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The Crystal Structure of $CaO.2Al_2O_3$

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The possible use of 0·1% Nd^{3+} in $CaO.2Al_2O_3$ as a solid-state laser has made it necessary to determine the structure of this compound accurately and eliminate the uncertainty in previous publications. A full X-ray analysis has been performed on a single crystal using a four-circle diffractometer and the results have shown the crystal to have a space group $C2/c$. A comparison with the published structure of the supposed isomorphous strontium compound gave an initial structure which was found to refine satisfactorily to give a reliability index, $R=0{\cdot}064$, from which the atomic parameters were obtained. The local symmetries of the calcium and aluminum sites are then discussed with respect to the effect on the crystalline electric fields at substituted Nd^{3+} ions.

There has been a certain amount of controversy over the exact crystal structure of the $CaO.2Al_2O_3$ phase of the calcium aluminate system CaO–Al_2O_3. Cockayne (1966) and Cockayne & Robertson (1964) report that this phase is complex hexagonal, whereas Boyko & Wisnyi (1958) report that both $CaO.2Al_2O_3$ and $SrO.2Al_2O_3$ form isomorphous monoclinic crystals with a space group $C2/c$ (C_{2h}^6).

In view of the fact that $CaO.2Al_2O_3$ appears to be a suitable host lattice capable of being doped with small quantities of the Nd^{3+} ion, which is of interest because it forms the basis of a number of the most efficient solid state laser systems, it was decided to attempt an accurate determination of its structure. Once determined one can then make useful estimates of the local symmetry of the substituted Nd^{3+} ions which is essential in calculating the crystalline electric fields which determine the energy levels important to the laser properties. The most important result of our investigation is that the basic structure proposed by Boyko & Wisnyi (henceforth referred to as B.W.) is correct for this phase of the system, while the work of Cockayne appears to be in error.

A number of small crystals, varying in size from about 0·3 mm up to 1 mm, were cut from a single 10 mm dimension crystal grown by the Czochralski technique (Cockayne, 1966). Using a selection of the larger cut crystals, the space group was determined by taking a number of X-ray photographs on a single-crystal precession camera using Cu $K\alpha$ radiation. From the exposed plates it was a simple matter to identify the three principal zones $hk0$, $h0l$ and $0kl$. Of the possible unit cell types proposed by previous authors only a monoclinic unit cell with $\beta=107°$ fitted the observed symmetry. In addition a photograph of the entire $h0l$ zone was taken on a Weissenberg camera, which clearly showed that we had chosen the most sensible monoclinic axes having $\beta=107°$, and that it was impossible to fit the observed symmetry to a hexagonal type structure involving an angle of 120°, as proposed by Cockayne.

The systematic absences observed on the plates indicated that the space group could be either Cc (C_s^4) or $C2/c$ (C_{2h}^6). Since the plates showed definite evidence of absorption of the Cu $K\alpha$ radiation, additional data were collected on a Hilger & Watts computer controlled four circle X-ray diffractometer using Mo $K\alpha$ radiation. The linear absorption coefficient for $CaO.2Al_2O_3$ using Cu $K\alpha$ radiation is $\mu=143$ cm^{-1}, compared with $\mu=15{\cdot}8$ cm^{-1} for Mo $K\alpha$ radiation. Hence by using Mo $K\alpha$ radiation the effects of absorption could be very much reduced. However, it was not possible to make an accurate assessment of the correction factor for the measured intensities because of the irregular shape of the crystal. This does not appear to be serious as an estimate of the correction for a sphere of equivalent size (0·3 mm across) indicated variations in intensity of some 2% compared with experimental errors of about 5%.

The positions of 14 strong low-angle X-ray reflexions were measured manually on the diffractometer and were then used as the basis to determine a set of accurate unit-cell parameters by a least-squares fit starting with the parameters of the monoclinic unit cell from precession photographs. The results of this fit are shown in Table 1 together with the previously published values of B.W. The errors quoted are from the least-squares fit which are rather optimistic, and the actual standard deviations are probably about 3 or 5 times greater.

Table 1. *Unit cell parameters of* $CaO.2Al_2O_3$

	This work	B.W.
a	12·8398 ± 0·0057 Å	12·89 Å
b	8·8624 ± 0·0032	8·88
c	5·4311 ± 0·0018	5·45
α	90°	90°
β	106° 50′ ± 2′	107° 3′
γ	90°	90°

Using the data of Table 1 to define the unit cell of the crystal, the computer control of the diffractometer was set to perform a step scan of ω and θ over all pos-

sible X-ray reflexions within a diffraction angle 2θ from 0 to 80° and within the two octants of diffraction indices defined by h, k, l and $\bar{l}$. A total of 1901 reflexions were measured in this way of which only about ten pairs were crystallographically equivalent.

A set of standard computer programs for the University of York, Elliott 4130 computer, was then employed to analyse the experimental data to produce structure factors from the integrated X-ray intensities.

The close similarity between our results and those of B.W. for the unit cell data, as shown on Table 1 makes it seem likely that their interpretation of the structure would form a suitable basis for interpreting our structure factors. B.W. published a set of atomic parameters for the structure of $SrO.2Al_2O_3$ which they concluded was isomorphous with the calcium compound. By using these values as a starting point we performed a full-matrix fit to the 1901 measured structure factors on the University of York computer with a modified version of the Oak Ridge Fortran least-squares program of Busing, Martin & Levy (1962).

Approximately 55 structure factors were unobserved on analysing the intensity data, but in view of the large number correctly observed these few were omitted in the least-squares fit. A Rollett weighting scheme was used to weight each reflexion in the fitting program. The appropriate ionic scattering factors for the calculation were taken from *International Tables for X-ray Crystallography* (1965), where the ionization states were assumed to be Ca^{2+}, Al^{3+} and O^{2-}.

With isotropic temperature factors for all the atoms the proposed structure was found to refine satisfactorily, and produced a reliability index of $R(hkl)=0{\cdot}093$. On conversion to anisotropic temperature factors the structure was refined even further to produce a minimum value of $R=0{\cdot}064$ at which point the calculated variations in the parameters were smaller than their standard deviations. The satisfactory low value of $R(hkl)$ indicates that the structure is correct and that the space group is $C2/c(C_{2h}^6)$ as proposed by B.W. The refined atomic parameters are given in Table 2. Both the positions x, y, z and the anisotropic temperature factors, β, are included. For completeness the general and special positions for the space group are listed at the bottom of the Table.

