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The Structures of the Aluminum Carbonitrides. II

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The results of three-dimensional single-crystal structure analyses are reported for Al_4C_3, Al_5C_3N, $Al_6C_3N_2$ and $Al_8C_3N_4$. These structures, which with AlN and $Al_7C_3N_3$ form a homologous series, have Al–Al first neighbour distances ranging from 2·56 to 3·33 Å, Al–C distances from 1·87 to 2·30 Å, and Al–N distances from 1·86 to 1·99 Å. The carbon atoms are five- and six-coordinated to nearest neighbor aluminum atoms. The relationship of these structures to that of AlN, the *B*4 type, is discussed in terms of the inversion and shear of blocks of tetrahedral coordination polyhedra. An attempt is made to describe the electronic structure qualitatively in terms of metallic and covalent interatomic bonding. The structure of the disordered Al_2CO is reinterpreted.

Introduction

Aluminum forms a series of structures in which there is tetrahedral first-neighbor coordination of carbon, nitrogen or oxygen atoms about the metal atom. The simplest of these is that of AlN, which has one of the two basic tetrahedral structures, *i.e.* the *B*4 or wurtzite type. The other simple tetrahedral structure, *B*3, that of zinc-blende, is formed by the more metallic binary combinations such as AlP and AlAs. The combination rules for the formation of structures of one or the other of these two 'normal' tetrahedral types have recently been reviewed and discussed by Parthé (1963). More complex, but related, structures are those of Al_2CO (Amma & Jeffrey, 1961), Al_4O_4C (Jeffrey & Slaughter, 1963), Al_4C_3 (Stackelberg, Schnorrenberg, Paulus & Spiess, 1935), Al_5C_3N (Stackelberg & Schnorrenberg, 1934), $Al_6C_3N_2$, $Al_7C_3N_3$, $Al_8C_3N_4$ (Jeffrey & Wu, 1963).

In this paper we present the results of a refinement of the Al_4C_3 and Al_5C_3N structures from new three-dimensional data, and the complete structure analyses of $Al_6C_3N_2$ and $Al_8C_3N_4$. The structure analysis of the other member of the series, $Al_7C_3N_3$, was reported in detail in our previous paper on these compounds. We also discuss the relationship of the aluminum carbide and carbonitride structures to the normal tetrahedral arrangements, and show how the former can be built up from blocks of the latter by alternating corner and edge-sharing tetrahedra, so as to fulfil the requirement of electroneutrality.

An attempt is made to interpret the detailed stereochemistry of these structures in terms of metallic and covalent bonding. The disordered structure of Al_2CO is interpreted in more detail in the light of our observations concerning these structures.

Crystal data

Stoichiometrically and structurally the aluminum carbonitrides can be expressed as members of a homologous series $(AlN)_nAl_4C_3$ where $n=1$ to 4, and the end members, $n=0$ and ∞, are Al_4C_3 and AlN. The members for which n is odd have space group symmetry $P6_3mc$ with two formula units per cell. Al_4C_3 and members for which n is even have space group symmetry $R\bar{3}m$ and one formula unit per rhombohedral cell. In the odd series, the atoms are in positions (*a*) $0, 0, z; 0, 0, \frac{1}{2}+z$ (*b*) $\frac{1}{3}, \frac{2}{3}, z; \frac{2}{3}, \frac{1}{3}, \frac{1}{2}+z$, of $P6_3mc$. In the $R\bar{3}m$ series, all atoms lie in positions (*c*) at xxx, $\bar{x}\bar{x}\bar{x}$. The aluminum atoms lie in regular stacking sequences, which are given in Table 1, together with the unit-cell dimensions referred to the hexagonal axis. These dimensions can be empirically related to better than 0·1 Å by the following formulae;

$$a_n = a_{n-1} - \left(\frac{1}{n+1}\right)^2 (a_0 - a_\infty)$$

$$c_n = \tfrac{3}{2}\,(c_{n-1} + c_\infty)$$

$$c_{n'} = \tfrac{2}{3}\,c_{n'-1} + c_\infty$$

where c_n and $c_{n'}$ refer to the axial lengths of the even and odd valued members of the series, $(AlN)_nAl_4C_3$, and 0 and ∞ refer to Al_4C_3 and AlN respectively.

Structure analysis

Three-dimensional diffraction data were obtained photographically from single crystals of Al_4C_3, Al_5C_3N, $Al_6C_3N_2$, $Al_8C_3N_4$ by the same methods as those described for the structure analysis of $Al_7C_3N_3$. The structures previously proposed by Jeffrey & Wu (1963) on the basis of the isotypic series were confirmed by Fourier syntheses and structure factor calculations. The structure refinements were carried out isotropically with the IBM 7070 differential synthesis program of Shiono (1963). For Al_4C_3 and Al_5C_3N, three cycles of isotropic least squares were also computed on the IBM 7070 machine, using Carpenter's (1963) program. The odd series of compounds is non-centric ($P6_3mc$), and the even series is either centric ($R\bar{3}m$) or pseudo-centric ($R3m$). The refinement calculations were carried out in *Cm*, which is the monoclinic space group of lower non-centrosymmetrical symmetry common to both types of structure. The deviations from centrosymmetry in the even series were less than three times the estimated standard deviations, thereby confirming the higher space-group symmetry $R\bar{3}m$ within the experimental errors.

The number of observed reflections, final agreement indices and structural parameters are reported in Table 2. The estimated standard deviations were calculated from the atomic curvatures (Cruickshank & Rollett, 1953). The first-neighbor Al–C and Al–N distances and second neighbor Al–Al distances are given in Table 3. The interbonding angles are given in Fig. 1. The observed and calculated structure factors are given in Table 4.

As pointed out in the previous paper, crystals of the same compound varied in color and in density, and the densities were always less than the calculated values, often by as much as five per cent, and in the case of the Al_4C_3 sometimes by twenty per cent. The crystals were difficult to manipulate and not ideal for intensity measurements. From the spread of the measurements of symmetry-related intensities, it was estimated that the reliability of the structure factors was about nine per cent. The final *R* values ranged from 0·12 to 0·18. The refinements were terminated at the isotropic stage because this level of uncertainty in stoichiometry and experimental measurements did not warrant further computational treatment of the data. We did, however, explore the peak heights in the terminal differential Fourier series. Table 5 shows the values of $(\varrho_o - \varrho_c)\varrho_o$. Discrepancies as large as eighteen per cent were noted, but there was no rationale about their distribution to suggest that what we were observing was other than the result of a combination of experimental error and stoichiometric defect of the particular crystal that was used in the experiment. Similarly the variations in the isotropic temperature factors shown in Table 2 are a related consequence pertaining to the particular crystal intensity data. To explore this interesting problem of non-stoichiometry further what is needed, quite clearly, is several high precision structure analyses of different crystals of the same compound and this lies beyond the scope of the present investigation.

Table 1. *Observed and calculated values of the cell dimensions of the aluminum carbonitrides*

Formula	Metal layer stacking sequence*	[*a*] axis (Å) Obs.	Calc.†	Diff.	[*c*] axis (Å) Obs.	Calc.†	Diff.
Al_4C_3	$[13]_3$	3·330			24·89		
Al_5C_3N	$[113]_2$	3·281	3·225	+0·006	21·67	21·58	+0·09
$Al_6C_3N_2$	$[1113]_3$	3·248	3·256	−0·008	40·03	39·99	+0·04
$Al_7C_3N_3$	$[11113]_2$	3·226	3·234	−0·008	31·70	31·66	+0·04
$Al_8C_3N_4$	$[111113]_3$	3·211	3·215	−0·004	55·08	55·02	+0·06
AlN	11	3·11			4·98		

* Zhdanov notation. (*International Tables for X-ray Crystallography*, 1959)
† Calculated from formulae given in text.

