e_g symmetry over the two-to-three spherical admixture becomes apparent. This latter conclusion had been drawn from trial and error analysis of the experimental data; its confirmation in the projection 5(*b*) is purely a result of extrapolating the data, and here serves only as an example of the type of detail that could become recognizable if more data were available.

The error in the density for two-dimensional centrosymmetric projections depends differently on the standard error of the structure factors depending on whether $\sigma(F)$ is proportional to F or independent of it, though the difference does not amount to much in practical cases (Lipson & Cochran, 1953). $\sigma(F)$ fluctuated somewhat in the polarized beam data mentioned here but for the present purposes it may be considered constant. For this case, Lipson & Cochran (1953) give

$$\sigma(\varrho)=[\pi S^2_{\max}/A_c]^{\frac{1}{2}}\sigma(F)$$

where A_c is the area of the projected plane. If $\sigma(F)$ is taken to be constant at one per cent of the strongest structure factor, an overgenerous estimate, we find that $\sigma(\varrho)=0{\cdot}034\mu_B/\text{Å}^2$, which is approximately one-half the spacing of the contours in 5(*a*).

Conclusion

It may be concluded that, although termination and observational errors are not completely removed from current projections of unpaired electron densities, over-all features are nevertheless recognizable in sufficient detail to give reliable information about the symmetry of the unpaired electron distribution. Improvement can of course be made by collecting three-dimensional data, as Shull & Yamada (1961) have done for Fe, though this will be more advantageous in cases where the structure is of enough complexity that superposition in the projection is a real problem. In cases such as discussed here, the obvious next step would be to extend the measurements to higher scattering angles so as to improve the resolution.

During this work the author had numerous and valuable discussions with Dr R. Nathans and Dr H. A. Alperin. Thanks are also due to Dr B. C. Frazer for commenting on the manuscript.

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The Structure of Aluminum Tetroxycarbide

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Aluminum tetroxycarbide, Al_4O_4C, is a high temperature reaction product in the aluminum oxide carbide system. Its structure has been determined by single crystal analysis of three-dimensional Cu $K\alpha$ data. The structure was solved from the Patterson synthesis, and refined by differential Fourier synthesis methods.

The structure is based on $Al(O_3C)$ tetrahedra which share corners and edges. The unusual feature of the structure is a chain of tetrahedra which are linked alternately by sharing edges and corners. The observed Al–O bond lengths range from 1·71 to 1·87 Å, the Al–C from 1·91 to 1·98 Å, with standard deviations of 0·01 Å. There are two short non-bonded distances associated with the shared edge of the tetrahedra, Al · · · Al 2·63 Å, and O · · · O 2·53 Å.

Introduction

Aluminum tetroxycarbide, Al_4O_4C, was first recognized by Foster, Long & Hunter (1956) as a chemically distinct phase formed by high temperature reaction at about 1800 °C. in the aluminum oxide and carbide system. The other phases identified were δ-Al_2O_3, Al_2CO and Al_4C_3. The conditions for the formation of δ-Al_2O_3 by high temperature reactions have been dis-

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Table 1. *X-ray powder data for* Al_4O_4C

Powder data (Foster, Long & Hunter, 1956)		Single crystal data	
d_o	I_o	d_c (Å)	*hkl*
—	—	4·774	(110)
—	—	4·561	(002)
—	—	4·269	(020)
4·22	100	4·230	(111)
3·87	90	3·866	(021)
3·30	70	3·298	(112)
3·11	80	3·116	(022)
—	—	2·880	(200)
2·57	70	2·565	(113)
—	—	2·551	(130)
2·48	50	2·476	(023)
—	—	2·456	(131)
2·43	50	2·435	(202)
—	—	2·387	(220)
2·32	70	2·310	(221)
—	—	2·280	(004)
2·23	20	2·227	(132)
—	—	2·115	(222)
—	—	2·134, 2·078	(040), (041)
2·02	30	2·057, 2·011	(114), (024)
1·96	50	1·954	(133)
—	—	1·933	(042)
1·88	20	1·877, 1·873	(223), (310)
1·84	20	1·835	(311)
1·78	10	1·788	(204)
1·73	10	1·747, 1·732	(043), (312)
—	—	1·715, 1·704	(240), (115)
—	—	1·700	(134)
1·68	30	1·685, 1·677	(241), (025)
1·65	20	1·648	(224)
—	—	1·637	(150)
1·61	30	1·611, 1·605	(151), (242)
—	—	1·594, 1·592	(313), (330)
1·56	20	1·568, 1·558	(331), (044)
—	—	1·541	(152)
—	—	1·520	(006)
1·49	60	1·503, 1·494, 1·484	(332), (243), (135)
1·45	70	1·449, 1·448 1·447, 1·441	(225), (116) (314), (153)
—	—	1·440	(400)
—	—	1·432	(026)
—	—	1·423	(060)
1·41	30	1·410, 1·406	(333), (061)
1·39	20	1·387	(045)
—	—	1·373	(402)
—	—	1·370	(244)
1·36	30	1·364, 1·358	(420), (062)
—	—	1·349	(421)
1·34	30	1·344	(206)
—	—	1·330	(154)
1·31	40	1·307, 1·307 1·306, 1·305	(315), (422) (136), (334)
1·28	20	1·288, 1·282	(063), (226)
—	—	1·376, 1·276	(350), (260)
1·26	20	1·263, 1·263 1·257	(261), (351) (117)
1·24	40	1·249, 1·246 1·245, 1·238	(245), (027) (423), (046)

cussed further by Long & Foster (1961). The powder data for δ-Al_2O_3 have recently been indexed on the basis of a large tetragonal cell containing sixteen molecules, but its detailed structure is unknown (Rooksby & Rooymans, 1961). The structure of Al_2CO has been studied by Amma & Jeffrey (1961). That of Al_4C_3 was determined by von Stackelberg & Schnorrenberg (1934) and has recently been reexamined in connection with its relationship to the aluminum carbonitrides by Jeffrey & Wu (1961). In their phase equilibrium study, Foster, Long & Hunter (1956) characterized these compounds by chemical analysis and by X-ray powder diffraction patterns of specimens separated from the matrix of the equilibrium products. A few single crystals of Al_2CO and Al_4O_4C were also sometimes formed from the vapor as a condensate on the reactor walls not in contact with the melt. These crystals were made available to us for crystal structural studies through the courtesy of Dr L. M. Foster of the ALCOA Research Laboratories.

