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The average crystal structure of $\gamma\text{-Na}_2\text{CO}_3$. By G.C. DUBBELDAM and P.M. DE WOLFF, *Delft University of Technology, Werkgroep Microstructuur, Lorentzweg 1, Delft, Netherlands*

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$\gamma\text{-Na}_2\text{CO}_3$ is a deformed version of the hexagonal α -phase structure. This was shown by successful refinement of a corresponding trial structure (symmetry $C2/m$) to $R=12.8\%$ for 313 independent reflexions, the indices hkl being integers. The satellite reflexions which correspond to the actual modulated structure were not included in this refinement, so that it refers to the average structure only. The main feature of the modulation is apparent from the fact that the average structure contains two CO_3 ions with half atoms. The modulation can, accordingly, be described as an ordered distribution of anions over two orientations.

Though it is one of the most common compounds, Na_2CO_3 is still a white patch on the map of crystal structures. The present analysis shows a possible cause for this remarkable fact: the room temperature or γ -phase possesses a modulation anomaly, so unexpected in such a chemically trivial compound that it may have baffled early workers and just been forgotten afterwards.

At room temperature, Na_2CO_3 crystallizes in a C -centred monoclinic lattice with the following parameters (23°C):

$$a = 8.90, b = 5.24, c = 6.04 \text{ \AA}, \beta = 101.2^\circ; Z = 4.$$

This phase was termed the γ -phase by Brouns, Visser & de Wolff (1964; 'BVW'). It shows up to 6 sharp satellites for each normal reflexion, corresponding to rows in the reciprocal lattice. The row containing the normal reflexion hkl is given by

$$(i) \quad \mathbf{h} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{p}^* \quad (1)$$

where m is a small integer and $\mathbf{p}^* = 0.182\mathbf{a}^* + 0.318\mathbf{c}^*$.

Further properties of these satellites are:

(ii) With increasing temperature, the fractional components of \mathbf{p} decrease continuously from the above values to, e.g. $\mathbf{p}^* = 0.154\mathbf{a}^* + 0.286\mathbf{c}^*$ at 300°C .

Table 1. Atomic coordinates for $\gamma\text{-Na}_2\text{CO}_3$

First three columns: final averaged structure.

Last three columns: $\alpha\text{-Na}_2\text{CO}_3$ on orthohexagonal axes.

	x	y	z	x	y	z
$4 \times \frac{1}{2}\text{Na}(1) \quad g$	0.000	0.018	0.000	0.000	0.000	0.000
$4 \times \frac{1}{2}\text{Na}(2) \quad h$	0.000	0.022	0.500	0.000	0.000	0.500
$8 \times \frac{1}{2}\text{Na}(3) \quad j$	0.172	0.544	0.749	0.167	0.500	0.750
$8 \times \frac{1}{2}\text{C} \quad j$	0.163	0.488	0.251	0.167	0.500	0.250
$8 \times \frac{1}{2}\text{O}(1) \quad j$	0.123	0.255	0.314	0.101	0.300	0.250
$8 \times \frac{1}{2}\text{O}(2) \quad j$	0.291	0.491	0.173	0.300	0.500	0.250
$8 \times \frac{1}{2}\text{O}(3) \quad j$	0.079	0.676	0.255	0.101	0.700	0.250

Table 2. Measured and calculated structure factors

The columns are L , F_o , F_c .

