A CONTRIBUTION to the STUDY of the CRYSTAL STRUCTURE of SALT HYDRATES.

(Crystal Structure of Rochelle Salt)

Thesis for the Degree of Ph.D.

submitted by

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I N D E X.

LIST of FIGURES.

INTRODUCTION.

It has become evident from a study of the structure of crystalline hydrates that the function of water in those compounds is much more important than is implied in the manner of writing the formulae for these substances. In some structures however the water molecules play a very small part, and merely fill gaps in the crystal structure from which they may sometimes, but not always, be expelled without any breakdown or major alteration of the structure. Nevertheless, in a great number of salt hydrates the primary function of water is to co-ordinate the cations and thereby increase their effective radius so that their charge may be distributed over a greater number of anions. The difference in radius between the smaller cations and the comparatively complex anions would prohibit the formation of any simple and highly co-ordinated structure such as is actually found in many crystalline hydrates, were it not for the co-ordinating influence of the water molecules.

Looked at from a geometrical standpoint, the function of water in inorganic salt hydrates is to form a complex with the smaller ion so that the latter may be effectively increased in size and thus incorporated in a relatively simpler structure. From the point of view of energetics the function of water of crystallization is to spread the charge of the ion over a larger area and thus lower the electrostatic energy, leading to a more stable system.

Water molecules play this part because of their small size and high dipole moment. The latter is an essential requirement for stability. Non-polar molecules can presumably co-ordinate a highly polarising ion but the resulting complex is so unstable that such structures are not actually found.

It has been shown by Bernal and Fowler[1] from theoretical and experimental considerations that the water molecule is probably tetrahedral in structure after the following fashion: If the water molecule be regarded as a sphere then its high polarity is due to the tetrahedral disposition of the two protons and two negative areas on its surface. That this model is essentially correct has been verified by numerous analyses of crystalline hydrates in which it has been shown that the water molecules have a tetrahedral disposition of bonds, two coming from positive regions and two going to negative regions of the structure.

Such a molecule can co-ordinate with itself and this assists materially in the building up of a stable configuration.

In many cases the tetrahedral form becomes modified so that the two negative areas apparently coalesce, thus giving rise to a three bonded water molecule which is approximately plane.[2]

The ammonia molecule can, to a lesser extent fill the same role as water in some cases. Such compounds have evidently been regarded in a truer light than have the salt hydrates, since these ammonia compounds have always been assigned formulae which indicate a close connection between the cation and the ammonia molecules. Thus, taking an example from the Cobalt Ammines we have :- $[Co(NH_3)_6]I_2$, while Berylium Sulphate Tetrahydrate is always written:- $BeSO_4.4H_2O$. It would be much more accurate to write $[Be(4H_2O)]SO_4$, as a study of the crystal structure of this hydrate shows.[3] It is evident that in the majority of cases the formation of salt hydrates must not be ascribed, as the formulae indicate, to the existence of weak residual valencies but to a strong tendency towards complex formation betweenwater molecules and polarising ions, due to the rather unique properties of the former.

Few hydrates other than those of inorganic salts have been studied, but the structure of Oxalic Acid Dihydrate illustrates the type of function which the water molecule may be expected to fulfil in such crystals.[4,5] Here, hydrogen bonds are formed between the carbonyl oxygen atoms and the water molecules and the latter form the sole medium of linkage between the oxalic acid molecules. The water molecules are of the three bonded type described above.

The present work was undertaken primarily as a development of earlier work on hydrates to see how far the established ideas could be extended to more complicated cases, particularly in the field of organic salts, where the anions are of course very much more complicated than in the inorganic field. Such structures cannot be expected to be formed on the basis of packing, close or otherwise, of approximately spherical groups, and it is of interest to see how far the cation co-ordinating function of water is affected by the presence of organic molecules, which presumably can be linked together through water molecules.

Rochelle Salt, the principal salt studied in this work, is also of great interest as being optically active not only in the crystalline state but also in solution, on account of the asymmetric tartrate molecule.

It has remarkable electric properties. The dielectric constant parallel to the a-axis reaches abnormally high values between the temperatures -10 and +25°C, and it exhibits a hysteresis similar to that exhibited by ferromagnetic substances. This property has attracted much attention to which reference will later be made. It may be noted here, however, that the crystal structure of this salt will, no doubt, decide where the seat of these anomalies lies.

In the following investigation four salts comprising the isomorphous series to which Rochelle Salt belongs, have been studied, and though only the structure of Rochelle Salt has been accurately determined, this is a sufficiently close approximation to the structures of the other members as to make their ~~their~~ accurate elucidation a routine matter.

Apart from determinations of cell dimensions and space group no work on the crystal structure of Rochelle Salt has been previously published, but some work on variation of reflected X-ray intensities with temperature and applied electric fields has been done; this will be considered later.

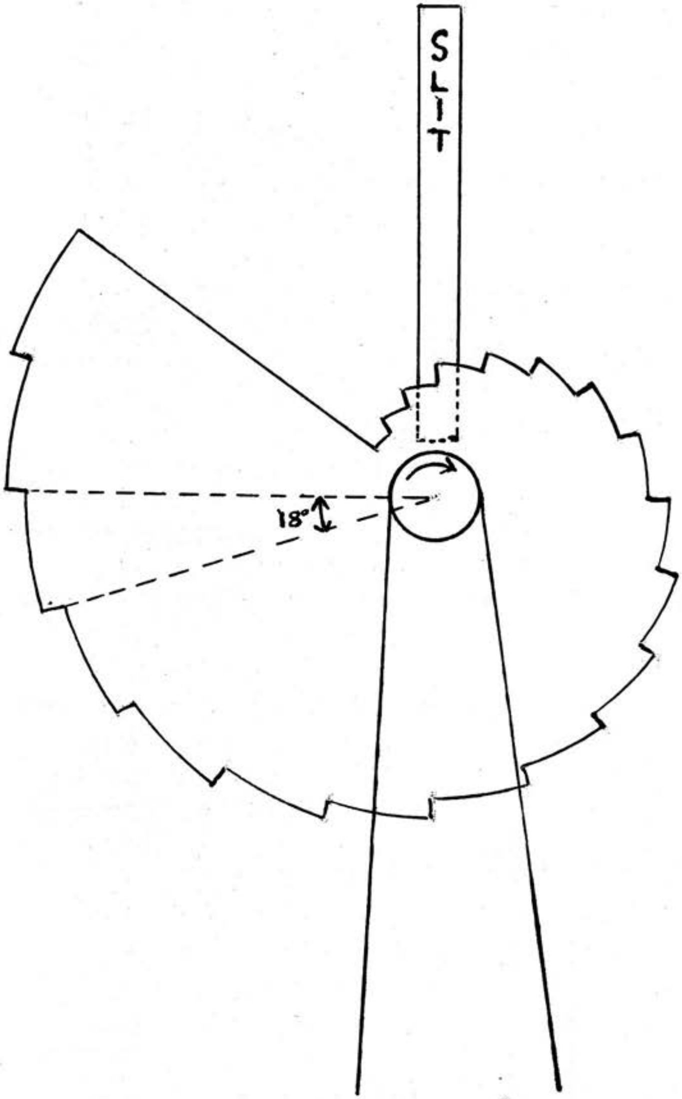


Figure 1.

Starting at the circumference, arcs of 360°, 342°, 324°...18°, have been successively cut away. Exposure of the slit while the wheel is rotating at constant speed results in a stepped wedge whose steps are exposed for times proportional to 1, 2, 3, ...20.

EXPERIMENTAL.

(a) Photography, Indexing, and Assignment of Intensities.

The X-rays were produced by a Metropolitan-Vickers crystallographic X-ray unit, run at 60 K.V., 25 m.a. Copper K_α radiation was used throughout, the K_β radiation being absorbed by a filter of nickel foil.

The film used was Ilford double coated X-ray film with developer and fixing solution as recommended by the makers. Each film was developed for five minutes at 18°C.

The camera was a cylindrical Weissenberg of radius 5.0 cm. and vertical travel 13.3 cm. per 180° rotation of the crystal. It was so constructed that a vertical blank strip was left in the centre of each film. After the photography of a crystal the film was mounted about ten feet from the X-ray source in a brass holder which exposed a vertical slit of this blank portion to X-rays. In front of the slit was placed a brass wheel cut as shown in Figure 1, which rotated at constant speed about an axis perpendicular to the plane of the film.

The slit was then exposed for a definite period of time to an X-ray beam of constant intensity. A wedge was thus produced on the film giving a range of intensities proportional to the numbers 1,2, ...20. The procedure was repeated after inverting the film in the holder, the slit being exposed for twice the initial time and to a beam twice as intense, giving a second range of intensities proportional to the numbers 4,8, ...80. For the light wedge the tube was run at 60 K.V., 5 m.a. exposure 30 sec. For the dark wedge; 60 K.V., 10 m.a. exposure 60 sec.

In effect the method of assignment of intensities depends on the following argument:- Successive steps in the wedge receive amounts of energy proportional to the numbers 1,2, ...etc. The spots on the photographs are classified as closely as possible by visual comparison with those steps in the wedge most similar to them in appearance. The energy received by each spot is then proportional to the numbers assigned to the appropriate steps. If the energy received is proportional to the intensity, the relative intensity may then be represented by the numbers assigned.

Errors due to variations in the intensity of of the X-ray beam and unequal development are negligible. Errors due to inefficient visual comparison are

WEISSENBERG CHART.

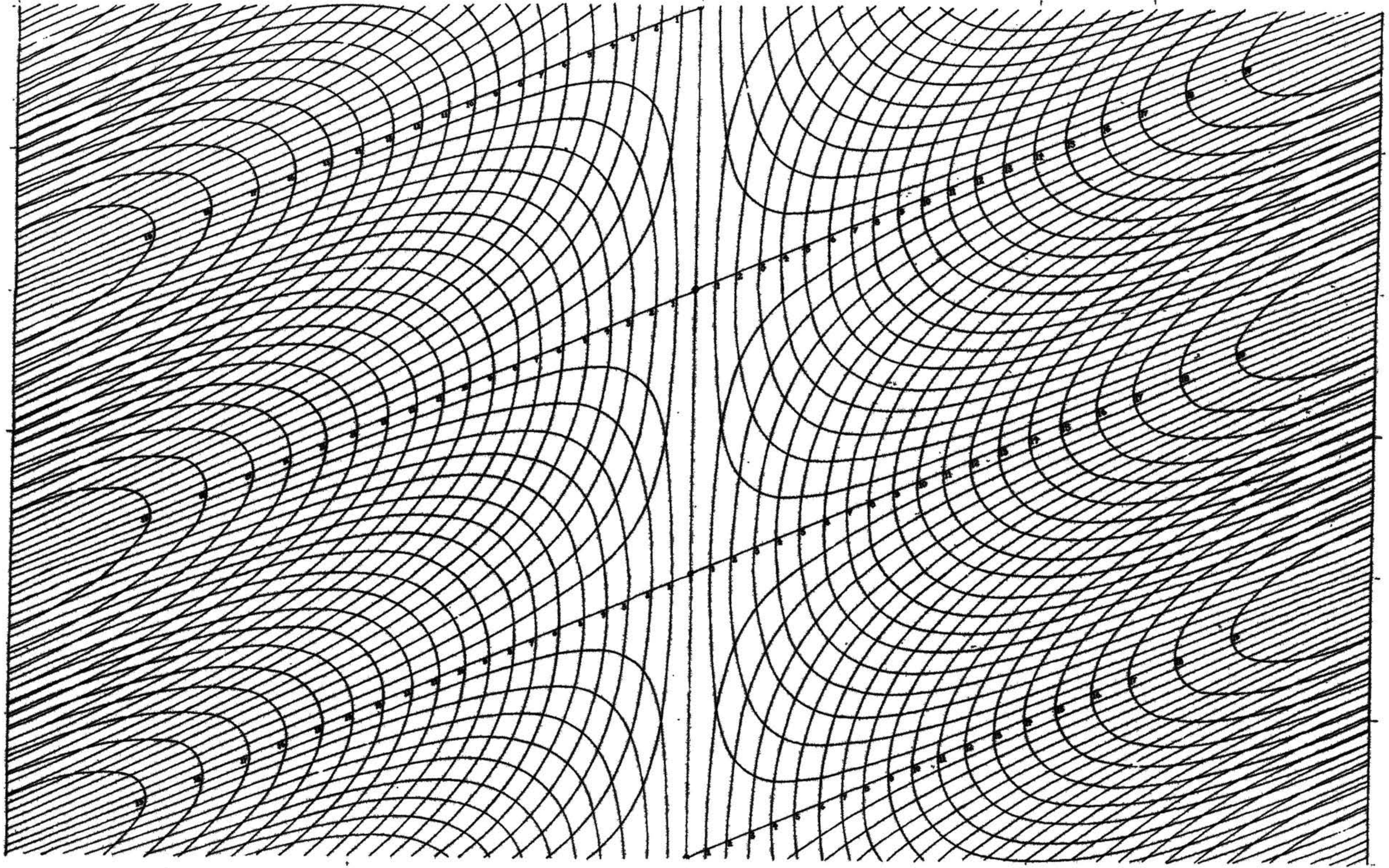


Figure 2.

probably not greater than 20 o/o of the values assigned and in many cases they are much smaller than this as was found by comparison of values obtained by independent observers. Errors are also due to the fact that when the absorption is high the spots are not uniform across their breadth. Because of this state of affairs each spot may be given a range of relative intensities. In actual practice the intensities assigned corresponded rather closely to the blackest portion of the spot. This in effect constitutes an absorption correction which is apparent in the later stages of the work.