Table 2. *Structural data on aluminum carbide and the aluminum carbonitrides*

Fractional coordinates are $\frac{1}{3}$, $\frac{2}{3}$, *z*, in cases marked with an asterisk, others are 00*z* or *xxx*. Isotropic temperature factors, *B*; number of reflections, *N*; agreement index, *R*.

	Al_4C_3		Al_5C_3N		$Al_6C_3N_2$		$Al_7C_3N_3$		$Al_8C_3N_4$	
R	0·12		0·13		0·18		0·15		0·17	
N	151		198		266		318		327	
	x	*B*	*x*	*B*	*x*	*B*	*x*	*B*	*x*	*B*
Al(1)	0·705	0·2	0·045*	0·5	0·6910	0·2	0·0299*	1·0	0·6852	0·5
Al(2)	0·129	0·5	0·155	0·5	0·0850	0·7	0·1085	1·1	0·0633	0·4
Al(3)	0·869	0·5	0·261*	0·6	0·8069	0·6	0·1844*	1·0	0·7752	0·1
Al(4)	0·296	0·2	0·345	0·3	0·1911	0·1	0·2615	1·1	0·1494	0·6
Al(5)			0·455*	0·4	0·9137	0·8	0·3166*	1·3	0·8522	0·8
Al(6)					0·3092	0·4	0·3915	1·4	0·2268	0·4
Al(7)							0·4659*	1·0	0·9365	0·2
Al(8)									0·3150	0·3
N(1)			0·137*	0·4	0·7406	0·2	0·0939*	1·0	0·7212	0·5
N(2)					0·2597	1·0	0·1686	1·0	0·0993	0·8
N(3)							0·4069*	1·4	0·9005	0·1
N(4)									0·2788	0·6
C(1)	0·000	0·7	0·000	0·7	0·0000	0·2	0·0000	1·3	0·0000	0·9
C(2)	0·781	0·7	0·248	0·0	0·1351	0·6	0·2448*	0·5	0·8112	1·2
C(3)	0·217	1·2	0·367*	1·7	0·8641	1·2	0·3267	0·8	0·1898	1·0
e.s.d.										
Al	0·001	0·2	0·001	0·3	0·0008	0·4	0·0006	0·4	0·0010	0·3
C, N	0·002	0·4	0·002	0·6	0·0015	0·6	0·0010	0·9	0·0018	0·7

The structural relationships

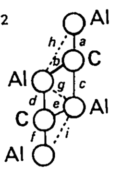
In our previous paper we described the general features of these structures in terms of three structural segments or blocks which are regularly arranged in different stacking sequences. These blocks are $[AlN]_n$, $[Al_2C_2]_n$, $[Al_2C]_n$. The rhombohedral structure of $Al_8C_3N_4$ is described, for example, as $([Al_2C_2]_n[AlN]_n[AlN]_n[Al_2C]_n[AlN]_n[AlN]_n)_3$. This description has been confirmed by completing the three-dimensional structure analyses of all the other members of the series so far observed, and detail concerning interatomic distances has been added. An analogous homologous series also formed from three different structural blocks has recently been reported by Kohn & Eckart (1964) for some hexagonal ferrites.

In this paper we wish to discuss the aluminum carbide and carbonitride structures in terms of their tetrahedral coordination polyhedra. This is an equivalent but alternative point of view, which illustrates more clearly their relationship to the basic tetrahedral wurtzite and zinc-blende structures. Since the aluminum atoms invariably have four non-metallic first neighbours disposed in a more or less distorted tetrahedral arrangement, we can recognize four different types of AlX_4 coordination tetrahedra in the carbide and carbonitride structures, *i.e.* AlC_4, AlC_3N, $AlCN_3$, AlN_4. The aluminum nitride tetrahedra occur only in members of the series above $Al_6C_3N_2$. The well-known *B*4 or wurtzite-type structure of AlN can be described as a regular stacking sequence of hexagonal layers of *corner-sharing* tetrahedra as illustrated at *A* in Fig. 2. All the $[AlN_4]$ tetrahedra have the same orientation and the structure is polar in the stacking direction, which is the hexagonal axis in the space group $P6_3mc$. The valence electron to atom ratio is 4:1 (or valence electron concentration, VEC = 4, Parthé, 1963) in accordance with the Grimm–Sommerfeld valence rule condition for a binary tetrahedral compound. In the absence of stacking faults or other defects, the corner-sharing of the tetrahedra is preserved throughout the crystal.

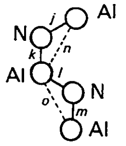
In Al_4C_3 the electron to atom ratio is 24:7 (VEC = 3·43), and to preserve electroneutrality in the association of the tetrahedra it is necessary to have an arrangement which also includes some *edge-sharing* tetrahedra. This is achieved by *inverting* alternate double-layer blocks of corner-sharing tetrahedra and then translating or shearing them so that edge-sharing takes place. There are two types of edge-sharing in the Al_4C_3 structure; edge-sharing produced by a shear in the basal direction and edge-sharing from a shear in a lateral direction. In illustration *B*, Fig. 2, the polar directions of the double-layer blocks are distinguished

Table 3. *Bond lengths of segments of aluminum carbide, nitride and carbonitrides*

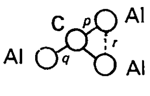
Al_2C_2



AlN



Al_2C



		AlN	Al_5C_3N	$Al_7C_3N_3$	Al_4C_3	$Al_6C_3N_2$	$Al_8C_3N_4$	Mean values
Al–C	*a*		1·91	1·91	1·89	1·99	1·98	1·936
	b		1·95	1·94	1·95	1·89	1·87	1·920
	c		2·30	2·28	2·19	2·29	2·26	2·266
	d		2·09	2·06	2·19	2·24	2·23	2·075† 2·220′‡
	e		1·92	1·89	1·95	1·89	1·87	1·904
	f		2·02	2·06	1·97	2·01	2·04	2·020
Al–Al	*g*		2·63	2·56	2·66	2·77	2·72	2·595,† 2·717‡
	h		3·04	3·06	2·95	2·92	2·91	2·976
	i		2·98	3·02	3·01	2·91	2·93	2·970
Al–N	*j*	1·89	1·93	1·93		1·94 1·93	1·92 1·92	1·930*
	k	1·92	1·99	1·86		1·98 1·99	1·98 1·98	1·963*
	l			1·92			1·91 1·91	1·920
	m			2·03			1·98 1·99	2·000
Al–Al	*n*		3·04	3·04		3·11 3·09	3·11 3·10	3·082
	o			3·10			3·08 3·01	3·063
Al–C	*p*		2·13	2·17	2·15	2·11	2·12	2·136
	q		2·13	2·08	2·14	2·11	2·11	2·114
Al–Al	*r*		2·83	2·76	2·81	2·81	2·86	2·81

mean e.s.d. Al–Al 0·04 Å
Al–C 0·06
Al–N 0·06

* Excluding AlN.
† Mean for odd series.
‡ Mean for even series.