Crystal data

The individual crystals of Al_4O_4C are formed as colorless transparent laths up to two mm in length with optical extinction directions at 35° and 55° to their long axis. These directions correspond to two of the orthorhombic axes (*a* and *c* respectively) and the third axis is normal to the flat face of the lath. A similar habit is occasionally found in AlN crystals, instead of the more usual hexagonal needles. The length of the lath shaped AlN crystals is also at 35° to one of the principal crystal axes, (*i.e.* the *c* axis).

The unit-cell dimensions of Al_4O_4C are

$$a = 5{\cdot}76 \pm 0{\cdot}01,\ b = 8{\cdot}537 \pm 0{\cdot}005\ ,$$
$$c = 9{\cdot}121 \pm 0{\cdot}005\ \text{Å},\ V = 448{\cdot}5\ \text{Å}^3,\ Z = 4\ ,$$
$$D_x = 2{\cdot}724\ \text{g.cm.}^{-3},\ D_m(\text{flotation}) = 2{\cdot}70\ \text{g.cm.}^{-3}\ .$$

The systematic extinctions are hkl absent for $h+k$ odd and $h0l$ absent for l odd, and the corresponding space groups are $Cmc2_1$, $C2cm$, $Cmcm$. Subsequent structure analysis established $Cmc2_1$.

The powder data calculated from the single crystal parameters are compared in Table 1 with those measured from powder specimens as reported by Foster, Long & Hunter (1956).

Experimental

Equi-inclination Weissenberg photographs were taken about the principal axes with Cu $K\alpha$ radiation, using crystals which were small trapezoidal plates 0·5 mm in edge and 0·1 mm. thick. Four layers about [*a*], six layers about [*b*] and the zero layer about [*c*] were recorded, and from these 275 independent reflexion intensities were obtained by visual estimation on multiple films. These intensities were reduced to structure amplitudes using Shiono's IBM 650 program (1957). No corrections were made for absorption.

The structure determination

A comparison of the calculated distribution of symmetry peaks on the three-dimensional Patterson with those observed led to an unequivocal assignment of

