

- I. THE CRYSTAL STRUCTURES OF WULFENITE
AND SCHEELITE.
- II. THE CRYSTAL STRUCTURES OF SODIUM CHLORATE
AND SODIUM BROMATE.
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THE CRYSTAL STRUCTURES OF SODIUM CHLORATE AND SODIUM BROMATE

I. Introduction.

In the study of the crystal structures of wulfenite and scheelite a number of possible sources of difficulty came to light which either would not be encountered or could be avoided in the study of sodium chlorate by the Bragg method. Large crystals could be obtained without serious difficulty and on these any desired face could be ground, a necessary precaution that could not be taken with the borrowed specimens of the previous research. This would eliminate gross ambiguities as to the amount of absorption suffered by the X-ray beam, and also permit definition of the relative areas of crystal operating in the successive orders of reflection. On the interpretive side, although the various atoms involved differ in atomic number sufficiently for their effects to be easily distinguishable, they are all included within a sufficiently limited range so that their contributions to the amplitude of the reflected wave would be expected to be sufficiently near proportional to their atomic numbers. It seemed advisable to make measurements on sodium bromate also since this salt is completely isomorphous with the chlorate.

2. Crystallography of Sodium Chlorate and Bromate.

Since due regard for symmetry must be had in making measurements as well as interpreting the data a brief description of the crystallography of these salts is not out of place at this point;

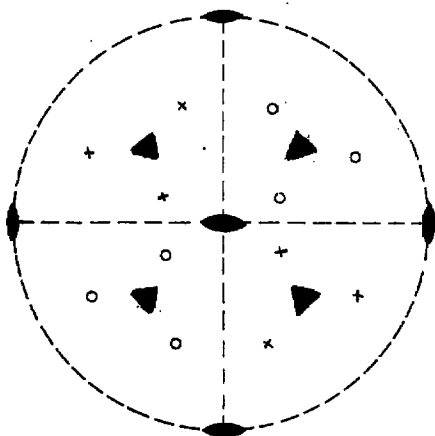


Fig. 1.

for a fuller discussion Groth's "Physikalische Krystallographie" and his "Chemische Krystallographie" may be consulted.

The forms of the salts here studied belong to the tetrahedral pentagonal dodecahedral class of the cubic system; this is the class of lowest possible symmetry in the

cubic system being characterized by the possession of only digonal and trigonal axes. The stereographic projection of the position of these axes is shown in Fig. 1.

In this class the form $\{100\}$ constitutes the six faces of a cube. All twelve faces of the rhombic dodecahedron $\{110\}$ are equivalent. $\{111\}$ and $\{\bar{1}\bar{1}\bar{1}\}$ are represented by positive and negative tetrahedra respectively; in their position of derivation, faces of one form are parallel to those of the other. Hence, in the absence of difference of change in phase on reflection from different atoms, these two forms should be indistinguishable in their spectra.¹

¹ See W. H. and W. L. Bragg "X-rays and Crystal Structure" p. 137; also data on these faces given below.

$\{h k o\}$ and $\{k h o\}$ are represented by left and right pentagonal dodecahedra, respectively. In their position of derivation no face of one form is parallel to any face of the other form; hence the two may give distinct X-ray spectra. Removed from their position of derivation the two forms are geometrically indistinguishable; hence there is less ambiguity in the data obtained if all pentagonal dodecahedral forms studied are in effect cut from a single specimen.

The absence of a center of symmetry in this class implies the existence of two enantiomorphously distinct structures. Since both the chlorate and the bromate are optically active, it is very easy to distinguish the two forms by the direction of rotation of the plane of polarized light. It does not, however, seem possible to determine by X-rays which of the two structures is possessed by a right-handed crystal and which by a left, either in this particular case or in any case of enantiomorphy. For consider the spectra from any face (hkl) of any enantiomorphous crystal. If we operate on the structure by an inversion about any convenient point, the enantiomorphously distinct structure is obtained. The effect on the atom-planes parallel to (hkl) is, however, simply a reversal of order and not a change in character or spacing. Hence a passage from one enantiomorphous form to the other produces no change in the X-ray spectra, and enantiomorphy does not exist for these properties. The validity of this generalization is evidently dependent on that of the absence

of difference of change of phase on reflection mentioned above.

Other possible forms in this class were not measured.

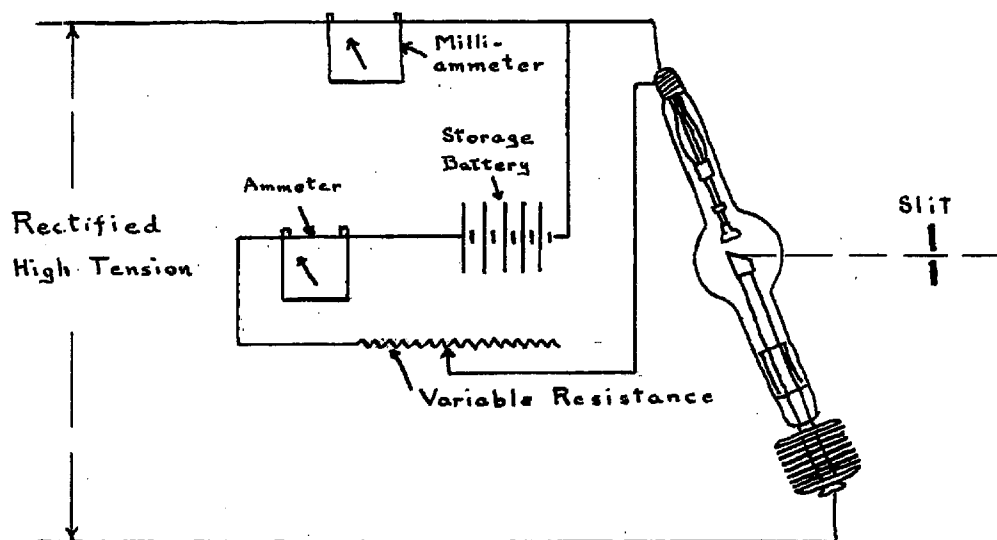


Fig. 2.