hkl	F_o	F_c	L	F_o	F_c	L	
1 0 0	326	331	4 40 27	4 225 216	1 31 95	0 29 26	4 136 135
2 0 0	323	312	5 11 19	5 11 19	0 22 20	1 14 8	5 13 17
3 0 0	324	305	6 12 23	6 12 23	3 122 121	2 41 34	6 29 20
4 0 0	327	294	7 13 28	7 13 28	4 157 145	3 122 121	7 43 46
5 0 0	321	281	8 14 33	8 14 33	5 149 135	4 157 145	8 59 55
6 0 0	317	268	9 15 38	9 15 38	6 122 121	5 149 135	10 75 71
7 0 0	311	255	10 16 43	10 16 43	7 13 15	6 39 44	12 91 87
8 0 0	305	242	11 17 48	11 17 48	8 14 42	7 14 12	14 107 103
9 0 0	299	229	12 18 53	12 18 53	9 15 38	8 30 50	16 123 119
10 0 0	293	216	13 19 58	13 19 58	10 16 43	9 46 62	18 139 135
11 0 0	287	203	14 20 63	14 20 63	11 17 48	10 62 78	20 155 151
12 0 0	281	190	15 21 68	15 21 68	12 18 53	11 78 94	22 171 167
13 0 0	275	177	16 22 73	16 22 73	13 19 58	12 94 110	24 187 183
14 0 0	269	164	17 23 78	17 23 78	14 20 63	13 110 126	26 203 199
15 0 0	263	151	18 24 83	18 24 83	15 21 68	14 126 142	28 219 215
16 0 0	257	138	19 25 88	19 25 88	16 22 73	15 142 158	30 235 231
17 0 0	251	125	20 26 93	20 26 93	17 23 78	16 158 174	32 251 247
18 0 0	245	112	21 27 98	21 27 98	18 24 83	17 174 190	34 267 263
19 0 0	239	99	22 28 103	22 28 103	19 25 88	18 190 206	36 283 279
20 0 0	233	86	23 29 108	23 29 108	20 26 93	19 206 222	38 299 295
21 0 0	227	73	24 30 113	24 30 113	21 27 98	20 222 238	40 315 311
22 0 0	221	60	25 31 118	25 31 118	22 28 103	21 238 254	42 331 327
23 0 0	215	47	26 32 123	26 32 123	23 29 108	22 254 270	44 347 343
24 0 0	209	34	27 33 128	27 33 128	24 30 113	23 270 286	46 363 359
25 0 0	203	21	28 34 133	28 34 133	25 31 118	24 286 302	48 379 375
26 0 0	197	8	29 35 138	29 35 138	26 32 123	25 302 318	50 395 391
27 0 0	191	-5	30 36 143	30 36 143	27 33 128	26 318 334	52 411 407
28 0 0	185	-12	31 37 148	31 37 148	28 34 133	27 334 350	54 427 423
29 0 0	179	-19	32 38 153	32 38 153	29 35 138	28 350 366	56 443 439
30 0 0	173	-26	33 39 158	33 39 158	30 36 143	29 366 382	58 459 455
31 0 0	167	-33	34 40 163	34 40 163	31 37 148	30 382 398	60 475 471
32 0 0	161	-40	35 41 168	35 41 168	32 38 153	31 398 414	62 491 487
33 0 0	155	-47	36 42 173	36 42 173	33 39 158	32 414 430	64 507 503
34 0 0	149	-54	37 43 178	37 43 178	34 40 163	33 430 446	66 523 519
35 0 0	143	-61	38 44 183	38 44 183	35 41 168	34 446 462	68 539 535
36 0 0	137	-68	39 45 188	39 45 188	36 42 173	35 462 478	70 555 551
37 0 0	131	-75	40 46 193	40 46 193	37 43 178	36 478 494	72 571 567
38 0 0	125	-82	41 47 198	41 47 198	38 44 183	37 494 510	74 587 583
39 0 0	119	-89	42 48 203	42 48 203	39 45 188	38 510 526	76 603 599
40 0 0	113	-96	43 49 208	43 49 208	40 46 193	39 526 542	78 619 615
41 0 0	107	-103	44 50 213	44 50 213	41 47 198	40 542 558	80 635 631
42 0 0	101	-110	45 51 218	45 51 218	42 48 203	41 558 574	82 651 647
43 0 0	95	-117	46 52 223	46 52 223	43 49 208	42 574 590	84 667 663
44 0 0	89	-124	47 53 228	47 53 228	44 50 213	43 590 606	86 683 679
45 0 0	83	-131	48 54 233	48 54 233	45 51 218	44 606 622	88 699 695
46 0 0	77	-138	49 55 238	49 55 238	46 52 223	45 622 638	90 715 711
47 0 0	71	-145	50 56 243	50 56 243	47 53 228	46 638 654	92 731 727
48 0 0	65	-152	51 57 248	51 57 248	48 54 233	47 654 670	94 747 743
49 0 0	59	-159	52 58 253	52 58 253	49 55 238	48 670 686	96 763 759
50 0 0	53	-166	53 59 258	53 59 258	50 56 243	49 686 702	98 779 775