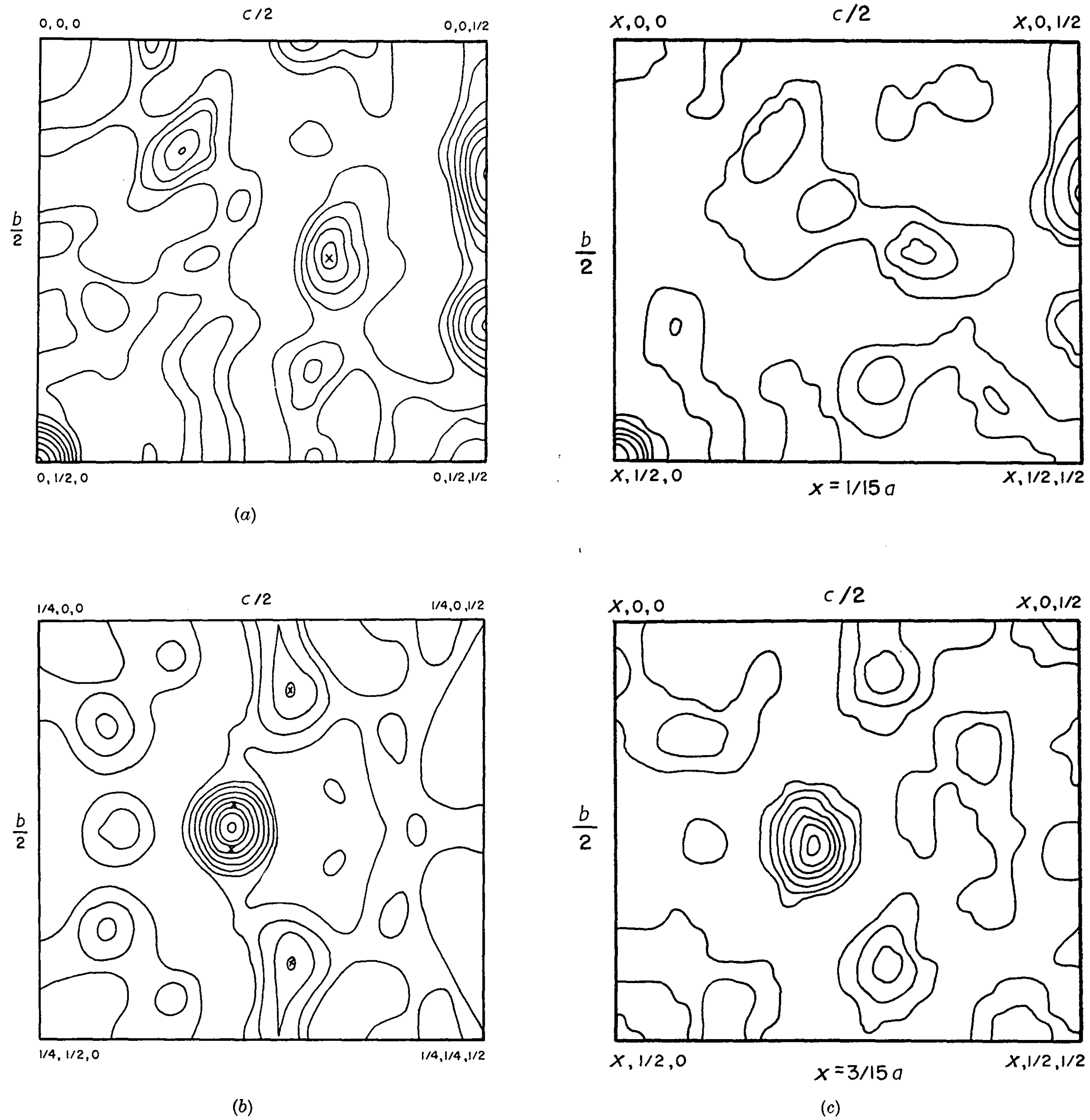

Fig. 1. The Patterson synthesis; (*a*) section at $x=0$, (*b*) section at $x=1/4$, (*c*) sections at $x=1/15$ and 3/15.

the space group as *Cmc*2_1. In particular the vector peaks of the type $(0, 0, \frac{1}{2}-2z)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}-2z)$ required by the symmetry *C*2*cm* and *Cmcm* were not observed.

The four carbon atoms in the cell must therefore lie in special positions on the mirror planes at $x=0$ and this provided a starting point for interpreting the Patterson synthesis, the important sections of which are shown in Fig. 1. It was assumed that the carbon atoms would form four tetrahedral C–Al bonds and the vectors corresponding to a tetrahedron of aluminum atoms centered on an atom in the mirror planes were sought. These were found corresponding to the four aluminum positions around the carbon shown in Fig. 2. Two of these positions, Al(1) and Al(2), also lie on the mirror plane and the other two, Al(3) and Al(3′), are in the mirror-related general positions. Oxygen atom positions were then sought so as to complete either a tetrahedral or an octahedral coordination around the aluminum atoms and also satisfy the criterion that the Al–O vectors lie on maxima or large positive areas in the Patterson synthesis. In this way, the tetrahedral coordination was deduced and the atomic positions shown in Fig. 2 were obtained.

As a check on this interpretation of the Patterson synthesis, a two-dimensional vector convergence pro-

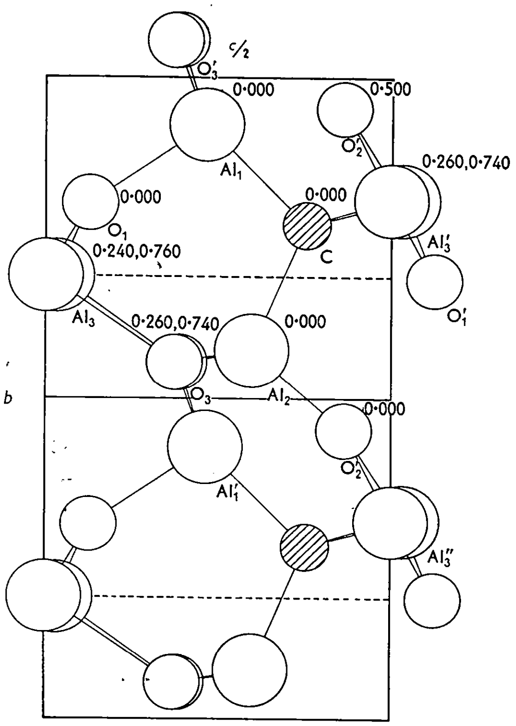

Fig. 2. The atomic positions deduced from the Patterson synthesis.

cedure was applied to the three-dimensional map by projecting the vectors on (100). The result is shown in Fig. 3. Comparison with Fig. 2 shows that all the atoms except the carbons were revealed by this method, although the interpretation of the final vector convergence map was made somewhat more obvious by the previous indirect interpretation.

The first trial coordinates from a model based on these interpretations gave reasonable qualitative agreement between the observed and calculated structure factors and an overall agreement index of 0·37. The arbitrary choice of origin in the z direction was made by placing Al(3) at $z=0$. A three-dimensional Fourier synthesis was then computed and atomic peaks corresponding to all the atoms were observed. The coordinates of these formed the basis for the subsequent refinement stage of the analysis.

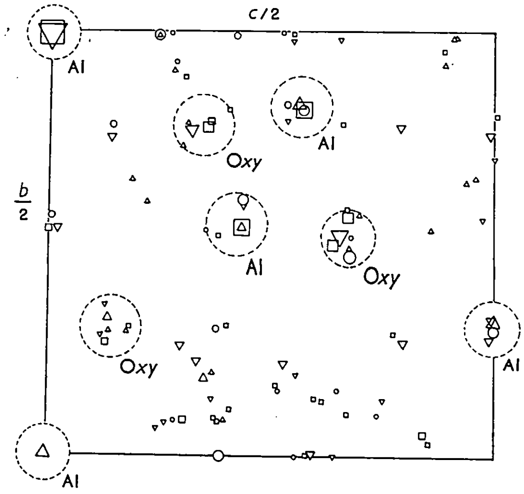

Fig. 3. Vector convergence interpretation of Patterson synthesis; (the diagram corresponds to the structure between dotted lines in Fig. 2).

The structure refinement

The structure refinement was carried out by differential Fourier synthesis with individual isotropic temperature factors, using Shiono's (1957) IBM 650 programs. The initial refinement cycles were carried out omitting many of the stronger reflexions in the lower sin θ range, which were severely affected by extinction errors, as shown by plots such as that in Fig. 4. When these low orders were included at a later state, there were only slight changes in the positional parameters of the atoms but the temperature factors began to diverge, those of the aluminum atoms decreasing and the oxygen and carbon atoms increasing to values of about $B=4A^2$, which seemed unreasonable for a structure of this type.

