A

Thesis

entitled-

I. THE CRYSTAL STRUCTURE OF SODIUM PERIODATE.

II. THE SPACE GROUP SYMMETRY OF SODIUM NITRITE.

III. THE CRYSTAL STRUCTURE OF THE CUBIC MODIFICATION OF TELLURIC ACID.

Presented

by

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In partial fulfilment of the requirements

for the degree of Doctor of Philosophy

California Institute of Technology

Pasadena California

1926.

# THE CRYSTAL STRUCTURE OF SODIUM PERIODATE.

by

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## Introduction.

Sodium periodate has been investigated crystallographically by Rammelsburg[1] and by Eakle[2] and is reported as being ditetragonal bipyramidal, its axial ratio being a;c = 1:1.5900. There are a number of salts having similar formulas that crystallize in the tetragonal system and have very closely the same axial ratios. These salts are given in Table I.[3]

Table I.

| salt | axial ratios | symmetry |
|---|---|---|
| $KRuO_4$ | 1:1.6340 | |
| $LiIO_4$ | 1:1.5272 | |
| $NaIO_4$ | 1:1.5900 | bipyramidal |
| $AgIO_4$ | 1:1.6318 | |
| $KIO_4$ | 1:1.5534 | |
| $RbIO_4$ | 1:1.5576 | |
| $NH_4IO_4$ | 1:1.5211 | bipyramidal |
| $CaMoO_4$ | 1:1.5437 | bipyramidal |
| $SrMoO_4$ | 1:1.5738 | bipyramidal |
| $BaMoO_4$ | 1:1.6232 | bipyramidal |
| $PbMoO_4$ | 1:1.5777 | pyramidal |
| $CaWO_4$ | 1:1.5268 | bipyramidal |
| $SrWO_4$ | 1:1.5582 | bipyramidal |
| $BaWO_4$ | 1:1.6046 | bipyramidal |
| $PbWO_4$ | 1:1.5606 | |

1) Rammelsburg, Pogg. Ann. d. Phys. 134, 373,(1868)
2) Eakle, Zeit. f. Krystall. 26, 565,(1896)
3) P. Groth, " Chemische Krystallographie" Engelman,Leipsig 1908. Vol. II, pages 174, 384.

The tungstates of lead, strontium, calcium, and barium are known to be isomorphous with the molybdates of these same metals; the periodates of sodium and ammonium are also isomorphous. It is thought that very probably all the salts listed in Table I are isomprphous and should therefore have the same symmetry. Crystallographers, however, do not assign the same class of symmetry to these different salts. It is then of interest to study the crystal structure of sodium periodate and to compare it with the structure of wulfenite, $PbMoO_4$, which has already been studied and reported by R. G. Dickinson.[4]

## The Preparation of the Crystals.

Sodium periodate was prepared by passing chlorine into a hot solution of iodine and sodium hydroxide[5] made by dissolving 20 g. of iodine and 80 g. of sodium hydroxide in 300 cc. of water. After several hours a fine crystal meal separated, which after filtering and washing was found to liberate iodine from a slightly basic solution of potassium iodide.[6] It was then dissolved in dilute sulfuric acid and slowly reprecipitated by adding sodium hydroxide until basic. The crystals were obtained by the slow evaporation, at 40°C to 45°C, of a solution of the salt containing a small amount of sulfuric acid. Under these conditions the faces which develop are $(111)_c$ and $(101)c$.

4) R. G. Dickinson, J.A.C.S., 42, 85, (1920)
5) See Gmelin-Kraut, "Handbuch der Anorganischen Chemie" Carl Winter, Heidelburg, 1909, Vol. I2, p. 364.
6) Treadwell-Hall "Analytical Chemistry" Wiley, New York Vol. II, p. 670.

One of the crystals was measured on a goniometer. The mean of two measurements of the angles between similar faces gave 47° 50'. The calculated value of the angle between $(111)_c$ and $(11\bar{1})_c$ is 47° 56'. Throughout this paper the subscript "c" indicates that the indices are referred to the same set of axes used by the crystallographer; the indices without designation are referred to the space group axes.

## Experimental Procedure.[7]

Spectral photographs were made by reflecting the K-radiation of Molybdenum from $(111)_c$, $(001)_c$, and $(110)_c$ while the crystal was being rotated at a constant angular velocity. The desired faces were obtained by grinding the crystal at the proper angle. To insure precision in measurements a reference spectrum of calcite was photographed at the same time. The spectral data are listed in Table II.

Laue photographs were taken with the white radiation from a tungsten target, the tube being operated at a peak voltage of 51.5 kv. hence the lower wave length limit was 0.24 Å. Photographs were taken with the X-ray beam incident upon $(001)_c$, $(111)_c$, and $(110)_c$. Gnomonic projections were made to assist in assigning indices to reflecting planes. The results were treated with the aid of the theory of space groups.[8] The Laue data are given in Table III .

7. R.W.G. Wycoff, "The Structure of Crystals" Chem. Catalog Co. New York, 1924.
8. R.W.G. Wycoff, "The Analytical Expression of the Results of the Theory of Space Groups" Pub. Carnegie Inst. No.318, 1922.

## The Unit of Structure.

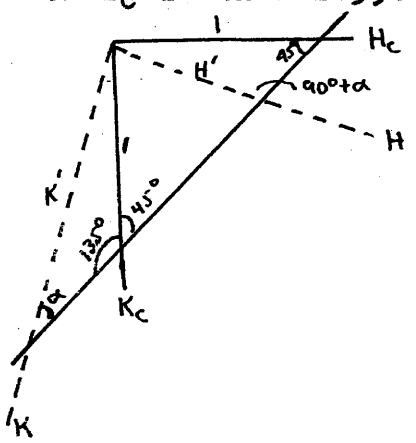
Table II.

| Line | | $(hkl)_c$ | angle of reflection. | $d_{hkl}/n$ | n | Intensity. |
|---|---|---|---|---|---|---|
| $\beta$ | 0.6311Å | 110 | 6° 51' | 2.644 | $n_2$ | 0.2 |
| $\alpha$ | 0.710 Å | 110 | 7° 39' | 2.666 | $n_2$ | 0.9 |
| $\beta$ | 0.6311Å | 110 | 13° 43' | 1.330 | $2n_2$ | 0.25 |
| $\alpha_1$ | 0.7078Å | 110 | 15° 25' | 1.331 | $2n_2$ | 1.0 |
| $\alpha_2$ | 0.7121Å | 110 | 15° 31' | 1.331 | $2n_2$ | 0.6 |
| $\gamma$ | 0.6197Å | 001 | 5° 59' | 2.978 | $n_1$ | 0.05 |
| $\beta$ | 0.6311Å | 001 | 6° 5' | 2.977 | $n_1$ | 0.4 |
| $\alpha$ | 0.710 Å | 001 | 6° 49' | 2.990 | $n_1$ | 1.8 |
| $\beta$ | 0.6311Å | 001 | 12° 10' | 1.489 | $2n_1$ | 0.2 |
| $\alpha_1$ | 0.7078Å | 001 | 13° 43' | 1.492 | $2n_1$ | 1.0 |
| $\alpha_2$ | 0.7121Å | 001 | 13° 48' | 1.493 | $2n_1$ | 0.3 |
| $\beta$ | 0.6311Å | 001 | 18° 32' | 0.993 | $3n_1$ | 0.3 |
| $\alpha$ | 0.710 Å | 111 | 4° 12' | 4.846 | $n_3$ | 1.0 |
| $\alpha$ | 0.710 Å | 111 | 8° 24' | 2.432 | $2n_3$ | 0.1 |
| $\beta$ | 0.6311Å | 111 | 11° 17' | 1.612 | $3n_3$ | 0.05 |
| $\alpha_1$ | 0.7078Å | 111 | 12° 39' | 1.616 | $3n_3$ | 0.3 |
| $\alpha_2$ | 0.7121Å | 111 | 12° 44' | 1.616 | $3n_3$ | 0.1 |
| $\gamma$ | 0.6197Å | 111 | 14° 51' | 1.209 | $4n_3$ | 0.05 |
| $\beta$ | 0.6311Å | 111 | 15° 7' | 1.210 | $4n_3$ | 0.3 |
| $\alpha_1$ | 0.7078Å | 111 | 17° 1' | 1.210 | $4n_3$ | 0.8 |
| $\alpha_2$ | 0.7121Å | 111 | 17° 8' | 1.209 | $4n_3$ | 0.5 |

The spectral measurements lead to the following values: $d_{(001)_c}/n_1 = 2.982$Å; $d_{(110)_c}/n_2 = 2.659$Å; and $d_{(111)_c}/n_3 = 4.843$Å.

