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The Crystal Structure and Anomalous Dispersion of γ-LiAlO$_2$

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γ-LiAlO$_2$ is tetragonal, space group $P4_12_12$ (or $P4_32_12$) with four molecules in a cell of dimensions $a=5{\cdot}1687 \pm 0{\cdot}0005$, $c=6{\cdot}2679 \pm 0{\cdot}0006$ Å. The bond lengths have been determined with an accuracy of 0·002 Å for Al–O bonds and 0·019 Å for Li–O bonds and the final R index is 3·2 %. Each atom is tetrahedrally coordinated and the structure consists of an infinite three-dimensional array of tetrahedra having certain edges and vertices in common. Experimental values of $\Delta f''$ for aluminum ($0{\cdot}22 \pm 0{\cdot}02$) and oxygen ($0{\cdot}028 \pm 0{\cdot}005$) for Cu $K\alpha$ radiation were calculated by using the Bijvoet inequalities (differences in intensity between the reflections hkl and $\bar{h}\bar{k}\bar{l}$).

Introduction

The crystal structure of γ-LiAlO$_2$ has been determined as part of a continuing program in this laboratory to study the solid state properties of oxide compounds with the general formula $A^{+1}B^{+3}O_2$. Single crystals of γ-LiAlO$_2$ were grown from a flux and were found to be piezoelectric by J. P. Remeika of this laboratory (Remeika & Ballman, 1964).

The crystals are tetragonal with cell dimensions $a=5{\cdot}1687 \pm 0{\cdot}0005$, $c=6{\cdot}2679 \pm 0{\cdot}0006$ Å. These values are in agreement with those of Théry, Lejus, Briançon & Collongues (1961), whose cell dimensions from powder data were $a=5{\cdot}181$, $c=6{\cdot}309$ Å. The cell contains four molecules and the calculated density is 2·615 g.cm^{-3}. The only systematic absences are: $00l$ when $l \neq 4n$, and $h00$ when $h \neq 2n$, leading to space group symmetry $P4_12_12$ (D_4^4) or its enantiomorph $P4_32_12$ (D_4^8), in which the lithium and aluminum atoms are in the special positions (4*a*) and oxygen atoms in the general positions (8*b*) [*International Tables for X-Ray Crystallography*, 1952].

In addition to this tetragonal form, LiAlO$_2$ has a second modification, α, which is trigonal and isostructural with NaHF$_2$. This phase was first prepared by Lehmann & Hesselbarth (1961).

Experimental

The symmetry, the space group, and the approximate lattice parameters were determined from zero, first, and second layer-line equi-inclination Weissenberg photographs taken with Cu $K\alpha$ radiation and from a zero level precession photograph taken with Mo $K\alpha$ radiation. For these studies a crystal with the shape of a pyramid was oriented along the pyramidal axis (which turned out to be the c axis).

All intensity measurements were made with a General Electric XRD-3 spectrometer rebuilt for single-crystal work and equipped with a proportional counter and filtered Cu $K\alpha$ radiation. All data were taken on one crystal which had been ground into a sphere of radius $R=0{\cdot}0206 \pm 0{\cdot}0005$ cm, corresponding to $\mu R=1{\cdot}38$, and the intensities of all possible reflections were measured. Absorption and Lorentz-polarization corrections were applied, using the tables given in *International Tables for X-ray Crystallography* (1959).

Precise lattice parameters were obtained by measuring the 2θ values for 11 reflections in the back-reflection region of a powder photograph taken at room temperature with a Norelco camera of 114·6 mm diameter, using Cu $K\alpha$ radiation. The lattice constants were calculated by the least-squares method of Mueller, Heaton & Miller (1960). Their program was modified by J. L. Bernstein of this laboratory for use on the IBM 7090 computer.

A comparison of observed and calculated interplanar spacings and intensities based on the tetragonal structure reported herein is given in Table 1.

Determination of structure

The first step in solving the structure was based on determining the position of the aluminum atom which had to be necessarily in the special position (x, x, 0) of the $P4_n2_12$ ($n=1$ or 3) space groups. The aluminum contribution to the $h00$ and $hh0$ reflections is proportional to $\cos 2\pi hx_{\rm Al}$ and $\cos 2\pi hx_{\rm Al}$ respectively. It was evident from the corresponding experimental structure factors that the aluminum atom was very nearly at ($\frac{1}{6}$, $\frac{1}{6}$, 0).