To facilitate the indexing of the photographs a chart was constructed, suitable for use with our camera, giving the co-ordinates of any point belonging to the equatorial layer of the reciprocal lattice, by laying the chart over the film. It was based on a reciprocal square net of interval 0.1 and was mainly of use in indexing high order reflections. Figure 2 shows the chart.

(b) Production of Crystal Cylinders.

Specimens of Sodium Potassium Tartrate Tetrahydrate (Rochelle Salt), Sodium Ammonium Tartrate Tetrahydrate, Sodium Rubidium Tartrate Tetrahydrate, and Sodium Thallium Tartrate Tetrahydrate were prepared by

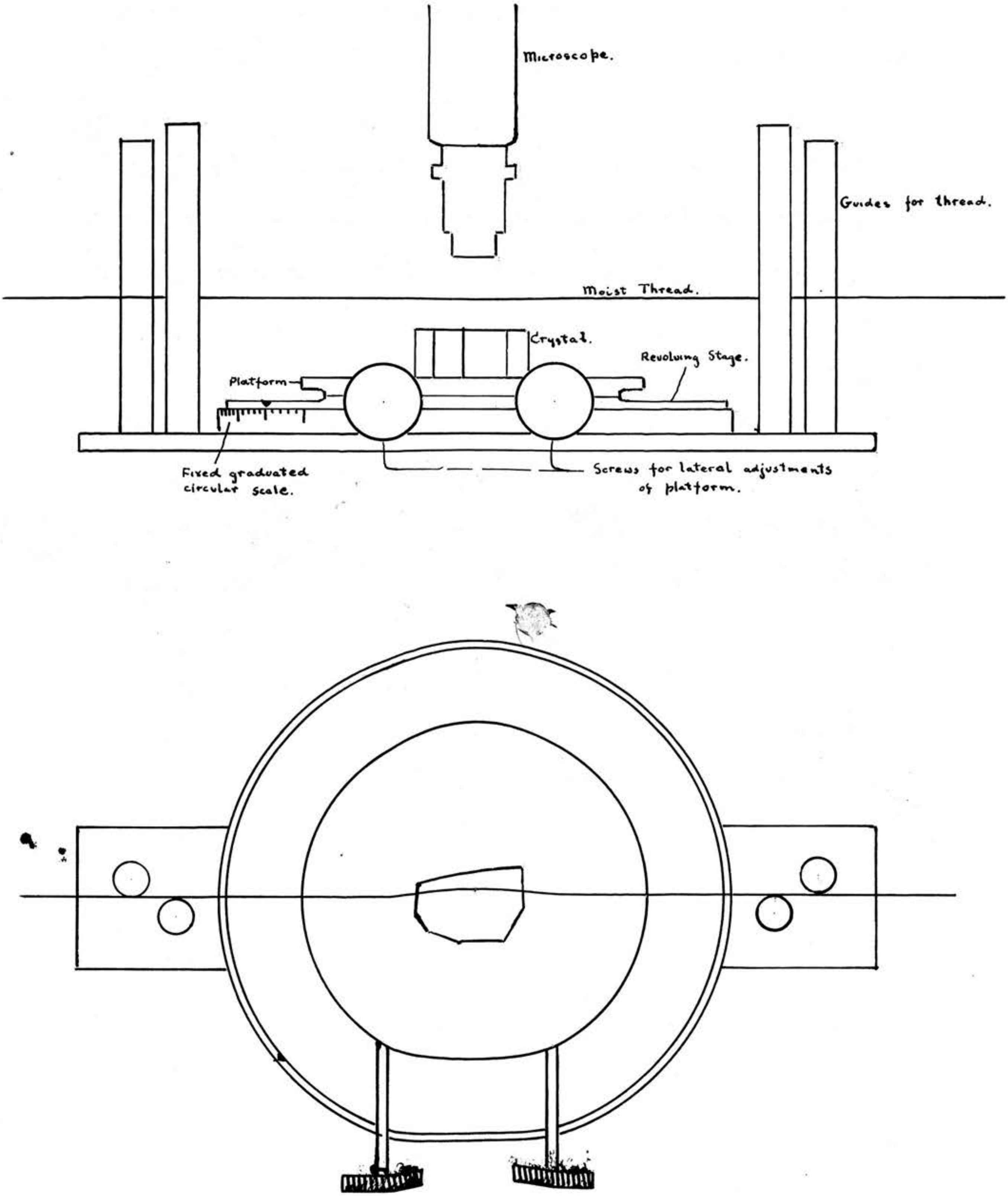

Microscope.
Guides for thread.
Moist Thread.
Crystal.
Revolving Stage.
Platform
Fixed graduated circular scale.
Screws for lateral adjustments of platform.

Figure 3.

evaporation of saturated solutions in vacuo over concentrated sulphuric acid, in a room maintained at approximately constant temperature.

The crystals were mounted on a microscope stage capable of rotation and transverse movement in two mutually perpendicular directions, and carrying guides for a moist thread. (Figure 3) Using the moist thread as a saw a crystal could be cut into long prisms parallel to any required direction. These prisms were then rolled into cylinders beneath the finger on a ground glass plate. Accurately cylindrical specimens of diameter 0.025 cm. can be obtained in this way, to which the absorption corrections calculated by Bradley[6] may be applied.

(c) Weissenberg Photographs.

All the photographs dealt with in this section were of the Weissenberg type. In the case of the Ammonium and Potassium salts, photographs about the three crystallographic axes of the zero and several other layer lines were taken. The Rubidium salt was similarly photographed about the b- and c-axes. The cleavage pafallel to (100) was very troublesome in the attempted production of a-axis cylinders in this case. The axial zero layer lines of the Thallium salt were photographed.

The diameters of the cylinders were measured by a microscope carrying a graduated eyepiece. The departure from truly cylindrical form in terms of the diameter of cross-section, was in the best case ± 0.001 cm. and in the worst case ± 0.004 cm.

The following table contains the details of the zero layer line photographs. r is the radius of cross-section of the cylinders.

Salt	Axis	r (cm)	μ r	Exposure (hours)
Potassium	a	0.031	1.7	4.00
Ammonium	a	0.038	0.7	4.00
Thallium	a	--	-	6.00
Potassium	b	0.029	1.6	4.00
Ammonium	b	0.028	0.5	1.00
Thallium	b	--	-	3.50
Potassium	b	0.018	0.97	4.00
Rubidium	b	0.013	0.98	4.00
Potassium	c	0.032	1.7	4.00
Ammonium	c	0.031	0.6	4.00
Rubidium	c	0.025	1.9	3.50
Thallium	c	0.045	-	10.00

μ is the linear absorption coefficient.

Space Group, Unit Cell, Density.

According to Groth III p. 332, all four salts are rhombic bisphenoidal. There are therefore twofold or twofold-screw axes parallel to each crystallographic axis. Several other workers have shown that for individual members of the series of salts studied in this work,

(h00) reflections are absent with h odd,

(0k0) reflections are absent with k odd,

and there are no other systematic absences.
In the present work this has been confirmed and shown to be true for all four salts. The space group is thus $P\,2_1 2_1 2$.

The unit cell dimensions were determined by the Bradley method[7] and by measuring layer line spacings. The following table summarises the measurements made.

	a_o	b_o	c_o	$V = a_o b_o c_o$
Potassium salt	11.93	14.30	6.17*	1053×10^{-24} cc.
Rubidium salt	12.05	14.40	6.21*	1077 "
Ammonium salt	12.15	14.40	6.18*	1082 "

* From layer line separations.

Cell dimensions in Angstrom units.

Using accepted values of the density, Z = 4 is obtained for these three salts, and rougher measurements produce the same conclusion for the Thallium salt.

From Internationale Tabellen the equivalent points of the space group P $2_1 2_1 2$ are:

Twofold special. (a) $(00z)$ $(\frac{1}{2}\frac{1}{2}\bar{z})$; (b) $(0\frac{1}{2}z')$ $(\frac{1}{2}0\bar{z}')$

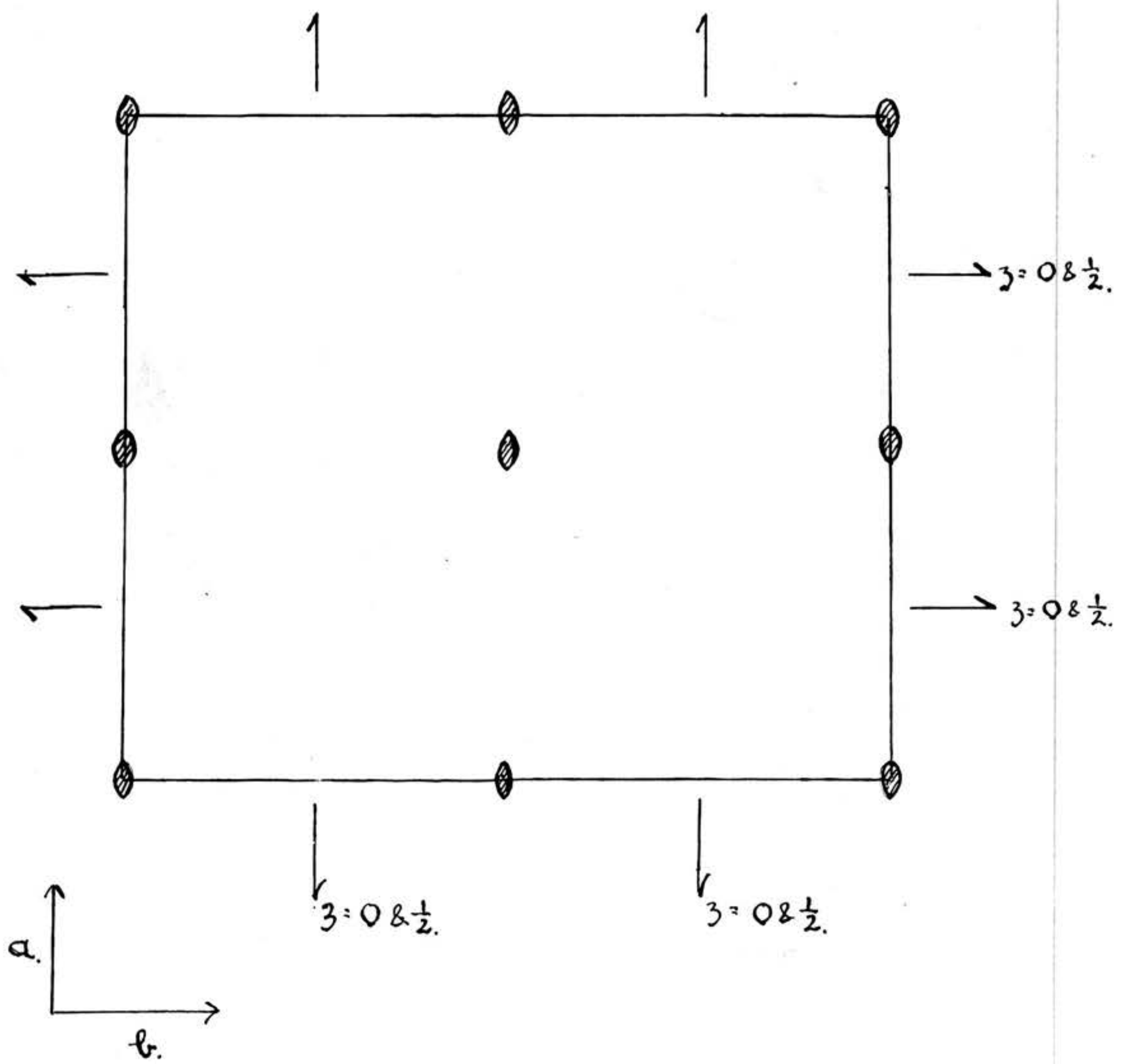
Fourfold general. (xyz) $(\overline{xy}z)$ $(\frac{1}{2}+x\ \frac{1}{2}-y\ \bar{z})$ $(\frac{1}{2}-x\ \frac{1}{2}+y\ \bar{z})$

The structure factor is given by:

$$A = 4 \cos 2\pi(hx+[h+k]/4) \cos 2\pi(ky-[h+k]/4) \cos 2\pi lz$$

$$B = -4 \sin 2\pi(hx+[h+k]/4) \sin 2\pi(ky-[h+k]/4) \sin 2\pi lz$$

The following diagram shows the symmetry elements of the unit cell.



Absorption Coefficients.

The following data was used in the absorption corfections. The linear absorption coefficient (μ) was calculated from the formula:-

$$\mu = n/V.\Sigma\mu_a$$

n = number of molecules in unit cell.
μ_a = absorption per atom.
V = volume of unit cell.

The values of μ_a for the various atoms were taken from Internationale Tabellen II p. 575. The values of V used are those on p.11. The absorption per ($NaC_4H_4O_6.4H_2O$) is 496×10^{-23}, and the absorption per molecule of the various salts is:

Thallium salt	8256×10^{-23}
Rubidium salt	2036 "
Potassium salt	1419 "
Ammonium salt.	516 "

The linear absorption coefficients are therefore:

Rubidium salt	75.6 cm.$^{-1}$
Potassium salt	54.0 "
Ammonium salt	19.1 "

It is appropriate to mention here that since Cu K_a radiation has an absorption edge between Rubidium and Potassium the absorptions of these two salts for this radiation are not very dissimilar. For this reason these two salts are well suited for direct photographic comparison, and the same may be said of any pair of isomorphous Rubidium and Potassium salts.