3. Apparatus and Procedure.

Several changes in the apparatus used in studying scheelite were made in the present investigation. The source of X-rays was a fine-focus Coolidge tube of the radiator type provided with a molybdenum target. The target was inclined 45° to the beam of cathode rays but when set up made an angle of not more than 20° with the line of slits. No difficulty was experienced that seemed assignable to a wandering of the anticathode spot.

The apparatus for controlling the tube current is indicated in Fig. 2. The filament current in the Coolidge tube was supplied by a 10-volt storage battery in series with a continuously variable

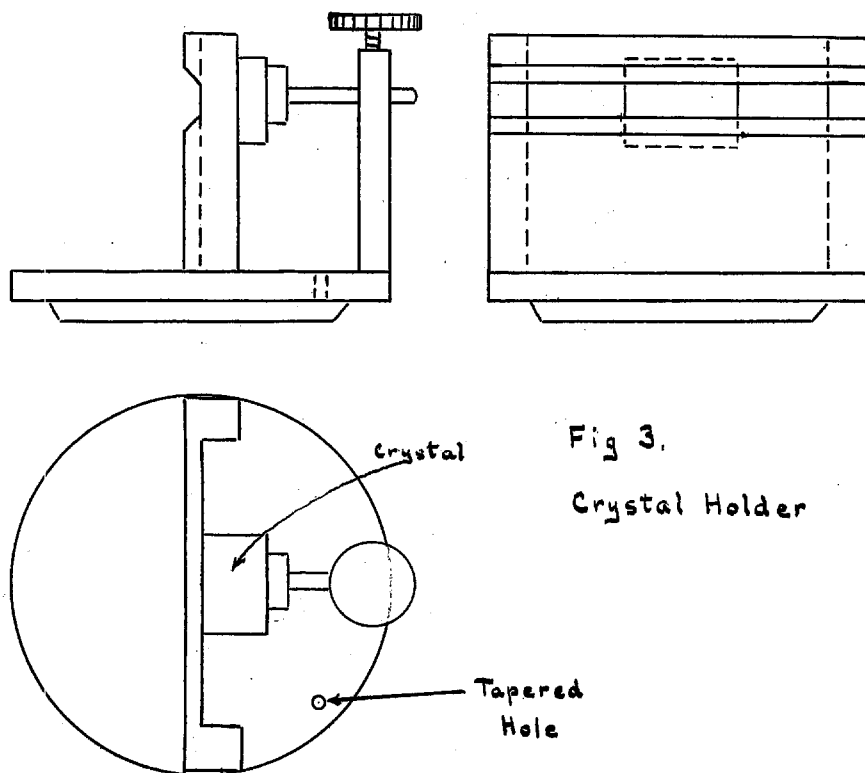
small resistance so insulated that it could be altered while the tube was in operation. The tube current was maintained constant by placing a milliammeter in series with the tube and keeping the readings of this instrument constant with the aid of the variable resistance. The ~~filament~~ tube current varies too rapidly with and is not sufficiently uniquely determined by the filament current to permit adequate control of the former by simply fixing the value of the latter. The tube was ordinarily operated with 2.5 milliamperes at 70,000 volts.

With the angles once determined, a set of intensity measurements could ordinarily be made in the course of half or three-quarters of an hour. A given reflection measured several times in such an interval showed a percentage deviation of 2.0, 0.5, 1.1, and 0.9% in several sets of data chosen at random; the electroscope deflection in these cases was moderately large. With weaker reflections the percentage deviation was probably somewhat greater. These values indicate the reproducibility of the measurement of relative intensities so far as fluctuations in the electrical parts of the apparatus and the ionization-chamber contents are concerned.

The crystals of sodium chlorate were prepared from a U. S. P. product by slow cooling of a saturated solution in a thermostat. The crystals were formed between 40° and 30° and had chiefly cube faces. Only a comparatively small amount of the salt was allowed

to crystallize from the solution. The sodium bromate was prepared electrolytically from the bromide, and recrystallized. The crystals were formed on suspended seeds by slow evaporation of a saturated solution in a desiccator at room temperature, and were chiefly tetrahedra. In at least one case of each face studied, the face was ground off with fine emery on plate glass using carbon tetrachloride as a lubricant, the crystal being mounted on a tripod with legs of adjustable length permitting the angle of grinding to be varied. With the aid of this device it was found possible easily to grind the face to within less than $15'$ of the desired angle, this accuracy apparently being adequate for the present purpose. After this apparatus was developed, a Fuess instrument identical with it in principle was found described in Groth's "Physikalische Krystallographie," 4th edition, p. 798. Details can be found in that place.

In order to make definite the relative areas of crystal which took part in successive reflections from a given face a slit defining the incident beam was moved up to 3.5 cm. from the crystal. As the distance from the target to this slit was about 28 cm. and as the anticathode spot was small, the beam on reaching the crystal could be very little wider than the slit. A crystal face was used having a horizontal dimension sufficiently great to cover the entire incident beam. With an angle of incidence of 5° and a $0.3/\text{mm.}$ slit



the minimum length of face permissible is $0.3/\sin 5^\circ$ or 3.5 mm. The length of face used was usually at least twice this amount. The one slit used to define the incident beam was not so placed as to get the benefit of the focussing effect described by Bragg. The specimens used were, however, sufficiently perfect that this caused no trouble.

Attempt was also made to compare the intensities of reflection from various faces of the crystals. With this end in view two crystal holders such as is shown in Fig. 3 were constructed. The area of crystal taking part in the reflection was limited vertically

by the slotted brass shield against which the crystal was placed. In each holder was a conical hole through which passed a conical pin into a corresponding hole in the spectrometer table. This last device permitted the removal of the holder from the spectrometer after the determination of angles, and its accurate replacement. With the aid of two holders, intensities of reflection from two separate crystals could be measured in immediate succession. On one holder was permanently mounted a crystal whose intensity of reflection was used as a reference unit throughout the investigation. On the other holder was temporarily mounted the specimen under consideration. By always measuring intensities of reflection in terms of this arbitrary reference crystal unit, the intensities of reflection from various faces could be compared with each other. The reference reflection chosen was that of the second order from a cubic cleavage face of rock salt; the intensity of this was of the order of magnitude of many of those to be compared with it.

