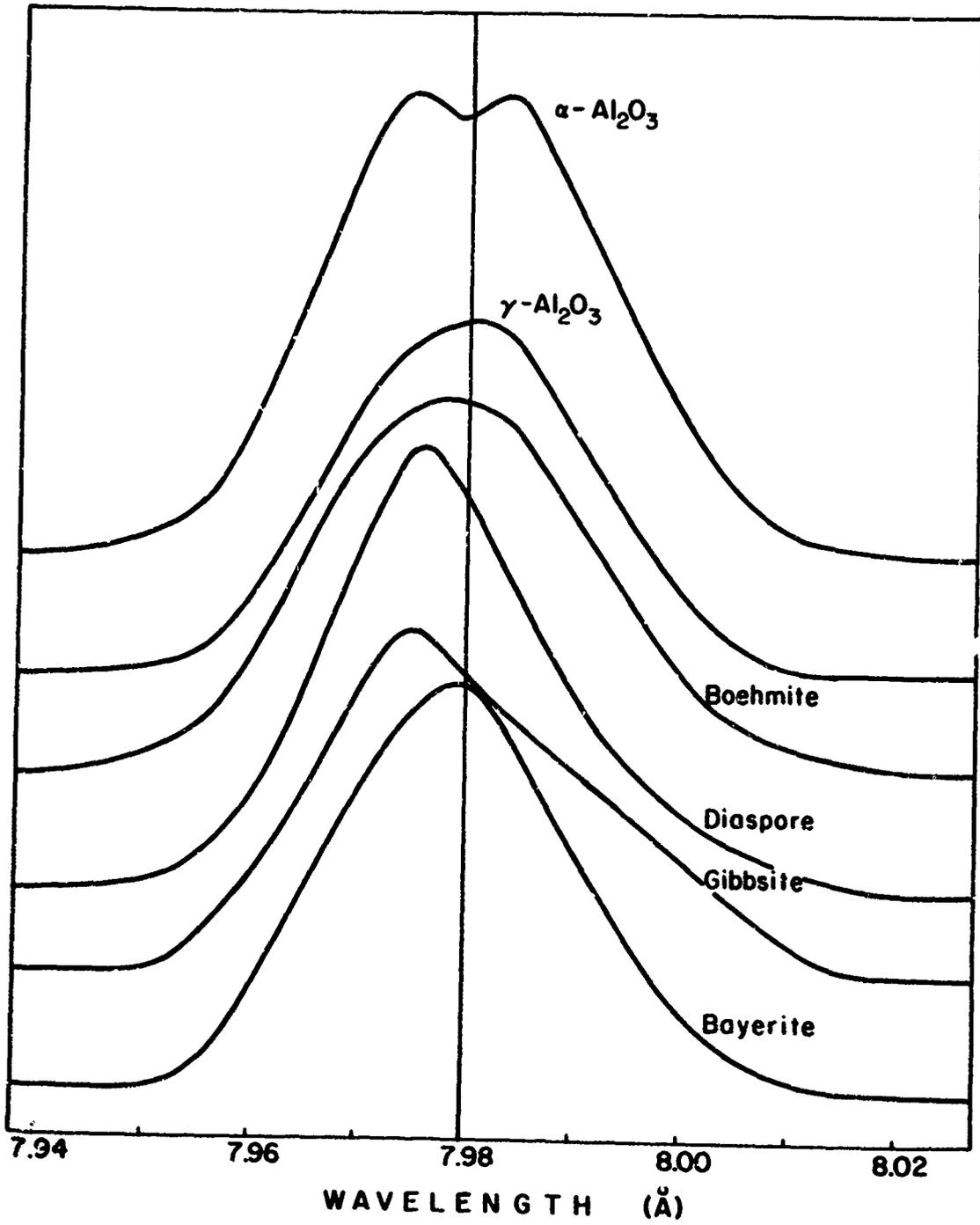


Fig. 1 AlK β peaks of aluminum-oxide-hydroxide compounds

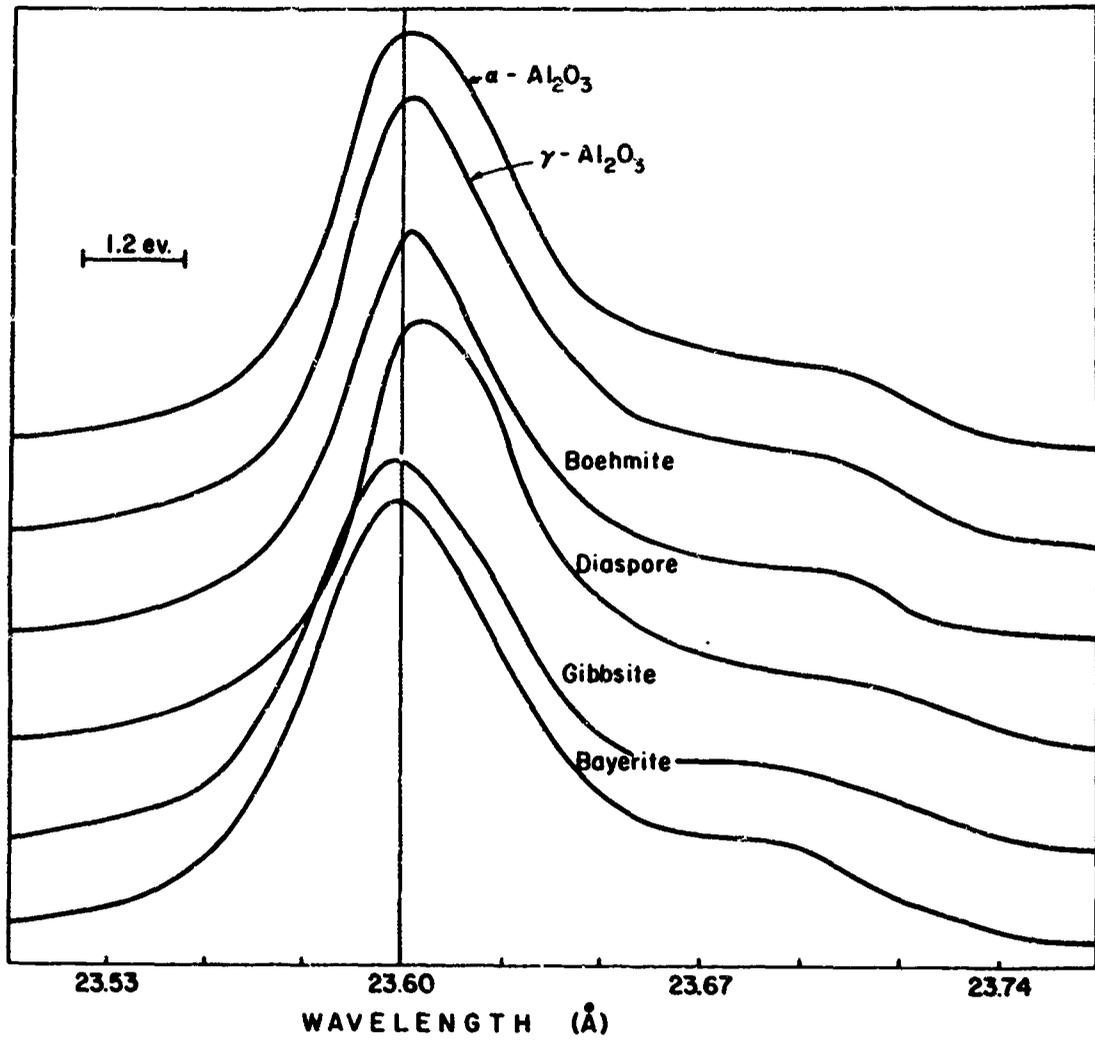


Fig. 2 OK α peaks of aluminum-oxide-hydroxide compounds

The formation of separate energy level diagrams for each type of atom present in an insulator solid is a well-known phenomenon (Parratt). Cross transitions of electron from the aluminums to oxygen and visa versa are probably of no consequence in the wavelength region included in this study. In fact, cross transitions are generally not dominant features in soft x-ray spectra (Parratt).

