

Physics. — "*Investigation by means of X-rays of the crystal-structure of sodium-chlorate and sodium-bromate*". Communication N°. 5 from the Laboratory of Physics and Physical Chemistry of the Veterinary College at Utrecht. By N. H. KOLKMEIJER, J. M. BIJVOET and A. KARSSSEN. (Communicated on behalf of Prof. W. H. KEESOM, Director of the Laboratory, by Prof. KAMERLINGH ONNES).

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§ 1. *Introduction.* For biological science every deepening of our insight into the nature of the chemical bindings of the element carbon, so important for the organic world, will be of great value. In connexion with the investigation of the structure of the modifications of the element carbon itself this point has already been in discussion¹⁾. Also the close connexion between the atoms of the group CO₂ that has been stated in calcite²⁾ forms an important datum for the purpose. Therefore we originally intended to investigate the crystal-structure of other carbon-compounds. Sodium-carbonate and sodium-hydrocarbonate first came into consideration because of their importance for animal life. Considering however that we could expect to meet with great difficulties in these investigations especially in the calculations as a consequence of the crystal-water resp. the monoclinic crystal-system, we first investigated some substances with analogous structure, for which these difficulties were not to be expected. We chose sodium-chlorate and sodium-bromate both crystallizing in the cubic system. We also hoped that these substances might give us some indications on the remaining together of the atoms of the acid-radical.

§ 2. *Present knowledge on NaClO₃ and NaBrO₃.* In P. GROTH's *Chemical Crystallography*, the crystalforms are described into which NaClO₃ and NaBrO₃ can crystallize under different circumstances. When crystallized from solutions in water these substances give at

¹⁾ P. DEBIJE and P. SCHERRER, *Phys. ZS.* **19**, (1918) p. 476.

D. COSTER, *These Proceedings*, **28**, (1919) p. 391.

N. H. KOLKMEIJER, *Comm.* N°. 4; *These Proceedings*, **28**, (1920) p. 767.

²⁾ W. H. and W. L. BRAGG, *X-Rays and Crystal-Structure*. London, 1918.

roomtemperature cubic tetartohedral forms. Both of the chlorate and of the bromate two enantiomorphous forms occur. In connexion with this phenomenon the crystals themselves show rotation of the plane of polarisation for every direction of the rays, while the solutions are non-active. The polar ternary axes are electric axes. With regard to these properties we thought it desirable to determine the structure of these crystals.

BECKENKAMP¹⁾ investigated already this structure theoretically; his conclusions were however not confirmed by our investigations.

W. H. and W. L. BRAGG²⁾ simply mention, that in the crystals of sodium-chlorate the places of the sodium- and Cl-atoms differ very little from those in sodium-chloride. From the following it will be evident that on the whole we agree with this opinion.

JAEGER and HAGA³⁾ took LAUE-photograms of NaClO₃; they did not derive details on the structure from them.

§ 3. *The apparatus used.* This was equal to that, described in a preceding communication⁴⁾. This time the finely powdered substance was divided as equally as possible by means of a little collodion on a glass rod (diameter $\pm 0,1$ mm.) in a layer less than 0,5 mm. The rod was fixed to the lid of the camera; by means of this lid it could be turned about its length axis during the exposure in order to avoid the scratches on the interference fringes caused by greater crystal-particles, which hinders the determination of the intensities⁵⁾. Because of the small depth of the layer the correction for the thickness of the rod, given in Communication N°. 2⁶⁾, was now much smaller than it was then. The glass core of the rod gave no difficulties.

§ 4. *Calculation of the crystal-structure.* In the tables I and II are to be found for the chlorate resp. the bromate in the columns

¹⁾ Comp. J. BECKENKAMP, *Z. f. anorg. u. allg. Chemie*, **110**, (1920) p. 290.

²⁾ W. H. and W. L. BRAGG, *X-Rays and Crystal-Structure*, London 1918. p. 173.