An interesting difficulty was encountered in studying the reflections from a (110) face of sodium chlorate.. A large crystal was set up, not using one of the holders described above, with two cube faces vertical and the other four making 45° angles with a horizontal plane. The vertical dimension of the prepared face was over 10 mm. The chamber and crystal angles for two reflections were found; with the aid of these, the reflections in the entire region

between chamber angles of 2° and 33° were measured rotating the crystal half as fast as the chamber. In this manner peaks were found at chamber angles of $9^\circ 10'$, $13^\circ 40'$, $18^\circ 0'$, and $27^\circ 0'$. If each of these is divided by two and a correction of $11'$ subtracted from each of the results, the glancing angles $4^\circ 24'$, $6^\circ 39'$, $8^\circ 49'$, and $13^\circ 19'$ are obtained. These seemed to be the angles of reflection for the second, third, fourth and sixth orders respectively, consistently with the fundamental equation $n \lambda = 2d \sin D$; for on dividing the sines of these angles by 2, 3, 4, and 6 respectively the numbers 0.0384, 0.0386, 0.0384, 0.0384 are obtained.

Now any face of a crystal may be regarded as made up of a great number of obliquely set planes of some other indices; consequently a given crystal boundary is capable of giving reflections corresponding to a number of different planes. If the crystal and slits have moderately large vertical dimensions, reflections from a number of different planes, but from the same boundary of the crystal, may enter the ionization chamber; moreover, analytical investigation has shown that when the crystal is set with an important zone axis horizontal, as in the above case, these reflections, although coming from faces whose spacings have irrational ratios, may enter the ionization chamber at angles very nearly in accord with the sine law and thus appear to come from a single face.

That this was taking place in the case of the (110) spectra was clearly shown photographically. A photographic plate was set up perpendicular to the incident beam and in place of the ionization chamber. The crystal (with the same setting as above) was rotated slowly and uniformly through a region sufficient to include the above lines. The reflections which had been called the second, fourth and sixth orders showed on the plate. The line which had been called the third order showed strongly but was not in a row with the others and clearly did not belong to the (110) spectra. Other lines from other faces were also in evidence. Now if the crystal is moved in such a way that (110) remains vertical but other faces are rotated, and a photograph taken as before, the real reflections from (110) should persist but those from other faces undergo alteration. A photograph was made in the same manner as the previous one but with 2 cube faces horizontal and 4 vertical. The lines previously called the second, fourth and sixth orders, were the only ones common to the two photographs. By setting up the crystal with no important zone axis horizontal, it was found possible to isolate these three lines for intensity measurement. All of the lines recorded below were given similar tests to insure their coming from the plane under consideration.

In the measurement of intensities an integration method similar to that described by Bragg¹ was employed. The ionization

¹W. H. Bragg, Phil. Mag. 27, 881, (1914)

chamber with not too wide a slit was set on a previously measured angle of maximum reflection; then the crystal was uniformly rotated through an angular range (usually 1°) sufficient to give substantially all of the peak in question, and the total deflection of the electroscope was read. To correct for general radiation similar integrations were made through the proper angles on each side of the peak where no strong homogeneous radiation was included and a mean subtracted from the deflection at the peak. The imperfections of the crystals in the present research were probably not sufficiently great to render very necessary the employment of an integration method; however, it eliminated the possibility of errors from this source and any that might have arisen in the intensities from small errors in the crystal angles.

In determining the chamber angles the slit next to the crystal was kept at 0.3 mm. and the chamber slit at 0.5 mm. In measuring the intensities the chamber slit was opened to 1.0 mm. to avoid affecting the intensities by crystal imperfections or small errors in the chamber angle.

4. The Experimental Data.

Observations on sodium chlorate and sodium bromate, all of which were obtained using the crystal holders described above, are given in Tables I and II, respectively. The chamber angles have been treated in the same way as those for wulfenite and

scheelite. Exception to this was made in the case of the 201 and $10\bar{2}$ faces where only one reflection was found in each case, and in the case of the 301 face where the second order reflection was too weak to give precision to the measurement of angle; in these instances the zero correction applied was the mean of the corrections found in other cases, the same crystal holder being used throughout. In the eighth column are given the relative intensities of various orders from single faces; in the ninth column are given the intensities of the separate reflections as compared with that of the reference unit.

It will be noticed that the intensity of the first order from the cube face of sodium chlorate is much less from the natural face than from a face whose surface has been ground off; the same is true of the bromate. In the case of another chlorate crystal not recorded in the table the intensity from a natural face was found to be 0.43 whereas the same face after slight grinding gave an intensity of 1.12. A similar phenomenon was observed by Compton¹, who says "if the reflecting surface of a crystal of calcite is roughened by grinding, the reflection coefficient is some three times as great as from a cleavage face. The grinding makes the surface of the crystal imperfect, and thus greatly

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A. H. Compton, Phys. Rev. 10, 95, 1917.