Derivation of F's.

Sinθ for the various planes was calculated for the Ammonium salt and the values taken as being the same for the Potassium and Rubidium salts. The values assigned to the intensities of the reflections were corrected for polarization by dividing by the appropriate θ for the plane in question. They were also corrected for absorption using the values of 100A quoted by Bradley[6]. This was done in the first instance only for the Potassium and Ammonium salts.

In the case of $F^2(hk0)$, it is shown by the reasoning in the following section that for all planes of this zone containing an odd index, the values of this quantity should be roughly equal in passing from salt to salt of the series. The F^2's derived as described above do not fulfil this condition. The divergence, or part of it, can be accounted for since the spots on the Potassium photograph were not uniform across their breadth, while those of the Ammonium photograph were. The values of the Potassium intensities were assigned on the basis of the blackest portion. This clearly constitutes an absorption correction, and consequently the Potassium F^2's will be too large relative to the Ammonium F^2's after the Bradley correction has been applied. Accordingly, the ratio $F_K^2/F_{NH_4}^2$ was plotted against $\sin\theta$ and a correction curve obtained.

Since the Ammonium values were regarded as being more reliable, the F_K^2's were divided by the factors obtained. These factors are:-

$\sin\theta < 0.4$	Correction factor, 2.4
$0.4 < \sin\theta < 0.8$	" " 1.8
$\sin\theta > 0.8$	" " 1.0

C

In the following table F_K is therefore:

$$\sqrt{(I_K \times 1000/(A_K \times \Theta \times C)}$$

and F_{NH_4} is:

$$\sqrt{(I_{NH_4} \times 1000/(A_{NH_4} \times \Theta))}$$

where I_K and I_{NH_4} are the Potassium and Ammonium intensities respectively, and C is the correction factor quoted above.

F(hk0) for the Ammonium and Potassium salts.

h	k	sinθ	θ	A_K	A_{NH_4}	I_K	I_{NH_4}	F^2_K	$F^2_{NH_4}$	F_K	F_{NH_4}
0	2	.107	9.2	7.3	37.0	6.5	30.0	40	88	6	9
	4	.214	4.4	7.6	37.2	28.0	7.5	350	46	19	7
	6	.321	2.7	8.3	37.5	5.0	1.5	93	15	10	4
	8	.427	1.8	9.3	38.0	51.0	40.0	1260	585	36	24
	10	.535	1.3	10.4	38.5	22.0	14.0	910	280	30	17
	12	.640	1.1	11.6	39.2	8.5	4.0	370	93	19	10
	14	.745	1.0	13.1	40.1	3.5	0.5	148	12	12	4
	16	.855	1.4	15.1	41.3	1.0	0.0	47	0	7	0
	18	.960	3.2	17.2	42.8	0.0	4.0	0	29	0	5
2	0	.127	7.6	7.3	37.0	34.0	>50.0	255	>178	16	>13
4		.253	3.6	7.9	37.5	28.0	10.0	408	75	20	9
6		.379	2.2	8.7	38.0	1.5	17.0	33	208	6	14
8		.510	1.4	10.0	38.0	7.0	0.0	277	0	17	0
10		.630	1.1	11.5	40.0	0.0	2.5	0	57	0	8
12		.760	1.1	13.4	40.0	1.5	0.0	56	0	8	0
14		.890	1.7	15.6	42.0	3.0	3.5	113	49	11	7
1	1	.083	12.0	7.2	37.0	-	-	-	-	-	-
	2	.124	7.9	7.3	37.0	17.0	28.0	123	95	11	10
	3	.172	5.6	7.5	37.0	0.0	4.0	0	19	0	4
	4	.223	4.1	7.7	37.0	6.5	16.0	86	105	9	10
	5	.275	3.3	8.0	37.5	4.5	8.0	71	65	8	8
	6	.327	2.6	8.3	37.5	24.0	31.0	460	317	22	18
	7	.379	2.2	8.7	38.0	7.0	11.0	150	132	12	12
	8	.432	1.8	9.2	38.0	1.0	4.0	33	58	6	8
	9	.485	1.5	9.8	38.0	2.0	7.0	75	123	9	11
	10	.540	1.3	10.3	38.0	3.5	6.5	145	131	12	11
	11	.590	1.2	11.0	40.0	4.5	7.0	190	145	14	12
	12	.650	1.1	11.7	40.0	3.0	5.5	130	125	11	11
	13	.685	1.0	12.3	40.0	10.0	14.0	450	350	21	19
	14	.750	1.0	13.2	40.0	5.5	14.0	230	350	15	18
	15	.800	1.1	14.1	40.0	0.0	0.0	0	0	0	0
	16	.855	1.4	15.0	42.0	2.0	2.0	96	34	10	6
2	1	.138	7.1	7.3	37.0	38.0	>50.0	306	>190	17	>14
	2	.166	5.8	7.4	37.0	20.0	8.0	193	37	14	6
	3	.205	4.6	7.6	37.0	4.0	7.0	48	41	7	6
	4	.248	3.7	7.8	37.0	10.0	40.0	146	292	12	17
	5	.296	3.0	8.1	37.5	29.0	40.0	495	356	22	19
	6	.345	2.4	8.4	37.5	10.5	0.0	217	0	15	0
	7	.395	2.0	8.9	38.0	0.0	2.0	0	26	0	5
	8	.446	1.7	9.4	38.0	2.0	3.5	70	54	8	7
	9	.497	1.5	9.9	38.0	6.0	10.5	225	184	15	14
	10	.550	1.3	10.5	38.0	3.5	0.0	142	0	12	0
	11	.600	1.2	11.1	40.0	0.0	0.0	0	0	0	0
	12	.655	1.1	11.8	40.0	0.0	2.0	0	45	0	7
	13	.705	1.0	12.5	40.0	2.5	3.5	110	87	10	9

h	k	sinθ	Θ	A_K	A_{NH_4}	I_K	I_{NH_4}	F^2_K	$F^2_{NH_4}$	F_K	F_{NH_4}
2	14	.760	1.1	13.4	40.0	2.0	1.0	75	23	9	5
	15	.810	1.2	14.3	40.0	0.0	0.0	0	0	0	0
	16	.860	1.4	15.2	42.0	1.0	2.0	63	34	8	6
3	1	.197	4.8	7.6	37.0	0.0	1.0	0	6	0	2
	2	.217	4.3	7.7	37.0	8.5	12.0	107	76	10	9
	3	.248	3.7	7.8	37.0	7.5	13.0	108	95	10	10
	4	.290	3.0	8.0	37.5	32.0	40.0	550	356	24	19
	5	.327	2.6	8.3	37.5	10.0	18.0	193	185	14	14
	6	.372	2.2	8.6	38.0	12.0	20.0	265	239	16	15
	7	.419	1.9	9.2	38.0	0.0	0.0	0	0	0	0
	8	.467	1.6	9.7	38.0	2.5	3.0	90	49	9	7
	9	.510	1.4	10.1	38.0	1.0	1.5	40	28	6	5
	10	.560	1.2	10.7	40.0	3.0	3.5	130	73	11	9
	11	.620	1.1	11.4	40.0	4.6	11.5	200	261	14	16
	12	.670	1.1	12.0	40.0	2.6	6.0	106	136	10	12
	13	.720	1.0	12.7	40.0	4.5	9.5	200	238	14	15
	14	.770	1.1	13.5	40.0	2.0	6.5	75	148	9	12
	15	.820	1.2	14.5	40.0	11.5	8.0	86	167	9	13
	16	.870	1.5	15.4	42.0	0.0	0.0	0	0	0	0
4	1	.258	3.5	7.9	37.5	50.0	>50.0	750	>382	27	>20
	2	.274	3.2	7.9	37.5	>50.0	>50.0	>825	>408	>29	>20
	3	.300	2.9	8.1	37.5	4.5	9.0	80	86	9	9
	4	.331	2.6	8.3	37.5	50.0	47.0	970	483	31	22
	5	.368	2.3	8.6	38.0	0.0	3.0	0	34	0	6
	6	.408	1.9	9.0	38.0	26.0	20.0	850	276	29	17
	7	.451	1.7	9.6	38.0	2.0	1.0	68	15	8	4
	8	.496	1.5	9.9	38.0	9.5	5.0	355	88	19	9
	9	.540	1.3	10.5	38.0	8.0	15.5	325	313	18	18
	10	.590	1.2	11.0	40.0	7.0	3.0	294	63	17	8
	11	.640	1.1	11.7	40.0	2.0	2.5	87	57	9	8
	12	.690	1.0	12.3	40.0	4.0	2.0	178	50	13	7
	13	.740	1.0	13.1	40.0	0.0	0.0	0	0	0	0
	14	.790	1.1	14.0	40.0	2.0	0.0	72	0	9	0
	15	.840	1.3	14.8	42.0	1.0	1.0	52	18	7	4
	16	.890	1.7	15.7	42.0	5.5	3.0	206	42	14	7
5	1	.321	2.7	8.3	37.5	0.0	1.0	0	10	0	3
	2	.334	2.6	8.4	37.5	15.0	34.0	290	350	17	19
	3	.354	2.4	8.5	38.0	7.0	18.0	140	198	12	14
	4	.381	2.1	8.7	38.0	1.0	3.0	23	38	5	6
	5	.414	1.9	9.1	38.0	11.0	18.0	360	250	19	16
	6	.450	1.7	9.5	38.0	1.5	5.0	52	78	7	9
	7	.489	1.5	9.8	38.0	1.5	2.0	57	35	8	6
	8	.530	1.3	10.2	38.0	3.5	9.0	145	182	12	14
	9	.570	1.2	10.8	40.0	0.0	1.0	0	21	0	5
	10	.620	1.1	11.4	40.0	0.0	1.0	0	23	0	5
	11	.660	1.1	12.0	40.0	0.0	2.5	0	57	0	8
	12	.710	1.0	12.6	40.0	9.5	20.0	420	500	21	22

h	k	sinθ	θ	A_K	A_{NH_4}	I_K	I_{NH_4}	F_K^2	$F_{NH_4}^2$	F_K	F_{NH_4}
5	13	.760	1.1	13.5	40.0	0.0	0.0	0	0	0	0
	14	.810	1.2	14.4	40.0	0.0	0.0	0	0	0	0
	15	.860	1.4	15.1	42.0	1.5	5.0	71	85	8	9
6	1	.383	2.1	8.8	38.0	5.0	3.0	110	38	10	6
	2	.394	2.0	8.9	38.0	7.0	32.0	165	422	12	21
	3	.412	1.9	9.1	38.0	5.0	14.0	161	194	13	14
	4	.435	1.8	9.3	38.0	9.0	2.0	300	29	17	5
	5	.464	1.7	9.6	38.0	2.0	6.0	68	93	8	10
	6	.496	1.5	9.9	38.0	15.0	6.0	560	105	24	10
	7	.530	1.3	10.3	38.0	0.5	3.0	21	60	5	8
	8	.570	1.2	10.8	40.0	3.0	0.0	128	0	11	0
	9	.610	1.1	11.2	40.0	3.0	45.0	136	102	12	10
	10	.650	1.1	11.8	40.0	2.0	11.5	93	262	10	16
	11	.700	1.0	12.4	40.0	0.0	1.0	0	25	0	5
	12	.740	1.0	13.1	40.0	1.5	0.0	63	0	8	0
	13	.790	1.1	13.9	40.0	2.5	4.0	91	91	10	10
	14	.840	1.3	14.8	42.0	3.0	2.0	156	37	13	6
	15	.880	1.6	15.6	42.0	0.0	3.0	0	45	0	7
	16	.930	2.3	16.7	42.0	3.5	1.0	91	10	10	3
7	1	.446	1.7	9.4	38.0	7.0	11.0	240	170	16	13
	2	.455	1.7	9.6	38.0	14.0	18.5	480	286	22	17
	3	.471	1.6	9.7	38.0	0.0	2.0	0	33	0	6
	4	.491	1.5	9.8	38.0	0.0	2.0	0	35	0	6
	5	.510	1.4	10.1	38.0	13.5	18.0	530	340	23	18
	6	.540	1.3	10.5	38.0	1.0	3.0	41	61	6	8
	7	.580	1.2	10.9	40.0	1.0	0.0	42	0	6	0
	8	.610	1.1	11.3	40.0	0.5	1.0	22	23	5	5
	9	.650	1.1	11.8	40.0	2.0	2.5	83	57	9	8
	10	.690	1.0	12.3	40.0	0.0	0.0	0	0	0	0
	11	.730	1.0	12.9	40.0	0.0	0.0	0	0	0	0
	12	.780	1.1	13.0	40.0	2.0	4.0	72	90	8	10
	13	.820	1.2	14.5	40.0	2.0	2.0	115	42	11	7
	14	.870	1.5	15.3	42.0	0.0	0.0	0	0	0	0
8	1	.510	1.4	10.1	38.0	7.0	17.5	280	330	17	18
	2	.517	1.4	10.2	38.0	31.0	31.0	1200	580	35	24
	3	.531	1.3	10.3	38.0	00.0	0.0	0	0	0	0
	4	.549	1.3	10.5	38.0	7.5	2.5	310	51	18	7
	5	.572	1.2	10.8	38.0	0.0	0.0	0	0	0	0
	6	.599	1.2	11.1	40.0	4.0	0.0	167	0	13	0
	7	.629	1.1	11.5	40.0	0.0	0.0	0	0	0	0
	8	.662	1.1	11.9	40.0	4.0	0.5	170	11	13	3
	9	.648	1.0	12.4	40.0	2.0	4.0	90	100	10	10
	10	.735	1.0	13.0	40.0	6.5	6.0	278	250	17	16
	11	.775	1.1	13.7	40.0	2.5	2.5	92	57	10	8
	12	.817	1.1	14.3	40.0	3.5	1.0	222	23	15	5
	13	.859	1.4	15.1	42.0	0.0	1.0	0	17	0	4