³⁾ F. M. JAEGER, *These Proceedings* Vol. 17 (1915) p. 1204.

⁴⁾ A. J. BIJL and N. H. KOLKMEIJER, *These Proceedings* **21** (1918) p. 408. Communication N°. 1.

⁵⁾ That these scratches touch the interference fringes has been explained l.c. p. 407. This time some films taken without turning of the rod showed also intersecting scratches; this intersecting can be explained in the indicated way when the height of the exposed part of the substance is taken into consideration. By decrease of this height the intersections vanished.

⁶⁾ A. J. BIJL and N. H. KOLKMEIJER, *These Proceedings*, **21** (1918) p. 496, Comm. N°. 1.

TABLE I.

Na Cl O₃

Distances in 0.1 mm and estimated intensities	$10^3 \sin^2 \frac{\theta}{2}$ (corrected)	Cu _{Kα_1} -radiation			Cu _{Kβ} -radiation		
		Σh^2	$10^3 \sin^2 \frac{\theta}{2}$ (calculated)	$h_1 h_2 h_3$	Σh^2	$10^3 \sin^2 \frac{\theta}{2}$ (calculated)	$h_1 h_2 h_3$
1.	2.	3.	4.	5.	6.	7.	8.
90 f	26	2	27	110			
114 f	41	3	41	111			
121 vf	47				4	45	200
132 s	56	4	55	200	5	56	210
147 vs	69	5	69	210	6	67	211
164 m	83	6	82	211			
				221			
199 m	125	9	124	300	11	124	311
				310			
211 vf	139	10	138	311	14	157	321
221 f	152	11	151	311			
241 vf	180	13	179	320			
250 vs	193	14	193	321			
				322			
278 f	234	17	234	410			
				331			
296 vf	262	19	261	331			
				421	26	292	431
312 f	288	21	289	421			510
				431			
353 m	358	26	358	510			

TABLE II.

Na Br O₃

Distances in 0.1 mm and estimated intensities	$10^3 \sin^2 \frac{\theta}{2}$ (corrected)	Cu _{Kα_1} -radiation			Cu _{Kβ} -radiation		
		Σh^2	$10^3 \sin^2 \frac{\theta}{2}$ (calculated)	$h_1 h_2 h_3$	Σh^2	$10^3 \sin^2 \frac{\theta}{2}$ (calculated)	$h_1 h_2 h_3$
1.	2.	3.	4.	5.	6.	7.	8.
98 fm	25	2	25	110			
119 vf	39	3	39	111			
136 fm	52	4	53	200	5	54	210
149 vs	64	5	66	210	6	65	211
165 f	79	6	79	211			
182 fff	97				9	97	221
							300
				221			
201 vf	119	9	119	300			
224 vf	152				14	151	321
250 vs	184	14	184	321			
				322			
274 vf	221	17	224	410			
				331			
293 vf	251	19	250	331			
308 f	275	21	276	421	26	280	431
							510
331 vf	313	24	316	422			
				431			
347 s	342	26	342	510			

1 the distance from the central part of the image on the film to the interference fringes, expressed in 0,1 mm. and the estimated intensities. In the columns 2 are given the values of $10^3 \sin^2 \frac{\theta}{2}$ calculated from these data. In the ordinary way the numbers, referring to β -lines, have been separated. In accordance with the cubic crystal-form of both substances it was then found that the values of $10^3 \sin^2 \frac{\theta}{2}$ of the α -lines possess a common factor viz. for the chlorate $A_\alpha = 13,79$ and for the bromate $A_\alpha = 13,16$. The columns 3, 5, 6, and 8 contain derived from these the indices triplets (resp. the sums of their squares) of the lines; the columns 4 and 7 the values of $10^3 \sin^2 \frac{\theta}{2}$ calculated with the mentioned values of A . From the obtained values of A_α we find, in connexion with the molecular weights, the densities (resp. 2,496 and 3,254), the number of Avogadro $6,062 \cdot 10^{23}$) and the wave-length of the $\text{Cu}_{K\alpha_1}$ -radiation ($1,537 \cdot 10^{-8}$ cm) for the number of molecules per elementary cell resp. 3,98 and 3,93. This number is therefore for both $4^{1)}$. This gives for the edge of the elementary-cell $6,55 \cdot 10^{-8}$ and $6,74 \cdot 10^{-8}$ for chlorate and bromate resp.