Table 4. *Observed and calculated structure factors for* Al_4C_3, Al_5C_3N, $Al_6C_3N_2$, $Al_8C_3N_4$

hkl refer to the orthogonal cell and are related to the *HKL* indices of the hexagonal cell by

$H=h,\ K=\frac{1}{2}h-\frac{1}{2}k,\ L=l.$

Al_4C_3

k=0			
0	3	12	8-
0	6	44	45
0	9	81	61
0	12	209	200-
0	15	17	12
0	18	48	43-
0	21	16*	10
0	24	124	112
0	27	32	28
0	30	68	60
-2	2	113	117-
-2	5	104	113-
-2	8	56	46
-2	11	89	92-
-2	14	105	127
-2	17	111	106
-2	20	16*	14
-2	23	112	100
-2	26	78	61-
-2	29	36	44-
2	1	83	76
2	4	9*	9-
2	7	141	162
2	10	101	96
2	13	37	42
2	16	46	47
2	19	103	103-
2	22	23	18-
2	25	57	49-
2	28	26	22-
-4	1	61	50
-4	4	29	18-
-4	7	121	128
-4	10	80	74
-4	13	32	30
-4	16	32	37
-4	19	89	84-
-4	22	18	17-
-4	25	46	42-
4	2	85	88-
4	5	96	99-
4	8	42	33
4	11	68	70-
4	14	96	101
4	17	79	85
4	20	14*	13
4	23	87	83
6	0	111	140
6	3	14*	5
6	6	21	21
6	9	28	17
6	12	86	100-
k=1			
-1	1	91	77
-1	4	7	10-
-1	7	135	161
-1	10	86	97
-1	13	34	41
-1	16	48	47
-1	19	112	104-
-1	22	20	19-
-1	25	51	49-
1	2	114	118-
1	5	108	112-
1	8	59	47
1	11	71	92-
1	14	137	128
1	17	107	106
1	20	14*	15
1	23	106	100
1	26	69	61-
3	0	215	225
3	3	4*	5-
3	6	33	32
3	9	44	29
3	12	158	153-
3	15	16*	11
3	18	38	35-
3	21	15	8
3	24	93	92
-5	2	71	68-
-5	5	83	82-
-5	8	40	23
-5	11	58	56-
-5	14	67	80
-5	17	73	71
-5	20	9	9
5	1	51	37
5	4	22*	13-
5	7	97	104
5	10	60	59
5	13	25	28
5	16	26	29
5	19	68	68-
-7	1	37	25
-7	4	8	7-
-7	7	53	70
7	2	54	50-
7	5	53	54-
7	8	15	16
k=2			
0	0	240	225
0	3	6*	4-
0	6	25	32
0	9	35	30
0	12	125	154-
0	15	13	8
0	18	32	36-
0	21	10*	8
0	24	97	93
0	27	24	25
-2	2	78	86-
-2	5	89	100-
-2	8	42	32
-2	11	60	70-
-2	14	70	99
-2	17	79	86
-2	20	9*	12
-2	23	95	82
2	1	56	49
2	4	27	17-
2	7	115	130
2	10	73	73
2	13	23	32
2	16	35	37
2	19	77	83-
2	22	15	16-
2	25	51	41-
-4	1	48	39
-4	4	24	14-
-4	7	90	103
-4	10	54	61
-4	13	18	26
-4	16	28	29
-4	19	70	69-
4	2	67	70-
4	5	80	80-
4	8	38	25
4	11	57	55-
4	14	59	83
4	17	70	71
4	20	7*	11
6	0	97	117
6	3	7*	5
6	6	15	18
6	9	17	14

Al_5C_3N

h=0			
0	2	8	8-
0	4	15	12
0	6	37	41
0	8	52	52
0	10	155	172-
0	12	10*	21
0	14	22	23-
0	16	38	24-
0	18	41	24
0	20	94	86
0	22	26	23
0	24	50	37
0	26	46	39
2	0	43	33
2	1	66	71
2	2	45	37-
2	3	38	33
2	4	44	39-
2	5	66	65
2	6	76	77
2	7	23	27
2	8	29	26
2	9	62	74
2	10	15	14-
2	11	20	22-
2	12	61	80
2	13	28	32-
2	14	45	44
2	15	51	53-
2	16	47	42-
2	17	31	30-
2	18	15	18
2	19	46	40-
2	20	37	28
2	21	22	21-
2	22	68	55-
2	23	23	20
2	24	9	11-
2	25	37	28
2	26	36	27
2	27	16	24
4	0	31	20
4	1	53	48-
4	3	28	21-
4	4	49	38-
4	5	62	54-
4	6	67	60
4	7	20	21-
4	8	24	19
4	9	53	53-
4	10	11	11-
4	11	15	17
4	12	55	62
4	13	20	23
4	14	32	34
4	15	30	41
4	16	38	33-
4	17	20	24
4	18	8	14
4	19	36	32
4	20	34	23
4	21	20	17
4	22	60	46-
4	23	16	16-
6	0	97	114
6	2	8*	3-
6	4	8	7
6	6	15	17
6	8	17	17
6	10	71	82-
h=1			
1	0	37	31
1	1	67	71-
1	2	43	37-
1	3	40	33-
1	4	39	39-
1	5	62	65-
1	6	68	77
1	7	20	26-
1	8	25	26
1	9	60	74-
1	10	14	13-
1	11	18	22
1	12	78	81
1	13	35	31
1	14	51	44
1	15	58	52
1	16	49	43-
1	17	29	30
1	18	10	18
1	19	45	39
1	20	36	28
1	21	22	20
1	22	60	55-
1	23	20	20-
1	24	11	12-
1	25	37	28-
1	26	33	27
4	19	28	26
6	0	76	95
6	2	1	2-
6	4	7	6
6	6	11	14
6	8	13	14
3	0	190	189
3	2	8	4-
3	4	14	10
3	6	27	27
3	8	25	27
3	10	112	129-
3	12	8	16
3	14	12	19-
3	16	25	27-
3	18	16	19
3	20	70	70
3	22	21	19
3	24	36	32
5	0	23	19
5	1	45	37
5	2	28	23-
5	3	19	17
5	4	39	30-
5	5	47	43
5	6	50	46
5	7	14	17
5	8	16	16
5	9	42	42
5	10	9	11-
5	11	13	14-
5	12	43	49
5	13	17	19-
5	14	30	27
5	15	36	34-
5	16	27	26-
5	17	19	19-
5	18	9	11
5	19	29	26-
7	0	13	12
7	1	25	24-
7	2	15	17-
7	3	9	11-
7	4	19	18-
7	5	25	28-
h=2			
0	0	189	189
0	2	3	4-
0	4	6	10
0	6	17	27
0	8	21	27
0	10	111	129-
0	12	4	16
0	14	14	19-
0	16	24	27-
0	18	17	19
0	20	82	70
0	22	22	19
0	24	37	32
2	0	24	23
2	1	44	48
2	2	34	29-
2	3	25	22
2	4	41	38-
2	5	54	54
2	6	56	59
2	7	17	21
2	8	18	19
2	9	38	54
2	10	12	12-
2	11	12	17-
2	12	43	61
2	13	21	24-
2	14	36	34
2	15	41	42-
2	16	36	33-
2	17	21	24-
2	18	10	14
2	19	37	32-
2	20	31	24
2	21	19	17-
2	22	55	45-
2	23	18	17
4	0	21	17
4	1	40	36-
4	2	26	24-
4	3	18	16-
4	4	35	30-
4	5	42	42-
4	6	46	46
4	7	14	17-
4	8	15	16
4	9	34	42-
4	10	9	9-
4	11	11	14
4	12	38	51
4	13	16	19
4	14	27	27
4	15	35	33
4	16	31	37-
4	17	19	20
4	18	10	11