h	k	sinθ	θ	A_K	A_{NH_4}	I_K	I_{NH_4}	F_K^2	$F_{NH_4}^2$	F_K	F_{NH_4}
9	1	.572	1.2	10.8	40.0	1.0	4.0	43	83	7	9
	2	.579	1.2	10.9	40.0	0.0	2.0	0	42	0	7
	3	.592	1.2	11.0	40.0	0.0	0.0	0	0	0	0
	4	.608	1.1	11.2	40.0	0.0	0.0	0	0	0	0
	5	.629	1.1	11.5	40.0	0.0	3.0	0	68	0	8
	6	.653	1.0	11.8	40.0	0.0	0.5	0	12	0	4
	7	.681	1.0	12.1	40.0	9.5	19.0	440	475	21	22
	8	.712	1.0	12.5	40.0	0.0	0.0	0	0	0	0
	9	.745	1.1	13.1	40.0	0.0	0.5	0	12	0	4
	10	.781	1.1	13.8	40.0	0.0	0.0	0	0	0	0
	11	.818	1.3	14.4	40.0	3.0	3.5	165	67	13	8
	12	.858	1.4	15.0	42.0	0.0	0.0	0	0	0	0
	13	.898	1.8	16.0	42.0	0.0	1.0	0	13	0	4
10	1	.635	1.1	11.6	40.0	1.0	1.0	43	23	7	5
	2	.642	1.1	11.6	40.0	1.0	0.0	43	0	7	0
	3	.653	1.1	11.8	40.0	0.0	1.0	0	23	0	5
	4	.668	1.1	12.0	40.0	6.0	3.0	250	68	16	8
	5	.687	1.0	12.2	40.0	0.0	0.0	0	0	0	0
	6	.709	1.0	12.6	40.0	1.5	5.0	66	125	8	11
	7	.735	1.0	13.0	40.0	2.0	2.0	86	50	9	7
	8	.764	1.1	13.5	40.0	2.0	1.0	75	23	9	5
	9	.795	1.1	14.0	40.0	4.5	6.0	160	136	13	12
	10	.828	1.2	14.6	42.0	2.0	0.0	114	0	11	0
	11	.863	1.5	15.2	42.0	1.0	3.5	44	55	7	7
	12	.901	1.8	16.0	42.0	4.5	1.0	166	13	13	4
11	1	.698	1.0	12.3	40.0	2.5	2.0	110	50	11	7
	2	.704	1.0	12.5	40.0	5.0	9.0	210	225	15	15
	3	.714	1.0	12.6	40.0	2.5	2.5	110	662	11	8
	4	.728	1.0	12.9	40.0	0.0	0.0	0	0	0	0
	5	.745	1.1	13.2	40.0	3.5	2.5	130	57	11	8
	6	.766	1.1	13.5	40.0	2.0	2.0	75	45	9	7
	7	.790	1.1	13.9	40.0	0.0	1.0	0	23	0	5
	8	.817	1.3	14.6	42.0	1.0	1.5	53	29	7	5
	9	.846	1.4	14.9	42.0	1.0	0.0	48	0	7	0
	10	.877	1.6	15.4	42.0	0.0	0.0	0	0	0	0
12	1	.761	1.0	13.4	40.0	0.0	1.0	0	24	0	5
	2	.767	1.1	13.5	40.0	5.0	2.0	186	45	14	7
	3	.776	1.1	13.7	40.0	0.0	1.0	0	23	0	5
	4	.789	1.1	13.9	40.0	0.0	0.0	0	0	0	0
	5	.805	1.1	14.2	40.0	4.0	0.0	256	0	16	0
	6	.824	1.2	14.5	40.0	4.0	3.0	229	62	15	8
13	1	.824	1.2	14.5	40.0	0.0	2.5	0	52	0	7
	2	.829	1.2	14.6	42.0	0.0	0.0	0	0	0	0
	3	.838	1.3	14.7	42.0	0.0	1.0	0	18	0	4
	4	.849	1.4	15.0	42.0	0.0	0.0	0	0	0	0
	5	.865	1.5	15.2	42.0	2.0	4.0	88	64	9	8
14	1	.887	1.7	15.6	42.0	0.0	1.0	0	14	0	4
	2	.892	1.7	15.7	42.0	0.0	1.0	0	14	0	4
	3	.900	1.8	16.0	42.0	1.0	2.0	34	26	6	5
	4	.911	1.9	16.2	42.0	0.0	0.0	0	0	0	0
	5	.925	2.2	16.5	42.0	0.0	2.0	0	22	0	5

3

h	k	$\sin\theta$	θ	A_K	A_{NH_4}	I_K	I_{NH_4}	F^2_K	$F^2_{NH_4}$	F_K	F_{NH_4}
14	6	.942	2.5	16.8	42.0	6.0	0.0	140	0	12	0
15	1	.950	2.8	17.0	42.0	0.0	0.0	0	0	0	0
	2	.955	3.2	17.1	42.0	0.0	0.0	0	0	0	0
	3	.962	3.2	17.2	42.0	11.0	6.0	200	45	14	7
	4	.973	3.8	17.5	42.0	12.0	8.0	180	50	13	7

In a similar way F's were derived from the observed (0kl) intensities. The same correction factor C, obtained from the c-axis photographs, was used in the derivation of the following table.

$\frac{I_K \times 1000}{A_K \cdot \Theta C}$

ΘF

I

k	l	sinθ	Θ	A_K	A_{NH_4}	I_K	I_{NH_4}	F_K^2	$F_{NH_4}^2$	F_K	F_{NH_4}
0	1	.124	7.9	8.4	31.5	15.0	100.0	94	400	10	20
	2	.250	3.6	8.9	31.9	18.5	24.0	240	210	16	15
	3	.376	2.2	9.7	32.4	10.0	20.0	196	280	14	17
	4	.501	1.5	10.9	33.1	7.0	12.0	240	240	16	16
	5	.628	1.1	12.5	34.1	0.5	5.0	20	133	5	12
	6	.753	1.1	14.1	35.3	75.0	7.0	270	180	16	13
	7	.879	1.6	16.4	37.0	0.0	3.0	0	51	0	7
2	0	.106	9.3	8.3	31.3	5.5	40.0	29	137	5	12
4		.212	4.4	8.7	31.7	22.0	8.0	240	58	16	8
6		.318	2.7	9.3	32.1	55.0	2.0	92	23	10	5
8		.426	1.8	10.2	32.6	48.0	80.0	1450	1360	38	37
10		.532	1.3	10.9	33.3	20.0	18.0	770	415	28	20
12		.639	1.1	12.6	34.1	75.0	5.0	300	133	17	12
14		.744	1.0	14.0	35.2	35.0	2.0	140	57	12	8
16		.851	1.4	15.8	36.6	2.0	0.0	90	0	10	0
18		.957	3.1	18.2	38.4	0.0	4.0	0	34	0	6
1	1	.135	7.2	8.4	31.5	1.0	20.0	7	88	3	9
	2	.255	3.3	9.0	31.8	3.5	8.0	49	76	7	9
	3	.380	2.2	9.7	32.4	7.0	25.0	138	350	12	19
	4	.505	1.4	10.9	33.1	3.0	1.0	110	22	11	5
	5	.630	1.1	12.5	34.00	0.0	1.0	0	27	0	5
	6	.754	1.1	14.2	35.3	7.0	8.0	250	210	16	15
	7	.880	1.6	16.5	37.0	0.0	0.0	0	0	0	0
2	1	.164	5.9	8.5	31.5	10.5	0.0	88	0	9	0
	2	.271	3.3	9.0	32.0	32.0	50.0	450	473	21	22
	3	.391	2.1	9.9	32.5	50.0	90.0	1000	1320	32	36
	4	.513	1.4	10.9	33.1	65.0	20.0	236	430	15	21
	5	.636	1.1	12.5	34.0	2.0	7.0	81	190	9	14
	6	.760	1.1	14.1	35.3	4.0	3.0	145	77	12	9
	7	.885	1.7	16.5	37.1	0.0	1.0	0	16	0	4
3	1	.203	4.7	8.6	31.7	80.0	150.0	840	1000	29	32
	2	.296	3.0	9.1	32.0	40.0	70.0	610	730	25	27
	3	.408	1.9	10.0	32.5	0.0	0.0	0	0	0	0
	4	.527	1.4	11.0	33.2	20.0	14.0	720	300	27	17
	5	.648	1.1	12.7	34.2	7.0	3.0	280	80	17	9
	6	.770	1.1	14.4	35.5	5.0	5.0	175	127	13	11
	7	.893	1.7	16.7	37.3	0.0	0.0	0	0	0	0
4	1	.246	3.7	8.9	31.9	8.5	6.0	106	51	10	7
	2	.327	2.6	9.3	32.2	60.0	100.0	1040	1200	32	35
	3	.433	1.8	10.2	32.7	0.0	0.0	0	0	0	0
	4	.546	1.3	11.4	33.3	0.0	0.0	0	0	0	0
	5	.663	1.1	12.9	34.3	1.0	5.0	40	132	6	12
	6	.782	1.1	14.6	35.6	0.0	2.0	0	51	0	7
	7	.904	1.9	17.0	37.4	3.0?	7.0	93	98	10	10
5	1	.293	3.0	9.1	32.0	13.0	25.0	200	260	14	16
	2	.364	2.3	9.6	32.3	1.0	2.0	19	27	4	5
	3	.460	1.7	10.5	32.8	0.0	4.0	0	72	0	9
	4	.568	1.2	11.7	33.5	14.0	10.0	555	250	24	16
	5	.681	1.0	12.5	34.0	1.5	0.0	67	0	8	0
	6	.798	1.1	15.0	35.9,	0.0	1.0	0	25	0	5
	7	.928	2.2	17.5	37.8	1.5	2.0	39	24	6	5

k	l	sinθ	θ	A_K	A_{NH_4}	I_K	I_{NH_4}	F_K^2	$F_{NH_4}^2$	F_K	F_{NH_4}
6	1	.342	2.5	9.4	32.2	50.0	70.0	890	870	30	30
	2	.405	2.0	10.0	32.5	0.0	2.0	0	31	0	6
	3	.494	1.5	10.8	33.1	7.0	10.0	240	200	16	14
	4	.596	1.2	12.0	33.8	5.0	12.0	200	300	14	17
	5	.704	1.0	13.4	34.7	2.0	12.0	83	346	9	19
	6	.818	1.2	15.3	36.1	0.0	0.0	0	0	0	0
	7	.935	2.4	17.7	37.9	2.0	4.0	47	44	7	7
7	1	.392	2.1	9.8	32.4	5.5	5.0	110	73	11	9
	2	.448	1.7	10.4	32.8	1.0	6.0	32	108	6	10
	3	.529	1.3	11.2	33.2	0.0	0.0	0	0	0	0
	4	.625	1.1	12.4	34.0	0.5	1.0	21	27	5	5
	5	.729	1.0	13.8	35.0	1.5	1.0	60	29	8	5
	6	.840	1.3	15.6	36.4	6.0	9.0	290	190	17	14
	7	.954	2.9	18.2	38.2	2.0	12.0	38	108	6	10
8	1	.445	1.7	10.3	32.7	9.0	60.0	290	1080	17	33
	2	.495	1.5	10.9	33.0	0.6	2.0	17	40	4	6
	3	.570	1.2	11.7	33.6	0.0	0.0	0	0	0	0
	4	.659	1.1	12.9	34.2	1.5	1.0	59	27	8	5
	5	.759	1.1	14.3	35.3	1.0	2.0	36	51	6	7
	6	.866	1.5	16.9	36.8	0.0?	7.0	0	126	0	11
9	1	.497	1.5	10.9	33.0	0.0	2.0	0	40	0	6
	2	.543	1.3	11.4	33.3	1.0	1.0	37	23	6	5
	3	.611	1.1	12.2	33.9	0.0	1.0	0	27	0	5
	4	.696	1.0	13.3	34.6	8.0	8.0	330	230	18	15
	5	.791	1.1	14.8	35.8	1.5	10.0	51	254	7	16
	6	.894	1.7	16.8	37.2	0.0	2.0	0	32	0	6
10	1	.548	1.3	11.5	33.3	0.0	2.0	0	46	0	7
	2	.589	1.2	11.9	33.6	8.0	20.0	310	500	18	22
	3	.653	1.1	12.8	34.2	5.0	8.0	195	213	14	15
	4	.733	1.0	13.9	35.0	1.5	6.0	60	172	8	13
	5	.824	1.2	15.3	36.5	0.5	4.0	27	91	5	10
	6	.923	2.2	17.5	37.8	0.0	0.0	0	0	0	0
11	1	.600	1.2	12.0	33.8	2.0	6.0	78	148	9	12
	2	.638	1.1	12.6	34.1	0.0	0.0	0	0	0	0
	3	.697	1.0	13.3	34.6	0.0	0.0	0	0	0	0
	4	.772	1.1	14.4	35.6	3.5	2.0	120	51	11	7
	5	.859	1.4	16.0	36.7	1.0	0.0	44	0	7	0
	6	.955	3.0	18.2	38.3	0.0	4.0	0	35	0	6
12	1	.652	1.1	12.7	34.2	4.0	20.0	160	530	13	23
	2	.687	1.0	13.2	34.5	2.0	2.0	83	58	9	8
	3	.742	1.0	13.9	35.1	1.0	2.0	40	58	6	8
	4	.813	1.2	15.2	36.0	1.6	5.0	82	116	9	11
	5	.897	1.8	16.8	37.3	1.0	1.0	33	15	6	4
	6	.988	6.4	19.0	39.0	0.0	8.0	0	32	0	6