There are four formula units $CaO.2Al_2O_3$ in a unit cell, and the calcium atom and one of the oxygen atoms, O(1), lie on special positions. The volume of the unit cell is 591·54 Å^3 and so the calculated density is 2·915 g.cm^{-3}.

The observed structure factors (FO), and the calculated structure factors (FC) based on the parameters of Table 2 are listed in Table 3.

In order to assess the likely positions of dopant Nd^{3+} ions which were in fact present to the amount of 0·1% by weight in the measured sample, it is only necessary to consider the calcium and aluminum ions, as they have similar electric charge to Nd^{3+}. The calcium ions have a point group 2, with the axis along the crystallographic b axis. Each has seven nearest neighbour oxygen ions varying in distance between 2·33 and 2·88 Å, which are only about 5° away from forming a point group $2mm$ $(=C_{2v})$.

The aluminum sites, however, have no well defined symmetry and the local point group is 1 $(=C_1)$. Despite this the two inequivalent aluminum sites are at the centre of tetrahedra of oxygen ions which are very close to regular tetrahedra. The aluminum–oxygen bond distances and bond angles for the two sites are given in Table 4.

For a perfect tetrahedron the bond angles would all be equal to 109·46°, which shows that these sites are slightly distorted but will experience a predominantly cubic crystal field. Nevertheless, a point charge calculation for both these sites indicates that all crystal field terms up to V_6^6 will be required to describe the splitting of the magnetic energy levels, if the Nd^{3+} ion enters the lattice at these points.

An unambiguous assignment of the likely positions of the dopant Nd^{3+} ions is not possible from the structure alone. If the Nd^{3+} enters the calcium site the difference in charge, as calcium forms Ca^{2+} ions, will necessitate some form of charge compensation in the lattice similar to that required in the laser material Nd^{3+} in $CaWO_4$. If the Nd^{3+} enters at the aluminum sites no charge compensation would be necessary as aluminum forms Al^{3+} ions. A final assignment can

Table 2. *The atomic positional and thermal parameters of* $CaO.2Al_2O_3$

	Ca	O(1)	Al(1)	Al(2)	O(2)	O(3)	O(4)
X	0	0	0·1641	0·1198	0·1155	0·1185	0·1924
Y	0·8091	0·5231	0·0867	0·4406	0·0512	0·2553	0·4436
Z	0·25	0·25	0·3030	0·2410	0·5659	0·1491	0·5797
β_{11}	0·00147	0·00142	0·00122	0·00124	0·00169	0·00200	0·00130
β_{22}	0·00252	0·00228	0·00205	0·00200	0·00310	0·00210	0·00325
β_{33}	0·00809	0·01510	0·00715	0·00876	0·00990	0·00938	0·00839
β_{12}	0	0	0·00007	0·00001	0·00043	0·00016	0·00020
β_{13}	0·00173	0·00297	0·00183	0·00220	0·00261	0·00158	0·00177
β_{23}	0	0	0·00007	0·00012	0·00130	0·00022	0·00037

Positional error: ±0·0010
Temperature factor error: ±0·0005
General position: x,y,z; $\bar{x},\bar{y},\bar{z}$; $\bar{x},y,\frac{1}{2}-z$; $x,\bar{y},\frac{1}{2}+z$; $\frac{1}{2}+x,\frac{1}{2}+y,z$; $\frac{1}{2}-x,\frac{1}{2}-y,\bar{z}$; $\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$; $\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z$
Special position: $0,y,\frac{1}{4}$; $0,\bar{y},\frac{3}{4}$; $\frac{1}{2},\frac{1}{2}+y,\frac{1}{4}$; $\frac{1}{2},\frac{1}{2}-y,\frac{3}{4}$

Table 3. *Observed and calculated structure factors* (FO) *and* (FC)