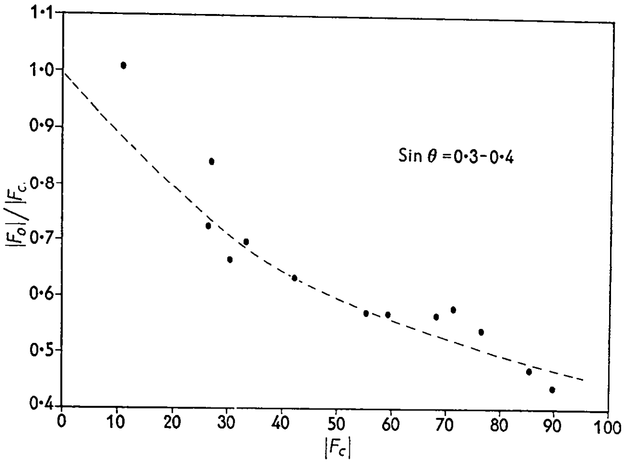

Fig. 4. $|F_o||F_c|$ versus $|F_c|$ for reflections in range sin θ 0·3 to 0·4, showing effect of extinction.

The semi-empirical method of Vand (1955) for the correction of extinction errors was then applied using an IBM 704 least-squares FORTRAN program written for this purpose (Slaughter, 1961). The values obtained for α, β and γ in Vand's relationship

$$F_{\text{corr.}} = F_{\text{obs.}} \exp\,(\alpha + \beta F^2_{\text{calc.}} + \gamma\,.\,Lp\,.\,F^2_{\text{calc.}})$$

were

$$\alpha = 0{\cdot}2714,\quad \beta = 0{\cdot}9692 \times 10^{-6},\quad \gamma = 0{\cdot}3828 \times 10^{-4}\,.$$

Sixty-five of the 275 observed amplitudes were significantly increased by the application of this formula. The corrected and uncorrected values are given in the structure factor Table 2. For the values marked

Table 2. *Observed and calculated structure factors*

First two columns are k and l, and the value for h appears above. The other columns are successively $|10F_o|$, including extinction corrections; $|10F_o|$, uncorrected, when different from values used; $|10F_c|$; $10A_c$; $10B_c$. Values marked * were not observed. Values marked ** were omitted from the refinement calculations