Table I. - Reflection Data

Plane and Specimen	Order n	Half of Observed Chamber angle	Zero Point $\frac{1}{2}^\circ$	Corrected Angle of Reflection, $\frac{1}{2}^\circ$	n
100 C	I II III	$6^\circ 11\frac{1}{2}'$ $12 \quad 27$ $18 \quad 52\frac{1}{2}$	$0'$	$6^\circ 11\frac{1}{2}'$ $12 \quad 27$ $18 \quad 52\frac{1}{2}$	
100 B	I II III IV	$6^\circ 17'$ $12^\circ 34$ $18 \quad 59$ $25 \quad 39$	$6'$	$6^\circ 11'$ $12 \quad 28$ $18 \quad 53$ $25 \quad 33$	
100 B	I II III IV	$6^\circ 18'$ $12 \quad 34$ $18 \quad 59$ $25 \quad 40$	$6\frac{1}{2}'$	$6^\circ 11\frac{1}{2}'$ $18 \quad 52\frac{1}{2}$	
110 A	I II III	$4^\circ 28\frac{1}{2}'$ $8 \quad 52\frac{1}{2}$ $13 \quad 20$	$6'$	$4^\circ 22\frac{1}{2}'$ $8 \quad 46\frac{1}{2}$ $13 \quad 14$	
111 B	I II III	$5^\circ 27\frac{1}{2}'$ $10 \quad 52\frac{1}{2}$ $16 \quad 23$	$6'$	$5^\circ 21\frac{1}{2}'$ $10 \quad 46\frac{1}{2}$ $16 \quad 17$	
111 B	I II III	$5^\circ 30'$ $10 \quad 54\frac{1}{2}$ $16 \quad 26$	$7'$	$5^\circ 23'$ $10 \quad 47\frac{1}{2}$ $16 \quad 19$	
111 B	I II III	$5^\circ 27'$ $10 \quad 51$ $16 \quad 21\frac{1}{2}$	$5\frac{1}{2}'$	$5^\circ 21\frac{1}{2}'$ $10 \quad 45\frac{1}{2}$ $16 \quad 16$	
201 C	I II	$7^\circ 12'$ Not found	$5\frac{1}{2}'$	$6^\circ 56\frac{1}{2}'$	
201 C	I	$7^\circ 1\frac{1}{2}'$	$5\frac{1}{2}'$	$6^\circ 56'$	
102 C	I II	Not found $14^\circ 2'$	$5\frac{1}{2}'$	$13^\circ 56\frac{1}{2}'$	
301 C	I II	$9^\circ 50'$ $20 \quad 4$	$5\frac{1}{2}'$	$9^\circ 44\frac{1}{2}'$ $19 \quad 58\frac{1}{2}$	
103 C	I II	$9^\circ 53'$ $19 \quad 58\frac{1}{2}$	$5\frac{1}{2}'$	$9^\circ 47\frac{1}{2}'$ $19 \quad 53$	

for Sodium Chlorate.

$\sin \frac{1}{2} n$	$\frac{1}{n} \sin \frac{1}{2} n$	Relative Intensities	Intensity in terms of Ref. Cryst = 1	Remarks
0.1079	0.1079	100	0.574	Natural face; not ground off.
0.2156	0.1078	8.4	0.048	
0.3235	0.1078	19.4	0.111	
0.1077	0.1077	100	1.09	Natural face freshly ground off
0.2159	0.1079	5.5	0.060	
0.3236	0.1078	11.9	0.130	
0.4313	0.1078	4.2	0.046	
0.1079	0.1079	100	1.21	Same as preceding but with face reversed
		2.9	0.035	
		10.2	0.135	
0.3235	0.1078	2.4	0.029	
0.0763	0.0763	100	0.251	Ground face
0.1526	0.0763	21	0.054	
0.2289	0.0763	24	0.060	
0.0934	0.0934	100	0.511	Ground face
0.1870	0.0935	16.1	0.082	
0.2804	0.0935	36	0.184	
0.0938	0.0938	100	0.500	Same as preceding but reversed
0.1872	0.0936	16.5	0.082	
0.2810	0.0937	39	0.195	
0.0934	0.0934	100	0.536	Ground face parallel to preceding
0.1867	0.0933	17.1	0.092	
0.2801	0.0933	42	0.225	
0.1208	0.1208		1.06	Ground face
0.1207	0.1207		1.13	Same as preceding face rotated 80°
0.2409	0.1205		0.112	Ground face
0.2409	0.1205		0.112	
0.1692	0.1692	100	0.085	Ground face
0.3416	0.1708	23	0.020	
0.1701	0.1701	100	0.101	Ground face
0.3401	0.1700	100	0.101	

Table II. - Reflection Data

Plane and Specimen	Order, n	Half of observed chamber angle	Zero point, $\frac{1}{2}^\circ$	Corrected angle of reflection, $\frac{1}{2}^\circ$ n
100	I	6° 14'	9'	6° 5'
Z	II	12 23 $\frac{1}{2}$		12 14 $\frac{1}{2}$
	III	18 41 $\frac{1}{2}$		18 32 $\frac{1}{2}$
100	I	6° 7'	2'	6° 5'
W	II	12° 16'		12 14
	III	18 34		18 32
111	I	5° 24'	8 $\frac{1}{2}$ '	5° 15 $\frac{1}{2}$ '
Z	II	10 41 $\frac{1}{2}$		10 33
	III	16 6 $\frac{1}{2}$		15 58

for Sodium Bromate

$\sin \frac{1}{2}$	n	$\frac{1}{n}$	$\sin \frac{1}{2}$	n	Relative Intensities	Intensity in terms of Ref. Cryst = 1	Remarks
0.1060		0.1060			100	0.326	Ground
0.2120		0.1060			28.4	0.093	face
0.3180		0.1060			28.4	0.093	
0.1060		0.1060			100	0.166	Natural
0.2199		0.1060			49	0.081	face not
0.3179		0.1060			51	0.085	ground off
0.0916		0.0916			100	0.323	Natural
0.1831		0.0916			47	0.153	face
0.2751		0.0917			47	0.153	slightly ground off.

reduces the selective absorption" selective absorption being supposed to occur at the angle of maximum reflection . It will be noticed further that the grinding produced a less violent effect on the intensities of the higher orders. It is difficult to see how Compton's explanation accounts for this, but it is easy to account for if we assume that the grinding simply removes an inert, non-reflecting but absorbing layer; for the path of the beam through this layer would be greater the smaller the angle of reflection. Attention does not seem to have been given previously to the effect of the character of the surface on the relative intensities from a single face.

How reproducible the surface is made by mere grinding always with the same grade of emery is not clear. The $\overline{(111)}$ plane of sodium chlorate gave intensities in good agreement with the (111) plane; on the other hand four different cube faces (not included in the table) gave intensities of 1.45, 1.23, 1.12, and 1.36. A reproducibility of better than 20 or 30% probably cannot be claimed for reflections taking place at small angles (i.e. up to 7 or 8°). More work on this point is desirable.