51 0 0	47	-173	54 60 263	54 60 263	51 57 248	50 702 718	100 795 791
52 0 0	41	-180	55 61 268	55 61 268	52 58 253	51 718 734	102 811 807
53 0 0	35	-187	56 62 273	56 62 273	53 59 258	52 734 750	104 827 823
54 0 0	29	-194	57 63 278	57 63 278	54 60 263	53 750 766	106 843 839
55 0 0	23	-201	58 64 283	58 64 283	55 61 268	54 766 782	108 859 855
56 0 0	17	-208	59 65 288	59 65 288	56 62 273	55 782 798	110 875 871
57 0 0	11	-215	60 66 293	60 66 293	57 63 278	56 798 814	112 891 887
58 0 0	5	-222	61 67 298	61 67 298	58 64 283	57 814 830	114 907 903
59 0 0	-1	-229	62 68 303	62 68 303	59 65 288	58 830 846	116 923 919
60 0 0	-7	-236	63 69 308	63 69 308	60 66 293	59 846 862	118 939 935
61 0 0	-13	-243	64 70 313	64 70 313	61 67 298	60 862 878	120 955 951
62 0 0	-19	-250	65 71 318	65 71 318	62 68 303	61 878 894	122 971 967
63 0 0	-25	-257	66 72 323	66 72 323	63 69 308	62 894 910	124 987 983
64 0 0	-31	-264	67 73 328	67 73 328	64 70 313	63 910 926	126 1003 1000
65 0 0	-37	-271	68 74 333	68 74 333	65 71 318	64 926 942	128 1019 1015
66 0 0	-43	-278	69 75 338	69 75 338	66 72 323	65 942 958	130 1035 1031
67 0 0	-49	-285	70 76 343	70 76 343	67 73 328	66 958 974	132 1051 1047
68 0 0	-55	-292	71 77 348	71 77 348	68 74 333	67 974 990	134 1067 1063
69 0 0	-61	-299	72 78 353	72 78 353	69 75 338	68 990 1006	136 1083 1079
70 0 0	-67	-306	73 79 358	73 79 358	70 76 343	69 1006 1022	138 1099 1095
71 0 0	-73	-313	74 80 363	74 80 363	71 77 348	70 1022 1038	140 1115 1111
72 0 0	-79	-320	75 81 368	75 81 368	72 78 353	71 1038 1054	142 1131 1127
73 0 0	-85	-327	76 82 373	76 82 373	73 79 358	72 1054 1070	144 1147 1143
74 0 0	-91	-334	77 83 378	77 83 378	74 80 363	73 1070 1086	146 1163 1159
75 0 0	-97	-341	78 84 383	78 84 383	75 81 368	74 1086 1102	148 1179 1175
76 0 0	-103	-348	79 85 388	79 85 388	76 82 373	75 1102 1118	150 1195 1191
77 0 0	-109	-355	80 86 393	80 86 393	77 83 378	76 1118 1134	152 1211 1210
78 0 0	-115	-362	81 87 398	81 87 398	78 84 383	77 1134 1150	154 1227 1227
79 0 0	-121	-369	82 88 403	82 88 403	79 85 388	78 1150 1166	156 1243 1243
80 0 0	-127	-376	83 89 408	83 89 408	80 86 393	79 1166 1182	158 1259 1259
81 0 0	-133	-383	84 90 413	84 90 413	81 87 398	80 1182 1198	160 1275 1275
82 0 0	-139	-390	85 91 418	85 91 418	82 88 403	81 1198 1214	162 1291 1291
83 0 0	-145	-397	86 92 423	86 92 423	83 89 408	82 1214 1230	164 1307 1307
84 0 0	-151	-404	87 93 428	87 93 428	84 90 413	83 1230 1246	166 1323 1323
85 0 0	-157	-411	88 94 433	88 94 433	85 91 418	84 1246 1262	168 1339 1339
86 0 0	-163	-418	89 95 438	89 95 438	86 92 423	85 1262 1278	170 1355 1355
87 0 0	-169	-425	90 96 443	90 96 443	87 93 428	86 1278 1294	172 1371 1371
88 0 0	-175	-432	91 97 448	91 97 448	88 94 433	87 1294 1310	174 1387 1387
89 0 0	-181	-439	92 98 453	92 98 453	89 95 438	88 1310 1326	176 1403 1403
90 0 0	-187	-446	93 99 458	93 99 458	90 96 443	89 1326 1342	178 1419 1419
91 0 0	-193	-453	94 100 463	94 100 463	91 97 448	90 1342 1358	180 1435 1435
92 0 0	-199	-460	95 101 468	95 101 468	92 98 453	91 1358 1374	182 1451 1451
93 0 0	-205	-467	96 102 473	96 102 473	93 99 458	92 1374 1390	184 1467 1467
94 0 0	-211	-474	97 103 478	97 103 478	94 100 463	93 1390 1406	186 1483 1483
95 0 0	-217	-481	98 104 483	98 104 483	95 101 468	94 1406 1422	188 1499 1499
96 0 0	-223	-488	99 105 488	99 105 488	96 102 473	95	