H	FO	FC
K = 1 L = -9		
1	48	-48
3	96	-89
5	163	-154
7	87	-84
9	20	30
11	124	-136
13	167	-196
15	20	1
K = 2 L = -9		
0	182	-172
2	22	23
4	10	12
6	165	-157
8	31	-22
10	40	-36
12	78	-88
14	9	-8
K = 3 L = -9		
1	24	-16
3	29	-4
5	17	16
7	67	64
9	146	154
11	92	-101
13	91	-104
K = 4 L = -9		
0	57	-52
2	174	168
4	155	153
6	15	-6
8	129	129
10	89	102
12	79	88
K = 5 L = -9		
1	59	52
3	96	-88
5	38	-41
7	75	70
9	140	145
11	75	-78
K = 6 L = -9		
4	33	-31
6	45	-43
8	61	-59
K = 0 L = -8		
0	48	45
2	212	207
4	107	102
6	42	-38
8	360	361
10	142	140
12	95	-100
14	230	260
16	152	180
18	25	32
K = 1 L = -8		
3	187	184
5	62	58
7	96	-92
9	49	-39
11	77	74
13	79	84
15	48	53
17	109	-135
K = 2 L = -8		
0	112	-108
2	97	-98
4	57	-60
6	69	-66
8	64	70
10	151	-146
12	184	-196
14	89	95
16	11	2
18	93	-130
K = 3 L = -8		
1	111	-108
3	77	-76
5	50	-45
7	164	-160
9	197	-198
11	41	-37
13	60	-63
15	118	-136
17	110	-135
K = 4 L = -8		
0	73	72
4	11	14
6	41	39
8	7	-25
10	39	39
12	91	92
14	35	-41
16	20	-12
K = 5 L = -8		
1	84	83
3	25	-25
5	156	150
7	125	126
9	13	12
11	118	123
13	84	90
K = 6 L = -8		
0	99	99
2	31	-29
4	84	86
6	208	202
8	91	-90
10	31	25
12	206	226
K = 7 L = -8		
3	159	-152
5	72	-73
7	18	18
9	11	-11
11	74	-79
13	83	-94
K = 8 L = -8		
0	46	-51
2	31	-26
4	75	-69
6	97	-93
8	193	-199
10	25	-9
12	31	38
K = 9 L = -8		
3	53	-48
5	102	-102
7	56	55
9	112	112
K = 1 L = -7		
1	34	18
3	43	43
5	312	285
7	129	119
9	30	23
11	170	157
13	148	146
15	107	101
17	99	108
19	53	73
K = 2 L = -7		
0	221	217
2	90	-84
4	51	-34
6	290	268
8	69	61
10	14	19
12	103	105
14	45	-50
16	155	172
18	130	157
20	105	-140
K = 3 L = -7		
1	187	-174
3	23	-11
5	253	228
7	271	-248
9	236	-218
11	179	182
13	38	38
15	161	-169
17	63	-66
19	38	42
K = 4 L = -7		
0	36	35
2	323	-294
4	328	-307
6	85	83
8	92	-86
10	241	-238
12	155	-149
14	213	-221
16	45	44
18	16	-20
K = 5 L = -7		
1	184	-179
3	23	-23
5	216	196
7	82	-86
9	130	-125
11	2	10
13	69	70
17	79	-93
K = 6 L = -7		
0	99	100
2	50	52
4	71	-68
6	149	145
8	196	193
10	17	-20
12	28	-18
14	63	67
16	148	165
18	39	46
K = 7 L = -7		
1	68	67
3	243	238
7	32	30
9	156	150
11	81	80
13	149	155
15	124	143
17	26	-30
K = 8 L = -7		
0	92	-92
2	32	33
4	88	-89
6	67	-67
8	89	86
10	97	-96
12	131	-138
14	57	64
K = 9 L = -7		
1	63	-64
3	59	-56
5	162	-160
7	20	12
9	2	10
11	216	-223
13	57	-64
K = 10 L = -7		
0	142	-138
2	3	20
4	5	-2
6	147	-144
8	66	-65
10	44	-42
12	66	-69
K = 11 L = -7		
3	70	63
5	26	-32
7	93	94
K = 0 L = -6		
0	332	-338
2	280	-272
4	108	108
6	157	-144
8	579	-543
10	198	-179
12	182	168
14	288	-275
16	297	-305
18	41	-46
20	125	-146
K = 1 L = -6		
1	36	-35
3	254	-252
5	172	164
7	84	-81
9	38	-35
11	129	122
13	228	-211
17	134	143
19	90	-101
21	52	-68
K = 2 L = -6		
0	154	-164
2	152	149
4	398	385
6	35	29
8	259	-240
10	80	83
12	431	397
14	31	18
16	152	155
18	76	89
20	98	116
K = 3 L = -6		
1	196	195
3	105	97
5	167	152
7	198	175
9	217	199
11	144	131
13	98	86
15	192	187
17	117	124
19	77	83
21	84	105
K = 4 L = -6		
0	55	-53
2	64	62
4	136	-126
6	74	-77
8	120	112
10	110	-102
12	111	-105
14	59	62
16	42	-43
18	61	-67
20	15	11
K = 5 L = -6		
3	65	24
5	279	-265
7	89	-76
9	67	-58
11	247	-226
13	13	3
15	49	-52
17	208	-223
19	22	-20
K = 6 L = -6		
0	63	-56
1	52	-48
2	50	49
4	250	-233
6	181	-165
8	120	109
10	119	-109
12	246	-241
14	39	25
16	31	-39
18	121	-138
K = 7 L = -6		
1	82	75
3	232	218
5	59	-50
7	110	99
9	74	77
11	30	-28
13	191	194
15	41	45
17	59	-67
K = 8 L = -6		
0	307	319
2	29	32
4	119	-119
6	173	166
8	343	340
10	124	123
12	156	-155
14	108	108
16	271	291
K = 9 L = -6		
1	51	-50
3	110	112
5	39	40
7	32	-27
9	46	-53
11	64	61
13	97	102
15	76	-80
K = 10 L = -6		
0	76	72
2	199	-198
4	112	-111
8	90	-91
10	16	8
12	132	-138
14	136	-151
K = 11 L = -6		
1	156	-149
3	113	-108
7	103	-105
9	141	-145
11	9	-10
13	76	-81