Since the axes of the true unit of structure may be coincident with the crystallographic axes or may be rotated about the "c" axis so as to make some angle (0° to 45°) with them, the following calculations were made to determine the smallest possible unit compatible with the spectral data and

and the orientation of the axes. Let $H_c$ and $K_c$ be the crystallographic axes, and H and K be the axes of the true unit. Let the indices of $(110)_c$ be (hk0); the indices of $(111)_c$ be (h'k'l') on the space group axes. Let also the intercepts of (h'k'l') on $H_c$ and $K_c$ be unity, the intercept on $L_c$ is then 1.590. Then the intercepts of this plane on the




the space group axes can be found from the figure:

$$\frac{H'}{\sin 45^\circ} = \frac{1}{\sin(\frac{\pi}{2}+\alpha)}\ ;\ \frac{K'}{\sin 135^\circ} = \frac{1}{\sin\alpha} \quad \text{or}$$

$H' = \frac{1}{\cos\alpha}\frac{1}{\sqrt{2}}$ and $K' = \frac{1}{\sin\alpha}\frac{1}{\sqrt{2}}$. Also it is clear that $H'/K' = \tan\alpha = k/h = \frac{\sin\alpha}{\cos\alpha}$ or $\frac{k^2}{h^2} = \frac{\sin^2\alpha}{1-\sin^2\alpha} = \frac{1-\cos^2\alpha}{\cos^2\alpha}$. Whence it results $\sin\alpha = \frac{k}{\sqrt{h^2+k^2}}$ and $\cos\alpha = \frac{h}{\sqrt{h^2+k^2}}$ and the intercepts are:

$H' = \frac{\sqrt{h^2+k^2}}{h\sqrt{2}}$ ; $K' = \frac{\sqrt{h^2+k^2}}{k\sqrt{2}}$ ; and $L' = 1.590$.

Now the length of the axes of the true unit are given by: H and K = $2.659n_2\sqrt{h^2+k^2}$ and L = $2.982n_1$. Hence h':k':l' = $\frac{nh\sqrt{2}\sqrt{h^2+k^2}\,2.659}{\sqrt{h^2+k^2}} : \frac{n_2k\sqrt{2}\sqrt{h^2+k^2}\,2.659}{\sqrt{h^2+k^2}} : \frac{2.982\,n_1}{1.590}$ which reduces to $2n_2h : 2n_2k : n_1$. Turning now to the general formula for the interplanar distance in terms of the indices of the plane and the lengths of the unit axes we can write:

$$d_{h'k'l'} = \sqrt{\left(\frac{h'}{d_{100}}\right)^2+\left(\frac{k'}{d_{010}}\right)^2+\left(\frac{l'}{d_{001}}\right)^2} = \sqrt{\frac{h'^2+k'^2}{(2.659n_2)^2(h^2+k^2)} + \frac{l'^2}{(n_1\,2.982)^2}}$$

if "r" is the common divisor of $2n_2k$; $2n_2h$; and $n_1$ then $(h'k'l') = \left(\frac{2n_2h}{r}, \frac{2n_2k}{r}, \frac{n_1}{r}\right)$. Substituting this into the above expression for $d_{h'k'l'}$ it reduces to $d_{h'k'l'} = 1.226\ r$. Comparing this with $d_{(111)_c}/n_3 = 4.843$ it is clear that $n_1$ must be a multiple

of four and $\frac{n_1}{4n_3}$ must be an integer. To obtain possible units it is now only necessary to assign values to $n_1$, $n_2$, $n_3$, h, and k remembering that $\frac{nh}{2n_3}$; $\frac{nk}{2n_3}$; and $\frac{n_1}{4n_3}$ shall be integral and also that the first two shall not both simultaneously be zero, further that $n_1 n_2^2(h^2+k^2)$ shall be a minimum since this is proportional to the size of the unit. Since it has already been shown that $n_1$ must be at least four; the only two units that give the samllest value to $n_1 n_2^2 (h^2+k^2)$ compatible with the other restrictions are: $n_1=4$; $n_2=2$; $n_3=1$; h=1; k=0; and $n_1=4$; $n_2=1$; $n_3=1$; h=2 and k=0. This last unit however is not possible as it does not give indices prime to one another. Hence the unit taken to be the true one is the first one given. The axes are at an angle of 45° with the crystallographic axes, hence $(110)_c = (100)$. A slightly different value for $d_{(110)_c}$ is taken rather than the observed value. This is calculated from the observed value of $d_{(001)_c}$ and the axial ratio, and is used because it gives a calculated value of $d_{(111)_c} = 4.847$ which agrees better with the observed value than does the one calculated on the basis of the observed value of $d_{(110)_c}$. This latter gives $d_{(111)_c} = 4.866$.

The true unit is then: $d_{001} = 11.926\text{Å}$ and $d_{100} = 5.304\text{Å}$. It contains four molecubes, calculated from the reported density and the molecular weight.

## The Space Group

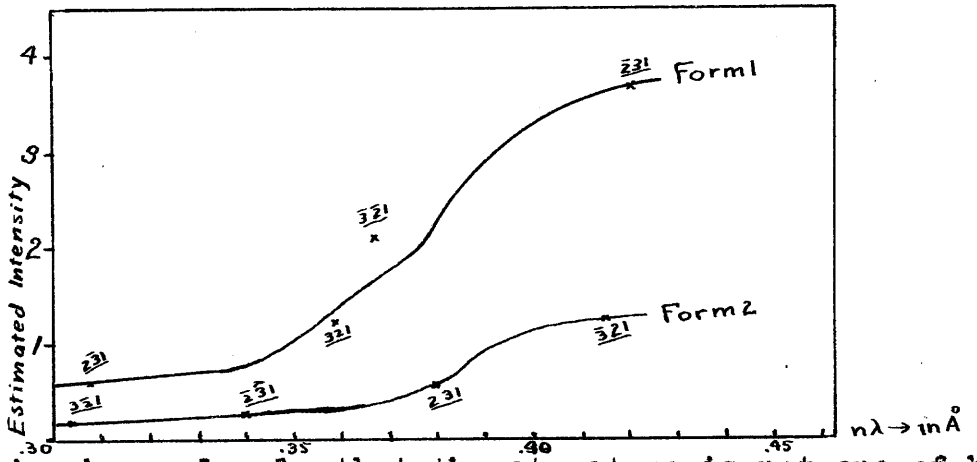
Table III.