5. The Crystal Structure.

It is convenient to examine first the ratios of the interplanar distances for various faces. Since the same wave-length

was used throughout, these are inversely proportional to the sines of the angles of first order reflection. For the chlorate¹

$$d_{100} : d_{110} : d_{111} : d_{201} : d_{10\bar{2}} : d_{301} : d_{10\bar{3}} =$$

$$\frac{1}{0.1078} : \frac{1}{0.0763} : \frac{1}{0.0935} : \frac{1}{0.1208} : \frac{1}{0.1205} : \frac{1}{0.1700} : \frac{1}{0.1700} =$$

$$1 : 1.413 : 1.153 : 0.892 : 0.895 : 0.634 : 0.634$$

$$1 : \frac{2}{\sqrt{2}} : \frac{2}{\sqrt{3}} : \frac{2}{\sqrt{5}} : \frac{2}{\sqrt{5}} : \frac{2}{\sqrt{10}} : \frac{2}{\sqrt{10}} =$$

$$1 : 1.414 : 1.155 : 0.894 : 0.894 : 0.632 : 0.632$$

For the bromate

$$d_{100} : d_{111} = \frac{1}{0.1060} : \frac{1}{0.0916} = 1 : 1.157$$

For a simple cubic lattice the corresponding ratios are:

$$1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}} : \frac{1}{\sqrt{5}} : \frac{1}{\sqrt{5}} : \frac{1}{\sqrt{10}} : \frac{1}{\sqrt{10}}$$

For a centered cubic lattice they are:

$$1 : \frac{2}{\sqrt{2}} : \frac{1}{\sqrt{3}} : \frac{1}{\sqrt{5}} : \frac{1}{\sqrt{5}} : \frac{2}{\sqrt{10}} : \frac{2}{\sqrt{10}}$$

For a face-centered cubic lattice they are:

$$1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}} : \frac{1}{\sqrt{5}} : \frac{1}{\sqrt{5}} : \frac{1}{\sqrt{10}} : \frac{1}{\sqrt{10}}$$

It is evident that the observed ratios do not agree with those of any single lattice; they likewise do not agree with those given by the diamond arrangement. It is possible, however, to associate 4 NaClO₃ with each point of a simple cubic lattice in such a way that the interplanar distance for the cube face will be halved while the rest remain unchanged. This will give an arrangement having the proper interplanar distance ratios.

¹ It is assumed here that the reflection found from the 201 plane was that of the second order.

The arrangement of the symmetry elements of the space group that enables this to be accomplished is shown in Fig. 4. The underlying simple cubic lattice has the translations $2\tau, 2\tau, 2\tau$. The solid black lines are trigonal

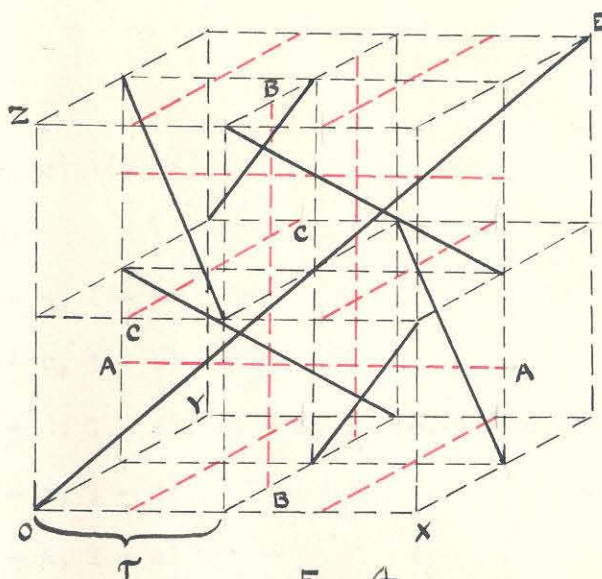


Fig. 4.

rotation axes; the red dotted lines are digonal screw axes of translation τ . Several of the latter parallel to those shown have been omitted from the figure to avoid confusion. There are no planes of symmetry. The mirror image of this arrangement of symmetry elements would, of course, serve as well. The group has the symmetry which has been assigned to NaClO_3 .

For convenience place $\tau = 1$. Place a sodium atom on the diagonal OE at (a, a, a) ; place a chlorine or bromine atom similarly at (b, b, b) ; finally place an oxygen atom in the general position (c, d, e) . Two successive operations with the trigonal axis OE introduces the new atoms:

$$\text{O at } (d, e, c), (e, c, d)$$

It remains to transform the five positions

The arrangement of the symmetry elements of the space group that enables this to be accomplished is shown in Fig. 4. The underlying simple cubic lattice has the translations a , 2τ , 2τ , 2τ . The solid black lines are trigonal

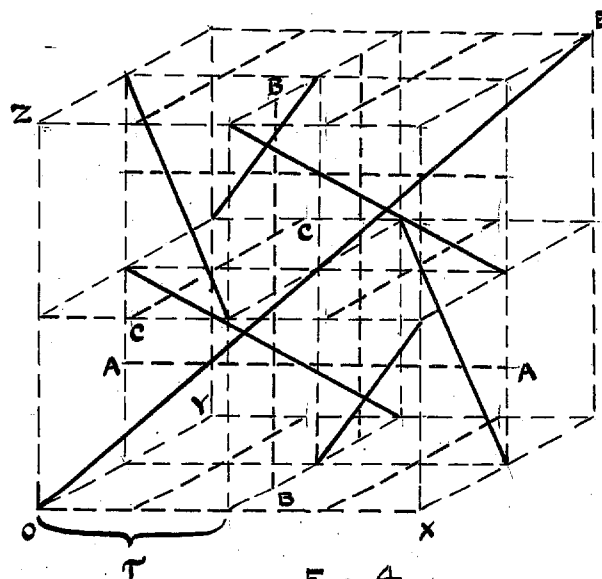


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rotation axes; the red dotted lines are digonal screw axes of translation τ . Several of the latter parallel to those shown have been omitted from the figure to avoid confusion. There are no planes of symmetry. The mirror image of this arrangement of symmetry elements would, of course, serve as well. The group has the symmetry which has been assigned to NaClO_3 .

For convenience place $\tau = 1$. Place a sodium atom on the digonal OE at (a, a, a) ; place a chlorine or bromine atom similarly at (b, b, b) ; finally place an oxygen atom in the general position (c, d, e) . Two successive operations with the trigonal axis OE introduces the new atoms:

O at (d, e, c) , (e, c, d)

It remains to transform the five positions

Na at (a, a, a) ;

Cl at (b, b, b) ;

O at $(c, d, e), (d, e, c), (e, c, d)$

by three digonal screw axes.

