

computed and used as multipliers for the matrices  $F(\lambda_i)$  in computing the expression (23). If positive signs for the roots are used we obtain

$$\gamma = \begin{pmatrix} 5.9969 & -0.8366 & -0.8894 \\ -0.8836 & 10.6565 & 0.4744 \\ -0.8894 & 0.4744 & 5.8842 \end{pmatrix}.$$

From this the adjoint  $\Gamma$  can be calculated, the determinant  $\gamma$  and hence the matrix

$$\gamma^* = \begin{pmatrix} 0.17220 & 0.01240 & 0.02503 \\ 0.01240 & 0.09507 & -0.00579 \\ 0.02503 & -0.00579 & 0.01622 \end{pmatrix},$$

which completes the solution to the problem.

### Discussion

The existence of the E-systems was first recognized in the course of the consideration of orthogonal systems suitable for use with triclinic and monoclinic crystals in the discussion of bond lengths and bond angles. It was realized if coordinate vectors only were under discussion, one matrix and its inverse were needed for transformation between the base lattice and the e-system. If, in addition, indices and direction vectors were needed, a second matrix and its inverse would be needed to provide the transformation between the reciprocal lattice and the e-system. Thus a total of four transformation matrices is required for work in terms of a general e-system while only two matrices  $\gamma$  and  $\gamma^*$  are needed if an E-system is used.

For those cases in which the  $\gamma$ -matrices can be written explicitly in terms of the lattice constants (e.g. Tables 1 and 2) the E-systems may prove to be very useful. In the orthogonal lattices the choice of the E-systems is obvious. In other systems a number of possible e-systems are available and it may be that the choice of the E-system will prove to be advantageous.

It is unfortunate that, for the triclinic system in which the use of an E-system would undoubtedly be the most profitable, the calculation of the  $\gamma$ -matrices is the most difficult. It is expected, however, that if the E-systems prove to be of value, the technique of the calculation of the  $\gamma$ -matrices can be improved considerably.

The existence of the E-systems introduces an interesting speculation. The problem of the diffraction analysis of structures depends on the interaction of data which belong in crystal space, such as atomicity, positivity, closest approach etc., with data, such as diffraction amplitude, phase, which belong in reciprocal space. The transformation of data from one space to the other always results in considerable increase in complication, as is indicated by the nature of the many ingenious methods of direct structural analysis which are now under consideration. The existence of an E-system 'midway' between the a-system and the a\*-system suggests the possibility of a function space occupying a similar position between crystal space and transform space. There seems to be little indication of the nature of the functional transformation needed, but the  $\gamma$ -matrix suggests a coordinate transformation which would provide a geometric basis for such a functional space.

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## The Crystal Structure of Phosgene, $\text{COCl}_2$

BY BERTRAM ZASLOW, MASAO ATOJI AND WILLIAM N. LIPSCOMB

*School of Chemistry, University of Minnesota, Minneapolis 14, Minnesota, U.S.A.*

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The crystal structure of phosgene is tetragonal  $C_{4h}^2-I4_1/a$  with 16 phosgene molecules in a unit cell of dimensions  $a = b = 15.82$ ,  $c = 5.72$  Å. At  $-160^\circ\text{C}$ ., the crystal is completely ordered, and the residual entropy of 1.63 e.u. remains unexplained. Parameters, referred to a center of symmetry as origin, are for  $\text{Cl}_1$ , (0.0394, -0.1417, 0.150); for  $\text{Cl}_2$ , (0.1038, -0.0528, -0.250); for O, (0.1982, -0.1306, 0.039); and for C, (0.1295, -0.1126, -0.004). Molecular dimensions are  $\text{C}-\text{Cl}_1 = 1.74 \pm 0.02$  Å,  $\text{C}-\text{Cl}_2 = 1.74 \pm 0.02$  Å,  $\text{C}=\text{O} = 1.15 \pm 0.02$  Å, and  $\text{Cl}_1-\text{C}-\text{Cl}_2 = 111.0 \pm 1.5^\circ$ .

### Introduction

As a result of a careful calorimetric study in which the spectroscopic assignment (Thompson, 1941;

Stevenson & Beach, 1938*a, b, c*) and molecular geometry (Brockway, Beach & Pauling, 1935) were employed, Giauque & Jones (1948) have attributed a residual entropy of 1.63 e.u. to phosgene. The purpose of the

present study was to investigate the solid for the structural disorder suggested by this residual entropy. In addition, our results are compared with those of the electron-diffraction studies (Brockway, Beach & Pauling, 1935; Schomaker, 1950) of the molecular structure.