Once the aluminum position was determined it was a simple task to locate the other two atoms. This is due to the fact that the four or six oxygen atoms surrounding the aluminum atom (initially the coordination of aluminum was not known) are crystallographically related. Therefore, many independent equations can be written on the basis that the oxygen–oxygen distance in a polyhedron around the aluminum is $\sim 2{\cdot}80$ Å and the aluminum–oxygen distance in the same polyhedron is $\sim 1{\cdot}80$ Å. The structure was readily seen when the tetrahedral coordination for aluminum was assumed. The coordinates so obtained were used as starting values in the first refinement in which only weak reflections were used, as high secondary extinction was expected. The Busing–Martin–Levy least-squares refinement program (1962), modified by B. B. Cetlin of this laboratory, was used with the f curves (for neutral atoms) given in *International Tables for X-ray Crystallography* (1962). The real anomalous dispersion correction was applied to aluminum.

In the first refinement individual isotropic thermal coefficients were used. The positional and thermal parameters obtained after four cycles, which gave an R index of 0·048, were used to calculate the structure factors of strong reflections. All the observed values were then corrected for secondary extinction. The Zachariasen (1963) formula was used: $F_{\text{corr.}} \simeq F_o[1+\beta(2\theta)CJ_o]$, where $F_{\text{corr.}}$ is the structure factor corrected for secondary extinction, F_o the observed one, J_o the observed intensity on an arbitrary scale, C is a constant to be found and $\beta(2\theta)$ takes into account the angular variation of the extinction correction. A range of C values was tried and the best agreement was obtained with $C=0{\cdot}28\times10^{-3}$. The final refinement, in which anisotropic thermal coefficients were used, gave an R index of 0·032 and the parameters shown in Tables 2 and 3. The agreement between observed and

Table 1. *Comparison of observed and calculated interplanar spacings and intensities*

	Present work				Debray & Hardy*		
hkl	$d_{\text{obs.}}$	$d_{\text{calc.}}$	$I_{\text{obs.}}$†	I/I_0 calc.	d	I/I_0	$h^2+k^2+l^2$
101	3·977	3·988	*vvs*	100	3·993	100	10
110	3·650	3·655	*w−m*	13·8	3·652	16	12
111	3·153	3·157	*m*	22·7	3·155	32	16
102	2·677	2·680	*vs*	65·3	2·683	55	22
200	2·584	2·584	*vs*	72·9	2·581	56	24
201	2·388	2·389	*vvw*	2·2			
112	—	2·379	n.obs.	0·0			
210	—	2·312	n.obs.	0·2			
211	2·168	2·169	*w*	8·3	2·167	12	34
202	—	1·994	n.obs.	0·1			
103	1·935	1·937	*vvw*	1·6	1·932	2	44
212	1·860	1·860	*m*	16·4	1·857	22	46
220	1·827	1·827	*w*	7·9			
113	1·814	1·814	*w*	8·0	1·819	20	48
221	—	1·754	n.obs.	0·0			
301	1·658	1·661	*vvw*	2·4	1·659	4	58
310	1·633	1·634	*w*	10·2	1·637	19	62
203	1·624	1·625	*vvw*	4·5			
311	1·580	1·582	*w*	9·8	1·581	17	64
322		1·579		1·4			
004	1·565	1·567	*w−m*	14·4	1·566	16	66
213	—	1·550	n.obs.	0·7			
302	1·508	1·510	*s*	50·3	1·510	38	70
104	—	1·500	n.obs.	0·1			
312	—	1·449	n.obs.	0·0			
114	1·440	1·440	*vvw*	1·4			
320	—	1·434	n.obs.	0·1			
321	1·396	1·397	*vw*	6·9	1·395	7	82
223	1·375	1·376	*vvw*	1·6	1·373	1	84
204	1·339	1·340	*m*	20·6	1·339	20	90
303	—	1·329	n.obs.	0·7			
322	1·303	1·304	*ms*	42·3	1·303	25	94
214	1·297	1·297	*vvw*	3·8			
400	—	1·292	n.obs.	0·7			
313	1·286	1·287	*m*	21·3	1·285	18	96
401	1·265	1·266	*vvw*	3·9	1·264	<1	100
410	1·253	1·254	*vvw*	2·1	1·252	<1	102
411	1·229	1·229	*w*	13·5	1·227	6	106
330 }	1·218	1·218	*ms*	28·7	1·217	19	108
105 }		1·218		16·0			
331 }	1·195	1·196	*vvw*	3·6			
402 }		1·195		0·4			
224	1·189	1·190	*w*	13·2	1·187	6	114
115	—	1·186	n.obs.	1·5			
323	1·182	1·182	*vw*	6·0			
412	—	1·164	n.obs.	0·5			
304	—	1·159	n.obs.	0·2			
420	1·156	1·156	*ww*	4·0	1·154	<1	120