k	l	sinθ	θ	A_K	A_{NH_4}	I_K	I_{NH_4}	F^2_K	$F^2_{NH_4}$	F_K	F_{NH_4}
13	1	.704	1.0	13.4	34.7	1.0	2.0	42	58	7	8
	2	.736	1.0	13.9	35.0	2.0	6.0	80	170	9	13
	3	.788	1.1	14.8	35.6	0.0	0.0	0	0	0	0
	4	.855	1.4	15.9	36.7	0.0	1.0	0	19	0	4
	5	.934	2.4	17.7	38.0	1.0	0.0	23	0	5	0
14	1	.754	1.1	14.2	35.3	0.0	0.0	0	0	0	0
	2	.785	1.1	14.7	35.6	1.0	2.0	34	51	6	7
	3	.834	1.3	15.5	36.2	4.0	5.0	200	106	14	10
	4	.898	1.8	16.9	37.3	3.0	8.0	100	119	10	11
	5	.974	4.1	18.7	38.7	0.0	5.0	0	31	0	6
15	1	.808	1.2	15.1	36.0	0.0	0.0	0	0	0	0
	2	.837	1.3	15.5	36.3	2.0	3.0	100	64	10	8
	3	.883	1.7	16.5	37.0	1.0	2.0	35	32	6	6
	4	.944	2.6	17.9	38.1	0.0	1.0	0	10	0	3

In the following table the (h0l) intensities have been treated by θ, A, and C factors exactly as before; they have also been multiplied by 1.4 to make the assigned values of the F's correspond with the (hk0) data (where the same reflections occur in both photographs). This latter factor must be due to a small shift in the position of the Weissenberg camera resulting in a slight change in the intensity of the X-ray beam incident on the crystal. Since the standard to which the assigned intensities were referred, was invariable (within experimental limits) the values assigned to the intensities in different photographs are only comparable if the X-ray beam incident on the crystal is constant, or if a factor which allows for variation is used.

F(h0l) for the Ammonium and Potassium salts.

h	l	$\sin\theta$	θ	A_K	A_{NH_4}	I_K	I_{NH_4}	F^2_K	$F^2_{NH_4}$	F_K	F_{NH_4}
0	1	.124	7.9	8.5	43.5	13.5	92.0	117	376	11	19
	2	.249	3.6	9.0	43.9	17.5	23.0	316	204	18	14
	3	.374	2.2	9.7	44.2	8.0	19.0	220	273	15	17
	4	.499	1.4	10.9	44.7	6.0	10.0	308	224	18	15
	5	.624	1.1	12.4	45.3	1.0	4.0	57	113	8	11
	6	.749	1.0	14.2	46.1	5.5	6.0	300	182	17	14
	7	.874	1.5	16.5	47.3	0.0	2.0	0	39	0	6
2	0	.127	7.6	8.5	43.7	40.0	128.0	366	560	19	23
4		.253	3.6	9.1	43.9	25.0	9.0	445	80	21	9
6		.379	2.2	9.7	44.2	1.0	13.0	27	188	5	14
8		.510	1.4	11.0	44.8	5.5	1.0	280	22	17	5
10		.630	1.1	12.4	45.3	0.0	2.0	0	56	0	8
12		.760	1.1	14.4	46.2	1.0	0.0	49	0	7	0
14		.890	1.7	16.6	47.3	3.0	1.0	148	17	12	4
1	1	.139	7.0	8.5	43.6	10.0	1.0	98	4	10	2
	2	.257	3.5	9.1	43.9	1.0	22.0	18	200	4	14
	3	.380	2.2	9.8	44.2	1.0	0.0	27	0	5	0
	4	.504	1.4	11.0	44.7	4.5	10.0	228	224	15	15
	5	.627	1.1	12.4	45.3	1.5	3.0	86	84	9	9
	6	.752	1.1	14.2	46.2	0.0	0.0	0	0	0	0
	7	.876	1.6	16.5	47.3	0.0	0.0	0	0	0	0
2	1	.177	5.4	8.8	43.8	45.0	56.0	550	330	23	18
	2	.280	3.2	9.2	44.0	18.0	15.0	160	148	13	12
	3	.395	2.0	9.8	44.3	8.0	6.0	58	95	8	10
	4	.515	1.4	11.0	44.8	1.0	2.0	51	45	7	7
	5	.637	1.1	12.5	45.3	4.5	5.0	255	140	16	12
	6	.760	1.1	14.4	46.2	0.0	1.0	0	28	0	5
	7	.882	1.6	16.5	47.3	2.0	0.0	104	0	10	0
3	1	.225	4.0	8.9	43.9	8.5	48.0	140	350	12	19
	2	.312	2.8	9.3	44.1	33.5	40.0	760	454	28	21
	3	.419	1.9	10.0	44.3	1.0	4.0	41	66	6	8
	4	.534	1.3	11.1	44.8	5.0	8.0	373	192	17	14
	5	.652	1.1	12.8	45.4	2.0	4.0	110	112	11	11
	6	.773	1.1	14.6	46.4	2.0	1.0	97	28	10	5
	7	.893	1.7	16.8	47.5	1.5	0.0	73	0	9	0
4	1	.280	3.2	9.2	44.0	75.0	78.0	1485	785	39	28
	2	.354	2.4	9.5	44.2	6.5	7.0	167	92	13	10
	3	.450	1.7	10.3	44.5	24.0	32.0	1070	590	33	24
	4	.559	1.3	11.6	45.0	1.5	1.0	78	24	9	5
	5	.673	1.1	13.0	45.6	0.0	1.0	0	28	0	5
	6	.790	1.1	14.9	46.5	2.0	1.0	95	28	10	5
	7	.909	2.0	17.1	47.7	0.0	0.0	0	0	0	0
5	1	.336	2.5	9.4	44.1	10.0	10.0	250	127	16	11
	2	.400	2.0	9.9	44.3	9.0	4.0	266	63	16	8
	3	.488	1.5	10.7	44.8	5.5	7.0	265	145	16	12
	4	.590	1.2	12.0	45.1	0.5	2.0	27	52	5	7
	5	.698	1.0	13.4	45.8	0.0	0.0	0	0	0	0
	6	.812	1.2	15.3	46.7	0.0	1.0	0	25	0	5

h	l	sinθ	θ	A_K	A_{NH_4}	I_K	I_{NH_4}	F_K^2	$F_{NH_4}^2$	F_K	F_{NH_4}
6	1	.396	2.0	9.8	44.3	6.5	0.0	194	0	14	0
	2	.451	1.7	10.5	44.5	19.0	34.0	845	630	29	25
	3	.531	1.3	11.5	44.8	9.5	28.0	500	672	22	26
	4	.626	1.1	12.4	45.33	1.0	1.0	57	28	8	5
	5	.729	1.0	13.8	46.0	0.0	0.0	0	0	0	0
	6	.839	1.3	15.6	47.0	0.0	1.0	0	22	0	5
7	1	.451	1.7	10.4	44.5	15.0	14.0	660	259	26	16
	2	.505	1.4	11.0	44.7	0.5	0.0	25	0	5	0
	3	.577	1.2	11.8	45.0	2.5	4.0	137	104	12	10
	4	.665	1.1	13.0	45.5	0.0	1.0	0	28	0	5
	5	.764	1.1	14.4	46.3	0.0	0.0	0	0	0	0
	6	.869	1.5	16.3	47.2	0.5	1.0	28	196	5	4
	7	.978	4.5	18.7	48.6	8.0	9.0	133	57	12	8
8	1	.517	1.4	11.1	44.7	0.0	3.0	0	67	0	8
	2	.650	1.3	11.6	45.0	0.5	3.0	26	71	5	8
	3	.626	1.1	12.4	45.3	4.5	7.0	258	196	16	14
	4	.709	1.0	13.5	45.8	1.5	1.0	58	31	8	6
	5	.801	1.1	14.2	46.6	0.0	1.0	0	27	0	5
	6	.902	1.8	17.0	47.6	0.0	0.0	0	0	0	0
9	1	.578	1.2	11.7	45.0	5.5	3.0	304	78	17	9
	2	.619	1.1	12.3	45.2	2.0	1.0	115	28	11	5
	3	.678	1.0	13.1	45.6	3.0	3.0	180	92	13	10
	4	.755	1.1	14.3	46.2	0.0	0.0	0	0	0	0
	5	.842	1.3	16.0	47.0	3.0	2.0	200	46	14	7
	6	.939	2.5	17.7	48.1	5.0	7.0	158	81	13	9
10	1	.640	1.1	12.6	45.4	0.0	1.0	0	28	0	5
	2	.675	1.0	13.1	45.6	1.0	2.0	59	62	8	8
	3	.731	1.0	13.9	46.0	0.0	1.0	0	31	0	6
	4	.803	1.1	15.2	46.7	2.0	2.0	168	55	13	7
11	1	.702	1.0	13.5	45.8	1.0	1.0	58	31	8	6
	2	.735	1.0	14.0	46.0	3.0	4.0	160	122	13	11
	3	.787	1.1	14.8	46.4	0.0	0.0	0	0	0	0
	4	.853	1.4	16.1	47.1	1.0	0.0	62	0	8	0
12	1	.765	1.1	14.5	46.3	0.0	0.0	0	0	0	0
	2	.796	1.1	15.0	46.5	0.0	0.0	0	0	0	0
	3	.844	1.3	16.0	47.0	0.0	0.0	0	0	0	0
	4	.906	1.9	17.1	47.7	1.0	3.0	43	46	7	7
13	1	.828	1.2	15.7	46.9	0.0	2.0	0	49	0	7
	2	.856	1.4	16.1	47.1	2.0	0.0	123	0	11	0
	3	.900	1.8	17.0	47.6	1.0	3.0	46	49	7	7
	4	.959	3.2	18.2	48.3	2.0	0.0	48	0	7	0
14	1	.890	1.7	16.8	47.5	1.0	0.0	49	0	7	0
15	1	.953	2.9	18.2	48.3	3.0	2.0	80	20	9	5

A second set of b-axis photographs was taken comparing the Potassium and Rubidium salts. In this case the cylinders were ground so that the product μr was the same for both, so that the same absorption corrections applied to both salts. They were also ground to a smaller diameter than the previous cylinders to ensure that the spots would be more uniform across their breadth. This unfortunately resulted in the loss of several high order reflections.

The following table shows the collected values of F(h0l) for the Ammonium, Potassium, and Rubidium salts. The agreement between the two sets of Potassium data is as good as can be expected from the method of derivation of F's, while the rise and fall of the F's in the three salts indicates that the latter are very similar in internal structure.

h	l	F_{NH_4}	F_K	F_K	F_{Rb}.
0	1	19	11	9	6
	2	14	18	16	16
	3	17	15	15	15
	4	15	18	14	11
	5	11	8	6	0
	6	14	17	14	14
	7	6	0	0	0
2	0	23	19	16	4
4		9	21	21	24
6		14	5	5	14
8		5	17	13	20
10		8	0	0	9
12		0	7	6	12
14		4	12	7	10
1	1	2	10	10	14
	2	14	4	4	11
	3	0	5	3	8
	4	15	15	11	10
	5	9	9	6	4
	6	0	0	0	0
	7	0	0	0	7
2	1	18	23	20	20
	2	12	13	14	14
	3	10	8	7	0
	4	7	7	4	0
	5	12	16	12	12
	6	5	0	0	4
	7	0	10	7	7
3	1	19	12	11	0
	2	21	28	26	26
	3	8	6	3	5
	4	14	17	12	8
	5	11	11	9	4
	6	5	10	6	6
	7	0	9	5	7
4	1	28	39	28	28
	2	10	13	13	13
	3	24	33	23	20
	4	5	9	6	4
	5	5	0	4	4
	6	5	10	8	12
	7	0	0	0	4
5	1	11	16	14	18
	2	8	16	16	17
	3	12	16	11	16
	4	7	5	0	0
	5	0	0	0	0
	6	5	0	0	0
6	1	0	14	12	15
	2	25	29	21	12
	3	26	22	18	14
	4	5	8	6	4
	5	0	0	0	6
	6	5	0	0	4
7	1	16	26	18	18
	2	0	5	4	11
	3	10	12	9	12
	4	5	0	0	0
	5	0	0	0	0
	6	4	5	3	0
	7	8	12	9	8
8	1	8	0	0	11
	2	8	5	4	8
	3	14	16	13	11
	4	6	8	5	0
	5	5	0	0	0
	6	0	0	0	4
9	1	9	17	14	14
	2	5	11	9	15
	3	10	13	11	11
	4	0	0	0	0
	5	7	14	8	5
	6	9	13	8	5
10	1	5	0	0	9
	2	8	8	7	5
	3	6	0	0	0
	4	7	13	8	6
11	1	6	8	6	9
	2	11	13	13	13
	3	0	0	0	0
	4	0	8	5	0
12	1	0	0	0	9
	2	0	0	0	0
	3	0	0	0	0
	4	7	7	4	0
13	1	7	0	0	4
	2	0	11	7	7
	3	7	7	0	0
	4	0	7	4	0
14	1	0	7	5	5
15	1	5	9	5	5