(iii) The $(h0l)$ plane $k=0$ is free from satellites.

These findings, reported without comment in BVW, can easily be translated into real space:

Re (i). Such a diffraction image is the well-known result of a modulation of the structure. A modulation can occur as a substitutional type, such as described recently by Jamieson, de Fontaine & Abrahams (1969). In Na_2CO_3 , however, such a defect seems hardly possible. The only remaining possibility is that of a displacement modulation. This means that the coordinates of the j th atom in the unit cell q, r, s , (taken from a fixed origin) can be written:

$$x_{jqs} = \bar{x}_j + x_j^d(w_{jqs})$$

with similar equations for y and z . Here \bar{x}_j is a fixed average coordinate value, whereas the displacement component x_j^d is a periodic function, averaging zero and with period 1, of

$$w_{jqs} = \mathbf{p}^* \cdot (qa + rb + sc).$$

Thus planes of constant displacement \bar{x}_j^d are perpendicular to \mathbf{p}^* , and repeat at a distance $1/|\mathbf{p}^*|$ which in the present case is 16.3 \AA .

Re (ii). Description of the structure as normal (unmodulated) based on some super-cell cannot be exact, since such a description is in conflict with the continuous change of \mathbf{p}^* with temperature.

Re (iii). The displacements are parallel to \mathbf{b} , since the b -projection is unmodulated. This means that the displacements must be parallel to the \mathbf{p}^* -wave front. In terms of the modulation function it means $x^d = z^d = 0$.

The present analysis is based upon normal reflexions [$m=0$ in equation (1)].

The resulting electron density – provided phases are assigned correctly – is the average of the actual distribution over all unit cells. Hence we expect each atom to show up in this distribution as a peak elongated in the y direction, or even split up into two peaks, depending on the amplitude and wave form of its modulation function y_j^d . Accordingly, we started by looking mainly at the b -projection, which can be expected to be unambiguous.

As a first trial structure we used a model derived from the hexagonal α -form (BVW; structure derived by Bijk & Wissler, 1969) because the γ -form, after loosing its satellites at 360°C , transforms into the α -form at 489°C without discontinuities in the cell parameters. The coordinates of the α -form with respect to orthohexagonal axes are given in Table 1. The space group $C2$ was arbitrarily chosen. Though eventually disproved (see below) it gave the correct symmetry in the $(h0l)$ projection; a later trial with Cm did not lead to a good refinement.