* Debray & Hardy (1960) reported $LiAlO_2$ as cubic with a lattice parameter of 12·650 Å. As can be seen, the stronger lines of the pattern can be indexed on a cubic cell, in agreement with Debray & Hardy. However, there are several weak lines present which could not be indexed and these were not observed by Debray & Hardy.

† Visually estimated from a film taken with Cr $K\alpha$ radiation.

calculated structure factors is shown in Table 4, where F_o corresponds to $\frac{1}{2}(|F_H|+|F_{\overline{H}}|)$ and $|F_c|$ is the calculated scattering amplitude per unit cell, neglecting the imaginary anomalous dispersion term in the atomic scattering factors. Under conditions of low dispersion ($LiAlO_2$ and Cu $K\alpha$ for example) the imaginary terms $\Delta f_j''$ may be neglected if the average intensity $\frac{1}{2}(I_H+I_{\overline{H}})$ is used to obtain the observed structure factors (Zachariasen, 1965).

Table 2. *Atomic coordinates* ($\times 10^4$)

	x	y	z
O	3369 ± 4	2906 ± 4	7723 ± 4
Al	1759 ± 2	(1759)	(0)
Li	8126 ± 9	(8126)	(0)

Table 3. *Anisotropic thermal coefficients** ($\times 10^4$)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O	45 ± 9	70 ± 8	18 ± 7	−12 ± 4	9 ± 4	−2 ± 4
Al	20 ± 6	(20)	5 ± 6	−0·2 ± 3	3 ± 3	(−3)
Li	107 ± 22	(107)	53 ± 22	−23 ± 21	0 ± 22	(0)

* By symmetry $\beta_{22}=\beta_{11}$ and $\beta_{23}=-\beta_{13}$ for Al and Li.