K = 12 L = -6		
0	142	140
2	110	-109
4	16	9
6	116	115
8	12	18
10	74	73
K = 1 L = -5		
1	181	-162
3	157	-136
5	304	-269
7	67	-65
9	172	-155
11	367	-338
13	36	-31
15	70	-62
17	228	-226
19	67	-77
21	64	-74
K = 2 L = -5		
0	260	-275
2	121	112
4	134	-125
6	45	-48
8	143	-131
10	309	-287
12	48	44
14	105	98
16	249	-232
18	184	-185
20	89	103
22	12	-15
K = 3 L = -5		
1	254	263
3	68	-69
5	364	-353
7	457	426
9	348	325
11	442	-410
13	70	64
15	243	225
17	26	-23
19	58	66
21	61	-63
K = 4 L = -5		
0	59	-65
2	365	374
4	297	286
6	312	301
8	28	20
10	9	-14
12	424	388
14	355	325
16	40	-39
18	29	-30
20	258	285
K = 5 L = -5		
3	11	-6
5	87	-82
7	189	175
9	102	95
11	280	-259
13	91	81
15	141	138
17	60	-61
21	36	-43
K = 6 L = -5		
0	221	-222
2	108	-108
4	86	83
6	27	24
8	357	-335
10	120	-110
12	115	105
14	59	-62
16	104	-104
18	128	-136
20	5	-5
K = 7 L = -5		
1	234	-231
3	243	-239
5	120	-120
7	152	-140
9	80	-71
11	190	-173
13	242	-236
15	74	-76
17	14	1
19	144	-158
K = 8 L = -5		
2	104	-102
4	244	232
6	134	127
8	184	-171
10	138	125
12	140	138
14	48	-49
16	87	95
18	30	31
K = 9 L = -5		
1	91	-89
3	148	137
5	323	310
7	74	-67
9	39	-36
11	243	241
13	73	74
15	31	14
17	88	98
K = 10 L = -5		
0	150	156
2	13	-17
4	91	86
6	77	77
8	89	91
10	160	158
12	17	11
14	13	-8
16	147	157
K = 11 L = -5		
1	66	-66
3	63	-61
5	29	-34
7	142	-142
9	122	-122
11	36	35
13	80	-88
15	113	-122
K = 12 L = -5		
0	17	-4
2	61	-57
4	164	-164
6	130	-128
8	77	75
10	63	-67
12	172	-173
K = 13 L = -5		
1	27	27
3	56	54
5	23	-12
7	55	-51
9	103	-99
K = 0 L = -4		
0	457	472
2	676	683
4	355	-331
6	443	390
8	749	701
10	76	-64
12	210	190
14	307	280
16	134	116
18	210	210
20	129	129
22	49	50
K = 1 L = -4		
1	114	107
3	356	332
5	37	23
7	206	-189
9	105	-90
11	52	47
13	360	328
15	87	-81
17	350	-322
19	229	229
21	141	148
23	132	-150
K = 2 L = -4		
0	198	202
2	262	262
4	676	-642
6	250	-213
8	304	263
10	105	-93
12	178	-160
14	187	-169
16	55	-35
18	73	70
20	87	-85
22	106	-117
K = 3 L = -4		
1	344	-334
3	59	-64
5	137	-118
7	520	-457
9	291	-249
11	90	-76
13	119	-111
15	220	-199
17	245	-233
19	57	-62
21	35	-37
K = 4 L = -4		
0	66	-61
2	106	-96
4	300	264
6	109	98
8	145	-124
10	124	111
12	90	84
14	22	-20
16	106	94
18	22	3
20	12	-27
22	93	99
K = 5 L = -4		
1	21	-3
3	143	132
5	282	253
7	226	209
9	273	253
11	91	-85
13	121	112
15	263	256
17	29	-23
19	25	24
K = 6 L = -4		
0	31	27
2	57	-56
4	472	465
6	159	-153
8	381	356
10	129	120
12	46	-41
14	154	147
16	63	63
18	38	35
K = 7 L = -4		
1	153	-147
3	254	-254
5	85	-84
7	10	-11
9	91	-86
11	281	-264
13	160	159
15	186	-197
K = 8 L = -4		
0	344	-355
2	334	-337
4	223	212
6	88	-83
8	415	-395
10	153	-140
12	45	-41
14	2	-11
16	164	-159
18	197	-201
K = 9 L = -4		
1	130	132
3	223	-219
5	195	-192
7	267	251
9	57	53
11	161	-162
13	100	-96
15	44	40
17	135	129
K = 10 L = -4		
0	74	67
2	117	119
4	108	109
6	85	80
8	99	99
10	17	28
12	74	79
14	178	175
16	27	-30
K = 11 L = -4		
1	228	241
3	28	-23
5	28	-25
7	355	357
9	84	85
11	74	-72
13	146	150
15	127	125
K = 12 L = -4		
0	75	-74
2	35	-37
4	81	-78
6	32	25
8	16	8
10	186	-185
12	38	-37
14	106	105
K = 13 L = -4		
3	89	-94
5	120	-125
9	73	-74
11	121	-119
K = 14 L = -4		
0	23	14
2	16	-22
4	154	-155
6	70	-73
8	36	31
K = 1 L = -3		
1	138	123
3	732	719
5	337	307
7	143	-127
9	290	249
11	466	406
13	144	134
15	65	58
17	147	133
19	111	110
21	131	132
23	91	92
K = 2 L = -3		
0	225	225
2	130	-130
4	400	365
6	72	58
8	19	4
10	507	447
12	135	-126
14	72	-66
16	382	351
18	13	5
20	54	-50
22	117	118
K = 3 L = -3		
1	806	-886
3	523	512
5	453	427
7	550	-493
9	344	-307
11	153	143
13	113	101
15	68	-68
17	137	-122
19	137	-128
K = 4 L = -3		
0	91	-90
2	541	-535
4	200	-176
6	393	-344
8	365	-327
10	134	119
12	485	-448
14	361	-329
16	154	139
18	200	-193
20	221	-215
22	49	-44
K = 5 L = -3		
1	299	-295
3	577	577
5	141	131