AA gives: Na at $(1 + a, 2 - a, 1 - a)$

Cl at $(1 + b, 2 - b, 1 - b)$

O at $(1 + c, 2 - d, 1 - e), (1 + d, 2 - e, 1 - d),$

$(1 + e, 2 - c, 1 - d)$

BB gives: Na at $(2 - a, 1 - a, 1 + a)$

Cl at $(2 - b, 1 - b, 1 + b),$

O at $(2 - c, 1 - d, 1 + e), (2 - d, 1 - e, 1 + c),$

$(2 - e, 1 - c, 1 + d)$

CC gives: Na at $(1 - a, 1 + a, 2 - a)$

Cl at $(1 - b, 1 + b, 2 - b)$

O at $(1 - c, 1 + d, 2 - e), (1 - d, 1 + e, 2 - c),$

$(1 - e, 1 + c, 2 - d)$

Twenty positions of atoms are thus obtained; if all possible even numbers are added to each of the above coordinates, these twenty atoms, whose grouping possesses the proper symmetry, are repeated on a simple cubic lattice.

That the interplanar distance for this arrangement is one-half of the lattice interplanar distance for the cube face and equal to the lattice interplanar distance for the other faces may

be seen from a consideration of the general expression for the intensity of reflection. It could be shown without the aid of this, but since the expression is necessary for the further development of the structure, it will be presented at this point.

It is clear that a plane will not give a reflection at an angle smaller than that calculated from the expression $n\lambda = 2d \sin \theta$ where $n = 1$ and d is the lattice distance for the plane in question, but that the first reflection may occur at a larger angle than that so calculated. In what follows, the order, n , will be based upon the lattice distance. The lattice spacing of the (hkl) planes in a simple cubic lattice of translation 2 is given by $\frac{2}{\sqrt{h^2+k^2+l^2}}$. Choose in the structure any (hkl) plane as a basis of reference; if it passes through the origin its normal equation is $\frac{hx+ky+lz}{\sqrt{h^2+k^2+l^2}} = 0$. The distance from this plane of any atom whose coordinates are (x_i, y_i, z_i) is $\frac{hx_i+ky_i+lz_i}{\sqrt{h^2+k^2+l^2}}$. For reflection of the n^{th} order, the phase of the waves from the atom at (x_i, y_i, z_i) referred to the initially chosen (hkl) plane is $2\pi n \frac{hx_i+ky_i+lz_i}{\sqrt{h^2+k^2+l^2}} \cdot \frac{2}{\sqrt{h^2+k^2+l^2}}$ or simply $n(hx_i+ky_i+lz_i)$. If then A_n is the amplitude of the resultant wave from all the atoms of the fundamental group,

$$A_n^2 = \left(\sum_i N_i \sin \pi n(hx_i+ky_i+lz_i) \right)^2 + \left(\sum_i N_i \cos \pi n(hx_i+ky_i+lz_i) \right)^2 \quad (1)$$

where N_i is a number proportional to the amount the atom i contributes to the amplitude, and is frequently taken as the atomic number; m is the number of atoms, 20 in the present case. The intensity of reflection is given by

$$I_n = f\left(\frac{\Phi}{2}\right) A_n^2 \quad (2)$$

where $f\left(\frac{\Phi}{2}\right)$ is some function of the angle at which reflection takes place, of the temperature, of the nature of the crystal, etc. It is ordinarily treated empirically.

We may now substitute in equation (1) the values of the coordinates of the twenty atoms of the fundamental group in place of x_i , y_i , and z_i , and the proper indices for h , k , and l in order to obtain special equations applicable to each of the faces measured. In the case of the (100) face the expression simplifies to

$$A_n^2 = 8(Na \cos \pi n a + Cl \cos \pi n b + O(\cos \pi n c + \cos \pi n d + \cos \pi n e))^2 \\ \times (1 + (-1)^n) \quad (3)$$

This expression vanishes when n is odd; hence the distance corresponding to the actually observed first order reflection is one-half of the lattice distance. In the case of the other faces, the first order reflections do not in general vanish; for particular values of the parameters they may of course become too small to be detected (as is known to be the case in the first order reflection from the octahedral face of KCl) and this is assumed to be true

for the 201 face in the present instance.

It can be seen that in the above structure there are 4 NaClO_3 associated with the volume $(2 d_{100})^3$ where d_{100} is the observed cube-face interplanar distance. If the structure is correct so far, it must give the crystals the proper density.

Taking λ for molybdenum as 0.712×10^{-8} cm. we may calculate d_{100} .

$$\text{For the chlorate } d_{100} = \frac{0.712 \times 10^{-8}}{2 \times 0.1078} = 3.30 \times 10^{-8} \text{ cm.}$$

$$\text{For the bromate } d_{100} = \frac{0.712 \times 10^{-8}}{2 \times 0.1060} = 3.36 \times 10^{-8} \text{ cm.}$$

The density of the structure is given by $\rho = \frac{4 M}{N (2d_{100})^3}$ where M is the formula weight and N is Avogadro's number, 6.06×10^{23} .

For the chlorate the density thus calculated is 2.45 g. per cc. to be compared with the values 2.467, 2.488, 2.490, and 2.496 given by Groth as determined by various experimenters. For the bromate, the calculated value is 3.28 and the experimental values 3.254 and 3.339. The structure described accordingly gives the crystals the proper density, gives probably the correct interplanar distance ratios, and accounts fully for the crystallographic symmetry. Completion of the knowledge of the structure requires the determination of the values of the five parameters a , b , c , d , and e with the aid of the intensity measurements.

6. The Values of the Parameters.

The determination of the values of these parameters requires the solution of simultaneous equations involving the trigonometric expressions for the amplitudes. It seems necessary to obtain the solutions by trial; since there are five variables involved, and since slight changes in these frequently produce considerable changes in the amplitudes, the number of plausible values that will give substantially different amplitudes is obviously considerable. Although the labor of making the trials has been materially reduced by the introduction of a graphical method of calculation, it has seemed hardly worth while to spend a great amount of time in the search for suitable values until the mechanism of reflection is better understood. Nevertheless, as some progress has been made, the method of attack and the results so far obtained will be described.