| (hkl) | $d_{hkl}$ | $n\lambda$ in Å.u. | Estimated Intensity |
|---|---|---|---|
| 152 | 1.030 | 0.381 | 1.2 |
| 725 | 0.701 | 0.398 | 0.2 |
| 376 | 0.6598 | 0.459 | 0.5 |
| 231 | 1.468 | 0.381 | 0.9 |
| 163 | 0.857 | 0.396 | 0.1 |
| 705 | 0.725 | 0.421 | 0.1 |
| 529 | 0.793 | 0.437 | 0.5 |
| 1·2·15 | 0.756 | 0.440 | 0.5 |
| 721 | 0.730 | 0.455 | 0.9 |
| 723 | 0.720 | 0.437 | 0.35 |
| 725 | 0.701 | 0.423 | 0.6 |
| 736 | 0.659 | 0.434 | 0.7 |
| 7·3·10 | 0.603 | 0.382 | 0.5 |
| 318 | 0.116 | 0.433 | 0.05 |
| 514 | 0.985 | 0.445 | 0.05 |
| 2·2·11 | 0.732 | 0.386 | 0.3 |
| 5·2·13 | 0.672 | 0.454 | 0.3 |
| 833 | 0.616 | 0.387 | 0.1 |
| 129 | 1.160 | 0.314 | 0.4 |
| 237 | 1.116 | 0.315 | 0.2 |
| 3·1·10 | 0.975 | 0.289 | 2.0 |
| 3·3·10 | 0.866 | 0.295 | 0.15 |
| 1·1·14 | 0.831 | 0.379 | 1.6 |
| 372 | 0.694 | 0.444 | 0.9 |
| 1·7·10 | 0.636 | 0.388 | 0.6 |
| 118 | 1.385 | 0.296 | 0.2 |
| 059 | 0.830 | 0.383 | 0.7 |
| 459 | 0.705 | 0.399 | 0.4 |
| 0·5·13 | 0.695 | 0.389 | 0.4 |

Since first order reflections occurred only from those planes, the sum of whose indices is odd, it can be said that the lattice is a centered one, $\Gamma_t'$ . Turning to a tabulation of possible space groups it is found that the only ones that

are compatible with this lattice are: $S_4^2$; $C_4^5$; $C_4^6$; $C_{4h}^5$; and $C_{4h}^6$ which contain operations of the second sort, and: $V_d^9$; $V_d^{10}$; $V_d^{11}$; $V_d^{12}$; $C_{4v}^9$; $C_{4v}^{10}$; $C_{4v}^{11}$; $C_{4v}^{12}$; $D_4^9$; $D_4^{10}$; $D_{4h}^{17}$; $D_{4h}^{18}$; $D_{4h}^{19}$; and $D_{4h}^{20}$.

A Laue photograph made with the X-ray beam normal to the basal plane $(001)_c$ face showed evidences of hemihedry, that is certain corresponding spots had different intensities depending upon which side of the central image they lay. The intensities of several groups were carefully compared among themselves and then plotted against their $n\lambda$'s. Following is a typical plot:




This shows clearly that the structure is not one of high symmetry, although since but few such groups of spots were found, it indicates that probably only the oxygen atoms cause the disymmetry while the sodium and iodine atoms are arranged symmetrically. Hence the last group of spaces groups listed above are eliminated, leaving only $S_4^2$; $C_4^5$; $C_4^6$; $C_{4v}^5$; and $C_{4v}^6$ to be considered. Of these $S_4^2$; $C_4^5$; and $C_{4h}^5$ require no special absences other than those required by the lattice itself.

$C_4^6$ requires further that reflections from (001) be present only in orders which are multiples of four. $C_{4h}^6$ requires further that (001) reflect only in orders which are multiples of four, also that all planes (hk0) reflect only in the second order. It has already been shown from spectral data that (001) reflects in the fourth, eighth and twelfth orders. Furthermore several photographs showed the absence of (150) though it were in a position to reflect in the first order, (710) and (530) were also found to be absent when in a position to reflect in the first order. Likewise several photographs differing from one another only in the angle of incidence of the X-ray beam showed (130) to be strong when reflecting high in the second order and very weak when reflecting near the lower limit of the second order.

It seems therefore that the facts are best explained by space group $C_{4h}^6$, and this is taken to be the true space group. This space group provides the following positions:

Two equivalent positions:

(a) $0\frac{3}{4}\frac{1}{8}$; $0\frac{1}{4}\frac{1}{8}$; $\frac{1}{2}\frac{1}{4}\frac{5}{8}$; $\frac{1}{2}\frac{3}{4}\frac{3}{8}$; (b) $0\frac{3}{4}\frac{5}{8}$; $0\frac{1}{4}\frac{3}{8}$; $\frac{1}{2}\frac{1}{4}\frac{1}{8}$; $\frac{1}{2}\frac{3}{4}\frac{7}{8}$;

Eight equivalent positions:

(c) $000$; $\frac{1}{4}\frac{1}{4}\frac{3}{4}$; $\frac{1}{2}0\frac{1}{2}$; $\frac{1}{4}\frac{3}{4}\frac{1}{4}$; $0\frac{1}{2}0$; $\frac{3}{4}\frac{3}{4}\frac{1}{4}$; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; $\frac{3}{4}\frac{1}{4}\frac{3}{4}$;

(d) $00\frac{1}{2}$; $\frac{1}{4}\frac{1}{4}\frac{1}{4}$; $\frac{1}{2}00$; $\frac{1}{4}\frac{3}{4}\frac{3}{4}$; $0\frac{1}{2}\frac{1}{2}$; $\frac{3}{4}\frac{3}{4}\frac{3}{4}$; $\frac{1}{2}\frac{1}{2}0$; $\frac{3}{4}\frac{1}{4}\frac{1}{4}$;

(e) $0\frac{1}{4}u$; $\frac{1}{2},\frac{1}{4},u+\frac{3}{4}$; $\frac{1}{2},\frac{3}{4},u+\frac{1}{2}$; $0,\frac{3}{4},u+\frac{1}{4}$; $0\frac{3}{4}\bar{u}$; $\frac{1}{2},\frac{3}{4},\frac{1}{4}-u$;

$\frac{1}{2},\frac{1}{4},\frac{1}{2}-u$; $0,\frac{1}{4},\frac{3}{4}-u$.

Sixteen equivalent positions:

(f). $xyz$; $y+\frac{1}{4},\frac{1}{4}-x,z+\frac{3}{4}$; $\frac{1}{2}-x,\bar{y},z+\frac{1}{2}$; $\frac{1}{4}-y,x+\frac{3}{4},z+\frac{1}{4}$; $x,y+\frac{1}{2},\bar{z}$;

$y+\frac{1}{4},\frac{3}{4}-x,\frac{1}{4}-z$; $\frac{1}{2}-x,\frac{1}{2}-y,\frac{1}{2}-z$; $\frac{1}{4}-y,x+\frac{1}{4},\frac{3}{4}-z$; $x+\frac{1}{2},y+\frac{1}{2},z+\frac{1}{2}$;