Table 4. *Observed and calculated structure factors*

hkl	F_o	$\lvert F_c \rvert$	hkl	F_o	$\lvert F_c \rvert$	hkl	F_o	$\lvert F_c \rvert$	hkl	F_o	$\lvert F_c \rvert$	hkl	F_o	$\lvert F_c \rvert$
101	27.5	28.0	321	14.3	14.4	422	10.2	10.1	433	9.5	9.6	326	17.4	18.0
110	15.0	16.1	223	9.6	9.7	413	11.0	11.0	503	1.5	1.5	611	15.4	15.0
111	16.7	17.4	204	31.4	33.6	324	2.7	2.9	522	15.8	15.7	443	10.1	10.2
102	34.5	36.3	303	6.0	5.9	333	10.7	11.1	440	3.3	3.3	217	2.1	2.2
200	56.3	56.2	322	30.3	32.1	430	0.7	0.3	513	8.3	8.1	602	1.9	1.9
201	7.4	7.6	214	9.6	9.4	225	0.6	0.5	226	9.4	9.5	612	9.1	9.2
112	1.7	0.5	400	8.4	8.4	106	15.0	15.9	441	11.5	11.3	524	8.6	8.8
210	1.7	2.4	313	20.8	22.4	501	3.2	3.0	405	5.4	5.5	620	16.5	16.0
211	11.9	11.9	401	12.8	12.8	431	15.4	15.3	306	29.5	29.9	533	5.2	5.1
202	2.4	2.2	410	9.6	9.3	510	13.4	13.0	530	24.3	24.0	406	6.6	5.6
103	8.2	8.3	411	14.8	15.2	305	7.6	7.8	415	11.0	11.2	621	10.8	10.9
212	18.9	20.0	105	21.8	23.3	423	10.5	10.6	107	2.6	2.4	540	8.1	8.2
220	27.2	27.7	330	42.8	42.7	116	10.7	10.5	316	1.5	1.2	227	9.6	10.5
113	19.6	20.3	331	9.7	9.5	511	5.5	5.2	531	4.3	4.4	416	1.5	1.6
221	1.0	0.9	402	3.2	3.4	404	6.5	6.6	442	9.9	9.9	541	6.4	6.4
301	12.1	11.7	224	16.2	18.2	315	7.1	7.2	335	3.2	3.1	435	13.8	14.8
310	22.9	24.4	115	6.0	5.8	502	28.6	28.2	523	1.9	1.9	505	5.0	5.2
203	16.3	16.5	323	8.4	8.5	432	5.1	5.0	117	11.4	12.1	603	8.4	8.5
311	17.0	17.5	412	1.8	1.8	414	10.6	10.4	434	3.7	3.5	307	1.0	0.8
222	9.6	9.5	304	1.6	1.8	206	2.5	2.7	504	2.2	2.1	336	1.3	1.0
004	60.3	60.6	420	7.2	7.2	512	8.8	8.6	600	26.4	25.0	622	1.6	1.7
213	5.1	4.8	421	10.1	10.2	334	31.1	31.8	601	7.6	7.6	444	2.0	2.1
302	57.1	56.1	332	2.2	2.3	520	10.4	10.4	532	2.3	2.4	515	2.2	2.6
104	2.0	2.2	314	16.3	17.5	216	9.6	9.9	514	10.8	10.9	613	11.0	11.1
312	1.0	0.9	205	3.4	3.1	521	4.7	4.6	610	2.3	2.5	317	15.5	16.0
114	9.3	9.4	215	12.4	13.2	325	13.5	13.8	425	6.2	6.3	003	25.5	24.3
320	2.9	2.8	403	17.3	17.7	424	5.8	5.4	207	13.0	13.6	542	5.5	5.6

Discussion of the structure

The results of the final refinement give the interatomic distances and angles reported in Tables 5 and 6 respectively.

Table 5. *Bond lengths*

Tetrahedron about Al					
Al–O	(2)	1·755 ± 0·002	O–O	(2)	2·918 ± 0·004
	(2)	1·766 ± 0·002		(2)	2·896 ± 0·005
					2·737 ± 0·003
					2·874 ± 0·004
Tetrahedron about Li					
Li–O	(2)	2·059 ± 0·018	O–O	(2)	3·301 ± 0·005
	(2)	1·948 ± 0·019		(2)	3·296 ± 0·003
					3·430 ± 0·005
					2·737 ± 0·003
Tetrahedron about O					
Al–Al		3·118			
Li–Li		3·091			
Al–Li		2·656			
		3·055			
		3·153			
		3·135			

As can be seen from Fig. 1, the structure consists of an infinite three-dimensional array of distorted tetrahedra, with aluminum and lithium atoms at the centers and oxygen atoms at the vertices. Each tetrahedron shares one of its edges with another tetrahedron of different kind and each vertex of every tetrahedron is shared with two additional tetrahedra, one of each kind. Each oxygen atom is then shared among four tetrahedra, two Al-centered and two Li-centered. Actually the same scheme would be obtained if the tetrahedra were drawn by putting the aluminum and the lithium at the vertices and the oxygens at the centers. This means that in this structure each atom is tetrahedrally coordinated.

Table 6. *Bond angles**

O–Al–O	(2)	110·7°
	(2)	111·9°
		101·7°
		109·9°
O–Li–O	(2)	110·6°
	(2)	110·9°
		83·3°
		123·4°
Al–O–Li		87·5°
		110·5°
		114·5°
		115·6°
Al–O–Al		124·6°
Li–O–Li		100·9°

* Individual standard deviations were not calculated for the bond angles, but an estimate of the standard deviation of an O–Al–O is 0·2°, of an O–Li–O is 0·8° and of an Al–O–Li is 0·4°.