0						
0	2	178	138	194	104	164
0	4	910	415**	772	681	365-
0	6	628	426	594	486	341
0	8	215		216	26	214
0	10	466		528	511	132-
2	0	301	203	268	268	
2	1	861	441**	818	229	785-
2	2	1055	477**	975	960-	170
2	3	951	413**	716	462-	548-
2	4	585	340	590	204-	553-
2	5	236	175	214	193-	92-
2	6	174		132	106-	79
2	7	846	498	744	197	717-
2	8	332		310	310-	01
2	9	123		108	49-	96-
2	10	38		72	70	18
2	11	437		339	04	339-
4	0	517	316	559	559-	
4	1	295	229	320	224	229
4	2	154	115	120	95-	74
4	3	402	285	356	74	348
4	4	491	321	464	430-	174-
4	5	578	387	625	110-	615
4	6	234		341	271-	208
4	7	216		244	202	137
4	8	179		156	114-	107-
4	9	411		491	31	490
4	10	205		192	183-	57
6	0	2*		22	22-	
6	1	396	277	330	329-	24-
6	2	1013	543**	855	853	55-
6	3	303	217	260	28-	259
6	4	307		345	289	188
6	5	197		219	192-	107
6	6	196		236	236	11
6	7	53		83	82	07
6	8	373		375	369	64-
6	9	137		94	93	13-
8	0	359		529	529-	
8	1	335		401	183-	356-
8	2	186		144	16-	143-
8	3	263		272	131	238-
8	4	257		280	31-	278
8	5	247		318	25-	317-
8	6	255		300	67-	293-
8	7	115		88	28-	83-
10	0	141		152	152-	
10	1	204		179	26	177
10	2	163		149	117-	91-
10	4	256		269	101-	249
1						
1	0	109	84	86	86-	
1	1	613	301**	585	529-	251
1	2	543	290	570	124-	557
1	3	277	203	300	30	298
1	4	291	210	302	69	294
1	5	182	143	169	169-	02-
1	6	491	348	439	56	435
1	7	90		68	67-	14-
1	8	270		337	51-	333-
1	9	89		102	64	80-
1	10	97		100	64-	77
1	11	119		95	93-	19
3	0	104		52	52-	
3	1	334	268	420	406-	109
3	2	304	232	330	313-	102
3	3	560	387	672	667	76-
3	4	277	202	297	287	77-
3	5	158	120	167	78-	148-
3	6	190		221	172	139-
3	7	106		133	133-	09
3	8	80		89	06	88-
3	9	139		142	118	80
3	10	114		99	94	31
3	11	179		159	148-	58
5	0	367	267	402	402	
5	1	177	146	159	126-	97
5	2	206	172	197	61-	187-
5	3	334	281	394	300	256-
5	4	317	255	318	17-	317
5	5	47		47	22-	41
5	6	122		153	101-	115-
5	7	190		233	82-	218-
5	8	228		217	67-	207
5	9	102		105	19	103
5	10	119		110	34	105-
7	0	172		185	185-	
7	1	172		206	78	191
7	2	163		175	59	165-
7	3	136		139	95-	101-
7	4	119		129	97-	85
7	5	190		213	03-	213
7	6	171		194	42-	189-
7	7	185		205	19-	204-
7	8	147		120	20	119
9	0	159		147	147-	
9	1	144		140	140	05-
9	2	229		272	262	73-
9	3	61		65	09	64-
9	4	97		128	125-	31-
9	5	55		54	53	12
2						
0	0	204	154	185	185	
0	2	1035	384**	889	725-	514-
0	4	463	317	475	358-	313
0	6	856	499**	832	825-	108
0	8	332		367	360-	70
0	10	97		68	18-	65
2	0	266	191	261	261	
2	1	775	395	852	344-	779
2	2	281	231	274	87	260-
2	3	287	209	262	258-	45
2	4	423	302	397	388	85-
2	5	1071	514	1034	58	1032
2	6	44		66	42	51-
2	7	76		64	63-	04-
2	8	180		176	159	77-
2	9	257		247	57	240
2	10	263		265	227	137
2	11	146		110	28	106
4	0	308	228	192	192	
4	1	491	341	522	351-	387-
4	2	510	356	499	487	106
4	3	1052	478	981	174	966-
4	4	239	185	235	132	194-
4	5	235		235	135	193
4	6	240		282	200	198
4	7	344		389	89-	379-
4	8	213		208	189	88-
4	9	173		162	149	63-
4	10	79		65	52	38
6	0	539	367	517	517-	
6	1	501	342	508	506-	47-
6	2	240		268	201-	177
6	3	86		99	34	93-
6	4	401		483	477-	73-
6	5	131		147	67-	130
6	6	185		190	166-	93
6	7	91		86	51-	68-
6	8	229		209	209-	04
6	9	222		204	146	142-
8	0	2*		47	47-	
8	1	237		241	125-	206
8	2	116		59	12	58
8	3	302		345	110	327
8	4	105		95	81	49
8	5	110		121	44-	113
8	6	297		293	222	192-
8	7	301		262	02	262
10	0	199		222	222	
10	1	212		226	150	169-
10	2	112		99	98	14-
10	3	75		49	24-	43-
3						
1	0	74		47	47	
1	1	342	273	375	366-	82-
1	2	340	253	358	92	346
1	3	101		76	59	47-
1	4	299	225	279	183	211-
1	5	245		201	109-	169-
1	6	277		356	120	335
1	7	153		165	62-	153-
1	8	261		284	54	279-
1	9	199		186	56	178-
1	10	91		75	04-	75
3	0	258	191	270	270-	
3	1	338	262	380	373-	69
3	2	411	321	472	468-	58
3	3	442	352	514	503-	104-
3	4	33		41	10	40-
3	5	93		115	49-	104-
3	6	104		116	57-	101-
3	7	104		129	129-	05-
3	8	139		146	124-	76-
3	9	124		114	104	47
3	10	41		35	18-	31
5	0	352	261	406	406	
5	1	300	240	313	133-	283
5	2	141		139	13	139-
5	3	196		242	237	45-
5	4	221		248	68	239
5	5	198		204	06-	204
5	6	98		91	15-	89-
5	7	89		103	84-	49-
5	8	171		175	18-	174
5	9	164		166	21	165
7	0	34		22	22-	
7	1	61		66	58	31
7	2	163		177	135	114-
7	3	201		213	76-	199-
7	4	58		51	06	51
7	5	88		82	01	82
7	6	187		157	51	149-
7	7	268		246	19-	245-
9	0	202		213	213-	
9	1	139		128	124	32-
9	2	115		117	104	53-
9	3	76		70	08	70-
9	4	225		204	200	39-
4						
0	0	1453	710	1434	1434	
0	2	120		61	04-	61
0	4	337		436	402	167-
0	6	298		318	256	190
0	8	154		143	09-	142
2	0	178		150	150	
2	1	349	257	359	105	344-
2	2	447	313	487	480-	86
2	3	423		415	221-	351-
2	4	244		295	88-	281-
2	5	89		94	94-	01-
2	6	74		78	61-	49
2	7	431		450	123	433-
2	8	212		191	191-	01
4	0	252		319	319-	
4	1	183		176	83	155
4	2	82		63	34-	53
4	3	170		156	48	149
4	4	241		272	247-	115-
4	5	353		378	67-	372
4	6	209		205	153-	137
4	7	144		143	128	65
4	8	116		92	59-	71-
5						
1	0	118		101	101-	
1	2	222		291	156-	245
1	3	230		270	44	266
1	4	191		195	58-	186-
1	5	148		136	79-	111
1	6	243		236	21-	235
1	7	101		88	26-	84
1	8	229		199	85-	180-
3	0	207		196	196	
3	1	191		208	203-	46
3	2	61		53	16	51
3	3	243		307	307	02
3	4	241		279	276	36-
3	5	97		97	57-	79-
3	6	201		212	201	65-
3	7	62		64	63-	12
5	0	122		132	134	
5	1	124		98	56-	81-
5	2	155		139	84-	110-
5	3	246		273	149	228-
5	4	189		178	44-	172
5	5	93		87	20-	85-
5	6	134		116	98-	62-
6						
0	0	169		145	145	
0	2	297		315	277-	149-
0	4	135		126	86-	92
0	6	327		300	296-	50
2	0	172		120	120	
2	1	231		245	86-	229
2	2	66		67	08-	66-
2	3	102		100	97-	23-
2	4	166		142	136	41-
2	5	378		387	23	387
4	0	2*		36	36	
4	1	172		163	122-	107-
4	2	170		176	171	43
4	3	351		353	67	346-
4	4	102		88	24	85-
4	5	139		131	51	122
7						
1	0	99		47	47	
1	1	194		165	127-	105-
1	2	161		132	78	106
1	3	128		88	26	85-
3	0	186		166	166-	
3	1	168		144	142-	27

** the extinction corrections were particularly large and it appeared that they had been overcorrected. These terms were given zero weight, by substituting F_c, in the refinement calculations which gave the final parameters shown in Table 3. With the corrected amplitudes the isotropic temperature factors for the lighter atoms behaved normally and converged on reasonable values relative to those of the metal atoms. However, because of the necessarily empirical nature of this Vand treatment for extinction and the omission of absorption corrections, the significance of these temperature factors is somewhat uncertain. There was good agreement between the observed and calculated curvatures of the atomic peaks and no evidence of thermal anisotropy. The experimental data did not in fact justify the extension to an anisotropic refinement. The final agreement index with the 265 corrected structure amplitudes used in the refinement was 0·11. Without the Vand corrections it was 0·21, and the distribution of agreement versus sin θ ranges is shown in Table 4. The interatomic distances and angles in the structure are given in Table 5 and Fig. 5. The mean standard deviations given in parenthesis were calculated by Cruickshank's method using the extinction corrected values of F_o and including all observed reflexions.