$Al_6C_3N_2$

k=0			
0	3	8	13-
0	6	2*	7
0	9	28	26
0	12	73	81
0	15	105	94
0	18	315	327-
0	21	47	28
0	24	19	47-
0	27	26	13-
0	30	63	36-
0	33	33	15-
0	36	167	169
0	39	56	25-
0	42	44	83
0	45	47	50
0	48	70	46
2	1	135	145
2	4	8*	3-
2	7	9*	6-
2	10	180	194
2	13	79	62
2	16	143	169
2	19	26	34-
2	22	108	134
2	25	32	28
2	28	107	138-
2	31	57	13
2	34	49	72-
2	37	25	35
2	40	140	122-
2	43	3*	8-
-2	2	141	150-
-2	5	122	107-
-2	8	143	143-
-2	11	87	100
-2	14	7*	36-
-2	17	138	129-
-2	20	51	85
-2	23	146	133
-2	26	124	157
-2	29	10*	61-
-2	32	42	84
-2	35	100	100
-2	38	64	14
-2	41	80	51-
-2	44	42	72-
4	2	99	102-
4	5	79	73-
4	8	122	130-
4	11	56	74
4	14	9*	32-
4	17	91	85-
4	20	30	64
4	23	110	99
4	26	119	123
4	29	5*	47-
4	32	46	71
4	35	84	76
4	38	31	14
-4	1	97	88
-4	4	8	6-
-4	7	31	23-
-4	10	154	159
-4	13	76	46
-4	16	102	121
-4	19	19	23-
-4	22	85	100
-4	25	24	29
-4	28	110	109-
-4	31	32	12
-4	34	31	58-
-4	37	20	27
-4	40	95	97-
6	0	198	202
6	3	10*	6-
6	6	5*	16
6	9	15	10
6	12	24	29
6	15	36	28
6	18	165	148-
6	21	10	18
6	24	3*	27-
6	27	6	2-
k=1			
1	2	149	149-
1	5	126	107-
1	8	137	143-
1	11	82	101
1	14	13	38-
1	17	120	124-
1	20	41	85
1	23	165	135
1	26	136	156
1	29	12*	63-
1	32	43	86
1	35	101	98
1	38	69	14
1	41	79	53-
-1	1	146	139
-1	4	9*	1-
-1	7	7*	8-
-1	10	179	196
-1	13	81	61
-1	16	133	167
-1	19	26	31-
-1	22	121	133
-1	25	34	31
-1	28	107	140-
-1	31	63	13
-1	34	28	72-
-1	37	25	34
-1	40	143	121-
-1	43	6*	10-
3	0	330	342
3	3	9*	8-
3	6	9*	13
3	9	18	15
3	12	43	51
3	15	58	45
3	18	255	239-
3	21	32	24
3	24	11*	39-
3	27	25	9-
3	30	48	28-
3	33	23	11-
3	36	156	135
3	39	34	20-
5	1	86	76
5	4	12	8-
5	7	20	15-
5	10	118	123
5	13	53	38
5	16	94	101
5	19	14*	23-
5	22	75	81
5	25	11	18
5	28	84	83-
-5	2	89	80-
-5	5	72	54-
-5	8	113	102-
-5	11	52	54
-5	14	14*	21-
-5	17	82	72-
-5	20	30	53
-5	23	94	76
-5	26	88	100
-5	29	5*	34-
k=2			
0	0	352	342
0	3	9*	5-
0	6	5	12
0	9	28	18
0	12	48	49
0	15	61	47
0	18	218	238-
0	21	37	24
0	24	12*	39-
0	27	34	11-
0	30	58	27-
0	33	32	12-
0	36	119	135
2	1	93	96
2	4	12*	9-
2	7	33	20-
2	10	135	156
2	13	62	48
2	16	95	124
2	19	22	27-
2	22	86	101
2	25	30	24
2	28	94	106-
2	31	29	12
2	34	35	59-
2	37	21	29
-2	2	104	104-
-2	5	92	74-
-2	8	129	130-
-2	11	62	72
-2	14	10*	29-
-2	17	87	91-
-2	20	37	65
-2	23	121	97
-2	26	105	124
-2	29	12*	45-
-2	32	38	68
-2	35	80	79
4	2	77	78-
4	5	66	54-
4	8	91	103-
4	11	42	57
4	14	11	25-
4	17	68	64-
4	20	27	52
4	23	93	79
4	26	94	99
4	29	3*	36-
-4	1	77	67
-4	4	10*	6-
-4	7	22	19-
-4	10	116	125
-4	13	49	36
-4	16	74	97
-4	19	11	17-
-4	22	64	80
-4	25	9	23
-4	28	88	86-
6	0	185	166
6	3	5*	5-
6	6	6*	15
6	9	10	9
6	12	7*	23
k=3			
1	2	70	79-
1	5	58	54-
1	8	86	103-
1	11	57	56
1	14	10*	24-
1	17	79	67-
1	20	37	52
1	23	86	78
1	26	86	100
1	29	3*	36-
-1	1	73	70
-1	4	17*	6-
-1	7	37*	17-
-1	10	113	125
-1	13	43	37
-1	16	74	98
-1	19	23	19-
-1	22	73	81
-1	25	18	21
-1	28	77	85-
3	0	215	203
3	3	10*	5-
3	6	10*	15
3	9	64	11
3	12	19	28
3	15	25	29
3	18	150	147-
3	21	18	18

* Indicates an unobserved reflection. First and second columns are *h* and *l* with *k* values given above or *k* and *l* with *h* values given above. Third and fourth columns are $|F_{obs}|$ and F_{calc}.

Table 4 (*cont.*)