REFERENCES

1. G. V. Gibbs and E. W. White, in press.
2. E. W. White and Rustum Roy, "Use of X-ray Emission Spectroscopy in the Characterization of Thin Films of Aluminum Oxides and Hydroxides," *Mat. Res. Bull.* 2:395-398 (1967).
3. H. M. O'Bryan and H. W. B. Skinner, "The Soft X-ray Spectroscopy of Solids", *Proc. Roy. Soc. (London)* A176, 229 (1940).
4. D. W. Fischer, "Effect of Chemical Combination on the X-ray Emission Spectra of Oxygen and Fluorine", *Jour. Chem. Phys.* 42, 3814-3821 (1965).
5. H. V. Chun and D. Hendel, "X-ray Spectroscopic Study of Chemical Bonds in Oxides" *Z. Naturforsch.* 22a, pp. 1401-1407, (1967).
6. L. G. Parratt, "Electronic Band Structure of Solids by X-ray Spectroscopy", *Rev. Mod. Phys.* 31, pp. 616-645, (1959).

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) The Pennsylvania State University		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
3. REPORT TITLE Structural Characterization of Thin Aluminum Oxide-Hydroxide Layers by the Aluminum and Oxygen X-ray Emission Bands			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Technical Report Number 1			
5. AUTHOR(S) (Last name, first name, initial) Savanick, G. A., Gigl P. and White, E. W.			
6. REPORT DATE August 1, 1968		7a. TOTAL NO. OF PAGES 12	7b. NO. OF REFS 6
8a. CONTRACT OR GRANT NO. N00014-67-A-0385-0002		8a. ORIGINATOR'S REPORT NUMBER(S)	
A. PROJECT NO. NR 032-502			
c.		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.			
10. AVAILABILITY/LIMITATION NOTICES Distribution of this document is unlimited; reproduction in whole or in part is permitted for any purpose of the United States Government			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Department of the Navy Office of Naval Research, Metallurgy Program Washington, D. C. 20360	
13. ABSTRACT A new technique is outlined for the characterization of thin films of crystalline and amorphous aluminum oxides, aluminum oxyhydroxides and aluminum hydroxides. Shifts in AlK β and OK α X-ray emission lines of known examples of these compounds are presented and are used to identify unknown Al-O-OH compounds.			

DD FORM 1473
1 JAN 54

Security Classification

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
X-ray spectroscopy, thin films, aluminum oxides-hydroxides, structural characterization, short range order, corrosion layers						

INSTRUCTIONS

1. **ORIGINATING ACTIVITY:** Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.
- 2a. **REPORT SECURITY CLASSIFICATION:** Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.
- 2b. **GROUP:** Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.
3. **REPORT TITLE:** Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.
4. **DESCRIPTIVE NOTES:** If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.
5. **AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.
6. **REPORT DATE:** Enter the date of the report as day, month, year, or month, year. If more than one date appears on the report, use date of publication.
- 7a. **TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.
- 7b. **NUMBER OF REFERENCES:** Enter the total number of references cited in the report.
- 8a. **CONTRACT OR GRANT NUMBER:** If appropriate, enter the applicable number of the contract or grant under which the report was written.
- 8b, 8c, & 8d. **PROJECT NUMBER:** Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.
- 9a. **ORIGINATOR'S REPORT NUMBER(S):** Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.
- 9b. **OTHER REPORT NUMBER(S):** If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).
10. **AVAILABILITY/LIMITATION NOTICES:** Enter any limitations on further dissemination of the report, other than those

imposed by security classification, using standard statements such as:

- (1) "Qualified requesters may obtain copies of this report from DDC."
- (2) "Foreign announcement and dissemination of this report by DDC is not authorized."
- (3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through _____."
- (4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through _____."
- (5) "All distribution of this report is controlled. Qualified DDC users shall request through _____."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. **SUPPLEMENTARY NOTES:** Use for additional explanatory notes.

12. **SPONSORING MILITARY ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.

13. **ABSTRACT:** Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS), (S), (C), or (U).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, roles, and weights is optional.