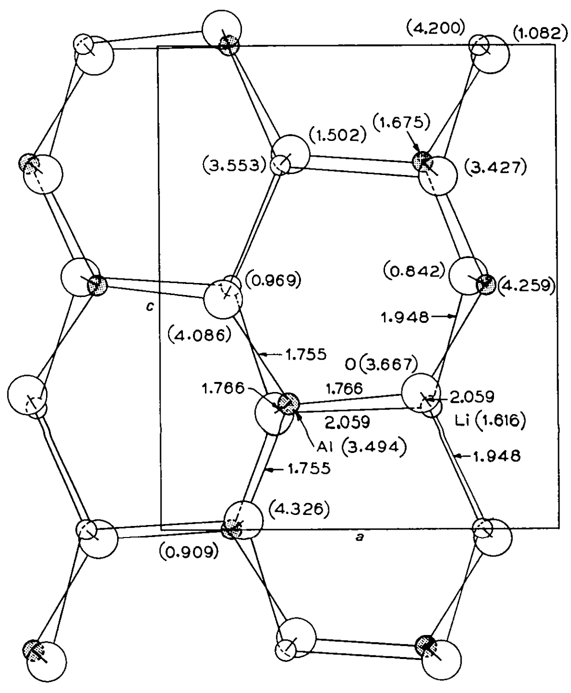

Fig. 1. Projection of the structure on XZ plane. The heights of the atoms (Å) are given in parenthesis. The bond lengths are also shown.

The common edge between the Li-centered tetrahedron and the Al-centered one is 2·737 Å. This value is a little shorter than the average (2·900 Å) of the other five edges of the Al-centered tetrahedron. But 2·737 Å is far shorter than the average (3·325 Å) of the other five edges of the Li-centered tetrahedron. In fact two Li–O distances are 2·059 Å and two 1·948 Å. The distortion of the Li-centered tetrahedron is thus much greater than that of the Al-centered one. The common edge must be this short (2·737 Å) in order to allow a reasonable Li–Al distance, which is itself rather short, 2·656 Å.

The mean bond lengths are Li–O 2·00 Å and Al–O 1·761 Å. The tetrahedral Li–O distance has been determined accurately in only a few compounds. For example, in Li_2CO_3 Zemann (1957) found 1·97 Å, in $LiBO_2$ Zachariasen (1964) also found 1·97 Å, and in $LiGaO_2$ the writer (Marezio, 1965) found 1·99 Å. There are other compounds in which Li^+ has tetrahedral coordination, such as $(LiAsO_3)n$, Li_2WO_4 *etc.*, whose structures have been refined accurately, but in these cases the standard deviations are very large because of the presence of heavy elements. The average tetrahedral Li–O distance given in *International Tables for X-ray Crystallography* (1962) is 1·98 Å.

Very few accurately determined values have been reported for the tetrahedral Al–O distance which is very important in the understanding of the crystal chemistry of the aluminum silicates. Smith & Bayley (1963) summarized the data on the tetrahedral Al–O distance in silicates and concluded that the most reliable values were in the range 1·75–1·80 Å. The average value given in *International Tables for X-ray Crystallography* (1962) is $1{\cdot}78_5$ Å, as compared with a value of 1761· Å in this work. There are many compounds in which Al^{3+} has tetrahedral coordination, such as $AlPO_4$, $CaAl_2O_4$, $CaAl_4O_7$, inverse aluminum spinels, aluminum garnets, but these structures have not yet been accurately refined.

The results for anisotropic thermal coefficients β_{ij} as obtained from the refinement program are listed in Table 3. Table 7 gives the thermal motion data in terms of the root mean square displacement Δ_i along principal axes, together with the direction cosines of the principal axes in the XYZ system of the crystal. The thermal displacements are small, as was to be expected from the hardness of the crystal. Although a detailed analysis of the data of Table 7 will not be presented, it can be stated that the results regarding anisotropy of thermal motion and orientation of the tensor ellipsoids are physically reasonable when correlated with the directions of the chemical bonds. For instance, the directions of minimum displacement observed for aluminum and oxygen are nearly parallel to the direction of the bond between the two atoms. In fact the direction cosines of this bond are: $\alpha=0{\cdot}474$, $\beta=0{\cdot}338$ and $\gamma=-0{\cdot}814$, compared with $\alpha=0{\cdot}443, \beta=0{\cdot}065, \gamma=-0{\cdot}894$ for the oxygen atom and $\alpha=0{\cdot}237$, $\beta=-0{\cdot}237$, $\gamma=-0{\cdot}942$ for the aluminum atom.