Then we investigated which grouping of these 4 Na-, 4 Cl- resp. Br- and 12 O-particles in the cell fulfils the symmetry demands that can be derived from the crystal-forms (viz. three binary axes, four polar ternary axes, rotation of the plane of polarisation). The model obtained in the following way fulfils these demands (see fig. 1).

Divide the cell into 8 cubes, draw in four of them that have only edges in common a cross-diagonal so that they do not intersect. Place on one of the diagonals arbitrarily a sodium- and a halogen-particle. The places of the other sodium- and halogen-particles are then found directly by means of the ternary axes.

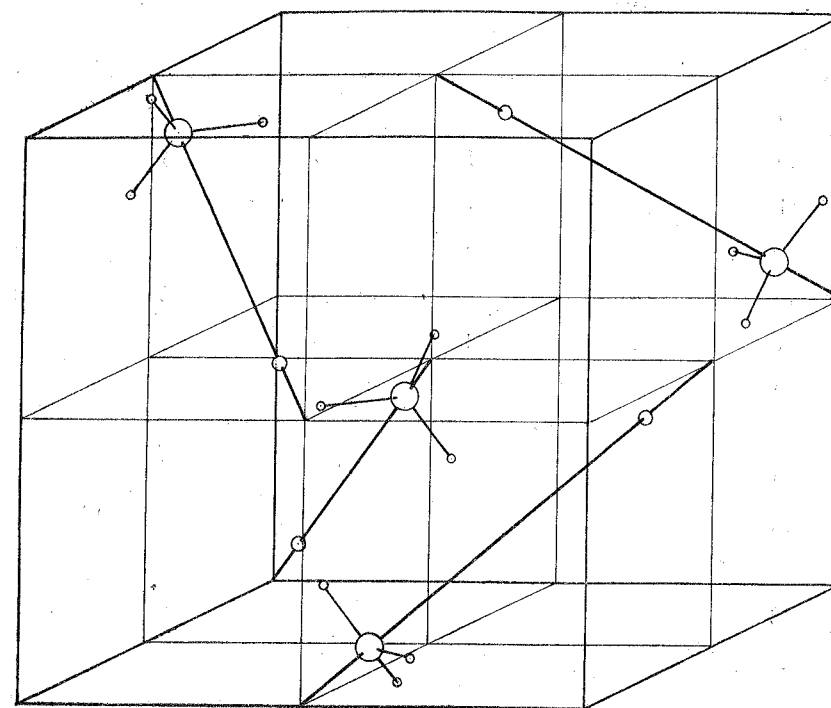
Place one oxygen-particle arbitrarily, the places of the other ones follow then again.

The described model cannot cover its mirror-image (see fig. 2) which is in agreement with the optical activity.

For the calculation of the places of the atoms we chose as parameters, one of the three equal rectangular coordinates of one of the sodium particles a (expressed in the side of the cell as unit), one of the three equal coordinates of one of the halogen particles

¹⁾ The essential difference with the model given by BECKENKAMP (l.c. p. 300) is that there this number is 16 (or 2 in a cube with an edge of half the value), which is in contradiction with our film.

$\frac{1}{2} - b$ and the three coordinates p , q and r of one of the oxygen particles. With the values $a = \frac{1}{12}$, $b = \frac{1}{12}$, $p = \frac{1}{2}$, $q = \frac{5}{12}$, $r = \frac{11}{36}$ we found intensities of the lines which suffice both for the chlorate and for the bromate, as is shown by the tables III and IV. The possible



$\bigcirc = \text{Cl}$

$\circ = \text{Na}$

$\cdot = \text{O}$

Fig. 1.