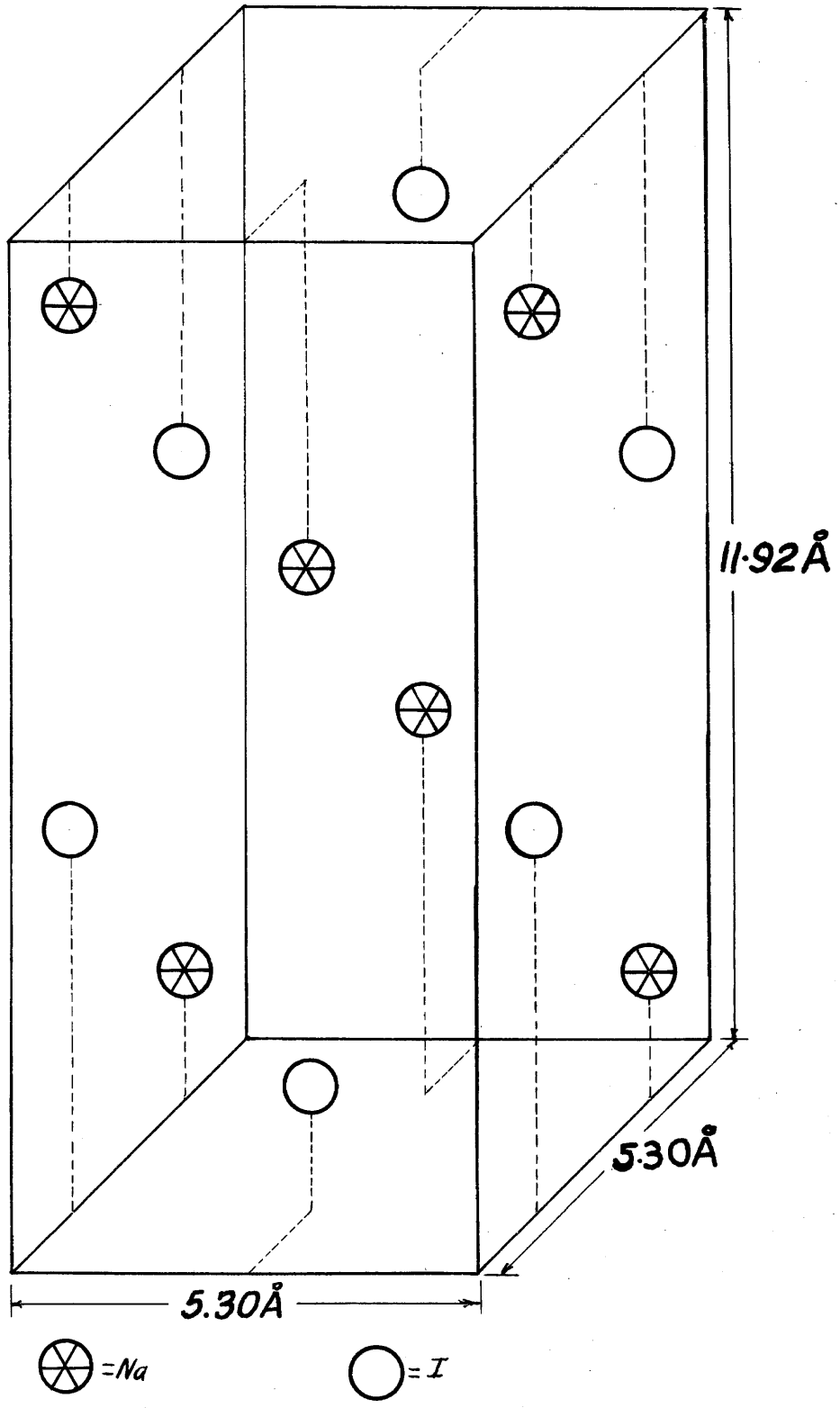
$y+\frac{3}{4},\frac{3}{4}-x,z+\frac{1}{4};\ \bar{x},\frac{1}{2}-y,z;\ \frac{1}{4}-y,x+\frac{1}{4},z+\frac{3}{4};\ x+\frac{1}{2},y,\frac{1}{2}-z;\ y+\frac{3}{4},\frac{1}{4}-x,\frac{3}{4}-z;\ \bar{x}\bar{y}\bar{z};$

$\frac{3}{4}-y,x+\frac{3}{4},\frac{1}{4}-z;$

The value of the structure factor S for any plane (hkl) is given by: $S=\sqrt{A^2+B^2}$, $A=\sum_i \overline{R}_i \cos 2\pi n(hx_i+ky_i+lz_i)$ and $B=\sum_i \overline{R}_i \sin 2\pi n(hx_i+ky_i+lz_i)$ where $\overline{R}_i$ is the relative reflecting power of the $i^{th}$ atom in the coordiante position $x_i y_i z_i$. It is to be noted that with each of the positions (a), (b), (c), (d), (e), and (f) the origin is a point of inversion hence the B term in the expression for S is always zero. This simplifies the considerations.

It is also noteworthy that if the sodium atoms are placed at (a) and the iodine atoms are placed at (b) the value of A is zero for planes of the type (hkl) where h and k are both odd and l is some multiple of four, for first order reflections. First order reflections, however, were observed from planes of the form: (114), (118), (138), and (154). These reflections must be due to the oxygen atoms alone. To determine whether these atoms were in the "eight" or the "sixteen" positions, A was evaluated for the above class of planes for each of the positions (c), (d), and (e). It was found that here too A vanished. Hence it can be said that the oxygen atoms are crystallographically equivalent and that the arrangement of atoms in the unit is: Na at (a), I at (b) and O at (f).

Although the determination of the exact positions of the Oxygen atoms would be a very difficult matter, something can be said of their general configuration.


11·92Å
5·30Å
5.30Å
=Na
=I

It is readily seen from the accomanying figure which shows the positions of the sodium and iodine atoms in the unit of structure, that cubes, 2.65 A on an edge with sides parallel to (100), (010), and (001), can be drawn so as to have two opposite corners on one side occupied by sodium atoms and two opposite corners on the opposite side occupied by iodine atoms. If the centers of these cubes were occupied by the oxygen atoms the whole space of the unit would be uniformly filled up and a wholly symmetrical tetrahedral arrangement of oxygen atoms would obtain. The Laue photographs, as was mentionned before show evidences of a slight hemihedral arrangement. Furthermore the field about the oxygen atoms is not homogeneous since on one side there are two iodine atoms while on the other there are two sodium atoms, hence one would expect the oxygen atoms to be shifted slightly from the center of these cubes toward the iodine atoms. They are then probably arranged not as tetrahedra but as tetragonal bisphenoids. These nearly regular tetrahedra are in parallel orientation in planes parallel to (010), but in the planes parallel to (100) they are arranged in alternate groups, one group being rotated 90° relative to the other about the "c" direction. The (100) faces of the unit contain no atoms while the (010) faces contain both iodine and sodium atoms.

That this structure is very probably the correct one gains additional support from the following considerations: The first and third orders of reflections from (100) should

be absent, the second and fourth orders should be present but with the fourth somewhat stronger than the second since in the former reflection the oxygen atoms are in phase with the sodium and iodine atoms while in the second order they are out of phase. Spectral photographs from $(110)_c = (100)$ show the first and third orders absent, also the fourth is slightly stronger than the second.

Also, since the reflecting power of iodine is so much greater than that of oxygen, and that of sodium is at least as great as that of oxygen one would expect that even complicated planes in which the sodium and iodine atoms are reflecting in phase would produce spots which are stronger than those produced by less complicated planes in which the iodine and sodium atoms do not reflect. It is found that the plane (736) reflects about ten times stronger than the much less complicated plane $(31\bar{8})$ which is due to oxygen atoms alone.

It is to be noted that each sodium atom is surrounded tetrahedrally by four other sodium atoms, likewise each iodine atoms is surrounded tetrahedrally by four other iodine atoms. This gives an interpenetrating diamond arrangement, the same type of structure assigned to wulfenite and scheelite[9]. These latter crystals belong to the group mentioned earlier in the paper, and presumably will have a very similar structure to that of sodium periodate.

9) See reference 4.

Finally it is worthy of mention that there is no basis for the formula $Na_2I_2O_8$ for the solid salt, it is $NaIO_4$.

## Summary

The crystal structure of sodium periodate was investigated by making the usual spectral and Laue photographs and treating the results from the standpoint of the theory of space groups.

It was shown that the true unit of structure contains four molecules and has the dimensions: $d_{001} = 11.92$ Å and $d_{100} = d_{010} = 5.30$ Å. The structure was shown to be of lower symmetry than that assigned by crystallographers, it was assigned to the space group $C_{4h}^6$. The sodium and iodine atoms are definitely placed, they form and interpenetrating diamond arrangement. The proabable positions of the oxygen atoms is also discussed.

# THE SPACE GROUP SYMMETRY OF SODIUM NITRITE.

By L. Merle Kirkpatrick.

## Introduction.

Crystallographic data[1] show that sodium nitrite is to be assigned to the orthorhombic class of crystals. Its axial ratios are 0.6399:1:0.9670. The faces usually developed are (001), (010), (101), and (110); furthermore since similar faces are equally developed it may be expected that the structure is one of high symmetry.

The crystals used for this investigation were fairly long flat plates obtained by the slow evaporation at room temperature of a saturated solution of the pure salt. The most regular ones were examined under a microscope between crossed Nicols and were found to show parallel extinction in three directions.

## Experimental Procedure[2].

Spectral photographs were taken both by reflection and by transmission of the K-radiation of Molybdenum, while the crystal was being rotated at a constant angular velocity, so as to give $d_{100}/n$; $d_{010}/n$; and $d_{001}/n$. To insure accuracy in measurements a reference spectrum of calcite or of sodium chloride was photographed at the same time. Furthermore a brass shield having a long slit

1. P. Groth, "Chemische Krystallographie" Engelman, Leipsig, 1908. Vol. II, page 18.
2. For a detailed description of X-ray technique see "The Structure of Crystals", by R. W. G. Wycoff. The Chem. Catalog Co., New York, 1924.