$Al_8C_3N_4$

k=0			
0	9	16	6
0	12	41	29
0	15	49	35
0	18	103	127
0	21	114	83
0	24	446	457-
0	27	52	47
0	30	36	73-
0	33	20	15
0	36	30	24-
0	39	31	15-
0	42	83	68-
0	45	81	36
0	48	202	213
0	51	70	48-
0	54	81	103
0	57	48	17
0	60	67	63
0	63	67	60
0	66	101	50
2	1	233	216
2	4	21	15
2	7	42	24-
2	10	9*	4
2	13	258	254
2	16	74	23
2	19	133	155
2	22	182	170
2	25	72	86-
2	28	70	80
2	31	146	148
2	34	16*	1-
2	37	168	206-
2	40	66	48
2	43	82	108-
2	46	43	35-
2	49	41	54
2	52	31	64-
2	55	152	138-
2	58	13*	19
2	61	80	123
-2	2	192	179-
-2	5	117	108-
-2	8	134	134-
-2	11	174	163-
-2	14	132	137
-2	17	29	12-
-2	20	15	18-
-2	23	177	181-
-2	26	94	111
-2	29	49	39
-2	32	203	250
-2	35	159	156
-2	38	56	106-
-2	41	25*	68
-2	44	73	45
-2	47	120	125
-2	60	43	24-
-2	53	58	65
-2	56	187	182-
-2	59	61	59-
-2	63	11	71
4	2	118	126-
4	5	82	71-
4	8	101	103-
4	11	172	157-
4	14	89	104
4	17	14*	4-
4	20	14*	19-
4	23	122	127-
4	26	63	86
4	29	70	27
4	32	151	191
4	35	88	125
4	38	14*	84-
4	41	14*	49
4	44	48	36
4	47	81	96
4	50	31	20-
4	53	44	53
4	56	131	152-
-4	1	137	140
-4	4	13*	6
-4	7	32	35-
-4	10	37	24-
-4	13	201	208
-4	16	48	20
-4	19	90	114
-4	22	120	120
-4	25	59	65-
-4	28	51	61
-4	31	120	119
-4	34	14*	3
-4	37	108	161-
-4	40	37	35
-4	43	63	84-
-4	46	12*	28-
-4	49	11*	44
-4	52	10*	54-
-4	55	123	118-
6	3	13*	8-
6	6	13*	5-
6	9	13*	7
6	12	35	8
6	15	27	10
6	18	29	56
6	21	30	12
6	24	206	211-
6	27	10*	27
6	30	9*	32-
6	33	8*	9
6	36	7*	7-
6	39	5*	9-
k=1			
1	2	188	179-
1	5	119	108-
1	8	148	135-
1	11	190	163-
1	14	129	136
1	17	36	10-
1	20	14	15-
1	23	162	179-
1	26	79	111
1	29	59	40
1	32	244	251
1	35	175	156
1	38	36	106-
1	41	15*	66
1	44	74	43
1	47	108	123
1	50	45	25-
1	53	69	65
1	56	195	183-
1	59	60	59-
1	62	12*	70
-1	4	7*	13
-1	7	31	26-
-1	10	8*	4
-1	13	221	255
-1	16	69	20
-1	19	133	154
-1	22	155	170
-1	25	82	83-
-1	28	66	82
-1	31	181	150
-1	34	14*	1-
-1	37	184	205-
-1	40	68	47
-1	43	84	107-
-1	46	39	34-
-1	49	23	53
-1	52	48	65-
-1	55	183	139-
-1	58	14*	18
-1	61	94	122
3	0	492	469
3	3	14*	10-
3	6	14*	1-
3	9	14*	6
3	12	28	16
3	15	33	18
3	18	73	85
3	21	35	26
3	24	340	333-
3	27	57	39
3	30	50	55-
3	33	24	11
3	36	17*	17-
3	39	19	14-
3	42	54	56-
3	45	57	32
3	48	177	171
3	51	73	40-
3	54	63	83
5	1	130	111
5	4	16*	13
5	7	23	28-
5	10	23	20-
5	13	172	165
5	16	47	21
5	19	81	90
5	22	112	96
5	25	43	57-
5	28	36	43
5	31	78	95
5	34	13*	4-
5	37	118	130-
5	40	48	31
5	43	49	68-
-5	2	105	96-
-5	5	75	53-
-5	8	84	80-
-5	11	143	127-
-5	14	79	82
-5	17	22	2-
-5	20	22	23-
-5	26	43	67
-5	29	41	17
-5	32	153	153
-5	35	123	101
-5	38	12*	70-
-5	41	11*	41
-5	44	65	35
k=2			
0	0	460	469
0	3	5	9-
0	6	4*	1-
0	9	11	7
0	12	26	18
0	15	39	20
0	18	63	85
0	21	60	26
0	24	308	332-
0	27	55	39
0	30	27	55-
0	33	25	10
0	36	34	18-
0	39	35	14-
0	42	72	56-
0	45	66	32
0	48	136	170-
0	51	69	39-
0	54	49	82
2	1	130	144
2	4	9	10
2	7	35	31-
2	10	38	24-
2	13	217	208
2	16	69	24
2	19	103	115
2	22	120	120
2	25	41	68-
2	28	50	57
2	31	128	116
2	34	9*	3
2	37	137	161-
2	40	56	37
2	43	63	85-
2	46	32	29-
2	49	9*	46
2	52	8*	52-
2	55	147	116-
2	58	24	18
-2	2	118	125-
-2	5	78	72-
-2	8	100	102-
-2	11	160	157-
-2	14	98	104
-2	17	27	6-
-2	20	30	22-
-2	23	154	130-
-2	26	82	85
-2	29	45	24
-2	32	187	190
-2	35	141	125
-2	38	29	85-
-2	41	10*	51
-2	44	82	39
-2	47	97	98
-2	50	43	20-
-2	53	59	53
-2	56	155	151-
4	2	87	97-
4	5	65	52-
4	8	76	81-
4	11	145	127-
4	14	81	82
4	17	17	2
4	20	12	19-
4	23	117	99-
4	26	51	68
4	29	38	20
4	32	147	155
4	35	118	102
4	38	25	69-
4	41	7*	39
4	44	54	32
4	47	67	79
-4	1	110	107
-4	4	9*	8
-4	7	28	32-
-4	10	35	21-
-4	13	168	165
-4	16	41	18
-4	19	65	89
-4	22	109	95
-4	25	45	53-
-4	28	36	47
-4	31	104	99
-4	34	13	2-
-4	37	119	130-
-4	40	46	29
-4	43	56	67-
-4	46	24	24-
6	0	257	232
6	3	5*	7-
6	6	5*	6-
6	9	5*	7
6	12	5*	6

Table 5. *Ratios of differences between observed and calculated peak height and observed peak height*

	Al_4C_3	Al_5C_3N	$Al_6C_3N_2$	$Al_7C_3N_3$	$Al_8C_3N_4$
C(1)	0·02	−0·10	0·10	0·03	0·07
C(2)	0·05	−0·05	0·20	−0·04	0·10
C(3)	0·02	−0·09	0·20	−0·05	0·15
Al(1)	−0·07	0·01	−0·08	0·05	0·03
Al(2)	−0·05	0·06	0·08	0·02	−0·02
Al(3)	0·01	−0·01	−0·18	−0·01	−0·04
Al(4)	0·02	0·05	−0·15	0·01	−0·12
Al(5)		−0·01	0·03	−0·05	−0·09
Al(6)			−0·02	0·03	−0·02
Al(7)				0·05	0·02
Al(8)					0·02
N(1)		−0·05	−0·08	0·03	−0·07
N(2)			−0·10	−0·04	−0·14
N(3)				−0·01	−0·10
N(4)					−0·18

by their shade. After the $\bar{1}$ inversion of the double layers, the second and third layers of tetrahedra are brought to the same level by a diagonal translation (at $\twoheadleftarrow$ in illustration *B*) of $\frac{1}{2}(\bar{a}+\bar{c}')$ where the primed periodicity refers to that of the basic *B*4 structure. The next inversion is between the fourth and fifth layers, (relative to the original *B*4 structure), and there the shear (at $\leftarrow$ in *B*) is in the basal direction only; *i.e.* $\bar{a}$. There are three such inversions of each type before the lattice repeats with rhombohedral symmetry and a *c*-axis periodicity of 24·89 Å $\simeq 5\,c'$. The inversion and $\frac{1}{2}(\bar{a}+\bar{c}')$-type shear gives rise to the five-coordinated apices (carbon atoms), the inversion and $\bar{a}$-type shear forms six-coordinated carbon atoms. The detailed stereochemistry of the carbon coordination is discussed later.

In Al_5C_3N, shown at *C* in Fig. 2, an additional layer of corner-sharing tetrahedra is added, so that the blocks consist of alternately three layers and two layers of tetrahedra. In the illustration, the inversion and $\frac{1}{2}(\bar{a}+\bar{c}')$ shear takes place between the third and fourth layers; the next inversion and $\bar{a}$ translation takes place between the fifth and sixth layers. There are two inversions of each type before the lattice repeats with hexagonal symmetry and a *c*-axis length of 21·67 Å $\simeq$ 4·5 c'.