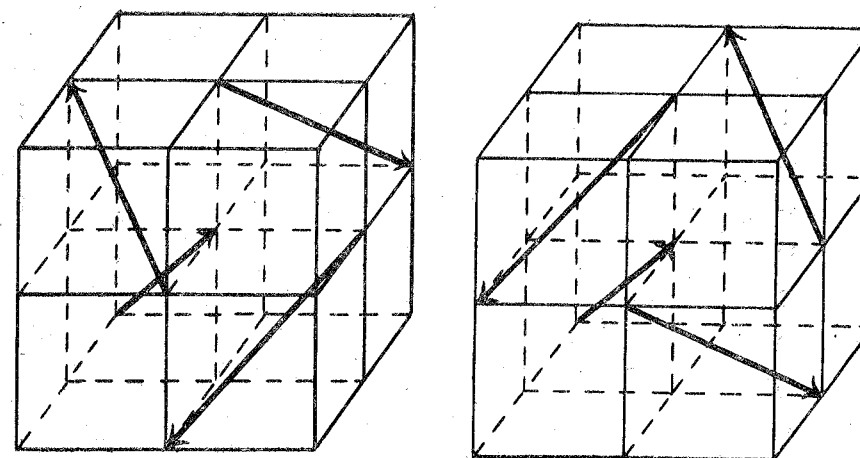


Fig. 2.

TABLE III.

Planes	INTENSITY				
	Observed	Calculated			
		A	B	C	D
100	?	0	0	0	0
110	f	137	146	55	5
111	f	47	70	22	4
200	s ¹⁾	80	95	57	32
210	vs	395	444	252	123
211	m	114	139	80	44
220	—	0	0	1	3
221	m	54	70	37	24
300		0	0	0	0
310	vf	5	10	2	0
311	f ²⁾	18	22	13	9
222	—	8	7	2	0
320	vf	12	8	4	1
321	vs	147	194	115	73
400	—	1	4	3	5
322	f	12	6	4	1
410		41	62	35	26
330	—	20	13	7	1
411		5	13	7	9
331	vf	36	47	24	23
420	—	31	26	15	6
421	f ³⁾	34	22	12	11
332	—	29	19	10	1
422	—	1	6	1	1
430	—	6	5	2	0
500		0	0	0	0
431	m	27	36	24	26
510		13	5	4	1

¹⁾ at the same time β -line of 210 vs. ²⁾ at the same time β -line of 321 vs.
³⁾ at the same time β -line of 431 m.

TABLE IV.

Planes	INTENSITY				
	Observed	Calculated			
		A	B	C	D
100	?	0	0	0	0
110	fm	376	391	228	97
111	vf	216	261	155	88
200	fm ¹⁾	179	197	143	100
210	vs	864	881	643	409
211	f	288	324	228	159
220	—	3	9	9	16
221	vf	149	179	107	97
300		0	0	0	0
310	—	53	91	54	46
311	f ²⁾	41	50	37	32
222	—	23	32	19	16
320	—	36	61	32	33
321	vs	393	471	338	260
400	—	11	19	15	1
322	vf	16	21	12	11
410		136	172	125	102
330	—	20	13	7	1
411		33	52	39	42
331	vf	92	115	85	73
420	—	46	43	30	19
421	f ³⁾	43	33	43	59
332	—	29	19	10	1
422	vf	30	50	30	25
430	—	19	32	19	17
500		0	0	0	0
431	s	78	144	96	112
510		8	10	6	6

¹⁾ at the same time β -line of 210 vs. ²⁾ at the same time β -line of 321 vs.
³⁾ at the same time β -line of 431 s.

error in the value of b for the bromate is about 0,01 of the cell-edge, the accuracy of the other parameters is much smaller¹⁾.