3 mm. wide cut in it, was set between the crystal and plate and was rotated through twice the angle of rotation of the crystal so as to screen off all but the desired pinacoid reflections. Other photographs were taken without the screen and reference spectrum in order to obtain intensity relations of the side spectra. Table I gives the summary of the spectral data.

Laue photographs were taken with the white radiation from a tungsten anticathode; the beam of X-rays being incident upon a (001) face. The position of the crystal was changed between photographs so as to obtain both symmetrical and unsymmetrical diagrams. The indices of the reflecting planes were obtained with the aid of gnomonic projections and the results were treated with the aid of the theory of space groups[3]. The Laue data are listed in Table II.

Table I.

| Line Mo-K | $\lambda$ | Angle of reflection | order | hkl | $\frac{d_{hkl}}{n}$ | Estimated intensity |
|---|---|---|---|---|---|---|
| $\gamma$ | 0.6197 | 10° 11' | n | 100 | 1.752 | weak |
| $\beta$ | 0.6311 | 10° 21' | n | 100 | 1.756 | med. weak |
| $\alpha_1$ | 0.7078 | 11° 37' | n | 100 | 1.758 | mod. strong |
| $\alpha_2$ | 0.7121 | 11° 42' | n | 100 | 1.756 | med. weak |
| $\gamma$ | 0.6197 | 6° 26' | n | 010 | 2.767 | weak |
| $\beta$ | 0.6311 | 6° 31' | n | 010 | 2.777 | med. weak |
| $\alpha$ | 0.710 | 7° 19' | n | 010 | 2.775 | mod. strong. |
| $\beta$ | 0.6311 | 6° 43' | n | 001 | 2.698 | 0.2 |
| $\alpha$ | 0.710 | 7° 32' | n | 001 | 2.709 | 0.8 |
| $\gamma$ | 0.6197 | 13° 13' | 2n | 001 | 2.711 | 0.08 |
| $\beta$ | 0.6311 | 13° 30' | 2n | 001 | 2.704 | 0.3 |
| $\alpha_1$ | 0.7078 | 15° 10' | 2n | 001 | 2.706 | 1.0 |
| $\alpha_2$ | 0.7121 | 15° 18' | 2n | 001 | 2.698 | 0.4 |

3. The nomenclature of Wycoff is used. See "The Analytical Expression of the Results of the Theory of Space Groups" by R. W. G. Wycoff. Pub. of Carnegie Inst. No. 318, 1922.

Table II.

| hkl | $d_{hkl}$ | n | nλ | Int. | hkl | $d_{hkl}$ | n | nλ | Int. |
|---|---|---|---|---|---|---|---|---|---|
| $\bar{2}\bar{5}1$ | 0.9261 | 1 | 0.426 | 0.7 > | $2\bar{1}1$ | 1.670 | 1 | 0.414 | 0.6 |
| $\bar{2}\bar{1}0$ | 1.684 | 2 | 0.620 | 0.25≥ | $\bar{1}20$ | 2.185 | 2 | 0.629 | 0.25 |
| $\bar{3}\bar{2}1$ | 0.679 | 1 | 0.391 | 0.13> | $\bar{4}51$ | 0.686 | 1 | 0.398 | 0.06 |
| $\bar{3}01$ | 0.701 | 1 | 0.429 | 0.25≥ | $\bar{4}13$ | 0.782 | 1 | 0.433 | 0.21 |
| $\bar{2}51$ | 0.9261 | 1 | 0.426 | 0.7 > | $\bar{3}10$ | 1.153 | 1 | 0.426 | 0.5 |
| $\bar{1}30$ | 1.642 | 1 | 0.401 | 4.0 ≫ | $\bar{2}11$ | 1.670 | 1 | 0.414 | 0.6 |
| $\bar{3}32$ | 0.932 | 1 | 0.414 | 0.6 > | $\bar{3}10$ | 1.153 | 1 | 0.426 | 0.5 |
| $\bar{4}51$ | 0.686 | 1 | 0.398 | 0.13> | $\bar{4}33$ | 0.729 | 1 | 0.392 | 0.10 |
| $\bar{2}\bar{7}1$ | 0.718 | 1 | 0.364 | 0.12> | $\bar{3}61$ | 0.722 | 1 | 0.352 | 0.07 |
| $\bar{3}31$ | 0.977 | 2 | 0.498 | 0.15≥ | $\bar{1}41$ | 1.257 | 1 | 0.257 | 0.15 |
| $\bar{1}50$ | 1.061 | 1 | 0.282 | 0.25> | $\bar{1}41$ | 1.257 | 1 | 0.257 | 0.15 |
| 252 | 0.889 | 2 | 0.591 | 0.05≥ | $\bar{3}41$ | 0.899 | 1 | 0.283 | 0.05 |
| 252 | 0.889 | 2 | 0.591 | 0.05≥ | $1\bar{6}1$ | 0.898 | 1 | 0.301 | 0.05 |
| $1\bar{3}1$ | 1.340 | 2 | 0.902 | 0.6 > | $1\bar{8}5$ | 0.775 | 1 | 0.453 | 0.1 |
| $1\bar{8}5$ | 0.575 | 1 | 0.453 | 0.1 > | $1\bar{9}2$ | 0.594 | 1 | 0.454 | 0.05 |
| $\bar{2}\bar{7}1$ | 0.719 | 1 | 0.399 | 0.3 > | $\bar{3}61$ | 0.730 | 1 | 0.401 | 0.02 |
| $\bar{1}63$ | 0.801 | 1 | 0.471 | 1.4 ≫ | $\bar{3}41$ | 0.890 | 1 | 0.463 | 0.6 |
| 321 | 1.071 | 1 | 0.322 | 0.7 > | $1\bar{2}0$ | 2.192 | 2 | 0.630 | 0.4 |
| 321 | 1.071 | 1 | 0.322 | 0.7 > | 231 | 1.249 | 1 | 0.325 | absent |
| $1\bar{2}0$ | 2.192 | 2 | 0.630 | 0.4 ≫ | $2\bar{3}1$ | 1.249 | 1 | 0.325 | absent |
| $1\bar{8}1$ | 0.676 | 1 | 0.385 | 0.1 ≫ | $3\bar{6}1$ | 0.730 | 1 | 0.372 | 0.05 |
| $\bar{1}61$ | 0.885 | 1 | 0.418 | 0.2 > | $2\bar{5}3$ | 0.834 | 1 | 0.432 | 0.05 |
| $3\bar{5}0$ | 0.812 | 1 | 0.417 | 0.25> | $2\bar{5}3$ | 0.834 | 1 | 0.432 | 0.05 |
| $1\bar{3}1$ | 1.572 | 2 | 0.661 | 0.2 ≥ | $\bar{2}10$ | 1.697 | 2 | 0.601 | 0.2 |
| $1\bar{4}1$ | 1.259 | 1 | 0.378 | 2.0 ≫ | $2\bar{1}1$ | 1.620 | 1 | 0.373 | 0.5 |
| $0\bar{5}1$ | 1.089 | 1 | 0.406 | 2.0 ≫ | $2\bar{1}1$ | 1.620 | 1 | 0.392 | 0.6 |
| $3\bar{5}0$ | 0.812 | 1 | 0.417 | 0.25≥ | $\bar{1}61$ | 0.885 | 1 | 0.418 | 0.20 |

## The Unit of Structure.

Spectral Measurements lead to the following values: $d_{100}/n \pm 1.755$Å; $d_{010}/n = 2.773$Å; and $d_{001}/n = 2.704$Å. These are in the ratios: 0.6329:1:0.9708 which agree reasonably well with the crystallographic axial ratios. Taking the density as 2.157 g/cc[4] the number of molecules in the unit is found to be 0.249 which necessitates increasing the size of the unit. A Laue photograph shoed the spot 321 at $\sin\theta = 0.152$, hence $n\lambda = 0.165$Å; and the spot 231 at $\sin\theta = 0.144$, hence $n\lambda = 0.179$Å. The X-ray tube was operated at an effective voltage of 40 kv. consequently the lower wave length limit of the X-rays in the beam was 0.24Å. These two spots together require the doubling of all three axes and as no further data were found that required a still larger unit the true unit may be taken as: $d_{100} = 3.510$A; $d_{010} = 5.546$A; and $d_{001} = 5.408$A. It contains two molecules of $NaNO_2$.