Table 3 (*cont.*)

H	FO	FC
6	92	-92
8	102	-102
10	89	-86
K = 15 L = 1		
1	55	-55
3	18	-6
5	182	-176
K = 0 L = 2		
0	879	H
2	653	-786
4	14	5
6	290	-329
8	172	-191
10	277	-323
12	297	-335
14	132	144
16	124	-135
18	289	-298
20	19	16
K = 1 L = 2		
1	488	534
3	97	-108
5	607	-727
7	309	348
9	324	353
11	232	-269
13	165	-176
15	82	87
17	83	82
19	58	-54
K = 2 L = 2		
0	20	-11
2	160	185
4	296	340
6	76	-89
8	69	69
10	121	143
12	19	12
14	134	144
16	8	15
18	18	-21
20	127	115
K = 3 L = 2		
1	497	535
3	99	105
5	93	97
7	370	399
9	219	251
11	106	112
13	62	65
15	102	110
17	179	178
19	65	59
K = 4 L = 2		
0	44	51
2	464	-499
4	462	-485
6	199	210
8	156	-162
10	106	-114
12	25	23
14	35	-33
16	12	-10
18	17	-8
K = 5 L = 2		
1	299	-299
3	333	-345
5	132	141
7	199	-214
9	287	-318
11	54	52
13	62	-62
15	174	-180
17	26	-31
19	38	-36
K = 6 L = 2		
0	244	257
2	175	-169
4	305	-317
6	49	-58
8	165	-179
10	9	-8
12	30	30
14	255	-265
16	58	-54
18	102	93
K = 7 L = 2		
1	182	-181
3	97	101
5	449	506
7	83	-93
9	160	-168
11	210	214
13	156	163
15	22	-15
17	31	-22
K = 8 L = 2		
0	329	355
2	161	175
4	50	-52
6	206	216
8	195	206
10	76	82
12	113	114
14	20	20
16	116	114
K = 9 L = 2		
1	161	-166
3	217	233
5	186	188
7	168	-176
9	58	-55
11	62	69
13	101	98
15	27	15
K = 10 L = 2		
0	104	-106
2	209	209
4	240	-247
6	270	-275
8	59	65
10	16	-14
12	111	-107
14	107	-100
K = 11 L = 2		
1	226	-223
3	82	84
5	100	-100
7	182	-190
9	66	-66
11	133	-132
13	14	-15
K = 12 L = 2		
0	83	-82
2	157	166
4	29	29
6	16	-15
8	123	124
10	10	-3
12	19	-18
K = 13 L = 2		
1	111	115
3	161	163
5	9	-9
7	46	41
9	131	127
K = 14 L = 2		
0	14	5
2	108	112
4	113	117
6	19	10
8	5	18
K = 15 L = 2		
1	30	-33
3	139	-140
5	95	-91
K = 1 L = 3		
1	91	-89
3	285	-313
5	163	-172
7	276	-302
9	107	-123
11	26	29
13	189	-203
15	148	-161
17	14	-5
19	50	-45
K = 2 L = 3		
0	229	-225
2	361	-387
4	99	107
6	24	23
8	271	-324
10	86	-100
12	91	95
14	107	-123
16	93	-96
18	9	15
K = 3 L = 3		
1	270	276
3	474	-530
5	131	145
7	84	98
9	100	116
11	139	150
13	186	-197
15	21	22
17	204	200
K = 4 L = 3		
0	95	90
2	100	98
6	242	280
8	46	-44
10	102	111
12	297	313
14	59	63
16	19	13
18	148	138
K = 5 L = 3		
1	398	400
3	202	-205
5	109	-119
7	58	-63
9	157	172
11	138	145
13	182	-193
15	34	-32
17	126	119
K = 6 L = 3		
0	332	-318
2	20	-26
4	19	-12
6	108	-117
8	70	-70
10	132	-139
12	10	-5
14	16	-9
16	117	-110
K = 7 L = 3		
1	22	32
3	276	-297
5	326	-366
7	35	-30
9	32	31
11	199	-214
13	179	-185
K = 8 L = 3		
0	71	-66
2	285	309
6	88	-87
8	177	186
10	9	16
12	10	-13
14	93	93
16	9	-10
K = 9 L = 3		
1	196	199
3	279	287
5	68	-65
7	61	62
9	137	146
11	27	26
13	101	97
15	66	61
K = 10 L = 3		
0	140	149
2	194	199
4	32	-31
6	25	22
8	187	198
10	73	72
12	31	-30
14	87	79
K = 11 L = 3		
1	232	-225
3	10	-18
5	33	-30
7	43	-44
9	127	-131
11	124	-116
K = 12 L = 3		
0	59	57
2	99	-106
4	129	-132
6	73	-73
8	76	-73
K = 13 L = 3		
1	175	-177
3	81	77
5	116	115
7	95	-95
9	146	-136
K = 14 L = 3		
0	219	220
2	55	-48
4	64	62
6	152	146
K = 15 L = 3		
1	79	-78
K = 0 L = 4		
0	476	472
2	27	-38
4	306	338
6	126	143
8	127	145
10	246	276
12	61	65
14	17	21
16	138	140
K = 1 L = 4		
1	355	-363
3	103	-106
5	407	474
7	40	-43
9	219	-252
11	144	158
13	41	41
15	5	-4
17	47	43
K = 2 L = 4		
0	205	202
2	326	-338
4	208	-212
6	73	-82
8	68	78
10	15	-15
12	171	-194
14	70	-77
16	45	44
K = 3 L = 4		
1	308	-297
3	217	-221
5	63	-68
7	108	-120
9	206	-231
11	103	-109
13	54	-58
15	69	-71
17	87	-82
K = 4 L = 4		
0	65	-61
2	214	209
4	25	21
6	26	-27
8	83	88
10	16	-16
12	20	20
14	72	74
16	33	-30
K = 5 L = 4		
1	322	350
3	153	159
5	111	-117
7	214	226
9	187	200
11	42	-43
13	88	92
15	103	101
K = 6 L = 4		
0	26	27
2	254	277
4	15	-25
5	170	177
6	100	108
10	31	-32
12	50	46
14	133	129
K = 7 L = 4		
1	147	152
3	75	-14
5	325	-352
7	25	-17
9	111	122
11	138	-144
13	61	-62
15	26	-22
K = 8 L = 4		
0	353	-355
2	24	-15
6	89	-86
8	232	-247
10	118	-122
12	51	49
14	58	-54
K = 9 L = 4		
1	87	78
3	22	-18
5	150	-149
7	43	-43
9	125	130
11	26	-25
13	81	-77
K = 10 L = 4		
0	73	67
4	140	151
6	144	148
8	67	-64
10	77	78
12	133	120
K = 11 L = 4		
1	60	67
3	109	113
5	107	112
7	23	-23
9	116	111
K = 12 L = 4		
0	73	-74
2	87	-86
4	80	78
6	20	-18
8	186	-174
K = 13 L = 4		
1	121	-116
3	80	-74
5	10	-5
K = 14 L = 4		
0	21	14
2	77	-72
K = 1 L = 5		
1	254	261
3	89	97
5	54	60
7	177	192
9	127	136
11	22	23
13	82	88
15	95	88
K = 2 L = 5		
0	272	275
2	325	336
4	236	-260
6	46	50
8	270	292
10	9	-14
14	57	57
K = 3 L = 5		
1	102	-105
3	8	-8
5	24	24
9	106	-114
11	109	-119
13	98	98
15	26	21
K = 4 L = 5		
0	69	65
2	76	79
4	519	-562
6	170	-176
8	144	146
10	146	-159
12	154	-158
14	100	-94
K = 5 L = 5		
1	60	-60
3	57	-61
5	25	27
7	15	9
11	63	-68
13	3	2
K = 6 L = 5		
0	224	222
2	136	140
4	99	-99
6	34	41
8	154	165
10	71	73
K = 7 L = 5		
1	83	-77
3	153	151
5	284	291
7	13	1
9	50	49
11	128	124
13	67	62
K = 8 L = 5		
2	134	-135
4	16	-5
6	49	-45
8	62	-63
10	43	42
12	38	-37
K = 9 L = 5		
1	122	-126
3	124	-124
5	49	-55
7	115	-117
K = 10 L = 5		
0	153	-156
2	175	-173
4	86	82
6	49	-48
8	170	-161
K = 11 L = 5		
1	98	100
3	83	79
5	40	35
7	52	48
K = 12 L = 5		
0	9	4
2	41	39
4	156	146
6	75	70
K = 13 L = 5		
1	191	179
K = 0 L = 6		
0	340	-338
2	73	-71
4	166	-171
6	58	-62
8	59	-65
10	250	-265
12	15	-15
K = 1 L = 6		
1	239	243
3	174	-181
5	109	-112
7	85	92
9	16	-3
11	53	-56
13	27	-24
K = 2 L = 6		
0	167	-164
2	16	27
4	155	155
6	168	167
8	25	28
10	107	-112
12	109	105
K = 3 L = 6		
1	183	180
3	74	78
5	120	115
7	94	102
9	103	108
11	83	82
13	22	28
K = 4 L = 6		
0	55	-53
2	58	-52
4	31	31
6	65	-70
8	31	-34
10	46	43
12	35	-32
K = 5 L = 6		
1	299	-293
3	25	-29
5	13	9
7	162	-168
9	71	-71
11	22	-20
K = 6 L = 6		
0	60	-56
2	171	-174
4	3	6
6	82	-84
8	106	-105
10	47	43
K = 7 L = 6		
1	110	-115
3	152	154
5	114	113
7	33	-27
9	34	30
K = 8 L = 6		
0	318	319
2	141	141
6	17	2
8	113	109
K = 9 L = 6		
1	50	-50
3	82	76
5	24	-21
7	18	19
K = 10 L = 6		
0	71	72
2	20	-23
4	171	-169
6	44	-44
K = 11 L = 6		
1	13	-1
3	58	-57
K = 12 L = 6		
0	143	140
K = 1 L = 7		
1	220	-209
3	98	-99
5	71	-69
7	84	-89
9	35	-32
K = 2 L = 7		
0	225	-217
2	143	-146
4	61	58
6	33	-30
8	114	-116
10	14	-19
K = 3 L = 7		
1	13	-12
3	106	109
5	43	-39
7	63	-64
9	178	171
K = 4 L = 7		
0	42	-35
2	12	6
4	209	212
6	165	163
8	3	-1
K = 5 L = 7		
1	47	-47
3	24	-18
5	19	-17
7	29	25
9	100	91
K = 6 L = 7		
0	104	-100
2	105	-102
4	60	-59
6	42	38
8	79	-74
K = 7 L = 7		
1	14	10
3	125	-121
5	170	-156
7	38	-35
K = 8 L = 7		
0	94	92
2	36	27
4	65	-59
6	110	97
K = 9 L = 7		
1	109	102
3	28	-17
K = 10 L = 7		
0	150	138
2	110	96
K = 0 L = 8		
0	54	45
2	155	154
4	90	85
6	26	22
K = 1 L = 8		
1	190	-180
3	129	119
5	146	133
7	93	-87
K = 2 L = 8		
0	113	-108
2	49	49
4	38	-37
6	118	-112
K = 3 L = 8		
1	159	-149
3	78	-76
5	16	-14
K = 4 L = 8		
0	76	72
2	18	-13
4	44	-42
6	79	72
K = 5 L = 8		
1	183	170
5	38	35
K = 6 L = 8		
0	108	99
2	44	36
4	44	38
K = 7 L = 8		
1	104	91
3	131	-115
K = 8 L = 8		
0	51	-51
K = 1 L = 9		
1	51	46
K = 2 L = 9		
0	193	172
2	14	13
K = 3 L = 9		
1	74	-68
K = 4 L = 9		
0	64	52