The main uncertainty was the orientation of the CO_3 ions. Using step-wise refinement (Bhuiya & Stanley, 1963) successively for the Eulerian angles of this group and for the other coordinates, a reasonable agreement between F_c and F_o (at this stage from integrated precession photographs) was obtained, first for the $h0l$ reflexions, then also for the $h1l$ reflexions. Higher k values were not used at this stage because the strength of the satellites in high k layers is such that to aim at a high accuracy of y coordinates is pointless until an explanation of the satellites has been found. Further refinements were based on integrated Weissenberg photographs (taken with $\text{Mo } K\alpha$ radiation) of a crystal rotating about the b axis. The largest dimension of the crystal was $\sim 0.5 \text{ mm}$; no absorption correction was applied. Atomic form factors were taken from Moore (1963), and the least-

squares refinement program used a single isotropic temperature factor. This led to a disagreement index $R = \Sigma |F_o - |F_c|| / \Sigma F_o = 17\%$ for 102 $h0l$ reflexions and 84 $h1l$ reflexions including those not observed. The corresponding structure is shown in Fig. 1.

Though all distances are reasonable – including those within a single CO_3 ion – the $h1l$ reflexions showed some large discrepancies. Moreover, in all these cases $\text{Im}(F_c)$ was large and $|F_c| > F_o$. Since the imaginary part arises from the departure of the structure from $C2/m$ symmetry (mainly caused by the two O atoms almost coinciding in the b -projection) and since the good agreement for $h0l$ reflexions shows that projection to be essentially correct, the solution is clear: there must be two alternative orientations [related by an (010) mirror plane] for each CO_3 ion. This hypothesis is corroborated by the drop in the R index to 14.35% for the same reflexions as before, just by doubling the anion in the way indicated. The last refinements (of the y coordinates only) have accordingly been performed in the space group $C2/m$. The R index became 12.8% using 102 $h0l$, 84 $h1l$, 72 $h2l$ and 55 $h3l$ reflexions. For these refinements a program of the Bhuiya–Stanley type has been used; the layer scale factors were obtained from a least-squares program. The results are shown in Tables 1 and 2.

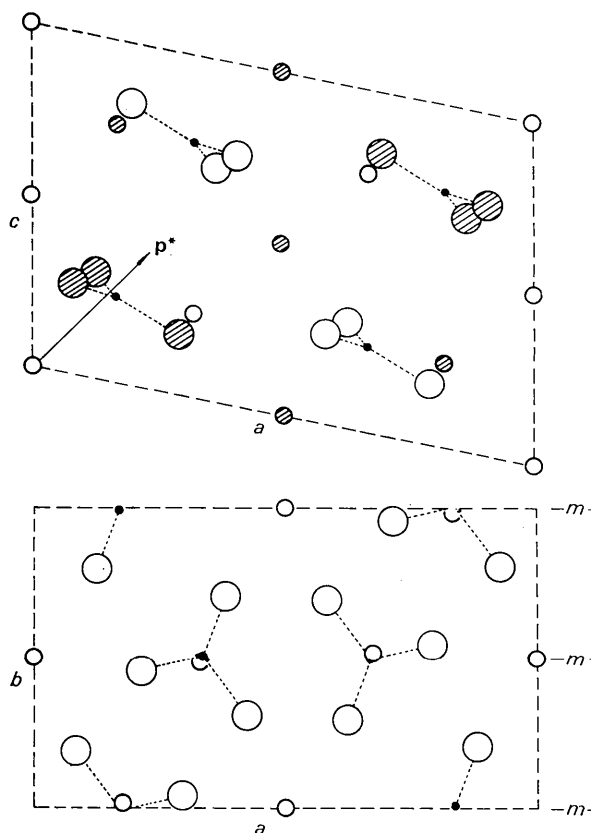


Fig. 1. Trial structure with $C2$ symmetry. Above: projection along b ; below: projection along c . Dots: C; large circles: O; small circles: Na. Na and O atoms at or near $y=0$ are open, those at or near $y=1/2$ are hatched in the b projection. The average structure with symmetry $C2/m$ is obtained from this Figure by superposing it with its mirror image formed by mirror planes m at the levels indicated in the lower Figure.