## The Space Group.

In the orthorhombic system no first order reflections can occur from the following types of planes with these lattices:

| | | | |
|---|---|---|---|
| Lattice | $\Gamma_o'$ | end centered on (001) | h+k odd |
| " | $\Gamma_o'$ | " " " (010) | h+l odd |
| " | $\Gamma_o'$ | " " " (100) | k+l odd |
| " | $\Gamma_o''$ | face centered | h, k, or l even. |
| " | $\Gamma_o'''$ | body centered | h+k+l odd |
| " | $\Gamma_o$ | simple | no general absences. |

First order reflections were obtained fromplanes belonging to all the above types except the one for which h+k+l is odd, hence it is more than probable that the structure is based upon

4. Landolt Bornstein, Physikalisch-Chemische Tabellen Vol.5 p 303

the body centered lattice $\Gamma_0'''$. The only space groups compatible with this lattice are: $C_{2v}^{20}$; $C_{2v}^{21}$; $C_{2v}^{22}$; $V^8$; $V^9$; $V_h^{25}$; $V_h^{26}$; $V_h^{27}$; and $V_h^{28}$. Of these only $C_{2v}^{20}$; $V^8$; and $V_h^{25}$ permit the placing of two molecules of $NaNO_2$. Furthermore $V^8$ and $V_h^{25}$ are identical as far as the "two" and "four" positions are concerned, hence only the space groups $C_{2v}^{20}$ and $V_h^{25}$ need be considered. Considering the morphology of the crystals the latter is the more probable.

$V_h^{25}$ requires but one parameter and it can occur in the h, in the k, or in the l direction. Referring to the results of the spectral measurements it appears that in the reflections from (00l) the second order is stronger than the first, hence one concludes that the parameter occurs in the l direction. There are, then, twenty-four possible structures; the different ways in which the following positions can be combined:

Two equivalent positions ( for the Na- and the N-atoms)

(a) 000; ½½½ ; (b) ½00; 0½½ ; (c) 00½; ½½ 0; (d) ½0½; 0½0.

Four equivalent positions ( for the O-atoms)

(i) 00u; 00$\bar{u}$; ½,½ u+½; ½,½,½ -u. (j) 0½u; 0½$\bar{u}$; ½,0,u+½; ½,0,½-u.

However, if certain translations of the origin of coordinates are made it is found that many of these structures are identical:

(000) to (00½) (a)=(c); (b)=(d); (i)=(i); and (j)=(j).
(000) to (0½0) (a)=(d); (b)=(c); and (i)=(j).
(000) to (½00) (a)=(b); (c)=(d); and (i)=(j).

The possible independent structures are reduced to six: (1) (a)(b)(i); (2) (a)(b)(j); (3) (a)(c)(i); (4) (a)(c)(j); (5) (a)(d)(i); and (6) (a)(d)(j). Where the first letter refers to the positions of the Na-atoms, the second to the positions of the N-atoms and the third to the positions of the O-atoms.

The structure factor expression for each of these structures for the case of first order reflections from planes for which the sum of the indices is odd are:

(1) $S= 2\bar{N}a + (-1)^{k} 2\bar{N} + 4\bar{O} \cos 2\pi lu.$

(2) $S= 2\bar{N}a + (-1)^{k} 2\bar{N} + 4\bar{O}\ (-1)^{k} \cos 2\pi lu.$

(3) $S= 2\bar{N}a + (-1)^{l} 2\bar{N} + 4\bar{O} \cos 2\pi lu.$

(4) $S= 2\bar{N}a + (-1)^{l} 2\bar{N} + 4\bar{O}\ (-1)^{k} \cos 2\pi lu.$

(5) $S= 2\bar{N}a + (-1)^{k} 2\bar{N} + 4\bar{O} \cos 2\pi lu.$

(6) $S= 2\bar{N}a + (-1)^{k} 2\bar{N} + 4\bar{O}\ (-1)^{k} \cos 2\pi lu.$

where $S=\sqrt{A^2+B^2}$ , $A=\Sigma\bar{R}_i \cos 2\pi n(hx_i+ky_i+lz_i)$ and $B=\Sigma\bar{R}_i \sin 2\pi n(hx_i+ky_i+lz_i)$ $\bar{R}_i$ being the reflecting power of the i'th atom in the coordinate position $x_i, y_i, z_i$.

Referring to Table II it is to be noted that $(\bar{2}\bar{5}1)_1 > (2\bar{1}1)_1$; $(\bar{1}\bar{8}1)_1 > (\bar{3}\bar{6}1)_1$; and $(051)_1 > (211)_1$. In each comparison the l index is the same, while the h indices and the k indices are the same for eveness or oddness. Consequently the value of S will be the same for each plane of the comparison for all the six structures. This definitely eliminates this space group and leaves only $C_{2v}^{20}$ as being compatible with the data found.

$C_{2v}^{20}$ provides the following positions:

Two equivalent positions, ( for the Na- and N-atoms ).

(a) 00u; $\frac{1}{2},\frac{1}{2},u+\frac{1}{2}$; and (b) $\frac{1}{2}$ 0u; $0,\frac{1}{2},u+\frac{1}{2}$.

Four equivalent positions, ( for the O-atoms ).

(c) w0v; $\bar{w}0v$; $w+\frac{1}{2},\frac{1}{2},v+\frac{1}{2}$; $\frac{1}{2}-w,\frac{1}{2},v+\frac{1}{2}$.

(d) 0wv; $0\bar{w}v$; $\frac{1}{2},w+\frac{1}{2},v+\frac{1}{2}$; $\frac{1}{2},\frac{1}{2}-w,\ v+\frac{1}{2}$.

There are eight possible ways of combining these positions, but if one translates the origin of coordinates from (000) to $(\frac{1}{2}00)$ it is clear that (a) becomes identical to (b) and (c) and (d) remain unchanged. This reduces the number of independent combinations to four:

$\alpha$:Na at (a), N at (b), O at (c); $\beta$:Na at (a), N at (b), O at (d).

$\gamma$:Na at (a), N at (a), O at (c); $\delta$:Na at (a), N at (a), O at (d).

However since this space group requires a unique choice of axes, the number of structures becomes twenty four since there are six ways of choosing the axes:[5]

$\mathrm{I}(hkl)_C = (hkl)_S$; $\mathrm{II}(hkl)_S = (hlk)_C$; $\mathrm{III}(hkl)_S = (khl)_C$; $\mathrm{IV}(hkl)_S = (klh)_C$;

$\mathrm{V}(hkl)_S = (lhk)_C$; $\mathrm{VI}(hkl)_S = (lkh)_C$.

Again using the spectral comparison $(001)_4 > (001)_2$ eight of these: $\alpha_{\mathrm{II}}, \alpha_{\mathrm{III}}, \beta_{\mathrm{V}}, \beta_{\mathrm{VI}}, \gamma_{\mathrm{II}}, \gamma_{\mathrm{III}}, \delta_{\mathrm{V}}, \delta_{\mathrm{VI}}$ are eliminated because the value of S becomes the same for each plane i.e. $S = 2\overline{Na} + 2\overline{N} + 4\overline{O}$.

Certain regions of the value of the parameter were investigated but with no conclusive results. To carefully con-

*

5. The subscript S refers to the Space Group axes, C refers to the crystallographic axes.

sider the entire range of parametral values for each one of the sixteen possible structures appeared not to be worth while.