Table 3 (*cont.*)

H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC
7	441	-385	K = 14 L = -3			6	136	128	1	110	94	14	64	63	10	20	-15	12	344	345			
9	190	-178	0	214	-220	8	207	194	3	948	-983	16	111	107	12	131	-136	14	155	150	K = 5 L = 1		
11	234	222	2	117	-119	10	425	-416	5	664	-625	18	54	-52	14	186	-183	16	133	-125	1	129	-142
13	201	191	4	56	54	12	183	-172	7	164	151				16	15	13				3	276	293
15	193	-178	6	123	-123	14	31	31	9	288	-268	K = 9 L = -1			18	14	16	K = 11 L = 0			5	215	233
17	121	-117	8	138	-141	16	129	-123	11	322	-291	1	71	-73	20	73	-72	1	269	281	7	176	-183
19	46	50	10	44	-46	20	94	-92	13	166	-162	3	281	292	22	109	-98	3	126	-123	9	217	-238
21	79	86							15	204	-196	5	101	99				5	189	186	11	117	126
			K = 15 L = -3			K = 7 L = -2			17	30	-22	7	38	-37	K = 3 L = 0			7	213	214	13	110	110
K = 6 L = -3			1	117	-113	1	197	189	19	76	-74	9	253	250	1	499	-521	9	39	15	15	31	-22
0	325	318	3	129	-129	3	54	48	21	192	-181	11	77	70	3	260	-263	11	127	128	17	120	-115
2	37	18				5	338	317				13	40	-37	5	455	-460	13	92	89	19	49	-39
4	29	-23	K = 0 L = -2			7	190	191	K = 2 L = -1			15	189	181	7	301	-302	15	46	41			
6	202	177	0	864	H	9	308	-302	0	117	-115	17	73	67	9	250	-251				K = 6 L = 1		
8	149	137	2	9	9	11	175	166	2	309	-283				11	216	-207	K = 12 L = 0			0	435	446
10	127	115	4	167	150	13	357	341	4	115	106	K = 10 L = -1			13	103	-102	0	42	50	2	233	236
12	26	-30	6	897	-849	15	49	-47	6	30	37	0	60	55	15	185	-182	2	115	-107	4	84	-88
14	79	72	8	997	H	17	73	-67	8	546	-517	2	170	178	17	145	-141	4	121	-118	6	126	-139
16	157	152	10	225	203	19	98	99	10	315	-286	4	116	114	19	83	-76	6	80	-83	8	278	303
18	9	13	12	35	-22				12	259	254	6	17	-25	21	89	-82	8	144	-139	10	200	211
20	30	32	14	449	-433	K = 8 L = -2			16	368	-349	8	191	189				10	72	66	12	51	-50
			16	172	-161	0	332	355	18	29	-34	10	199	191	K = 4 L = 0			12	38	-43	14	8	-6
K = -7 L = -3			18	261	-238	2	182	189	20	84	80	12	33	-33	0	287	279				16	71	67
1	136	141	20	45	-41	4	9	-6	22	107	-97	14	40	39	2	224	228	K = 13 L = 0			18	145	140
3	275	281	22	36	36	6	114	113				16	173	164	4	68	-63	1	81	-84			
5	272	272				8	380	377	K = 3 L = -1						6	173	-173	3	132	-134	K = 7 L = 1		
7	314	306	K = 1 L = -2			10	107	103	1	796	879	K = 11 L = -1			8	286	292	5	18	16	1	436	454
9	80	-76	1	79	-72	12	10	12	3	116	-111	1	283	-292	10	230	228	7	54	-56	3	135	129
11	95	86	3	327	288	14	157	155	5	258	-241	3	75	75	12	180	-185	9	186	-186	5	289	283
13	473	447	5	555	-499	16	103	99	7	432	410	5	51	54	14	5	8	11	33	-29	7	122	132
15	79	72	7	280	-247	18	156	150	9	168	-163	7	275	-277	16	158	149	13	18	20	9	17	14
17	35	-41	9	747	708	20	44	50	11	142	132	9	145	-151	18	8	1				11	328	340
19	155	156	11	131	-113				13	172	169	11	30	-19				K = 14 L = 0			13	149	142
			13	453	-434	K = 9 L = -2			15	223	-210	13	20	-14	K = 5 L = 0			0	30	-35	15	35	-35
K = 8 L = -3			15	127	121	1	163	-168	17	144	132	15	61	-57	1	104	105	2	86	-90	17	140	132
0	66	66	17	180	170	3	96	93	19	153	144				3	460	473	4	77	-79	19	133	121
2	39	42	19	53	-55	5	280	288	21	95	-89	K = 12 L = -1			5	34	27	6	23	-28			
4	273	-269	21	107	-102	7	63	-56				0	94	98	7	10	18	8	78	-74	K = 8 L = 1		
8	24	13	23	18	11	9	233	-224	K = 4 L = -1			2	102	-97	9	440	430	10	71	-71	0	187	173
10	214	-201				11	116	109	0	346	354	4	343	-349	11	56	56				2	228	-228
12	1	-3	K = 2 L = -2			13	122	119	2	308	300	8	87	90	13	48	-52	K = 15 L = 0			4	130	-135
14	35	30	0	19	-11	15	27	25	4	766	790	10	128	-129	15	252	243	1	22	21	6	62	67
16	154	-151	2	57	64	17	65	-63	6	476	455	12	147	-145	17	83	80	3	145	153	8	146	-158
18	30	-30	4	297	279	19	68	-64	8	188	-181	14	109	-106	19	21	-2	5	86	79	10	79	-81
20	34	34	6	217	183				10	126	115				21	129	116	7	41	47	12	74	73
			8	172	-164	K = 10 L = -2			12	561	557	K = 13 L = -1									14	106	-109
K = 9 L = -3			10	227	206	0	101	-106	14	298	277	1	75	-77	K = 6 L = 0			K = 16 L = 0			16	96	-92
1	176	180	12	184	168	2	264	-269	16	166	-157	3	112	-116	0	640	-697	0	142	144	18	68	57