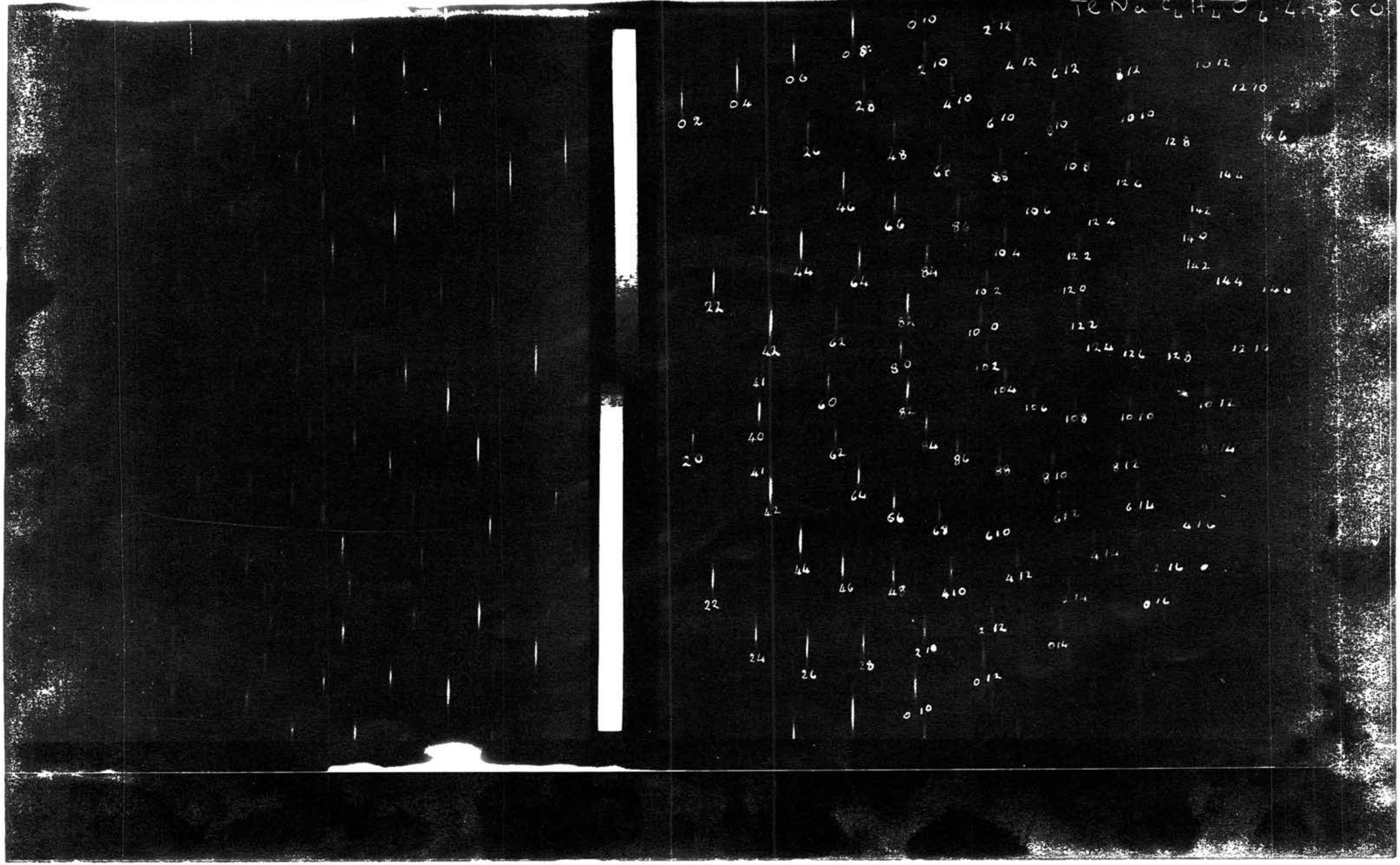


Figure 4.
Weissenberg photograph. Sodium Thallium Tartrate Tetrahydrate. c-axis, zero layer-line.
(Owing to the high absorbtion of this salt, the relatively weaker (hk0) reflections with no Thallium contribution are practically all absent

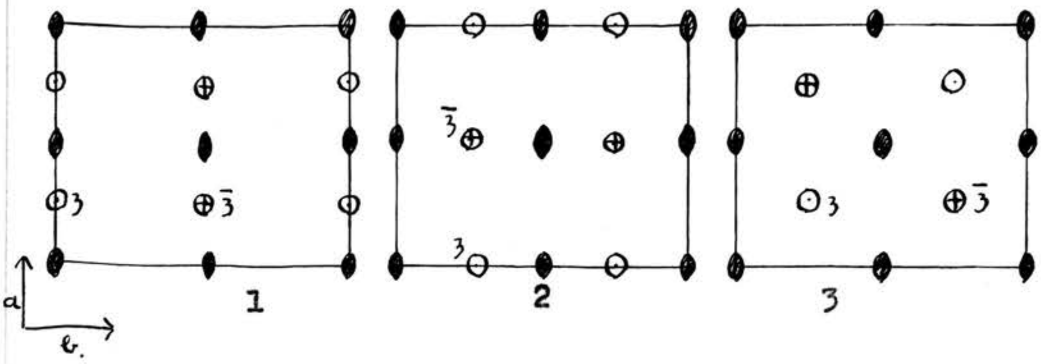
Location of Potassium Atoms.

(The deduction of the thallium and potassium positions was first made by Dr.R.C.Evans, to whom thanks are due for access to his unpublished work. They were deduced by means of Patterson methods. The following is an independent proof in support of his findings.)

An examination of the (hk0) intensities of Rochelle Salt shows that the intensities with both h and k even are as a class appreciably stronger than the other intensities. This effect shows up also in the Rubidium salt, while for the Thallium salt it is so marked that in some photographs few reflections outside this class can be observed. Figure 4 shows such a photograph.

It was therefore assumed that the Thallium atoms halved both the a and b directions, and that this was also true for the Potassium, Rubidium, and Ammonium atoms. There are four possible arrangements which fulfil this condition;-

(a) Three general positions.



These possibilities were rejected on examination of the Thallium (0kl) and (h0l) intensities, which to a first approximation depend only on the position of the Thallium atoms:-

(0kl) intensities.

With k even, the structure factors of the Thallium atoms are in these arrangements:

(1) $\pm \cos lz2\pi$ (2) $\cos lz2\pi$ (3) $\pm \cos lz2\pi$

and with k odd:

(1) 0 (2) $\sin lz2\pi$ (3) 0

but the intensities with k even do not dominate the intensities with k odd in any of the a-axis zero layer line photographs. (1) and (3) were therefore rejected.

(h0l) intensities.

With h even, the structure factors of the Thallium atoms are in these arrangements:

(1) $\cos 2\pi lz$ (2) $\pm \cos 2\pi lz$ (3) $\pm \cos 2\pi lz$

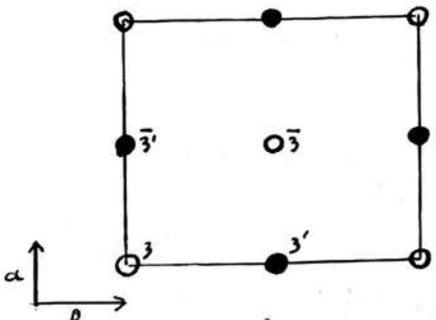
and with h odd:

(1) $\sin 2\pi lz$ (2) 0 (3) 0

but the intensities with h even do not dominate the intensities with h odd in any of the b-axis zero layer line photographs. (2) and (3) were therefore rejected.

(b) Special positions.

The fourth possibility consists of the two sets of special twofold positions, $(0\ 0\ z)$ and $(0\ \tfrac{1}{2}\ z')$.



4

The structure factors for this arrangement are:

(h0l)	h even,	$\cos 2\pi lz + \cos 2\pi lz'$
	h odd,	$\sin 2\pi lz + \sin 2\pi lz'$
(0kl)	k even,	$\cos 2\pi lz + \cos 2\pi lz'$
	k odd,	$\sin 2\pi lz - \sin 2\pi lz'$

An inspection of the Thallium (h0l) and (0kl) intensities gives approximate values of z and z' which account for the observed results quite well. The values adopted were:

$$z = 3/60.c_o$$

$$z' = 9/60.c_o$$

The following tables show how these values afford a reasonable explanation of the Thallium intensities, if the latter are regarded as being approximately due to the Thallium contributions alone.

Thallium (h0l) Intensities, h even.

					h				
l	cos $2\pi lz$+cos $2\pi lz'$	0	2	4	6	8	10	12	14
0	2.00		10	17	9	9	5	5	6
1	1.54	7	15	15	8	4	2	2	2
2	0.50	6	3	2	0	½	0	0	0
3	$\overline{0.36}$	2	0	3	0	½	0	0	0
4	$\overline{0.50}$	2	0	½	0	0	0	0	
5	0.00	0	½	0	0	0	0	0	
6	0.50	3	½	1	½	0	½		
7	0.36	0	½	0	0				
8	$\overline{0.50}$	0	4						

Thallium (h0l) Intensities, h odd.

					h				
l	sin $2\pi lz$+sin $2\pi lz'$	1	3	5	7	9	11	13	15
1	1.12	7	3	7	6	3	1	½	4
2	1.54	10	13	9	5	3	3	2	3
3	1.12	9	3	4	2	1	0	0	
4	0.36	1	0	0	0	0	0	0	
5	0.00	0	0	0	0	0	0	0	
6	0.36	0	0	0	0	0			
7	1.14	1	1	½	3				

Thallium (Okl) Intensities, k odd.

		k								
l	sin 2πlz-sin 2πlz'	1	3	5	7	9	11	13	15	17
1	0.50	½	5	4	3	1	0	1	0	0
2	$\overline{0.36}$	½	5	½	½	0	½	0	0	1
3	0.50	0	1	½	½	½	½	0	0	
4	1.54	10	16	12	7	8	6	3	3	
5	2.00	10	13	11	10	5	8	10		
6	1.54	6	6	4	7	7	3			

Thallium (Okl) Intensities, k even.

		k									
l	cos 2πlz+cos 2πlz'	0	2	4	6	8	10	12	14	16	18
0	2.00		12	20	18	26	18	10	7	4	4
1	1.54	5	5	12	12	4	6	2	4	3	0
2	0.50	4	5	6	½	1	2	½	½	0	2
3	$\overline{0.36}$	2	6	½	1	½	1	½	½		
4	$\overline{0.50}$	2	0	½	0	½	0	0	0		
5	0.00	0	0	0	0	0	0	0	0		
6	0.50	2	1	½	1	3	1	4			

Since atoms on the twofold axes contribute only to the (hk0) reflections with h, k, both even, one would expect that any particular experimentally observed F(hk0) outside this class would have approximately the same value for all four salts, if the salts are strictly isomorphous. An inspection of the intensity of such reflections showed that they rose and fell in step, in the different salts, while the table of F's (pp.17-21) shows how close to equality they can be easily brought, bearing in mind the limitations of the method used in the derivation of the F's. The same table shows the expected large changes in F(hk0) with h, k, both even, in passing from one salt to an other.

It was therefore concluded that the Thallium, Rubidium, Potassium, and Ammonium atoms occupied the two special twofold positions,

(a) (0 0 3) associated with (30 30 57),
and (b) (0 30 9) " " (30 0 51)

Parameters in 60ths of the cell edges.

METHOD OF ANALYSIS.

Both Fourier and Patterson methods were used in the determination of the structure. The Fourier method used is a general one applicable whenever the crystal is a member of an isomorphous series. From a knowledge of the position of the replaceable atoms in the lattice and observations of the changes of intensity between the different salts, the signs of the F's can be obtained. It has been assumed on the basis of a fairly substantial amount of evidence that all the replaceable atoms occupy the same positions, viz. those given on p.34, so that the sign of each F may be taken to be the same as the sign of the Thallium structure factor if there is an increase in the intensity as an atom is replaced by a heavier one. If there is a decrease in the intensity then the sign is opposite to the sign of the Thallium contribution.

The first difficulty in this method is due to the effect of the varying absorption coefficients on the intensities, which makes it impossible to compare photographs of different salts directly. The application of absorption corrections however produced self consistent results in the case of all reflections with a Thallium structure factor $\geq$ 1, so that the signs of such F's could be obtained without any ambiguity. The second difficulty arises from the fact that many of the structure factors are small, and in the particular case of Rochelle Salt rather a high proportion are actually zero. The signs of reflections having zero Thallium contribution are of course indeterminate by this method. Of particular interest are those F's having a small Thallium ~~contribution~~ S.F. and a large contribution from the rest of the unit cell. The signs of these F's can in many cases be obtained by inspection of the Thallium intensities. Thus if we have a number of Potassium F's of high magnitude and small Potassium contribution, the corresponding Thallium reflections should fall into two fairly well marked classes, a strong class where the sign of the F is the same as that of the Thallium S.F., and a weak class where the sign of the F is opposite to that of the Thallium S.F. In this way a considerable number of large magnitude terms were added to the Fourier series.