## Summary.

The crystal structure of orthorhombic sodium nitrite was studied by means of spectral and Laue photographs. The results were treated from the stand point of space group theory. The unit rectangular parallelopiped was shown to contain two molecules and to have these dimensions: $d_{100} = 3.510$ Å; $d_{010} = 5.546$ Å; and $d_{001} = 5.408$ Å. The structure was shown to be built upon a body centered lattice $\Gamma_o^{m}$ and that it was to be assigned to the space group $C_{2v}^{20}$.

# THE CRYSTAL STRUCTURE OF THE CUBIC MODIFICATION OF TELLURIC ACID.[1]

By L. Merle Kirkpatrick and Linus Pauling.[2]

## Introduction.

Telluric acid $Te(OH)_6$, crystallizes in both the cubic and monoclinic systems.[3] The structure of the cubic form was investigated by the use of spectral and Laue photographs interpreted with the aid of the theory of space groups.

The crystals were prepared as follows: tellurium metal was treated with hot nitric acid and chromic anhydride. The resulting telluric oxide, $TeO_3$, was then dissolved in hot nitric acid whose specific gravity was 1.32. This solution upon slow cooling, yielded small octahedral crystals of $Te(OH)_6$, which were optically isotropic and were therefore cubic.

## Experimental Procedure.

The X-ray methods employed have been described by Wycoff[4]. The spectral photographs were taken by causing a beam of the K-radiation of Molybdenum to pass through an octahedral, [1 1 1] face while the crystal was being rotated at a constant angular velocity. The Laue photographs were also taken through a [1 1 1] face using the white radiation from a tungsten anticathode. The crystal was mounted directly over the second of the two pin holes used to define the beam of X-rays.

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1. This paper has been accepted for publication in the Zeitschrift für Krystallographie und Mineralogie.
2. National Research Fellow.
3. Groth, "Chemische Krystallographie" Engelman Leipzig, 1906. I, 123
4. R.W.G.Wycoff, "The Structure of Crystals" The Chemical Catalogue Co. New York, 1924, pp. 109-177.

Gnomonic projections were made of the Laue Photographs and indices were assigned to the planes producing the spots. The crystals used to make these photographs were less than 0.3 mm. on an edge. It is remarkable that such small specimens will give clear photographs as fig. 1 and fig. 2. show.

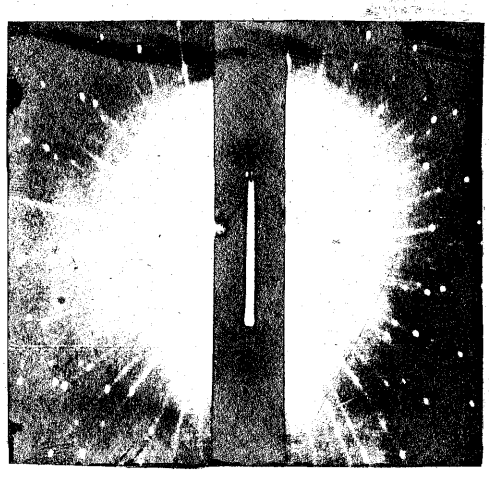

Fig1

Fig 2.

## The Unit of Structure.

In table I, are listed the spectral data from (110). Using the equations $\lambda n = 2d_{hkl}\sin\theta$ and $d_{100} = d_{hkl}\sqrt{h^2+k^2+l^2}$, one finds a value of 3.87 Å for $d_{100}/n$. Table II, gives the data froma Laue photograph taken with the X-ray tube operated at a peak voltage of 40kv. Therefore, the low wave length limit of the X-rays present in the incident beam is 0.31 Å. In order to explain the production of certain spots on this photograph it is necessary to take n=4 in which case $d_{100} = 15.48$ Å. No other data were found requiring a larger unit , hence the true unit of structure may be taken as a cube 15.48 Å on an edge. All data in Table II are calculated on this basis.

The density of the crystals, using the Retgers' suspension method, was found to be 3.12 g/cc. somewhat higher than the value 3.053 g/cc which is usually given. Assuming that there are 32 molecules of $Te(OH)_6$ in the unit the density calculated on the X-ray data is 3.26 g/cc which is in sufficiently good agreement with the experimentally determined value.

The Space Lattice and the Space-group.

Since the only planes which produce first order reflections are those whose indices are all odd, the structure is based upon the face centered cubic lattice $\Gamma_c'$. Moreover a Laue photograph taken with the incident beam inclined only a few degrees from [111] showed a plane of symmetry containing this three-fold axis. This shows that the crystal is isomorphous with the point group $T_d$, O or $O_h$.

The only space groups which will place 32 molecules of $Te(OH)_6$, are $O_h^5$, $O_h^6$, $O_h^7$, and $O_h^8$. Using space group criteria one can decide between these possibilities;

(a) No first order reflections from planes all of whose indices are odd and with $h=\pm k$ were found although planes of the forms {533}, {551}, {733}, {773}, {755}, {775}, {955}, and {11·3·3} were in a position favorable to reflection.

(b) No second order reflections from planes of the form (0kl) were observed, although planes of the forms {023}, {043}, and {047} were in positions favorable to reflection.

Fact (a) is explained only by the space groups $O_h^6$ and $O_h^8$. Fact (b) is required by $O_h^8$ and is not explained by $O_h^6$. Hence X-ray data show that the crystal is to be assigned to the space group $O_h^8$.

## The Atomic Arrangement.

There are 32 tellurium atoms, 192 oxygen atoms and 192 hydrogen atoms to be placed in the unit of structure. Assuming that all atoms of one kind are crystallographically equivalent it is found by reference to a tabulation of the results of the theory of space groups[5] that the space group $O_R^8$ provides two possible positions for the tellurium atoms:

32 d. $\frac{1}{8}\frac{1}{8}\frac{1}{8}$; $\frac{1}{8}\frac{7}{8}\frac{7}{8}$; $\frac{7}{8}\frac{1}{8}\frac{7}{8}$; $\frac{7}{8}\frac{7}{8}\frac{1}{8}$;
$\frac{3}{8}\frac{1}{8}\frac{3}{8}$; $\frac{1}{8}\frac{3}{8}\frac{3}{8}$; $\frac{3}{8}\frac{3}{8}\frac{1}{8}$; $\frac{5}{8}\frac{5}{8}\frac{5}{8}$;
$\frac{5}{8}\frac{7}{8}\frac{7}{8}$; $\frac{7}{8}\frac{5}{8}\frac{5}{8}$; $\frac{7}{8}\frac{7}{8}\frac{5}{8}$; $\frac{3}{8}\frac{5}{8}\frac{5}{8}$;
$\frac{5}{8}\frac{3}{8}\frac{3}{8}$; $\frac{3}{8}\frac{3}{8}\frac{5}{8}$; $\frac{5}{8}\frac{3}{8}\frac{3}{8}$; $\frac{1}{8}\frac{1}{8}\frac{5}{8}$;
$\frac{3}{8}\frac{5}{8}\frac{7}{8}$; $\frac{3}{8}\frac{5}{8}\frac{5}{8}$; $\frac{5}{8}\frac{3}{8}\frac{3}{8}$; $\frac{1}{8}\frac{5}{8}\frac{1}{8}$;
$\frac{1}{8}\frac{3}{8}\frac{3}{8}$; $\frac{3}{8}\frac{1}{8}\frac{3}{8}$; $\frac{5}{8}\frac{5}{8}\frac{1}{8}$; $\frac{5}{8}\frac{1}{8}\frac{1}{8}$;
$\frac{5}{8}\frac{1}{8}\frac{5}{8}$; $\frac{3}{8}\frac{3}{8}\frac{5}{8}$; $\frac{3}{8}\frac{5}{8}\frac{3}{8}$; $\frac{1}{8}\frac{1}{8}\frac{3}{8}$;
$\frac{3}{8}\frac{7}{8}\frac{1}{8}$; $\frac{3}{8}\frac{3}{8}\frac{1}{8}$; $\frac{1}{8}\frac{5}{8}\frac{5}{8}$; $\frac{3}{8}\frac{3}{8}\frac{3}{8}$;