### Experimental

Samples of phosgene (99.5% pure), obtained from the Matheson Company, East Rutherford, New Jersey, were distilled under vacuum into thin Pyrex capillary tubes less than 1 mm. in diameter. These tubes were sealed off after freezing the material with liquid nitrogen, and were then mounted on the Buerger precession camera. Single crystals were grown (Abrahams, Collin, Lipscomb & Reed, 1950) in a stream of cold nitrogen obtained by evaporation of liquid nitrogen by use of a heating coil. Phosgene freezes at  $-127.8^\circ \text{C}$ . Because the solid is characterized by an anomalous coefficient of expansion for about a  $25^\circ \text{C}$ . range below its melting point (Giauque & Jones, 1948), the photographs were taken at  $-160^\circ \text{C}$ . The intensity data were obtained from single crystals grown over a period of about one hour, and maintained at  $-160^\circ \text{C}$ . for 6–72 hr. Thus, the exposures for  $\{hk0\}$  data began 48 hr. after the single crystal had been grown, while those for  $\{h0l\}$  data began 6 hr. after the single crystal had been grown. No systematic orientation was observed for different crystals grown under essentially the same conditions. Mo  $K\alpha$  radiation was used throughout this study and the photographs were taken at a precession angle of  $28^\circ$ . Corrected Lorentz and polarization factors (Waser, 1951*a, b*) were employed for reduction of the visual estimates to structure factors.

### Determination of the structure

The unit cell is tetragonal with

$$a = 15.82 \pm 0.05, c = 5.72 \pm 0.02 \text{ \AA}.$$

The symmetry of the reciprocal lattice is  $C_{4h}$ . The following conditions for non-extinction occur, where  $n$  is an integer:  $h+k+l = 2n$  for  $\{hkl\}$ ;  $h = 2n$  and  $k = 2n$  for  $\{hk0\}$ ;  $l = 4n$  for  $\{00l\}$ . These uniquely determine the space group  $C_{4h}^s - I4_1/a$ , which is centrosymmetric. The number of molecules in the unit cell and the number of general positions in the unit cell are both 16.

The  $\{hk0\}$  data were initially examined because of the possibility of complete resolution of all the atoms in the molecule by projection along the relatively short  $c$  axis. The  $x$  and  $y$  parameters of the chlorine atoms were approximately located from the  $\{hk0\}$  Patterson synthesis analyzed on the basis of a molecule consisting of two chlorine atoms only. The oxygen and carbon atoms later showed up in the Fourier projection for which the signs of  $F_o$  were determined

by this model. Refinements were carried out until no further sign changes occurred. This final Fourier summation is shown in Fig. 1. A calculated Fourier

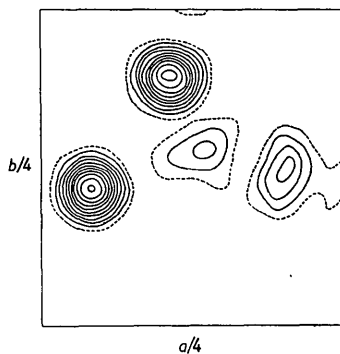


Fig. 1. Projection of the asymmetric unit in the unit cell along the  $c$  axis. Each contour line represents a density increment of  $3 \text{ e.}\text{\AA}^{-2}$ , the three-electron contour line being broken.

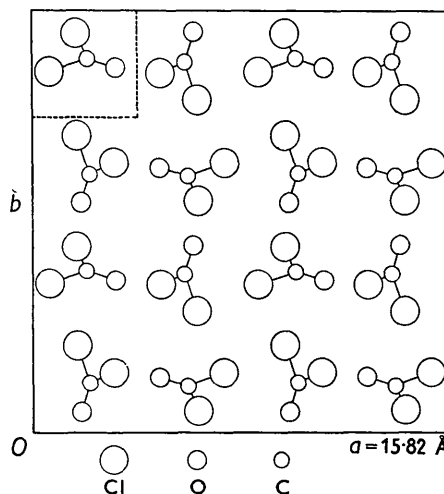


Fig. 2. Arrangement of the molecules in the  $c$ -axis projection. The asymmetric unit is shown by broken lines.

was computed, and a backshift was applied to correct the positions of the atoms for termination error. No further sign changes resulted from the backshift correction.