W. H. Bragg, in the article previously referred to, showed that if the intensities of the reflections from the (100) and (110) faces, and those of the second and fourth orders from the (111) face of rock salt were plotted against the sine of the angle at which reflection occurs, a reasonably smooth curve could be drawn through the points, and that this curve deviated systematically from one whose ordinates were inversely proportional to the

square of the sine of the angle.

All of these reflections take place from planes where no interference occurs. In Fig. 5 the ordinates of the dotted curve are inversely proportional to the squares of the sines of the angles.

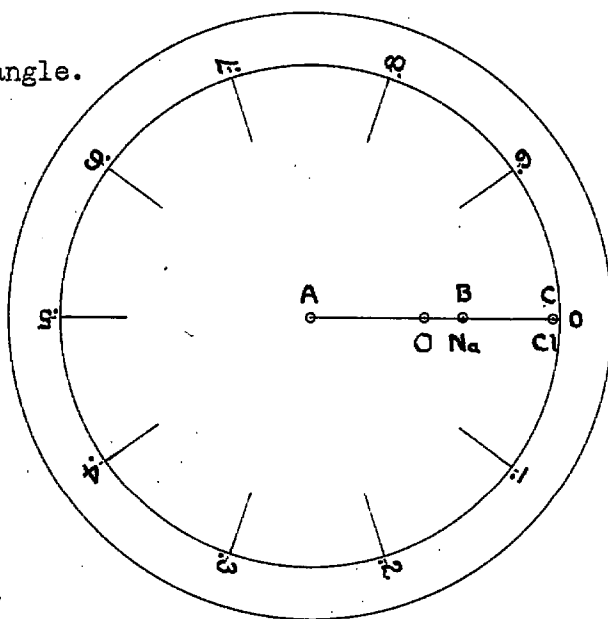
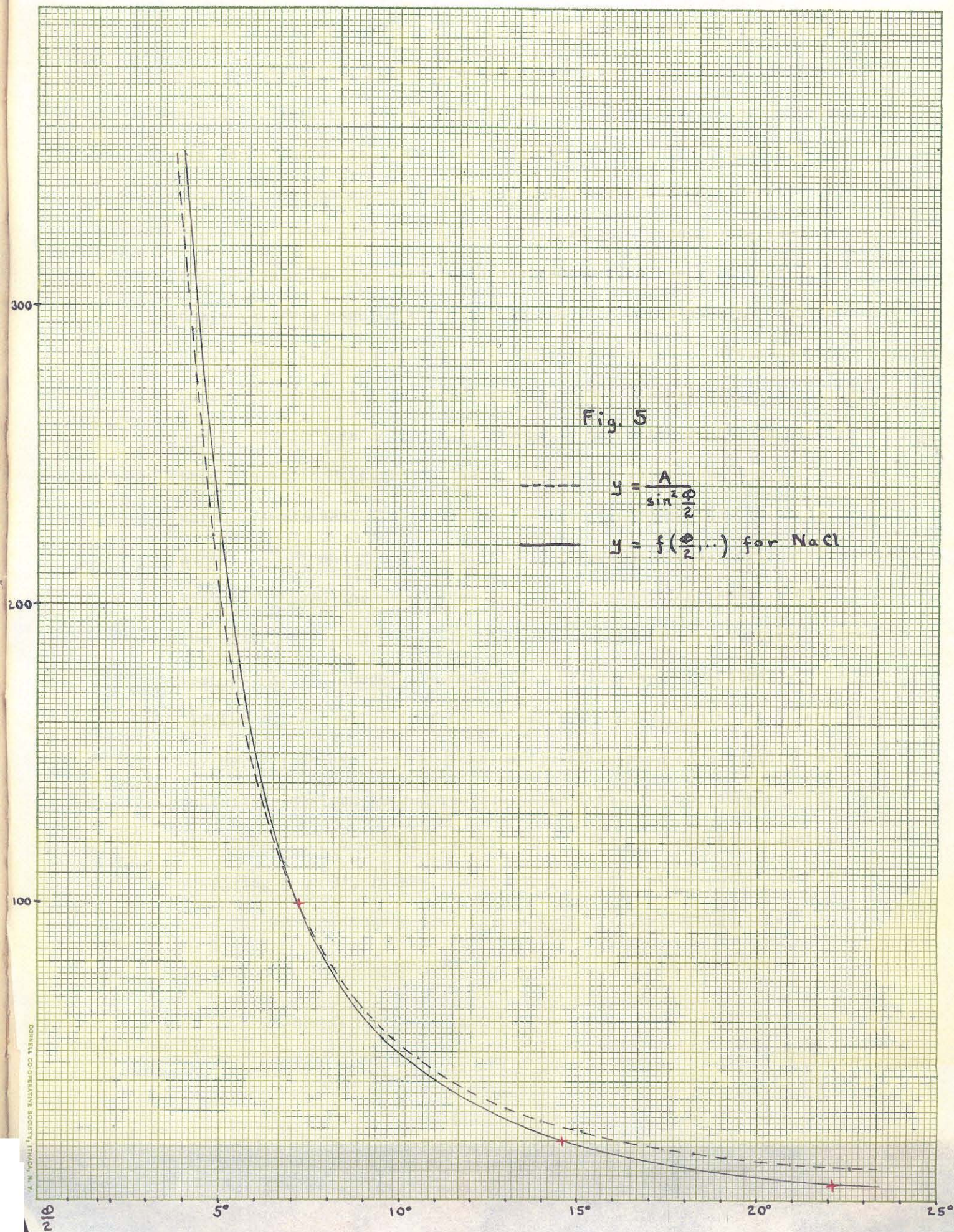


Fig. 6.

The solid curve is drawn to deviate systematically from it and to pass through experimentally determined points representing the relative intensities from the cube face of rock salt using the molybdenum target. The ordinates of this curve have been taken as $f(\frac{\phi}{2}, \dots)$ in equation (2). To make the comparison between the experimental and calculated intensities for sodium chlorate a series of amplitudes have been calculated from (2) using the observed values of the intensities, and their ratios compared with the ratios of those calculated from (1).