32 e. $\frac{3}{8}\frac{3}{8}\frac{3}{8}$; $\frac{7}{8}\frac{7}{8}\frac{7}{8}$; $\frac{7}{8}\frac{7}{8}\frac{3}{8}$; $\frac{3}{8}\frac{3}{8}\frac{7}{8}$;
$\frac{7}{8}\frac{3}{8}\frac{7}{8}$; $\frac{3}{8}\frac{7}{8}\frac{3}{8}$; $\frac{3}{8}\frac{7}{8}\frac{3}{8}$; $\frac{7}{8}\frac{3}{8}\frac{3}{8}$;
$\frac{3}{8}\frac{5}{8}\frac{5}{8}$; $\frac{5}{8}\frac{7}{8}\frac{5}{8}$; $\frac{3}{8}\frac{1}{8}\frac{1}{8}$; $\frac{1}{8}\frac{7}{8}\frac{1}{8}$;
$\frac{7}{8}\frac{1}{8}\frac{5}{8}$; $\frac{1}{8}\frac{3}{8}\frac{5}{8}$; $\frac{7}{8}\frac{5}{8}\frac{1}{8}$; $\frac{5}{8}\frac{3}{8}\frac{1}{8}$;
$\frac{5}{8}\frac{3}{8}\frac{5}{8}$; $\frac{7}{8}\frac{5}{8}\frac{5}{8}$; $\frac{1}{8}\frac{3}{8}\frac{1}{8}$; $\frac{7}{8}\frac{1}{8}\frac{1}{8}$;
$\frac{1}{8}\frac{7}{8}\frac{5}{8}$; $\frac{3}{8}\frac{1}{8}\frac{5}{8}$; $\frac{5}{8}\frac{7}{8}\frac{1}{8}$; $\frac{3}{8}\frac{5}{8}\frac{1}{8}$;
$\frac{5}{8}\frac{5}{8}\frac{3}{8}$; $\frac{5}{8}\frac{5}{8}\frac{7}{8}$; $\frac{1}{8}\frac{1}{8}\frac{3}{8}$; $\frac{1}{8}\frac{1}{8}\frac{7}{8}$;
$\frac{1}{8}\frac{5}{8}\frac{7}{8}$; $\frac{1}{8}\frac{5}{8}\frac{3}{8}$; $\frac{5}{8}\frac{1}{8}\frac{7}{8}$; $\frac{5}{8}\frac{1}{8}\frac{3}{8}$.

The oxygen and hydrogen atoms are to be assigned to the general positions.

It is obvious that by a translation of the origin from 000 to $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, 32 d, becomes identical with 32 e. In either case the unit cube can be said to be composed of 8 small cubes each one of which contains 4 tellurium atoms with the face centered arrangement 000, $\frac{1}{2}\frac{1}{2}0$, $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$. Hence one can say that the crystal is built up of approximately spherical $Te(OH)_6$ molecules with cubic close packing.

In neither 32 d, nor 32 e, do the tellurium atoms contribute either to the first order reflections from planes with all indices odd or to the second order reflections from other planes. This is clear after considering the structure factor expressions:

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5. R.W.G.Wycoff, "The Analytical Representation of the Results of the Theory of Space Groups", Pub. Carnegie Inst. #318, 1922.

$S=\sqrt{A^2+B^2}$, where $A=\overline{R}_i \cos 2\pi n(hx_i+ky_i+lz_i)$ and $B=\overline{R}_i \sin 2\pi n(hx_i+ky_i+lz_i)$. In these expressions $\overline{R}_i$ signifies the relative reflecting power of the " i'th " atom which is in the coordinate position $x_i\ y_i\ z_i$. h k l are of course the indices of any particular plane. The summations are taken over the whole unit for all the atoms. The hydrogen atoms, due to their very low reflecting power contribute nothing to any reflection, hence one should be able to locate the oxygen atoms by studying the intensities of the reflections from the above mentioned interesting planes. Although extensive calculations were carried through no unique value for the three parameters defining the positions of the oxygen atoms could be obtained, and it seemed useless to carry these calculations further.

With the tellurium atoms in 32 d, or in 32 e, the point group symmetry of the molecule[6] is $C_{3i}$ or $D_3$ respectively. This is in agreement with the formula $Te(OH)_6$ rather than $H_2TeO_4.2H_2O$; the former is supported by other evidence also.[7] It seems reasonable that the six oxygen atoms are arranged octahedrally about the the central tellurium atom in the molecule; however in default of a complete determination of the structure and atomic arrangement the shape of the molecule cannot be further determined.

## Summary of Results.

The crystal structure of cubic telluric acid $Te(OH)_6$ has been studied by interpreting the data from spectral and Laue photographs with the aid of the theory of space groups. The unit of structure is 15.48 Å on an edge and contains 32 molecules. The structure is based on the face centered lattice $\Gamma_c'$ and is to be

6. Niggli, "Geometrische Kristallographie des Discontinuums" Borntraeger, Leipsig, 1919, p.411.
7. Baker and Adlam, J. Chem. Soc. 99, 507, 1911.

assigned to the space group $O_h^8$. A discussion of the atomic arrangement is given.

Table I.

| Order | Wave length of line | angle of reflection | $d_{110}$ /n. |
|---|---|---|---|
| n | 0.6311 Å | 6°33.5' | 2.762 Å |
| n | 0.719 | 7°22.5' | 2.769 |
| 2n | 0.6311 | 13°14.2' | 2.755 |
| 2n | 0.7078 | 14°53.2' | 2.755 |
| 2n | 0.7121 | 14°57.6' | 2.756 |

Table II.

| (hkl) | n | $d_{hkl}$ /n | λ | estimated intensity |
|---|---|---|---|---|
| $5\bar{3}\bar{1}$ | 1 | 2.62 Å | 0.41 Å | 4 |
| $\bar{5}33$ | 1 | 2.36 | 0.43 | a |
| $\bar{5}51$ | 1 | 2.17 | 0.44 | a |
| $0\bar{2}3$ | 2 | 2.15 | 0.52 | a |
| $3\bar{7}\bar{3}$ | 1 | 1.89 | 0.40 | a |
| $42\bar{1}$ | 2 | 1.69 | 0.37 | a |
| $4\bar{1}\bar{2}$ | 2 | 1.69 | 0.41 | 0.05 |
| $5\bar{7}5$ | 1 | 1.56 | 0.40 | a |
| $\bar{3}40$ | 2 | 1.55 | 0.44 | a |
| $7\bar{7}\bar{3}$ | 1 | 1.50 | 0.40 | a |
| $5\bar{1}9$ | 1 | 1.50 | 0.43 | a |
| $5\bar{7}7$ | 1 | 1.40 | 0.61 | a |
| $9\bar{1}7$ | 1 | 1.35 | 0.43 | 0.3 |
| $\bar{3}\bar{4}3$ | 2 | 1.33 | 0.42 | 0.8 |
| $\bar{4}33$ | 2 | 1.33 | 0.53 | 0.4 |
| $0\bar{3}5$ | 2 | 1.33 | 0.42 | 0.1 |
| $11\bar{5}\bar{1}$ | 1 | 1.28 | 0.55 | 0.1 |
| $\bar{5}7\bar{9}$ | 1 | 1.24 | 0.41 | a |
| $\bar{5}11\bar{3}$ | 1 | 1.24 | 0.43 | 0.25 |
| $5\bar{1}4$ | 2 | 1.19 | 0.42 | a |
| $\bar{1}11\bar{7}$ | 1 | 1.18 | 0.40 | a |
| $43\bar{5}$ | 2 | 1.10 | 0.40 | 0.05 |
| $25\bar{5}$ | 2 | 1.06 | 0.40 | a |
| $4\bar{5}4$ | 2 | 1.03 | 0.39 | 0.15 |
| $\bar{2}27$ | 2 | 1.03 | 0.40 | 0.10 |

a signifies absent.