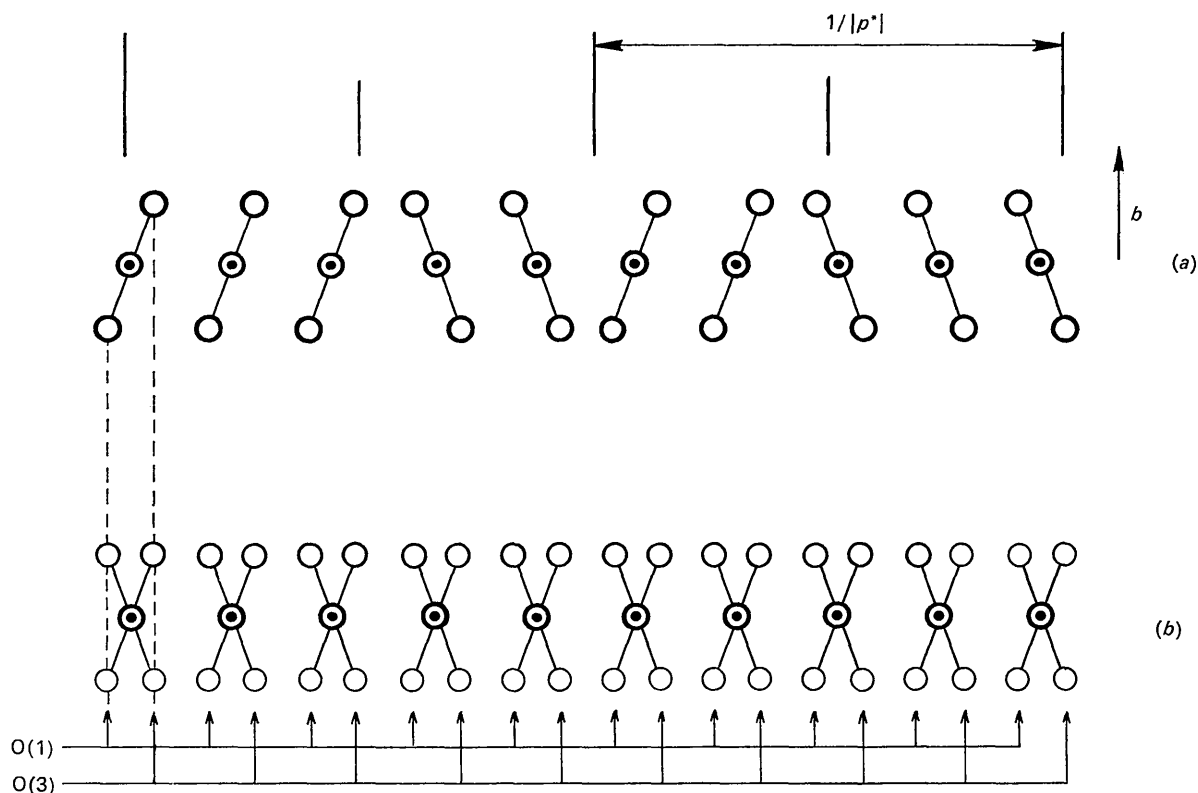


Fig. 2. Schematic projection of the anions: (a) in the actual modulated structure; (b) in the average structure. The projection direction is perpendicular to \mathbf{p}^* and \mathbf{b} , and the C-O(2) direction is supposed to be parallel to it so that C and O(2) coincide in the centre of each projected anion. As seen from Fig. 1, this is not quite true.

The presence of two 'half' carbonate ions at once makes clear the main feature of the modulation: the satellites of the γ -phase allow us to explain the double atoms of the anion as the split atoms representing an atom in the average electron density distribution of the structure, as discussed above. If there had been no satellites, the double anion would have had to have been ascribed to disorder in the anion orientation (this is most probably the situation for the β -phase above 360°C). Therefore the modulation can also be described as a complete ordering of the anion orientations.

The atoms O(1) and O(3) have a large modulation amplitude, and their modulation function y^d is roughly a square wave. A very schematic projection of the anions in a direction perpendicular to \mathbf{p}^* and \mathbf{b} (Fig. 2) illustrates this situation. The complete determination of the modulation amplitudes and wave forms of all atoms in the unit cell will require an elaborate analysis of the satellite intensities. So

far, attempts at such an analysis have shown that the order of magnitude of these intensities does agree with the proposed model.

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