In the calculation of the intensities we have taken into consideration besides the structure factor²⁾ only the number of planes and the LORENTZ-factor. We thus have neglected the absorption in the rod, the temperature-factor and the polarisation-factor. This is allowed, when only we compare the intensities of very close neighbouring interference fringes.

Starting from the assumption that the X-rays are deflected for the greater part by the electrons, we calculated the intensities under the following simplifying assumptions.

Round the sodium point we place 10 electrons (monovalent positive ion)³⁾; the weakening of the coöperation by mutual interference is neglected. Round the halogen particles we place in the cases *A*, *B*, *C*, and *D* of the columns 3, 4, 5, and 6 of the tables III and IV respectively 12, 18, 12, and 10 electrons for the chlorate and 30, 36, 30, and 28 electrons for the bromate, while again the same neglects were made; in the same way for an oxygen particle resp. 10, 8, 6, and 2 electrons. All this is based upon the following suppositions:

in case *A*: pentavalent positive halogen-ions and bivalent negative oxygen atoms;

in case *B*: monovalent negative halogen-ions and oxygen-atoms;

in case *C*: binding of oxygen in the halogenate-ion by a ring of four circulating electrons, of which two are derived from the oxygen-atom and two from the halogen-atom. The interference-effect by these binding-electrons has been neglected;

in case *D*: binding between halogen and oxygen, where the effect due to the total outer electron rings, to which the binding electrons belong, has been neglected.

From the tables III and IV we see that the agreement between the calculated and observed intensities is good from which of these suppositions we may start.

¹⁾ This must be ascribed to the fact that the displacements of the Br-particles can only be very small when their influence on the interference-result shall be compensated by displacements of the other particles. This is the case to a much less degree for the Cl-particle because of its low atomic number. Therefore we cannot give a limit of the accuracy of the parameters either for this particle or for the O- and Na-particles.

²⁾ In the calculation of the structure-factor we took into consideration, that for planes with three unequal indices for the symmetry of these crystals this factor depends on the succession of the indices. Comp. W. H. and W. L. BRAGG, l.c. p. 151.

³⁾ P. DEBIJE and P. SCHERRER, Phys. ZS. 19 (1918), p. 474.

From the values found for the parameters it is evident that each time three oxygen-particles are lying close round each halogen-particle; the plane of the three oxygen-particles perpendicular to a ternary axis contains, approximately at least, the halogen-particle. The distance between the centres of a halogen- and one of those neighbouring oxygen-particles is about $\frac{1}{7}$ of the parameter of the lattice¹⁾. The situation of the groups Na^+ and ClO_3^- resp. BrO_3^- can be found from the NaCl-model by diminishing the distance between the opposite ions all by about $\frac{1}{8}$ of their value.

Finally we wish to express our indebtedness to Prof. KEESOM for his kindness to place his laboratory at our disposal for this investigation and for his great interest and help.

¹⁾ (Note, added during translation). Quantitatively these values are not in accordance with the data of BRAGG (Phil. Mag. (6) 40 (1920) p. 169. The distances of the centres of an O- and a Cl-atom or a Br-atom, which, according to BRAGG's data ought to be $1.70 \cdot 10^{-8}$ and $1.84 \cdot 10^{-8}$ respectively are found by us as $0.910 \cdot 10^{-8}$ and $0.937 \cdot 10^{-8}$ respectively. This discrepancy is not astonishing, seeing 1 that in note 1) of the preceding page some reserve is made about the accuracy of the parameters for the O-particles; 2 that BRAGG expects a shortening of the distance in discussion in radicals in which there is strong binding.

We thought it desirable however, to investigate this point nearer, with this aim new photos will be taken and discussed by two of us (B. and Ka). The intensities of the lines with the smallest radii especially, lying in a dark part of the film, can perhaps be determined more accurately, when an antikathode is used, which gives a larger wavelength and when the radius of the camera is enlarged.