A least-squares treatment was then applied to the  $\{hk0\}$  data using the method described by Hughes (1941). The results are summarized in Table 1. The probable errors were calculated from the residuals on the assumption that the differences  $\nu\omega \cdot (F_c - F_o)$  were random. Weighting factors were  $\nu\omega = 1/F_o$  for  $F_o \geq 4F_{\text{min}}$ . and  $\nu\omega = \frac{1}{16} |F_o/F_{\text{min}}|^2$  for  $F_o \leq 4F_{\text{min}}$ . The final value of the constant  $B$  in the temperature-factor expression for  $\{hk0\}$  data was found to be  $1.6 \text{ \AA}^2$ .

Initial  $z$  coordinates were determined from spatial and symmetry considerations, assuming that the molecule is planar. A projection along  $[010]$  was then

Table 1. *Final atomic parameters\* of phosgene expressed as fractions of the unit cell*

	Fourier	Least squares	Average	Probable error (calculated)
$x_{Cl_1}$	0.0395	0.0393	0.0394	0.0003
$y_{Cl_1}$	-0.1416	-0.1418	-0.1417	0.0003
$x_{Cl_2}$	0.1036	0.1041	0.1038	0.0003
$y_{Cl_2}$	-0.0528	-0.0528	-0.0528	0.0003
$x_O$	0.1988	0.1975	0.1982	0.0007
$y_O$	-0.1305	-0.1308	-0.1306	0.0007
$x_C$	0.1292	0.1298	0.1295	0.0009
$y_C$	-0.1119	-0.1134	-0.1126	0.0010

	Trial and error	Probable error (estimated)
$z_{Cl_1}$	0.150	0.002
$z_{Cl_2}$	-0.250	0.002
$z_O$	0.039	0.004
$z_C$	-0.004	0.004

\*The parameters are referred to an origin which is at  $0, \frac{1}{4}, \frac{1}{8}$  with respect to: he origin in the *Internationale Tabellen*.

made (Fig. 3) which resolved only one chlorine atom,  $Cl_1$  (Fig. 4). A least-squares treatment of the  $\{h0l\}$  data was not profitable, even when the  $x$  and  $y$  parameters determined above were introduced as constraints, presumably because of the extremely poor resolution of atoms. Final  $z$  parameters and their

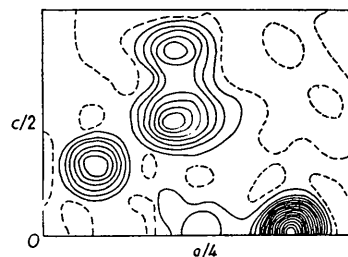


Fig. 3. Projection of the unit cell along the  $b$  crystal axis. Each contour line represents a density increment of  $5 e. \text{Å}^{-2}$ , the zero-electron contour line being broken.

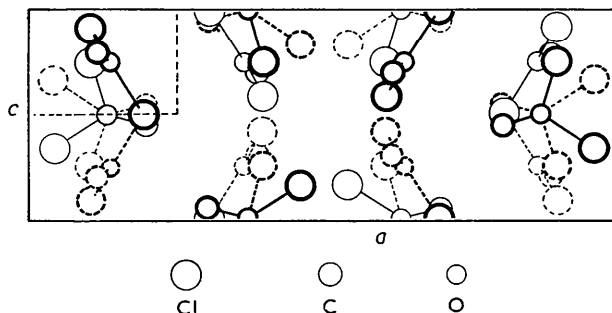


Fig. 4. Arrangement of the molecules in the  $b$ -axis projection.