3	183	-182	14	21	7	4	97	-89	18	113	110	5	94	96	2	366	368						
5	286	-283	16	119	109	6	142	-138	20	296	279	9	117	-118	4	679	729	K = 1 L = 1			K = 9 L = 1		
7	53	50	18	32	-27	8	86	79	22	52	46	11	60	-48	6	103	-106	1	86	93	1	101	-106
9	111	-108	20	69	63	10	76	-69				13	60	58	10	118	123	3	559	654	3	310	-329
11	153	-146	22	140	134	12	307	-308	K = 5 L = -1						12	114	116	5	419	468	5	61	63
13	11	9				16	89	84	1	558	585	K = 14 L = -1			14	237	226	7	139	147	7	30	-34
15	141	-138	K = 3 L = -2			18	96	-93	3	377	-382	0	254	266	16	15	18	9	119	120	9	267	-264
17	107	-104	1	537	543				5	422	-422	2	84	90	18	84	-80	11	135	150	11	15	-14
19	42	43	3	395	363	K = 11 L = -2			7	410	404	4	123	-127	20	136	125	13	197	210	15	147	-141
			5	74	60	1	322	-335	9	88	75	6	198	202				15	181	187	17	35	-28
K = 10 L = -3			7	365	327	3	46	35	11	68	-64	8	180	178	K = 7 L = 0			19	38	39			
0	142	-149	9	519	479	5	39	42	13	70	-75	10	23	-17	1	54	-53	21	175	164	K = 10 L = 1		
2	33	-31	11	164	148	7	296	-293	15	72	-67				3	103	-107				0	53	-55
4	144	-139	13	108	99	9	148	-156	17	179	176	K = 15 L = -1			5	275	-269	K = 2 L = 1			2	207	-214
6	38	-36	15	162	146	11	12	-4	19	14	9	1	49	49	7	148	-157	0	117	115	4	69	-76
8	91	-91	17	205	188	13	139	-133	21	116	-110	3	14	22	9	199	206	2	581	660	6	62	57
10	249	-248	19	173	167	15	37	-34				5	148	148	11	142	-146	4	74	74	8	249	-250
12	19	22	21	39	29				K = 6 L = -1			7	69	64	13	307	-300	6	424	-468	10	134	-136
14	30	21				K = 12 L = -2			0	434	-446				15	112	104	8	523	571	12	78	73
16	211	-205	K = 4 L = -2			0	82	-82	2	95	-92	K = 0 L = 0			19	139	-130	10	306	311	14	107	-102
18	67	-62	0	83	51	2	48	44	4	397	400	2	205	210				12	235	-254	16	112	-106
			2	185	177	4	201	210	6	266	-251	4	729	-780	K = 8 L = 0			14	109	114			
K = 11 L = -3			4	245	-227	6	76	-78	8	438	-421	6	721	763	0	632	-639	16	150	145	K = 11 L = 1		
1	182	186	6	102	-84	8	19	22	10	15	2	8	662	693	2	85	-85	18	31	33	1	218	226
3	103	-102	8	140	-128	10	156	154	12	64	61	10	406	413	4	97	94	20	73	65	5	32	-30
5	44	52	10	104	-98	12	19	-26	14	9	2	12	51	46	6	237	-248				7	144	144
7	236	240	12	135	127	14	30	21	16	207	-201	14	74	-82	8	225	-236	K = 3 L = 1			9	191	202
9	135	139	14	78	-72				18	137	-132	16	321	315	10	215	-212	1	263	272	11	29	34
11	20	-18	16	197	-179	K = 13 L = -2			20	98	94	18	337	334	12	22	-23	3	409	462	15	57	52
15	158	158	18	47	41	1	15	-17				22	75	-68	14	25	-18	5	291	-310			
			20	50	48	3	99	101	K = 7 L = -1						16	190	-185	7	326	-340	K = 12 L = 1		
K = 12 L = -3			22	81	-80	5	116	116	1	228	-227	K = 1 L = 0			18	133	-119	9	66	67	0	94	-98
0	55	-57				7	32	39	3	50	46	1	28	-23				11	39	45	2	63	64
2	134	136	K = 5 L = -2			9	113	108	5	384	-369	3	53	-46	K = 9 L = 0			13	72	-74	4	203	81
4	198	202	1	55	54	11	54	53	7	372	-370	5	2	1	1	108	118	17	112	-111	6	171	175
6	34	27	3	437	-419				9	58	-60	7	188	181	3	205	-218	19	48	-47	8	51	-48
8	28	20	5	176	-159	K = 14 L = -2			11	88	-86	9	368	-389	7	28	22	21	123	114	12	155	147
10	77	77	7	83	84	2	26	18	13	245	-234	11	107	101	9	15	14						
12	154	148	9	473	-420	4	107	116	15	138	-132	13	332	337	11	4	-6	K = 4 L = 1			K = 13 L = 1		
14	64	62	11	173	-165	6	99	106	17	76	-74	15	241	-237	13	106	-106	0	349	-354	1	35	-33
			13	120	114	8	13	25	19	134	-129	17	31	-29	15	36	32	2	42	44	3	56	56
K = 13 L = -3			15	231	-214	10	31	31				19	139	137	17	27	28	4	448	-481	5	59	-61
1	88	85	17	175	-173				K = 8 L = -1			21	55	-50				6	813	-895	7	63	62
3	67	-63	19	26	16	K = 15 L = -2			0	187	-173				K = 10 L = 0			8	230	244	9	148	144
5	35	-34	21	80	-77	1	16	-10	2	138	131	K = 2 L = 0			0	143	-153	10	30	29	11	125	-117
7	27	-15				3	104	-107	4	369	354	0	596	685	2	70	68	12	493	-523			
9	192	190	K = 6 L = -2			5	147	-145	6	155	-161	2	400	-408	4	317	328	14	129	-125	K = 14 L = 1		
11	51	50	0	238	257	7	32	-36	8	29	31	4	462	-474	6	250	253	16	48	-44	0	249	-266
13	206	-199	2	298	-296				10	231	236	6	92	90	8	136	-140	18	90	-88	2	29	-42
			4	634	-629	K = 1 L = -1			12	56	-56	8	81	-76	10	113	-111	20	77	-71	4	12	-15