Table 3. *Fractional atomic coordinates with standard deviations in Å (in parenthesis) and isotropic temperature factors*

Atom	x_n	y_n	z_n	B (Å^2)
Al_1	0·0000	0·0600 (0·004)	0·2093 (0·004)	1·60
Al_2	0·0000	0·3983 (0·004)	0·2903 (0·004)	1·55
Al_3	0·2288 (0·004)	0·3374 (0·004)	0·0000 (0·004)	1·65
O_1	0·0000	0·1937 (0·009)	0·0557 (0·009)	1·55
O_2	0·0000	0·5559 (0·009)	0·4070 (0·008)	1·55
O_3	0·2564 (0·008)	0·4340 (0·010)	0·1786 (0·008)	1·60
C	0·0000	0·1965 (0·010)	0·3853 (0·012)	1·60

Table 4. *Agreement index, R, for corrected and uncorrected structure amplitudes for various ranges of* sin θ

	R		Mean $|F|$		No.
sin θ	corrected	uncorrected	obs.	calc.	reflections
0·0–0·2	0·04	0·68	23	39	5
0·2–0·4	0·13	0·71	29	48	19
0·4–0·6	0·09	0·41	26	39	46
0·6–0·8	0·11	0·12	20	21	86
0·8–1·0	0·11	0·11	18	18	107
0·0–1·0	0·11	0·21	—	—	265

Description of the structure

The coordination element of the structure is the Al(O_3C) tetrahedron. The Al–C distances vary from 1·90 to 1·98 Å, and the extreme values are probably significantly different. With one exception the Al–O distances lie in the range of 1·80 to 1·87 Å, with a mean of 1·82 Å. One distance, that of Al(2)–O(2) at 1·72 Å, is significantly shorter. These bond lengths are about 0·08 Å less than the sum of the tetrahedral covalent radii, *e.g.* Al–C 2·03, Al–O, 1·92 Å, (Pauling,

Table 5. *Interatomic distances and angles in* Al_4C_4O

The coordinates given in Table 3 refer to the atoms in the asymmetric unit I, the symmetry related atoms are as follows:

I	x, y, z
II	$-x, y, z$
III	$\frac{1}{2}+x, \frac{1}{2}+y, z$
IV	$\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z$
V	$1-x, y, z$
VI	$-x, 1-y, \frac{1}{2}+z$
VII	$\frac{1}{2}+x, -\frac{1}{2}+y, z$
VIII	$\frac{1}{2}-x, -\frac{1}{2}+y, z$
IX	$\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$
X	$-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$
XI	$x, 1-y, -\frac{1}{2}+z$
XII	$-\frac{1}{2}+x, -\frac{1}{2}+y, z$
XIII	$x, 1-y, \frac{1}{2}+z$
XIV	$-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$

Interatomic distances

Aluminum–carbon distances

Al_1(I)–C(I)	1·98 Å	(0·012 Å)
Al_2(I)–C(I)	1·93	
Al_3(I)–C(IX)	1·90	

Aluminum–oxygen distances

Al_1(I)–O_1(I)	1·81 Å	(0·010 Å)
Al_1(I)–O_3(VIII)	1·79	
Al_2(I)–O_2(I)	1·72	
Al_2(I)–O_3(I)	1·82	
Al_3(I)–O_1(I)	1·87	
Al_3(I)–O_2(XI)	1·81	
Al_3(I)–O_3(I)	1·83	

Aluminum–aluminum distances

Al_1(I)–Al_2(I)	2·98 Å	(0·006 Å)
Al_1(I)–Al_2(VII)	3·28	
Al_1(I)–Al_3(I)	3·32	
Al_1(I)–Al_3(VIII)	3·11	
Al_1(I)–Al_3(IV)	3·20	
Al_2(I)–Al_3(I)	3·00	
Al_2(I)–Al_3(VI)	3·24	
Al_2(I)–Al_3(IV)	3·19	
Al_3(I)–Al_3(V)	3·12	
Al_3(I)–Al_3(II)	2·63	

Oxygen–oxygen distances

O_1(I)–O_2(XI)	2·53 Å	(0·013 Å)
O_1(I)–O_3(I)	2·77	
O_1(I)–O_3(VIII)	2·85	
O_2(I)–O_3(I)	2·76	
O_2(I)–O_3(VI)	2·89	
O_3(I)–O_3(II)	2·95	
O_3(I)–O_3(V)	2·81	

Oxygen to carbon distances

O_1(I)–C(I)	3·01 Å	(0·014 Å)
O_1(I)–C(IX)	3·40	
O_2(I)–C(I)	3·07	
O_2(I)–C(III)	3·13	
O_3(I)–C(I)	3·14	
O_3(I)–C(III)	3·25	
O_3(I)–C(IX)	3·22	

Bond angles

Central atom Al_1

O_1(I)–Al_1(I)–O_3(VIII)	105·0°	(0·09°)
O_1(I)–Al_1(I)–C(I)	104·9	
O_3(VIII)–Al_1(I)–C(I)	118·7	
O_3(VIII)–Al_1(I)–O_3(XII)	103·2	