Table 2. *Observed and calculated values of the structure factors\**

$hkl$	$F_o$	$F_c$	$hkl$	$F_o$	$F_c$	$hkl$	$F_o$	$F_c$
200	< 10.2	4.5	12,6,0	12.6	-11.5	12,14,0	19.1	-21.1
400	42.5	-50.8	14,6,0	3.3	5.9	14,14,0	14.0	-12.0
600	13.3	-12.6	16,6,0	13.5	12.6	2,16,0	10.2	-11.0
800	6.8	6.3	18,6,0	7.0	-9.0	4,16,0	< 6.9	3.6
10,0,0	34.1	35.8	280	5.4	6.6	6,16,0	10.5	11.5
12,0,0	37.8	-37.2	480	52.7	60.1	8,16,0	22.6	22.8
14,0,0	27.7	-28.7	680	14.4	11.6	10,16,0	< 6.2	-1.0
16,0,0	< 6.9	-0.9	880	21.4	-22.3	12,16,0	9.6	-10.0
18,0,0	< 6.6	-0.2	10,8,0	6.1	-4.7	2,18,0	6.8	8.9
20,0,0	16.5	15.8	12,8,0	7.4	-4.2	4,18,0	21.5	-24.0
220	< 3.0	3.0	14,8,0	17.2	17.9	6,18,0	8.2	-8.0
420	26.3	23.3	16,8,0	16.1	-15.2	8,18,0	6.0	5.9
620	13.3	10.4	18,8,0	23.3	-23.7	10,18,0	10.5	6.6
820	25.0	25.1	2,10,0	8.4	-7.4	2,20,0	< 6.0	-3.5
10,2,0	5.1	6.6	4,10,0	7.0	-6.6	4,20,0	14.7	-11.6
12,2,0	< 6.6	3.5	6,10,0	16.1	14.9	101	16.4	16.0
14,2,0	9.6	8.9	8,10,0	25.4	26.1	301	16.2	-15.6
16,2,0	13.0	-13.3	10,10,0	7.5	-9.4	501	41.6	52.8
18,2,0	7.0	-7.3	12,10,0	9.2	8.4	701	20.0	-19.6
20,2,0	8.4	-6.7	14,10,0	6.5	7.2	901	16.4	-14.4
240	42.7	49.0	16,10,0	4.6	4.7	11,0,1	5.4	-5.2
440	27.3	-26.0	18,10,0	8.2	5.7	13,0,1	13.0	-13.6
640	41.0	-43.4	2,12,0	6.8	-6.7	15,0,1	14.6	15.6
840	5.8	-4.5	4,12,0	3.2	-0.8	17,0,1	12.0	-12.8
10,4,0	6.1	6.7	6,12,0	7.4	8.8	19,0,1	6.2	6.8
12,4,0	44.3	46.1	8,12,0	21.4	-21.1	202	33.0	-35.0
14,4,0	3.3	-3.1	10,12,0	15.2	-18.2	402	23.0	23.2
16,4,0	8.4	-10.4	12,12,0	11.2	10.3	602	19.6	19.0
18,4,0	11.2	10.9	14,12,0	< 6.6	4.1	802	23.2	-25.8
20,4,0	< 5.8	3.0	16,12,0	15.2	13.2	10,0,2	13.6	11.6
260	22.6	-21.0	2,14,0	4.6	-4.5	12,0,2	6.6	-6.0
460	6.1	5.7	4,14,0	< 6.6	4.9	14,0,2	9.2	11.0
660	13.3	12.6	6,14,0	7.4	-8.4	16,0,2	11.4	11.2
860	33.8	-33.3	8,14,0	< 6.9	-2.2	18,0,2	9.2	-11.0
10,6,0	19.4	-18.3	10,14,0	10.5	11.9	20,0,2	2.2	2.0

\* Structure factors are calculated for 4  $COCl_2$  molecules. Reflections of the type  $\{hkk\}$  for  $k$  odd were also indexed, but the calculations were considered so lengthy that we felt it unprofitable to extend the list further.

Table 2 (cont.)