The square root of the right hand side of equation (1) is the resultant of a series of vectors of magnitude N_i , and angle $\frac{n}{2} (hx_i + ky_i + lz_i)$ where the angle is expressed in revolutions. The compounding of the vectors was accomplished by means of the



device indicated in Fig. 6. A circle was drawn on a piece of transparent celluloid, and was graduated clockwise to 0.01 revolution. A small hole with a fiber bushing was placed at the center and other similar holes on the zero line at distances from the center proportional to the atomic numbers of the atoms under consideration. Pins were made to fit the holes. The method of use may be seen from an example. Suppose it is desired to find the resultant of the waves from a sodium atom at 0.40 and a chlorine atom at 0.65 revolutions. A pin is placed at A' on a large sheet of cross-section paper. The hole A is slipped over the pin. The celluloid is rotated until the 0.40 graduation is horizontal and on the right. A pin is then placed in B (at B' on the cross-section paper) and the pin through A removed. The celluloid is then placed so that the hole at A is at B' and rotated until the 0.65 graduation is horizontal. A pin is passed through C (meeting the cross-section paper at C'). The distance from C' to A' is the resultant of the two vectors. More vectors may, of course, be added in the same way. Practically, the lifting of the celluloid from one position and replacing it in another may usually be avoided, and the manipulation made more rapid. Suppose it is desired to combine the waves from a sodium atom at 0.40 with those from a sodium atom at 0.65. Start as before but instead of moving A to B', rotate the celluloid with B at B' until the 0.65 graduation is horizontal but on the left. A pin through A is then

at a distance from A' equal to the magnitude of the resultant.

Before combining the vectors, it is, of course, necessary to calculate their angles by means of the expression $\frac{n}{2}(hx_i + ky_i + lz_i)$.

In Braggs' "X-rays and Crystal Structure" it is stated that the arrangement of sodium and chlorine atoms in the chlorate is approximately as in the chloride. No data are given. If $a = 0$ and $b = 1$ the arrangement of sodium and chlorine atoms would become the same as in sodium chloride, and the dissymmetry of the chlorate would be due to the placing of the oxygen atoms. If, however, the sodium and chlorine atoms are placed in these positions, it is impossible to account for the (111) intensities with the assumptions that have been made. Consequently, although the sodium and chlorine atoms in the chlorate may be arranged approximately as in sodium chloride it seems probable that they are not just as in the chloride.

By placing $a = 0.15$, $b = 0.86$, $c = 0.60$, $d = 0.94$, and $e = 1.19$ a general correspondence between the two sets of amplitudes obtained as above described, is found. This is indicated in Table III. The planes given in Table I as (201) , $(10\bar{2})$, (301) , $(10\bar{3})$ are given in Table III as $(10\bar{2})$, (201) , $(10\bar{3})$, (301) respectively. For the reasons given in Section 2 this permutation does no violence to the theory. For the (100) face, the orders previously given as I, II, III, and IV are here given as II, IV, VI, and VIII. The column headed I_n contains mean values of the

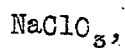


Table III. - $a = 0.15$, $b = 0.86$, $c = 0.60$, $d = 0.94$, $e = 1.19$

Plane	Order n	I_n	$f(\frac{\phi}{2} \dots)$	$\frac{I_n}{f} \times 10^4$	$k\sqrt{\frac{I_n}{f}}$	A_n	$k_{hkl}\sqrt{\frac{I_n}{f}}$
100	II	1.15	137.	84.	75	84	[84]
	IV	0.048	29.5	16.	33	36	37
	VI	0.133	9.2	145.	98	107	110
	VIII	0.038	3.5	110.	86	121	96
110	I	0.251	280	9.0	24	19	[19]
	II	0.054	66	8.2	23	20	18
	III	0.060	26	23.	39	26	30
111	I	0.516	184	28.0	[43]	43	[43]
	II	0.085	41	21.	37	12	37
	III	0.201	15	134.	95	133	95
$10\bar{2}$	I	1.10	108	102	83	91	
	II	0.02	22	9	25	20	
201	I	0.02	108	1.8	1.1	1.3	
	II	0.112	22	51	58	53	
$10\bar{3}$	I	0.085	54	16	32	22	20
	II	0.020	8	25	41	25	[25]
301	I	0.101	54	19	35	19	37
	II	0.101	8	130	93	97	[97]

intensities of the reflections in terms of that of the reference crystal taken as unity. The values of $f(\frac{\Phi}{2}, \pm 1.)$ were read from Fig. 5. In the column headed A_n are given the square roots of the right hand side of equation (1) obtained graphically. The values in the column headed $k\sqrt{\frac{I_n}{f}}$ have all been multiplied by a constant to make the values for the first order of (111) equal to that of A_n , this reflection was chosen as the basis of comparison since the value of I_n for it seemed best known. In the last column, the values of $\sqrt{\frac{I_n}{f}}$ have been so altered as to permit comparison of the relative amplitudes from single faces but not of the various faces with each other.

Between the two sets of values in the sixth and seventh columns, there are admittedly serious discrepancies. There is, however, a marked parallelism between the two sets; and the fact that this parallelism runs through such a range of data is taken as good evidence in favor of this type of structure. It is likely that slightly different values of the parameters could be found that would give somewhat better agreement.

It can be seen that with these values of the parameters the sodium and chlorine atoms are slightly displaced toward each other along cube diagonals from the relative positions they would occupy in sodium chloride. Three oxygen atoms are grouped

about each chlorine atom in such a way that the chlorine atom lies nearly in the plane of the oxygen atoms. Their distance from the chlorine atom is 1.41×10^{-8} cm. No other atoms in the structure are nearly so close together.

The parameters for the bromate are probably slightly different from those for the chlorate.

7. Summary

1. The experimental technique of investigating crystal structures by the Bragg method has been somewhat improved, both in the avoidance of wrong reflections and in measuring the intensities of the correct ones. A method of comparing the relative intensities of reflection from various faces of the same crystal has been suggested and used.

2. Reflection data for sodium chlorate have been collected and tabulated; a number of measurements have also been made on sodium bromate.

3. A type of structure has been developed which accounts for the interplanar distance ratios, the densities of the substances, and the crystallographic symmetry.

4. In the case of sodium chlorate, locations of the atoms have been given which account roughly for the observed intensities of reflection from various faces relative to each other.