Table 7. *Thermal motion data*

	i	Δ_i(Å)	α	β	γ
O	1	0·053 ± 0·012	0·443	0·065	−0·894
	2	0·078 ± 0·007	0·802	0·418	0·427
	3	0·101 ± 0·005	0·402	−0·906	0·134
Al	1	0·027 ± 0·024	0·237	−0·237	−0·942
	2	0·052 ± 0·009	0·707	0·707	0
	3	0·054 ± 0·009	−0·667	0·667	−0·336
Li	1	0·103 ± 0·021	0	0	−1·000
	2	0·107 ± 0·020	0·707	0·707	0
	3	0·133 ± 0·015	−0·707	0·707	0

In general, mixed oxides with the general formula $A^{+1}B^{+3}O_2$ have structural arrangements that can be considered distortions of some simple structures. For instance $LiFeO_2$, $LiInO_2$, $LiScO_2$, $LiEuO_2$, *etc.* have tetragonal structures which are NaCl-like; the departure from the cubic symmetry is due to the need for accommodating metallic atoms of different sizes. Some of these structures (for instance $LiFeO_2$) can exist in the disordered state. Other mixed oxides, such as $NaInO_2$, $LiVO_2$, $LiNiO_2$, $NaFeO_2$, *etc.*, have trigonal structures with the $CsCl_2I$ arrangement, which is also NaCl-like. There are, of course, exceptions to this classification and γ-$LiAlO_2$ is one example. In NaCl-like structures the cations are octahedrally coordinated, while in γ-$LiAlO_2$ lithium and aluminum are tetrahedrally coordinated.

Anomalous dispersion

As was previously stated, two space groups, $P4_12_12$ and its enantiomorph $P4_32_12$, are possible for the

Table 8. *Observed and calculated intensity inequalities for space group* $P4_12_12$*

hkl	$X_o\,.\,10^2$	$X_c\,.\,10^2$	hkl	$X_o\,.\,10^2$	$X_c\,.\,10^2$
211	−2·0	−2·6	424	−3·5	−2·0
212	−0·5	0·4	433	0·7	1·3
311	−0·8	−1·6	522	−1·4	−0·6
213	20·1	17·9	513	2·4	2·1
312	−11·5	−14·9	415	−2·0	−1·9
321	−1·5	−2·0	316	−13·1	−12·1
322	0·9	−0·3	531	−11·3	−10·3
214	3·9	4·0	523	53·0	54·1
313	1·1	0·9	434	8·7	8·8
411	−3·3	−2·4	532	5·5	5·6
323	3·3	3·7	514	2·9	2·6
412	1·9	−1·9	425	−14·5	−14·0
421	−8·3	−7·4	326	−1·1	−1·4
314	0·9	1·4	611	0·6	0·8
215	−1·0	−0·2	217	40·9	42·2
422	−3·3	−3·1	612	2·3	2·0
413	4·2	4·0	524	− 1·1	−0·6
324	−9·8	−9·6	533	7·3	6·9
431	−2·1	−1·7	621	1·0	1·1
423	5·0	3·6	416	−5·7	−4·3
511	−1·3	− 0·2	541	−7·0	−4·9
315	−2·1	−1·3	435	−1·0	−1·8
432	−4·0	−3·7	622	−30·4	−28·4
414	1·4	3·1	515	23·9	17·5
512	1·1	1·5	613	−0·7	−0·5
216	1·0	1·7	317	0·2	0·8
521	−11·5	−11·0	542	2·4	2·7
325	−1·1	−0·5			

* The X_c values for space group $P4_32_12$ have the same magnitude, but opposite sign.

crystal structure of γ-$LiAlO_2$. By making use of the anomalous dispersion effect, it is possible to determine the proper one, namely the absolute configuration. As a result of the work of Bijvoet (1951) and his school, it is now well known that when anomalous scattering occurs in an acentric structure, Friedel's law no longer holds, that is I_{hkl} and $I_{\overline{hkl}}$ have different values, and the absolute configuration can be determined by evaluating these inequalities. For instance, from Table 8 one can see that the proper space group for the $LiAlO_2$ specimen used in this investigation is $P4_12_12$.