<i>hkl</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>	<i>hkl</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>	<i>hkl</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>
103	4.4	2.0	112	33.3	34.2	822	4.1	3.0
303	36.6	-38.4	222	11.0	-9.7	10,2,2	12.6	-15.2
503	4.2	5.2	332	8.1	8.6	12,2,2	13.7	-13.5
703	7.0	-6.8	442	15.7	-12.8	14,2,2	11.7	12.1
903	19.2	18.4	552	17.3	-15.4	16,2,2	6.1	5.8
11,0,3	15.6	14.6	662	23.7	22.9	18,2,2	5.6	5.0
13,0,3	7.6	-7.2	772	2.8	2.4	242	26.0	26.0
15,0,3	14.8	17.2	882	3.5	3.1	262	27.5	-28.6
17,0,3	< 2.0	1.0	992	12.2	-12.2	282	20.8	-20.7
004	18.4	18.0	10,10,2	3.0	1.5	2,10,2	21.8	23.9
204	21.6	-20.8	11,11,2	6.2	6.2	2,12,2	22.6	22.1
404	13.6	-12.2	12,12,2	9.2	10.5	2,14,2	8.6	-8.8
604	3.4	3.4	13,13,2	12.3	12.4	2,16,2	3.2	-3.7
804	4.0	-2.0	14,14,2	7.0	7.2	2,18,2	12.1	14.2
10,0,4	19.0	19.4	114	< 2.6	-2.9	244	27.7	27.9
12,0,4	2.6	-2.2	224	9.6	10.0	644	4.5	4.3
14,0,4	9.2	7.4	334	12.9	-13.5	844	< 3.8	-1.3
16,0,4	8.0	8.0	444	9.2	9.1	10,4,4	14.7	-16.0
105	11.4	12.2	554	2.9	-3.2	12,4,4	9.6	9.5
305	14.6	-15.2	664	6.6	5.7	14,4,4	9.7	-8.1
505	5.8	2.6	774	11.2	8.7	16,4,4	8.1	-8.2
705	7.2	-6.6	884	3.1	-3.0	424	11.0	-12.5
905	8.2	9.2	994	2.1	-0.8	464	13.0	14.5
11,0,5	5.4	6.2	10,10,4	22.7	-25.5	484	< 3.8	3.3
13,0,5	11.2	-12.0	11,11,4	< 2.0	-0.3	4,10,4	13.1	13.8
15,0,5	6.4	3.2	12,12,4	< 2.0	-0.6	4,12,4	2.8	-2.5
206	6.0	-4.4	116	< 2.0	-7.0	4,14,4	5.3	5.6
406	19.4	19.6	226	< 2.0	0.5	4,16,4	9.6	-9.7
606	13.0	13.2	336	< 2.0	-5.5	266	6.2	-3.5
806	16.0	-16.8	446	12.5	-12.7	466	9.6	-8.9
10,0,6	8.0	-8.4	556	< 2.0	-0.8	866	12.1	-10.8
12,0,6	11.8	-7.0	666	< 2.0	2.3	10,6,6	< 2.4	0.9
107	14.0	12.4	776	< 2.0	1.7	626	< 2.8	-3.0
307	5.0	-3.8	886	10.2	11.8	646	11.8	10.4
507	3.2	4.0	422	20.1	20.1	686	< 2.6	1.5
707	6.2	-3.4	622	8.0	-4.9	6,10,6	10.8	-9.2

estimated probable errors (Table 1) were determined by trial-and-error refinements of the structure factors.

### Discussion

Molecular dimensions, calculated from the parameters listed in Table 1, are C-Cl<sub>1</sub> = 1.74 ± 0.02 Å, C-Cl<sub>2</sub> = 1.74 ± 0.02 Å, C=O = 1.15 ± 0.02 Å, and ∠ Cl<sub>1</sub>-C-Cl<sub>2</sub> = 111.0° ± 1.5°. These values may be compared with those of Brockway, Beach & Pauling (1935): C-Cl = 1.68 ± 0.02 Å, C=O = 1.28 ± 0.02 Å and ∠ Cl-C-Cl = 117 ± 2°; and with those of Schomaker (1950): C-Cl = 1.74 ± 0.02 Å, C=O = 1.18 ± 0.03 Å and ∠ Cl-C-Cl = 112.5 ± 1.5°. Thus our values are in reasonable agreement with, but probably less accurate than, the values given by Schomaker (1950).

Although these differences in molecular dimensions are interesting and important, the use of the values given by Brockway, Beach & Pauling (1935) in the entropy calculations produces a difference of less than 0.1 e.u. Giaque & Jones (1948) suggested that the residual entropy of 1.63 e.u. arises from random orientation of the molecule in which the oxygen assumes any one of three positions at the apices of the triangular molecules. This complete randomness would correspond to  $R \ln 3 = 2.18$  e.u., but partial ordering

was assumed in order to reduce the value to 1.63 e.u. The unusual thermal expansion, extending some 25° C. below the melting point, was thought to be related to the ordering process. Because the conditions under which our crystals were grown and maintained were somewhat different from those used in the calorimetric study, we cannot be sure that the degrees of order in the solids of these two studies are comparable. Nevertheless, we have carried out a study of the effect of the proposed disorder on the agreement between observed and calculated structure factors. We shall show that, apart from normal, essentially isotropic temperature motions, no disorder was present in our crystals, and therefore it is possible to achieve complete orientational order in the solid.