In $Al_6C_3N_2$ (*D*, Fig. 2) the blocks are all three-layer, and the inversions and shears are at the 3/4, 6/7, 9/10, 12/13, 15/16, 18/19 layers relative to the *B*4 lattice. The lattice has rhombohedral symmetry and *c*-axis periodicity of 40·03 Å $\simeq 8\,c'$. In $Al_7C_3N_3$ (*E*, Fig. 2) they are all four-layer. In theory, this process could be continued indefinitely to form the series of compounds $Al_{n+4}C_3N_n$. Where *n* is large, the compound could be described stoichiometrically as a defect structure of AlN, with a small substitution of carbon atoms. Structurally, it would be a definite ordered phase with a very long *c*-axial periodicity. This concept is consistent with the 'step-lattice', or 'shear' structure interpretation of the complex 'non-stoichiometric' formulae of certain transition metal oxides (*cf.* Wadsley, 1963, 1964). It is important to note that the insertion of the impurity carbon atoms in the AlN lattice would have the effect of reversing the polarity of adjacent blocks of struc-

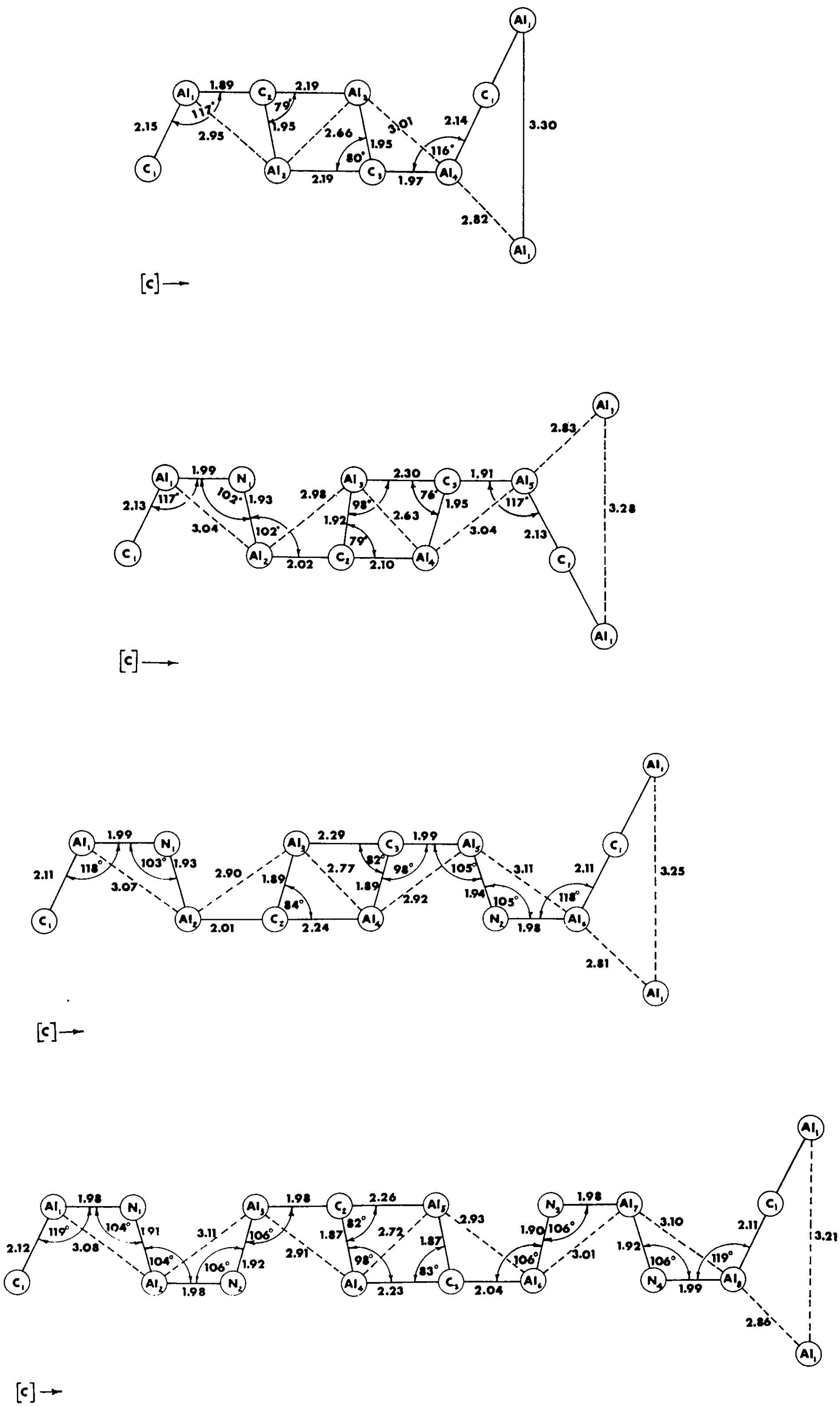


Fig. 1. Interatomic distances and angles in Al_4C_3, Al_5C_3N, $Al_6C_3N_2$, $Al_8C_3N_4$.

ture. The carbon atoms would have to be arranged regularly in a basal plane layer of a crystalline domain but there woud be no requirement for periodicity of substitution in the stacking (c-axis) direction. The inversion of blocks could occur irregularly, as a type of stacking fault, and result in a reversal of polarity across a basal plane boundary. It is an interesting hypothesis to generalize this to other normal tetrahedral lattices where the introduction of the foreign atom is such as to reduce the electron to atom ratio below 4 to 1, *e.g.* ZnO with C or N, GaAs with Ge. This may be the cause of the polarity twinning sometimes observed in wurtzite-type structures, in BeO (Austerman, 1962) for example.

When the substituted atom in a tetrahedral structure is such that the VEC exceeds 4, vacant sites, which may be ordered or disordered, are introduced into the long-range structure in order to preserve electroneutrality. These have been described as 'defect' tetrahedral structures (Parthé, 1963). We believe there is valid analogy in this case where the substituted atom reduces the VEC below 4 and shared edges rather than vacancy defects are introduced in the normal tetrahedral arrangements as an alternate means of preserving the electroneutrality of the crystal. Parthé (1964), however, classifies the aluminum carbonitrides as complex variations of the 'filled' tetrahedral structure. Indeed it is clear that the structural feature which we have described as an inversion and shear of $\frac{1}{2}(a+c)$ of the tetrahedral blocks can equally well be described by filling with Al atoms the set of tetrahedral sites which are vacant in a 'normal' tetrahedral structure. Thus at the levels of the type marked ↞ in B (Fig. 2), there is a double concentration of metal atoms relative to the level in the normal structure shown in A.

There are two first neighbour stereochemical consequences of the edge-sharing of tetrahedra; (i) it brings like 'cations', *i.e.* the aluminum atoms, within bonding interatomic distances, (ii) it increases beyond fourfold the coordination of the 'anions'. The interatomic distances and angles associated with these featuıes are shown in detail in Table 3 and Fig. 1, and are discussed below.

The interatomic distances and bonding

As described and illustrated in Fig. 2 of the paper by Jeffrey & Wu (1963), the aluminum atoms lie in hexagonal layers with an $ABAB\ldots$ stacking sequence which switches to $ABCB\ldots$ at $z=0, \frac{1}{3}, \frac{2}{3}$ in the even series, and $z=0, \frac{1}{2}$ in the odd series. Within the layers, the Al–Al distances are the a translation of the hexagonal unit cell, *i.e.* they range from 3·21 to 3·33 Å. Examination of the Al–Al interlayer distances, given in Table 3, shows a distinction between those metal layers which are separated by nitrogen atoms, those separated by carbon atoms, and those which have no intervening non-metallic atoms. The Al–Al distances in the nitrogen-separated layers, (n, o, in Table 3) range from 3·04 to 3·11 Å with a mean value close to that of AlN. The Al–Al distances in the carbon-separated layers are significantly shorter and vary between 2·76 and 3·06 Å (h, i, r, in Table 3) with a mean close to the value of 2·86 Å found in the h.c.p. structure of the pure metal. They fall into two well-defined groups; those separated by five-coordinated carbon atoms (h, i) at 2·91–3·06 Å, and those separated by the six-coordinated carbon atoms (r) at 2·76–2·86 Å, *i.e.* respectively greater than and less than the h.c.p. metal value.