Central atom Al_2

O_2(I)–Al_2(I)–O_3(I)	102·5°	(0·09°)
O_2(I)–Al_2(I)–C(I)	114·9	
O_3(I)–Al_2(I)–C(I)	113·7	
O_3(I)–Al_2(I)–O_3(II)	108·5	

Central atom Al_3

O_1(I)–Al_3(I)–O_3(I)	96·6°	(0·09°)
O_1(I)–Al_3(I)–C(IX)	128·7	
O_1(I)–Al_3(I)–O_2(XI)	86·0	
O_3(I)–Al_3(I)–C(IX)	119·2	
O_3(I)–Al_3(I)–O_2(XI)	96·8	
O_2(XI)–Al_3(I)–C(IX)	114·4	

Central atom O_1

Al_1(I)–O_1(I)–Al_3(I)	128·7°	(0·09°)
Al_3(I)–O_1(I)–Al_3(II)	89·6	

Central atom O_2

Al_2(I)–O_2(I)–Al_3(VI)	133·2°	(0·09°)
Al_3(VI)–O_2(I)–Al_3(XIII)	93·3	

Central atom O_3

Al_2(I)–O_3(I)–Al_1(III)	130·5°	(0·09°)
Al_2(I)–O_3(I)–Al_3(I)	110·6	
Al_3(I)–O_3(I)–Al_1(III)	118·5	

Central atom C

Al_1(I)–C(I)–Al_2(I)	99·3°	(0·10°)
Al_1(I)–C(I)–Al_3(IV)	110·8	
Al_2(I)–C(I)–Al_3(IV)	112·5	
Al_3(IV)–C(I)–Al_3(XIV)	110·4	

The standard deviations are given in parenthesis.

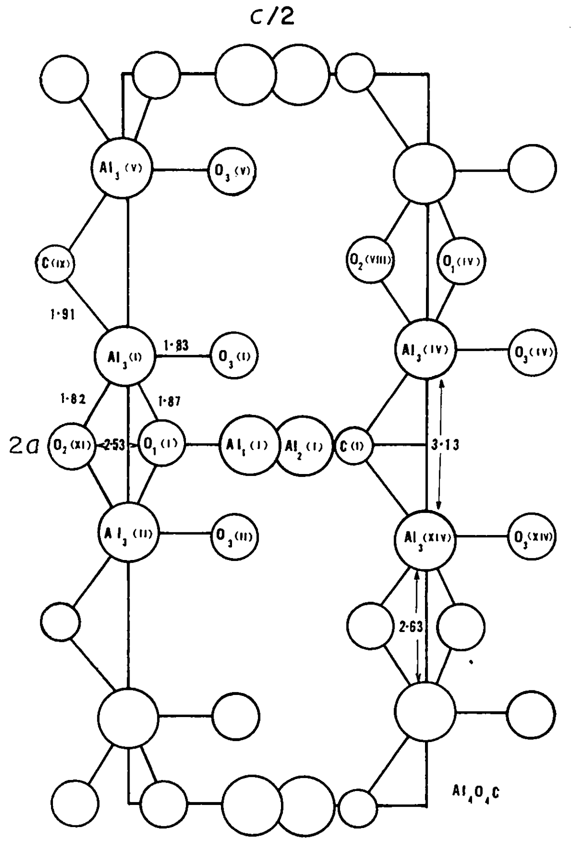

Fig. 5. Some interatomic distances in the Al_4O_4C structure. (The roman figures refer to symmetry related coordinates given in Table 5.)

1960). However, Smith (1954) in summarizing the data on Al–O bond lengths in silicates concluded that the most reliable values were in the range 1·75–1·79 Å. These were for AlO_4 tetrahedra in which each oxygen was bonded to two aluminum atoms. In this structure each oxygen is bonded to three aluminum atoms and it is interesting to note that the observed mean length is midway between the value of 1·77 Å for the coordination of two and the sum of the tetrahedral covalent radii for four coordinated atoms.

The angles at the center of the $Al(O_3C)$ tetrahedra lie within ±8° of the ideal value for Al(1) and Al(2), *i.e.* ranging from 102° to 119°. For Al(3) the variation is greater, 86° to 128°. Since the Al(3) tetrahedra are involved in edge-sharing in the structure, these distortions from the ideal coordination are to be expected.

The coordination around the carbon atoms is also approximately tetrahedral, with an angle variation between 100° to 113°.

The structure can be described in terms of a three-dimensional network of $Al(O_3C)$ tetrahedra which are associated by sharing edges and corners. In the unit cell of 4 formula units, the eight Al(3) atoms in the general positions are at the centers of two tetrahedra which share an O · · · O edge. These double tetrahedra are corner-linked through the carbon atoms to form a continuous chain in the *a* axis directions, as shown in Fig. 6(*a*). The chains are then crossed-linked laterally by the aluminum atoms in the special positions Al(1) and Al(2), which form corner-linked $Al(O_3C)$ tetrahedra, as shown in Fig. 6(*b*). This arrangement is also shown in the polyhedral diagrams in Fig. 7.

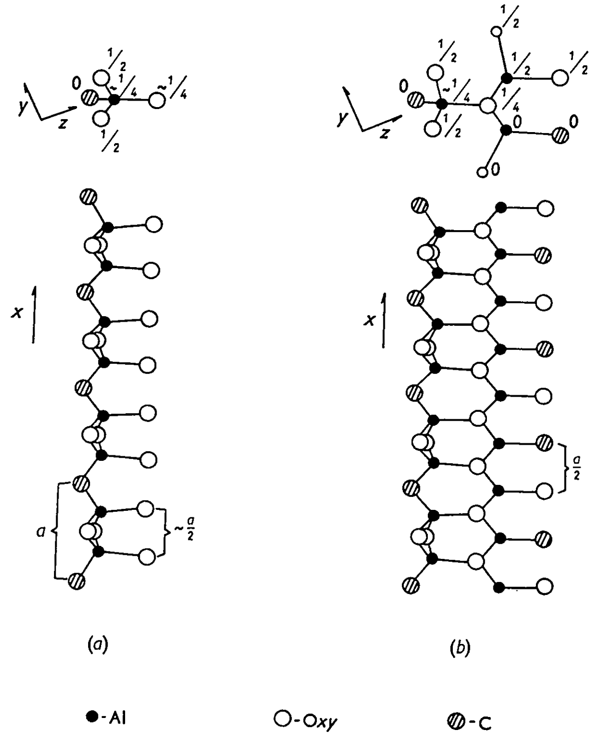

Fig. 6. The structure of Al_4O_4C. (*a*) Single chain of tetrahedra, linked alternately across edges and corners in the *a* axis direction. (*b*) The lateral arrangement of the tetrahedra.