The initial attempt at solving the structure of phosgene from the Patterson projection along the *c* axis was made assuming randomness of the above type. The reasonable approximation, that three equivalent atoms are the major contributors to the peaks in the {*h**h*0} Patterson synthesis, was made. The only plausible models that resulted did not fit the Patterson map as well as did the ordered model. These models yielded Fourier projections that did not refine, and poor structure factor agreement.

The reliability factor,  $\sum |F_c| - |F_o| \div \sum |F_o|$ , for the

$\{hk0\}$  data, omitting the structure factors for unobserved reflections is 9.9%; including these structure factors, the value is 12.6%. Disorder was put into the ordered model to observe its effect on the structure-factor agreement. Using the final atomic positions as determined, but weighting these so as to account for the residual entropy, the new reliability factors of 24.6% and 27.9% were found, corresponding to the two types of calculations described above. A more sensitive comparison of structure factors can be found in the function  $\Sigma(|F_o| - |F_c|)^2$ , which increased by a factor of 4.6 by the insertion of randomness into the ordered model. The signs of five small terms changed in the disordered set of structure factors. Applying the maximum possible contribution from each of these terms at peak maxima such that there is always a decrease in chlorine heights, and an increase in the oxygen height (a highly improbable occurrence), it would be possible to reach 0.7 of the height difference necessary to convert the ordered structure to a disordered one for the chlorine atoms, but only 0.35 of the difference necessary for the oxygen atom. Refinements of the  $\{hk0\}$  Fourier synthesis clearly showed, however, that peak coordinates and heights are insensitive to the sign changes of small terms.

Finally, the low value of the temperature-factor constant,  $B = 1.6 \text{ \AA}^2$ , does indeed suggest an ordered structure. At least part of the effect of the type of disorder considered above would be to produce an apparent abnormally high temperature factor because the molecule is not an equilateral triangle.

Intermolecular distances are  $\text{Cl}_1\text{-Cl}_1 = 3.64 \text{ \AA}$ ,

$\text{Cl}_2\text{-Cl}_2 = 3.76 \text{ \AA}$  and  $\text{Cl}_2\text{-O} = 3.12 \text{ \AA}$ . The slightly short  $\text{Cl}_2\text{-O}$  distance suggests that van der Waals bonding within the spirals around the screw axes is somewhat stronger than the bonding between these spirals.

The overall reliability factor omitting structure factors for unobserved reflections is 9.5%; including these, it is 12.2% (see Table 2).

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## Structure Cristalline du Metasilicate de Sodium Anhydre, $\text{Na}_2\text{SiO}_3$

PAR A. GRUND

*Laboratoire de Minéralogie de la Sorbonne, Paris, France*

ET MELLE M. PIZY

*Laboratoire de Cristallographie du S.R.C.T., Paris, France*

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The crystal structure of anhydrous sodium metasilicate,  $\text{Na}_2\text{SiO}_3$ , has been completely determined. The crystals are orthorhombic, pseudo-hexagonal, with space group  $Cmc-C_{2v}^{12}$ . The cell, of dimensions  $a = 10.43$ ,  $b = 6.02$ ,  $c = 4.81 \text{ \AA}$ , contains four formula units. Atomic positions have been determined from Patterson and Fourier-Bragg projections. Silicon and oxygen atoms form chains  $[\text{Si}_2\text{O}_6]^{4-}$  in the  $c$  direction similar to those in pyroxenes. The chains are linked through sodium atoms always co-ordinated by five oxygen atoms.

### Introduction

Au cours d'essais de synthèse du quartz par I. Franke au Laboratoire de Cristallographie du S.R.C.T., des questions de structure cristalline des silicates de sodium

se sont posées, en particulier celle du métasilicate de sodium anhydre.

Quelques études cristallographiques sur ce corps ont déjà été faites par van Klooster (1910), Niggli (1914), Kracek (1930), Morey & Fenner (1914a, b), Schwarz