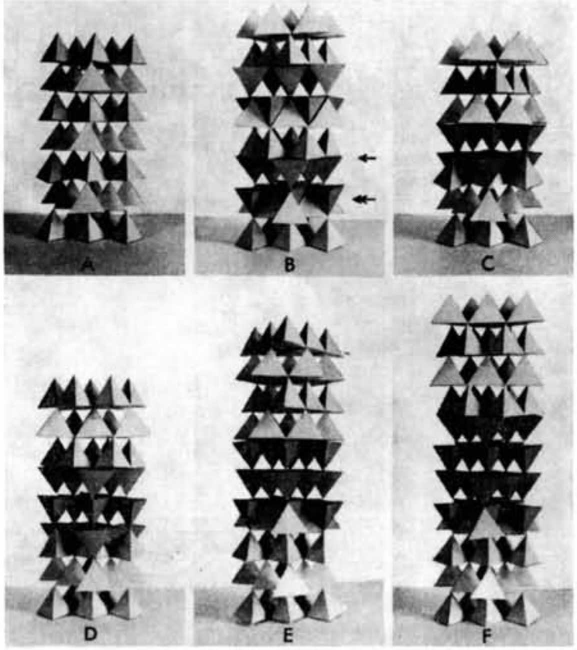


Fig. 2. Tetrahedral block stacking arrangements in aluminum nitride and the aluminum carbonitrides.

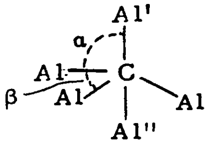
A. AlN	*D*. $Al_6C_3N_2$
B. Al_4C_3	*E*. $Al_7C_3N_3$
C. Al_5C_3N	*F*. $Al_8C_3N_4$

The shortest Al–Al distances are those when the layers are in direct contact, *i.e.* $g=2·56$ to 2·77 Å. The estimated standard deviations are such that the variations within these groups are unlikely to be significant, with the exception of the d and g distances, where there appears to be a distinction between the odd and even series of compounds.

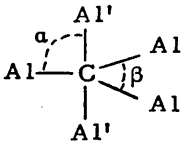
Since nitrogen is normally considered to have a slightly smaller radius than carbon, either in covalent or interstitial compounds, it can be inferred that the nature of the binding between the metal and non-metallic atoms must be somewhat different in the nitride and carbide segments of the structures.

The AlN segments, with small variations, have the same structure as that of AlN itself and can be described as mainly covalent non-conducting structure. The mean Al–N distances are 1·970 Å in the c-axial direction and 1·925 Å laterally, as compared with 1·917 and 1·885 Å in AlN (Jeffrey, Parry & Mozzi, 1956). The mean valence angles are Al′–N–Al = 105·5°. This flattening of the tetrahedra also indicates a significant trend toward the formation of atomic layers normal to the stacking direction, with the Al–N covalent binding significantly weaker between layers than within the same layer. This tendency toward plane layers is a general feature throughout the whole series of structures.

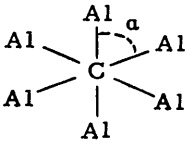
In the carbide blocks of the carbonitride structures and in Al_4C_3, the carbon atoms are four-, five- and six-coordinated to first nearest neighbour aluminum atoms, as illustrated in (*A*), (*B*) and (*C*) below, where the limits after the interatomic distances correspond to the spread of the observed values.



C–Al $=1{\cdot}91\pm0{\cdot}04$ Å
C–Al′ $=1{\cdot}94\pm0{\cdot}05$ Å
C–Al″ $=2{\cdot}25\pm0{\cdot}06$ Å
$\alpha=105°\pm2°$
$\beta=113°\pm3°$
(*A*)



C–Al (equat) $=1{\cdot}90\pm0{\cdot}02$ Å
C–Al′ (polar) $=2{\cdot}06\pm0{\cdot}04$ Å
$\alpha=101°\pm3°$
$\beta=117°\pm3°$
(*B*)



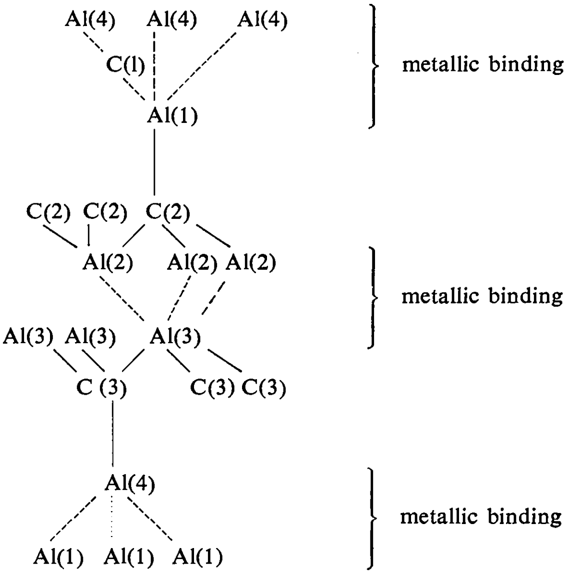
C–Al $=2{\cdot}13\pm0{\cdot}05$ Å
$\alpha=96°\pm2°$
(*C*)

- *A* is a distorted tetrahedron with a fifth long 'bond' in the stacking axis direction. It is found in all structures.
- *B* is a distorted trigonal bipyramid with the polar axis in the stacking direction. It is found only in the noncentric structures, Al_5C_3N and $Al_7C_3N_3$.
- *C* is a flattened octahedron, which is found in all structures.

Aluminum carbide is an electron deficient compound in the usual sense that there are 28 valence orbitals per formula unit and 24 valence electrons, excluding the 1*s* shells. This results in the increase in coordination number of the carbon atoms above their usual value of four (*cf.* Pauling, 1960). Since the aspects of the structures which are difficult to interpret are associated with the carbide blocks, we will first attempt to describe the nature of the binding in the carbide structure.

There are two alternative descriptions of the electronic distribution and bonding, either of which accounts qualitatively for the observed stereochemistry. One is a metallic block/covalent block description, the other is entirely covalent with two- and three-center bonding orbitals. The electronic distributions in structures which are intermediate between metallic and covalent in their bonding characteristics are particularly difficult to describe, and we will refer to these two descriptions as I and II, by analogy with valence-bond resonance representations.

In I, we assume that the metal layers with no intervening non-metallic atoms are in direct contact and cohere by metallic non-directional binding. We also assume that the metallic layers at the *ABC* stacking sequence are also in direct contact with metallic bonding, since the interlayer Al–Al distances are also less than those in the pure metal. The six-coordinated carbon atoms then occupy the octahedral sites (of diameter ~1·1 to 1·2 Å) interstitially. This bonding is indicated by the dotted lines in I. It corresponds to two closest-packed hexagonal layers of metal atoms with much stronger bonding between the layers than in the layers. Each Al atom has six neighbours in the same layer and three above (or below), but, of course, none below (or above) because the metallic structure does not extend beyond the double layer. This accounts for the shorter intermetallic distance between layers than in the h.c.p. elemental structure where the metallic coordination is 12. The Pauling (1960) bond numbers, calculated from the observed distances and R_1 for Al = 2·49 Å, are 0·93 between the layers and 0·05 in the layers.



I

Between these layers of intermetallic structure, there are blocks of covalent (CAl_4) tetrahedra linked cornerwise in the directions of the basal plane. The binding in these blocks is normal covalent two-center orbitals of the type $\{[sp^3]C+[sp^3]Al\}$. It should be noted that formally this uses up all the valence electrons, and there are none available for the metallic bonding between the Al(2) to Al(3) layers, unless the electrons are so distributed in the covalent orbitals to transfer them from the adjacent Al(4) $\cdots$ Al(1) metallic layers.