Some distortions from regularity in both angles and distances are necessary to obtain this packing of the tetrahedra and, as would be expected, the largest of these are associated with the edge-linked pair of tetrahedra. Both the oxygens forming the common edge and the aluminums opposite to the edge have close approaches, O · · · O 2·53 Å, Al · · · Al 2·63 Å. The corresponding bond angles are O(1) · · · Al(3) = 86° and Al(3) · · · O(1) · · · Al(3) = 90°. The other angles in the tetrahedra are accordingly greater than ideal, *i.e.* O(1) · · · Al(3) · · · C = 128°. These short distances are comparable with related situations in other structures, *e.g.* the O · · · O distance between the shared corners of the octahedra in rutile and the Al · · · Al distance across the shared faces in corundum. There is no obvious reason why the Al(2) · · · O(2) bond should be about 0·1 Å shorter than the other Al–O bonds. However, a shift in the oxygen atom position such as to increase this distance would lead to a greater departure from tetrahedral angles at the associated

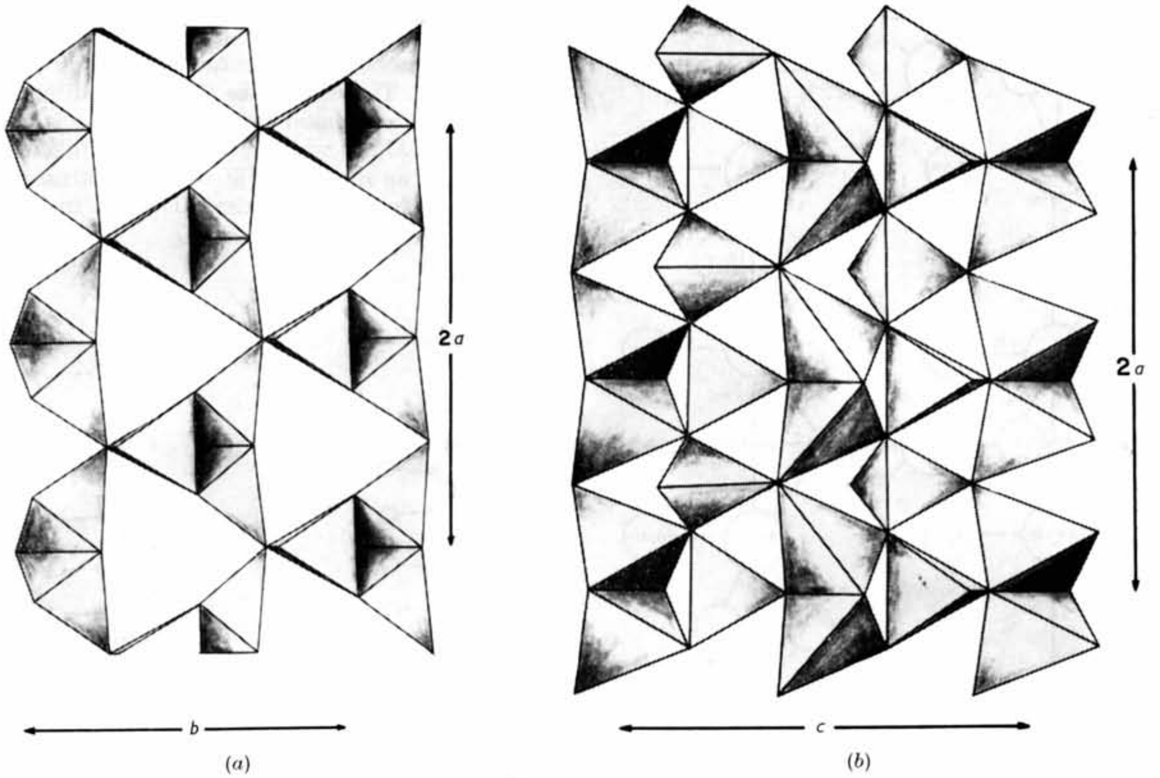

Fig. 7. Polyhedron diagrams of $Al(O_3C)$ tetrahedra in Al_4O_4C. (a) View in c axis direction. (b) View in b axis direction.

aluminum atoms, and this shorter distance may be the consequence of preserving more closely the tetrahedral coordination around the aluminum atoms.

The unique feature of this structure is the edge-linked double tetrahedra shown in Figs. 5, 6 and 7. We have found no counterpart in the AlO_4 tetrahedra of the aluminates or alumino-silicates, where tetrahedral coordination around the aluminum atoms is quite common but is invariably corner-linked. There appear to be no structures containing analogous $Al(O_3Si)$ groups. In the mineral structures, only the sulfides provide comparable examples of edge-sharing tetrahedra. For example, $KFeS_2$ and SiS_2 have structures with infinite chains of tetrahedra linked through a common edge, but no exact counterpart of the $[Al(O_3C)]_n$ chain with alternate shared edges and corners appears to occur naturally. This suggests that it is the presence of the carbon atoms in the structure which is essentially responsible for the formation of this 'unnatural' atomic arrangement, instead of one of the more common coordination patterns associated with the alumina tetrahedra or octahedra.

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