By an application of these methods three Fourier projections were obtainable.

(1) A projection on (001) containing only terms with h, k, both even, since the Potassium etc. atoms

contribute only to these planes. The resulting projection is unique over only one sixteenth of the cell projection and consists of the superimposition of the four quarters of the unit cell. The resolution is thus very low and the projection was of little value. (2) A projection on (100) and (3) a projection on (010). These, it was found later, were substantially correct and the three dimensional structure might have been derived from them immediately had it not been for the fact that in each projection two molecules were superimposed. The Fourier projections will be shown later in their final form which does not differ materially from that obtainable by the above methods.

The following table shows the collected values of F(h0l) with Thallium S.F. = 1, for the Ammonium, Potassium, and Rubidium salts. With few exceptions, the changes in F from Ammonium to Potassium agree in direction with the changes from Potassium to Rubidium. The outstanding exceptions are those in which there is an increase from Ammonium to Potassium and no change from Potassium to Rubidium. In all these cases however, the Rubidium F is comparatively large and consequently the sign of the Potassium F must be the same as that of the Rubidium contribution; otherwise the Rubidium F would fall off considerably.

Three signs, those of the (600), the (102), and the (303) cannot be determined because of a sign change from Ammonium to Rubidium; these F's are of necessity small and their effect negligible.

h	l	S.F.	F_{NH_4}	F_K	F_K	F_{Rb}	F_K sign.
0	1	1.54	19	11	9	6	-
2	0	2.00	23	19	16	4	-
4~~0~~	0	2.00	9	21	21	24	+
6	0	2.00	14	5	5	14	?
8	0	2.00	5	17	13	20	+
10	0	2.00	8	0	0	9	
12	0	2.00	0	7	6	12	+
14	0	2.00	4	12	7	10	+
1	1	1.12	2	10	10	14	+
1	2	1.54	14	4	4	11	?
1	3	1.12	0	5	3	8	+
1	7	1.12	0	0	0	7	
2	1	1.54	18	23	20	20	+
3	1	1.12	19	12	11	0	-
3	2	1.54	21	28	26	26	+
3	3	1.12	8	6	3	5	?
3	7	1.12	0	9	5	7	+
4	1	1.54	28	39	28	28	+
5	1	1.12	11	16	14	18	+
5	2	1.54	8	16	16	17	+
5	3	1.12	12	16	11	16	+
6	1	1.54	0	14	12	15	+
7	1	1.12	16	26	18	18	+
7	2	1.54	0	5	4	11	+
7	3	1.12	10	12	9	12	+
8	1	1.54	8	0	0	11	
9	1	1.12	9	17	14	14	+
9	2	1.54	5	11	9	15	+
9	3	1.12	10	13	11	11	+
10	1	1.54	5	0	0	9	
11	1	1.12	6	8	6	9	+
11	2	1.54	11	13	13	13	+
11	3	1.12	0	0	0	0	
12	1	1.54	0	0	0	9	
13	1	1.12	7	0	0	4	
13	2	1.54	0	11	7	7	+
13	3	1.12	7	7	0	0	?
14	1	1.54	0	7	5	5	+
15	1	1.12	4	9	5	5	+

A similar table was compiled for the rest of the (h0l) F's but it was obvious that the discrepancies would not permit the assignment of signs. Most of the stronger members of these remaining F's were determined by inspection of the Thallium intensities as described before.

In the same way by comparison of the Ammonium and Potassium F'(0kl)'s and consideration of the Thallium intensities the signs of a sufficient number of Potassium F(0kl)'s could be determined to enable a Fourier projection on (100) to be completed.

These Fourier projections suffer from a lack of resolving power, and it was felt that if more accurate atomic positions were obtainable, the structure would soon become apparent. An increase in resolving power was obtained by use of Patterson methods. The Patterson syntheses used in the work were:

(1) Sections at $z = 0$, $x = \frac{1}{2}a_0$, and $y = \frac{1}{2}b_0$, of the three dimensional synthesis of the Ammonium salt.

(2) Patterson synthesis of the (hk0) planes excluding those having both h and k even. This synthesis was done for the Potassium salt, and the fact that the combined use of both Ammonium and Potassium data produces concordant results, is adequate proof of the great similarity of the internal structures of these two salts.

The general intensities required for (1), numbering about 1400 in all were obtained mainly from layer line Weissenberg photographs about the a, b, and c-axes. These photographs gave all the intensities obtainable with Cu K_α radiation except those within cusps having axes parallel to [110] in the reciprocal space. The remaining intensities were obtained from a set of oscillation photographs with [110] as rotation axis. In this case the layer lines were so close together as to make the oscillation method the most advantageous.

The low absorption of the Ammonium salt and its small variation with $\sin\theta$, made this salt ideal for this type of work where very large numbers of intensities had to be dealt with. The intensities were corrected for polarization and by the geometrical correction factor D_1 described and calculated by Cox and Shaw (1930)[8]. No absorption corrections were applied.

The twofold screw axes in the structure are equivalent to twofold axes in the three dimensional Patterson. The symmetry thus becomes 2 2 2 and this combined with the centre of symmetry at the origin present in all Pattersons, makes the symmetry P2/m2/m2/m. (= mmm)

The unique volume of the Patterson synthesis is thus 1/8th of the unit cell, so that the resolving power in the sections perpendicular to a and b is the same as in the a and b-axis Fourier projections, except possibly for a slight improvement due to the complete nature of the data used in the Patterson synthesis. The resolving power in the direction of the c-axis is however much increased.

The equivalent points of the space group $P\,2_1\,2_1\,2$ are:

1	2	3	4
(xyz)	$(\frac{1}{2}+x\ \ \frac{1}{2}-y\ \ \bar{z})$	$(\frac{1}{2}-x\ \ \frac{1}{2}+y\ \ \bar{z})$	$(\overline{xy}z)$

The interatomic vectors between four equivalent atoms having these coordinates give rise to peaks in the Patterson synthesis at the points:

$$(0\ \ 0\ \ 0)\ \ (\tfrac{1}{2}\ \ \tfrac{1}{2}+2y\ \ 2z)\ \ (\tfrac{1}{2}+2x\ \ \tfrac{1}{2}\ \ 2z)\ \ (2x\ \ 2y\ \ 0)$$
$$(\tfrac{1}{2}\ \ \tfrac{1}{2}-2y\ \ 2\bar{z})\ \ (0\ \ 0\ \ 0)\ \ (2x\ \ 2\bar{y}\ \ 0)\ \ (\tfrac{1}{2}+2x\ \ \tfrac{1}{2}\ \ 2\bar{z})$$
$$(\tfrac{1}{2}-2x\ \ \tfrac{1}{2}\ \ 2\bar{z})\ \ (2\bar{x}\ \ 2y\ \ 0)\ \ (0\ \ 0\ \ 0)\ \ (\tfrac{1}{2}\ \ \tfrac{1}{2}+2y\ \ 2\bar{z})$$
$$(2\bar{x}\ \ 2\bar{y}\ \ 0)\ \ (\tfrac{1}{2}-2x\ \ \tfrac{1}{2}\ \ 2z)\ \ (\tfrac{1}{2}\ \ \tfrac{1}{2}-2y\ \ 2z)\ \ (0\ \ 0\ \ 0)$$

These reduce to the three unique peaks at:

$$(\tfrac{1}{2}\ \ \tfrac{1}{2}+2y\ \ 2z)\ \ (\tfrac{1}{2}+2x\ \ \tfrac{1}{2}\ \ 2z)\ \ (2x\ \ 2y\ \ 0),$$

lying one in each of the sections computed.

Thus, in the section at $x = \frac{1}{2}a_0$ a peak at Y Z corresponds to an atom at $\pm\frac{1}{2}(\frac{1}{2}-Y)$, $\pm\frac{1}{2}Z$. i.e. there are four possible atomic sites corresponding to a peak in the sections considered. The interpretation is further complicated by the existence of interatomic vectors whose x components are $\frac{1}{2}a_o$, due to atoms having by chance the same x coordinate. The peaks corresponding to these vectors are of double weight and though at first a complicating factor, they ultimately prove to be valuable in confirming some of the allocated atomic sites. Similar considerations apply to the other sections. The following table summarises the information obtainable from these sections where (X Y) etc. correspond to vectors between equivalent atoms.

Section	Peaks	Atomic coordinates.	
$x = \frac{1}{2}a_o$	(Y Z)	$\pm\frac{1}{2}(\frac{1}{2}-Y)$	$\pm\frac{1}{2}Z$
$y = \frac{1}{2}b_o$	(X Z)	$\pm\frac{1}{2}(\frac{1}{2}-X)$	$\pm\frac{1}{2}Z$
$z = 0$	(X Y)	$\pm\frac{1}{2}X$	$\pm\frac{1}{2}Y$

The series to be evaluated for this synthesis is:

$$\sum_{-\infty}^{+\infty}\sum_{hkl}\sum F^2_{hkl}\exp.(hx+ky+lz)2\pi$$

which reduces to $\sum_{0}^{+\infty}\sum_{hk}(\sum_{l,0}^{+\infty} F^2_{hkl}) \cos 2\pi hx \cos 2\pi ky$

for the section at $z = 0$,

to $\sum_{0}^{+\infty}\sum_{kl}(\sum_{h,0}^{+\infty} F^2_{hkl}) \cos 2\pi ky \cos 2\pi lz$

for the section at $x = \frac{1}{2}a_o$,

and to $\sum_{0}^{+\infty}\sum_{hl}(\sum_{k,0}^{+\infty} F^2_{hkl}) \cos 2\pi hx \cos 2\pi lz$

for the section at $y = \frac{1}{2}b_o$.

In the latter two syntheses F^2_{hkl} is taken as being -ve when h or k is odd respectively.

Confidence in the a and b-axis Fourier projections increased, when it was found that they agreed almost perfectly with the three dimensional Patterson sections, and the former were used with great effect in the interpretation of the latter. e.g. The Fouriers were used to discriminate between the two types of peak found in the Patterson sections.

The combined use of Fourier projections and Patterson sections enabled rather accurate atomic sites to be found which were, unfortunately, limited in value because of the existence of alternatives. Thus, ~~an~~ an atomic position might be at (xyz) or at $(\frac{1}{2}-x\ \frac{1}{2}-y\ \bar{z})$; i.e. there was left a centre of symmetry at (1/4 1/4 1/2) which **did not** exist in the structure. That this should be so is obvious from the symmetry of the sections and projections. It was here that the Patterson projection (2) was found to be of great value. It is of course the projection of the complete three-dimensional synthesis on (001), and could therefore be used to discriminate between the remaining alternatives. If the first atom is placed on one of the possible alternatives this projection shows which of the other alternatives are to be chosen for the remaining atomic positions. Since (2) contains no planes with h, k, both even, it does not give any information concerning interatomic vectors involving the Potassium atoms. The projection is thus much simplified.

In this way two structures can be built up related to each other by a centre of symmetry at (1/4 1/4 1/2) and these correspond to the d- and l-forms of the optically active compound. The X-ray evidence cannot of course distinguish between them.

The Patterson diagrams are shown at the end of this section. The procedure adopted in the analysis was as follows.

Since the a-axis Fourier synthesis was obviously the most open available projection, it was made the starting point. An isolated peak in this projection was chosen. The Patterson section at $x = \frac{1}{2}a_0$ was examined for confirmation of its approximate position, then the b-axis Fourier synthesis was investigated for an atomic site having the same z parameter. In the most favourable cases there existed at least two possibilities, because of the symmetry of the projection. Their positions were verified by the Patterson section at $y = \frac{1}{2}b_0$. The first atom to be inserted may be placed arbitrarily on either of these positions.

A second isolated peak in the a-axis Fourier synthesis was chosen, its position verified as before, and two or more possible positions in the b-axis Fourier synthesis found and verified. The correct position was determined by using the Patterson projection on (001), since the insertion of two atoms results in four unique peaks in the general Patterson synthesis (apart from the ~~three~~ six unique peaks in the sections computed) of which, the Patterson synthesis used, is the projection. These result from the four interatomic vectors between an atom (xyz) and the four equivalent atoms $(x'\ y'\ z')$, $(\frac{1}{2}+x'\ \frac{1}{2}-y'\ \bar{z}')$, $(\frac{1}{2}-x'\ \frac{1}{2}+y'\ \bar{z}')$, $(\bar{x}'\ \bar{y}'\ z')$. The four corresponding positions in the Patterson projection were examined and the sum of the heights of the four positions found. The insertion of a third atom increases to eight the number of conditions to be fulfilled in the Patterson projection. In this manner the correct alternatives were soon found. The extraction of single values of 'electron density^2' is not very sound; one should take the total volume of the peak , but the evaluation of this is impossible and of little value at this stage, in such a complicated superimposition as this Patterson projection. The success of the method proves that this procedure was sufficiently accurate to indicate the structure. In some cases the sum total was not very impressive, but note was taken of whether the coordinates in question fell near a high region.

In this way the positions of the atoms of one half of the tartrate molecule were progressively found, and thereafter the analysis was comparatively simple. The water molecules proved rather more difficult to find since they, of course, had no conditions of molecular structure to fulfil, as had the atoms of the tartrate molecule. Actually the last water molecule to be found was located by consideration of space available in a model of the structure.