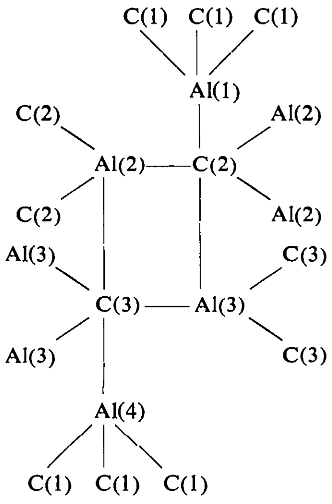
In the electronic description II, we assume that the carbon atoms in the octahedral sites are bonded covalently to the metal atoms by a resonating system of four three-center and two two-center bond orbitals of the type $\{[sp^3]Al+[p]C(1)-[sp^3]Al\}$ and $\{[sp^3]Al+[sp]C(1)\}$, as first proposed by Rundle (1948) for the interstitial metallic carbides. This gives a bond number of two-thirds in the Pauling nomenclature, or uses two of the three valence electrons of each Al(1) and Al(4) atom. The corresponding Al–C distances are 2·13 Å. We now use the other extreme covalent configuration for the remaining carbon atoms, the trigonal bipyramid, and complete the valence bond diagram II. The 24 electrons involved in the bonding of the C(2) and C(3) atoms are distributed in the following orbitals:

two three-center orbitals, *i.e.*

$$\{[sp^3]Al(1)+[p]C(2)-[p]Al(3)\}$$
$$\{[sp^3]Al(4)+[p]C(3)-[p]Al(2)\}$$

and ten two-center orbitals, *i.e.*

$$\text{five } \{[sp^2]C(2)+[sp^2]Al(2)\}$$
$$\text{and five } \{[sp^2]C(3)+[sp^2]Al(3)\}\,.$$



II

The ideal stereochemistry for maximum orbital overlap is a plane layer structure for the $[Al_2C_2]_n$ block, and this corresponds to the tendency towards the formation of layers which was remarked upon in the geometrical description of these structures. The trigonal symmetry in the basal plane fits perfectly the hexagonal lattice of the structure. The two-center bond orbitals and the $[sp^3]\,.\,[p]$ overlap of the three-center orbitals correspond to Al–C distances of 1·92 Å. The $[p]\,.\,[p]$ overlap of the three-center orbitals corresponds to the 'long' Al–C bonds of 2·25 Å.

The structures of $Al_6C_3N_2$ and $Al_8C_3N_4$ are similar to that of Al_4C_3 except that there are one and two blocks respectively of covalent AlN structure interposed between Al(1) and C(2) and Al(3) and C(4). The blocks of AlN structure involve normal $\{[sp^3]Al+[sp^3]N\}$. In Al_5C_3N and $Al_7C_3N_3$, however, there is an odd distribution of AlN blocks; in the former, one between Al(1) and C(2), none between C(3) and Al(4); in the latter, two between Al(1) and C(2), one between C(3) and Al(4). This asymmetrical distribution about the central $[Al_2C_2]$ structure results in an asymmetric bond distribution such that only one of the two carbon atoms is bonded as in Al_4C_3, *i.e.* configuration (*A*).

The other carbon has the configuration (*B*), with two equal polar bonds of 2·04 Å. This can be accounted for by a three-center orbital combination of the type $\{[sp^3]Al_2+[p]C(2)-[sp^3]Al(4)\}$ for these bonds. Since all the valence angles in the $[Al_2C_2]$ blocks lie between the 90° and 109°28′, there is probably little distinction between the effective overlap of $[sp^3]$ and $[sp^2]$ orbitals. However, beyond remarking upon the general sensitivity of the individual bonds to the electronic structure of the crystal as a whole, we do not feel justified at present in attempting to extend our already hard-pressed chemical bond description to include a more quantitative description of this additional complexity.

The structure of Al_2CO

Aluminum oxycarbide has a long-range disordered structure which is isostructural with that of AlN (Amma & Jeffrey, 1961). The short-range ordered structure could not be completely determined from the limited diffuse spectral data. The short-range periodicities of $\sqrt{3}a$ and $2c$, relative to the wurtzite-type lattice, were interpreted in terms of atomic sites which were not specified, (Fig. 9(*b*), (*c*), in the paper by Amma & Jeffrey, 1961). It now seems reasonable to suppose that this structure also consists of mixed blocks analogous to those of the carbonitrides. It can be described as $[AlO]_n[Al_2C_2]_n[AlO]_n$ with the carbon atoms in a similar environment to those in the aluminum carbide.

There are then two possible configurations for the oxygen atoms, as shown in Fig. 3(*a*) and (*b*). Both are three-coordinated to first neighbour Al atoms. In (*a*), the coordination is trigonal planar with the lone-pair electrons occupying a $2p$ orbital. In (*b*), the coordination to the adjacent aluminum atoms is trigonal pyramidal with the lone-pair electrons occupying the $[sp^3]$ orbital in the direction of the c axis, which completes the tetrahedron. This is the more likely electron configuration. The basal cleavage, which would be an obvious property of the short-range structure, would not

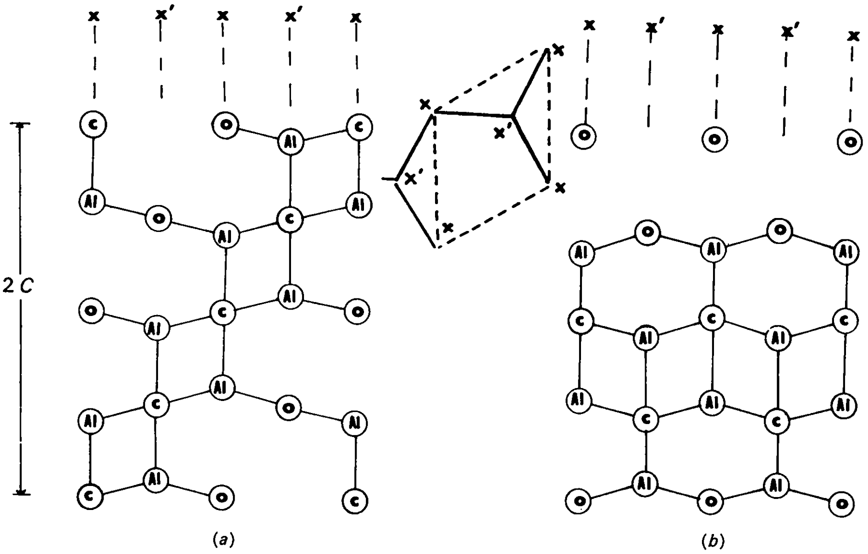


Fig. 3. Two possible short-range order structures for Al_2CO.

be apparent in the crystal owing to the long-range disorder.

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A Powerful Phase-determining Equation for the Invariant Structure Factors in the Centrosymmetric Projection of the Non-centrosymmetric Space Group $P2_1$

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A phase-determining equation is developed based on the Harker–Kasper inequality for a diad-screw axis. Probabilities for a given phase as high as 0·99 are obtained.

Introduction

A solution of the crystal structure problem involves solving the structure factor equation

$$F(\mathbf{h})=\sum_{i=1}^{N} f_i \exp(2\pi j\mathbf{h}\,.\,\mathbf{r}_i)$$

for the N triads (r_i). Hauptman & Karle (1953) have shown that for the special case of a centrosymmetric