Table 4. Al–O *bond distances and angles*

Al–O bond distances

Al(1)–O(3)	1·729 Å	Al(2)–O(3)	1·716 Å
Al(1)–O(2)	1·744	Al(2)–O(1)	1·752
Al(1)–O(2)†	1·753	Al(2)–O(4)†	1·779
Al(1)–O(4)*	1·789	Al(2)–O(4)	1·804

Bond angles

O(3)–Al(1)–O(2)	113·64°	O(3)–Al(2)–O(1)	121·07°
O(3)–Al(1)–O(2)†	104·37	O(3)–Al(2)–O(4)†	111·32
O(3)–Al(1)–O(4)*	118·18	O(3)–Al(2)–O(4)	105·64
O(2)–Al(1)–O(2)†	109·89	O(1)–Al(2)–O(4)†	109·63
O(2)–Al(1)–O(4)*	104·83	O(1)–Al(2)–O(4)	99·38
†O(2)–Al(1)–O(4)*	105·55	†O(4)–Al(2)–O(4)	107·75

The superscripts on the oxygen atoms indicate the positions relative to the basis atoms in Table 2.
* Position $\frac{1}{2}-x,\frac{1}{2}-y,\bar{z}$.
† Position $x,\bar{y},\frac{1}{2}+z$.

only be achieved after additional electron spin resonance and optical measurements have been performed on the doped sample, when the exact symmetry of the sites should become obvious.

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A Study of the Crystal structure of β-Cyclotetramethylene Tetranitramine by Neutron Diffraction

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The crystal structure of β-cyclotetramethylene tetranitramine has been reinvestigated by means of neutron diffraction. Least-square refinement of all positional and anisotropic thermal parameters with 545 non-zero reflections yielded a final R value of 0·059. The heavy-atom parameters obtained agree with those from X-ray determinations except for slight position shifts of a few atoms. The positions of the hydrogen atoms have been determined for the first time. All hydrogen atoms are located close to nearby oxygen atoms, a few of which form intramolecular or intermolecular hydrogen bonds of the type C–H···O. Several short intramolecular and intermolecular distances between oxygen and other atoms have been measured.

Introduction

Cyclotetramethylene tetranitramine, known as HMX, is a well-known explosive and a high-melting-point by-product in the manufacture of RDX. β-HMX is the room temperature stable phase of the four known polymorphic forms, whose crystallographic data are summarized in the paper of Cady, Larson & Cromer (1963). The positions of the heavy-atoms were reported by Eiland & Pepinsky (1955) from a three-dimensional X-ray investigation using an isotropic bulk temperature factor. The same data were further refined by Cady, Larson & Cromer (1963) using anisotropic temperature factors, but hydrogen positions were not reported. In the present work, the structure is reinvestigated to

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