Experimental values for $\Delta f''_{\rm Al}$ and $\Delta f''_{\rm O}$ can be calculated from the observed intensity inequalities. In a recent paper Zachariasen (1965) has shown that the anomalous dispersion effect can be conveniently expressed by the dimensionless quantity X_H defined by:

$$X_H=\frac{I_H-I_{\overline{H}}}{\frac{1}{2}(I_H+I_{\overline{H}})}$$
$$=\frac{4}{|F_H|^2+|\Psi_H|^2}\{\sum_{j>k}\sum|F_j||F_k|(\delta_j-\delta_k)\sin(\alpha_k-\alpha_j)\}$$

where F_H is the structure factor associated with the f's ($f=f_o+\Delta f'$) and Ψ_H is the structure factor associated with the $\Delta f''$'s, F_j (or F_k) is the contribution to F_H due to the atoms of the jth (or kth) chemical species, α is the phase angle and $\delta=\Delta f''/f$. Since Ψ_H is negligible with respect to F_H, and $\delta_{\rm Li}$ is negligible with respect to $\delta_{\rm Al}$ and $\delta_{\rm O}$, the above equation can be written as follows:

$$X_H\simeq\frac{4}{|F|}\{|F_{\rm Al}|\delta_{\rm Al}\sin(\alpha-\alpha_{\rm Al})+|F_{\rm O}|\delta_{\rm O}\sin(\alpha-\alpha_{\rm O})\}$$
$$=\frac{4}{|F|^2}\{\delta_{\rm Al}(BA_{\rm Al}-B_{\rm Al}A)+\delta_{\rm O}(BA_{\rm O}-B_{\rm O}A)\}.$$

For each reflection one can write an observational equation of the form:

$$P_i\Delta f''_{\rm Al}+R_i\Delta f''_{\rm O}=X_{oi}\,,$$

where

$$P=\frac{4}{f_{\rm Al}}\,\frac{BA_{\rm Al}-B_{\rm Al}A}{|F|^2}\,,\qquad R=\frac{4}{f_{\rm O}}\,\frac{BA_{\rm O}-B_{\rm O}A}{|F|^2}\,.$$

The two parameters $\Delta f''_{\rm Al}$ and $\Delta f''_{\rm O}$ can be determined by least-squares, assuming that they do not vary with θ. By using only those reflections for which $X_o\geq0{\cdot}05$, and using unit weights, we obtained for Cu $K\alpha$ radiation $\Delta f''_{\rm Al}=0{\cdot}22\pm0{\cdot}02$ and $\Delta f''_{\rm O}=0{\cdot}028\pm0{\cdot}005$. These values were used to calculate the X_H's reported in Table 8.

Fairly accurate values for $\Delta f''$ can be obtained from the atomic absorption coefficients, $\mu_a=(2e^2\lambda/mc^2)\Delta f''$, on the assumption that true absorption is the predominant process (Zachariasen, 1965). By using the values for atomic absorption coefficients in *International Tables for X-ray Crystallography* (1962) for aluminum and oxygen the above formula gives 0·25 and 0·035 respectively.

The experimental $\Delta f''$ values obtained from the anomalous dispersion effect are much smaller than those given in *International Tables for X-ray Crystallography* (1962), ($\Delta f''_{\rm Al}=0{\cdot}3$, $\Delta f''_{\rm O}=0{\cdot}1$), slightly smaller than those obtained from the atomic absorption coefficients ($\Delta f''_{\rm Al}=0{\cdot}25$, $\Delta f''_{\rm O}=0{\cdot}035$) and in good agreement with the values ($\Delta f''_{\rm Al}=0{\cdot}24$, $\Delta f''_{\rm O}=0{\cdot}028$) calculated from Hönl's (1933) theory.

The experimental data for this work were taken at the University of Chicago and I am deeply indebted to Professor W. H. Zachariasen for permission to use his X-ray equipment.

Note added in proof:– Since the submission of this paper an article has appeared which is pertinent to the subject of this work. Bertant, Delapalme, Bassi, Durif-Varambon & Toubert (1965) have determined the structure of γ-$LiAlO_2$ by neutron and X-ray diffraction on a powder sample. Their determinations and the present one are in good agreement.

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