Once the approximate structure was found, the calculation of F(hk0), F(h0l), and F(0kl) enabled the a and b-axis Fourier syntheses to be improved by the inclusion of a number of new terms, while an unrestricted c-axis Fourier synthesis was obtained for the first time. That all the expected positions showed up in this projection, was excellent verification of the proposed structure suggested mainly by the projections down the other axes. The F's were recalculated using slightly improved positions indicated by the three Fourier projections, and the final set of Fourier projections obtained.

The following table is a list of the positions determined. (Parameters in 100ths of the cell edges)

Parameters of the Structure of Rochelle Salt.

2 K on (a)		(00 00 05)
2 K on (b)		(00 50 15)
4 Na on		(23 99 52)
4 O on	(1)	(12 10 37)
4 O on	(2)	(22 20 12)
4 O on	(3)	(23 40 82)
4 O on	(4)	(06 37 85)
4 OH on	(5)	(16 36 32)
4 OH on	(6)	(29 24 63)
4 H_2O on	(7)	(40 08 50)
4 H_2O on	(8)	(25 05 87)
4 H_2O on	(9)	(44 30 05)
4 H_2O on	(10)	(42 40 45)
4 C on		(15 18 28)
4 C on		(12 28 42)
4 C on		(17 27 65)
4 C on		(15 35 80)

(Parameters in 100ths of the cell edges)

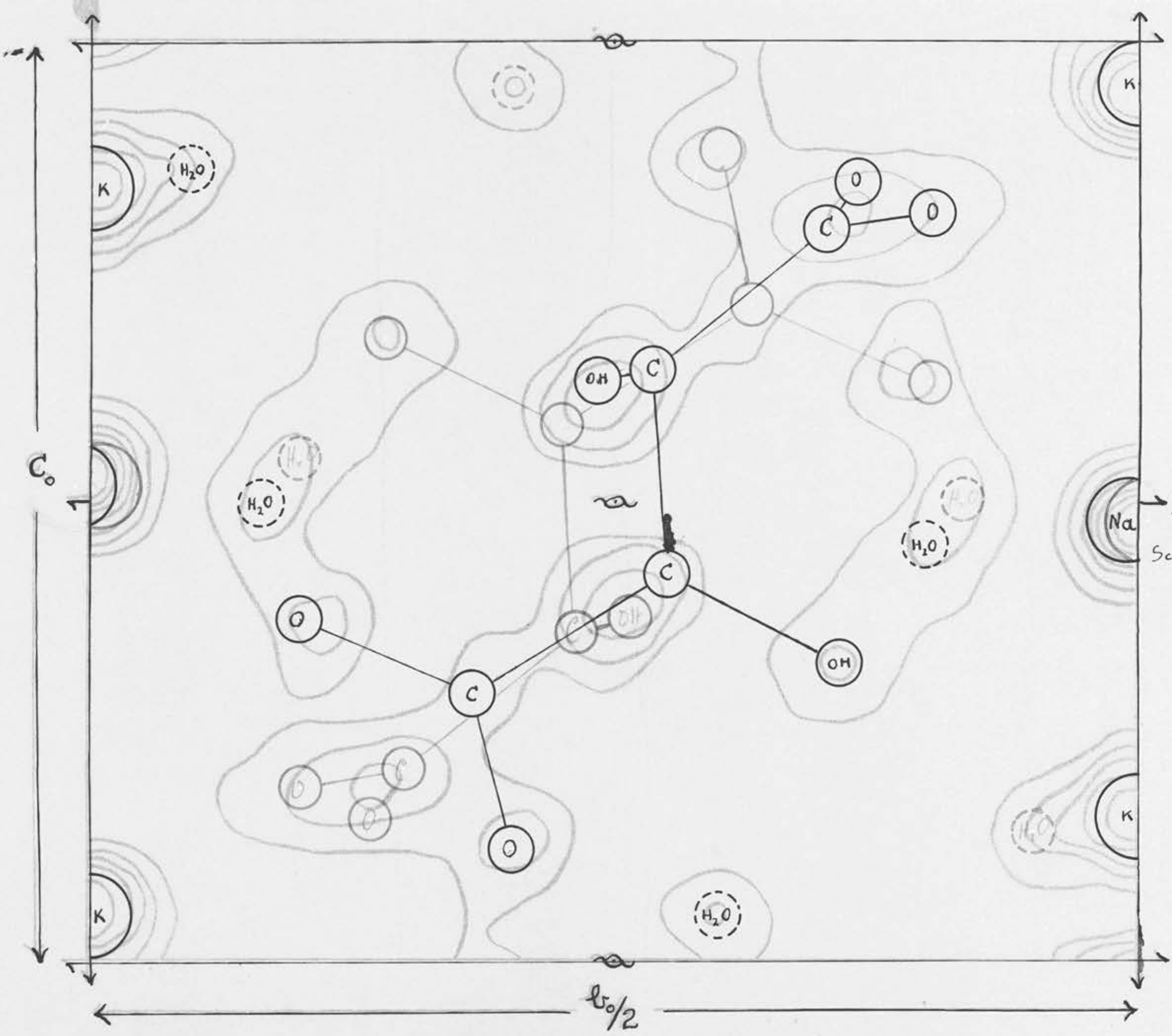
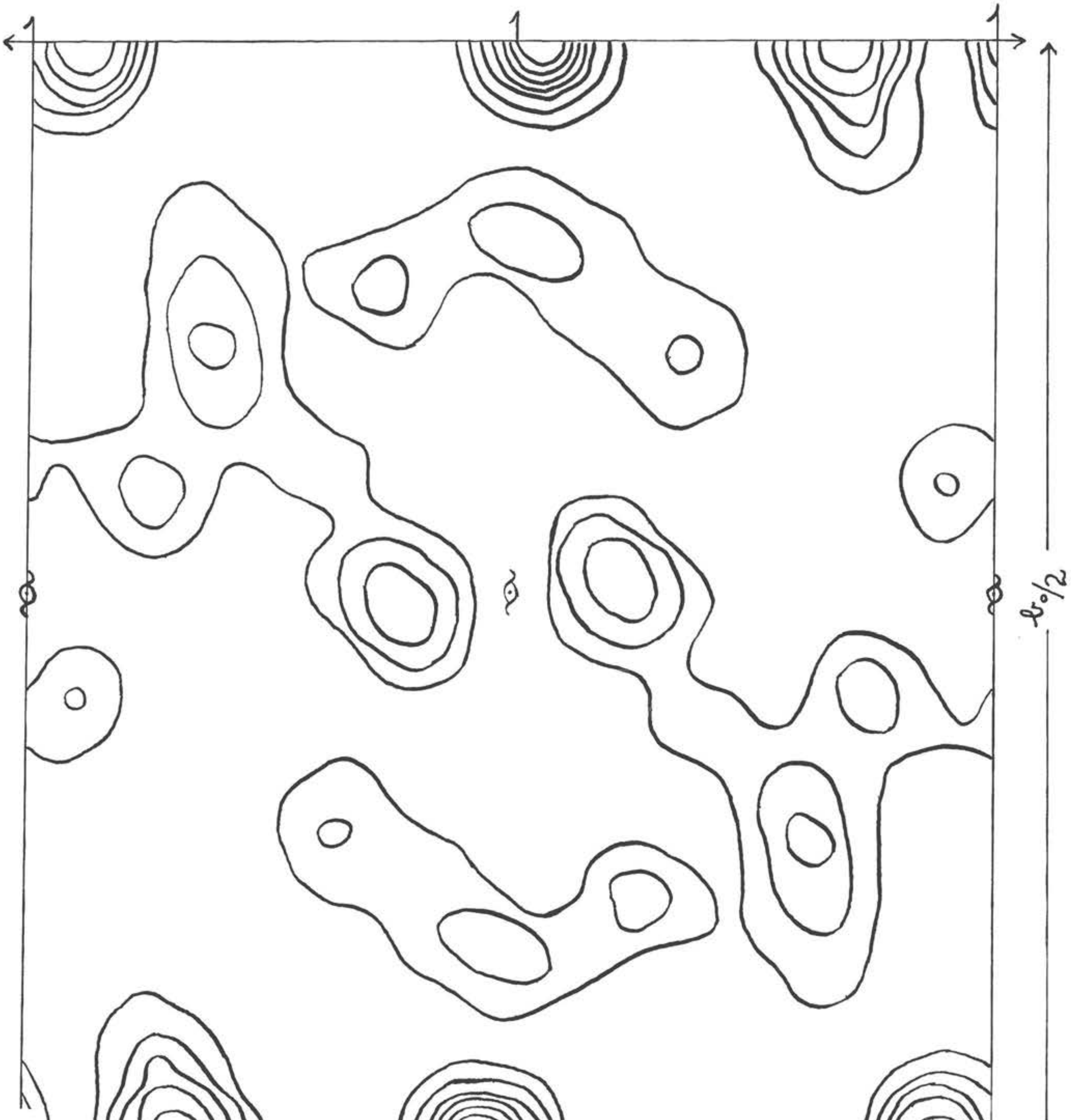


Figure 5.

Scale 1" ≡ 1 Å.


b₀/2
c₀

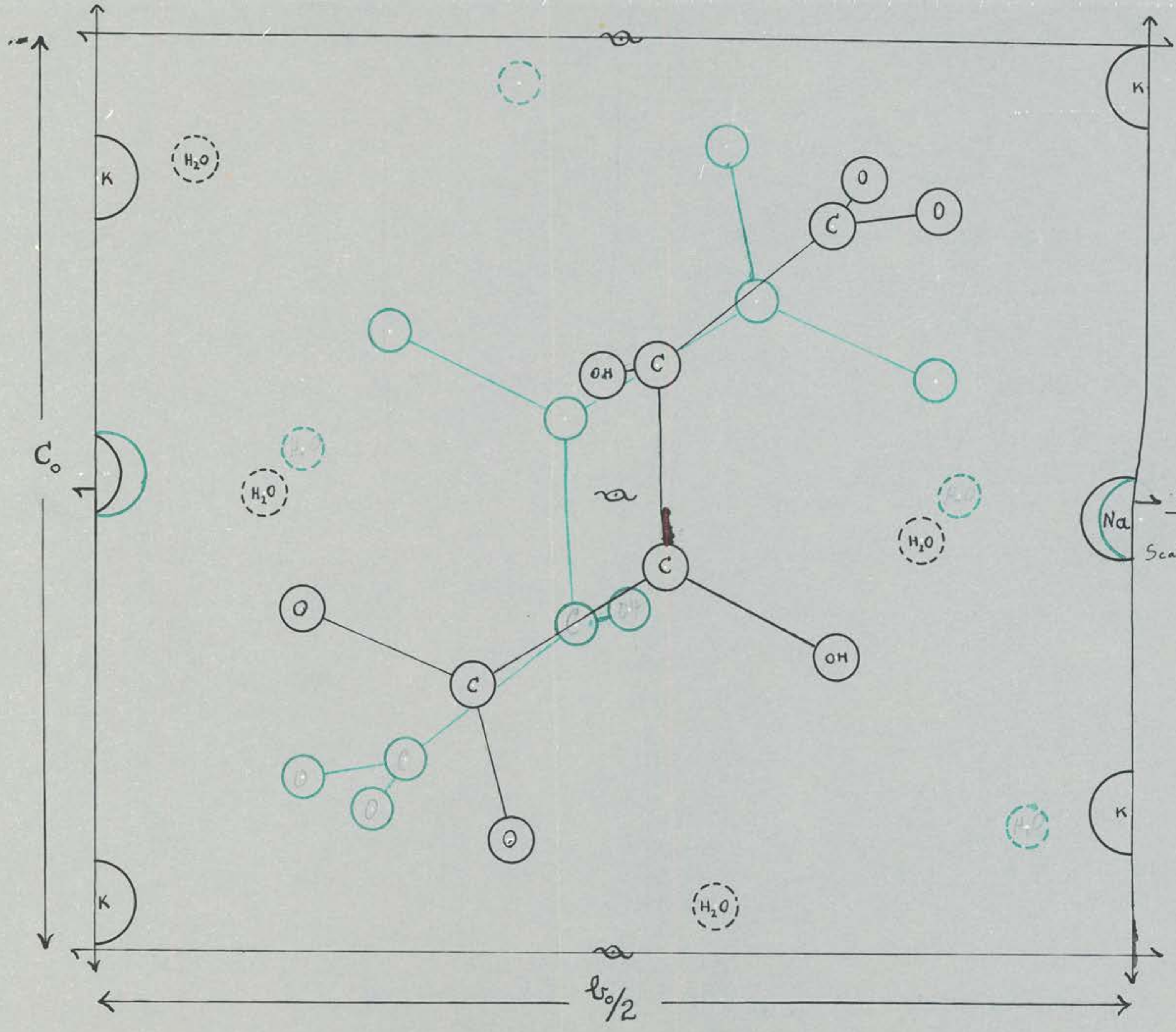


Figure 5.

Scale 1" ≡ 1Å.

Diagrams of Fourier and Patterson Syntheses.

Figure 5.

Fourier projection of Rochelle Salt on (100). Projection of half cell shown. The black atoms are those lying in the near quarter of the unit cell. The green atoms are those in the far quarter. Contours are drawn at 10, 60, 110, 160, 210, 260, 310. The background is quite good, averag~~e~~ing about -40.

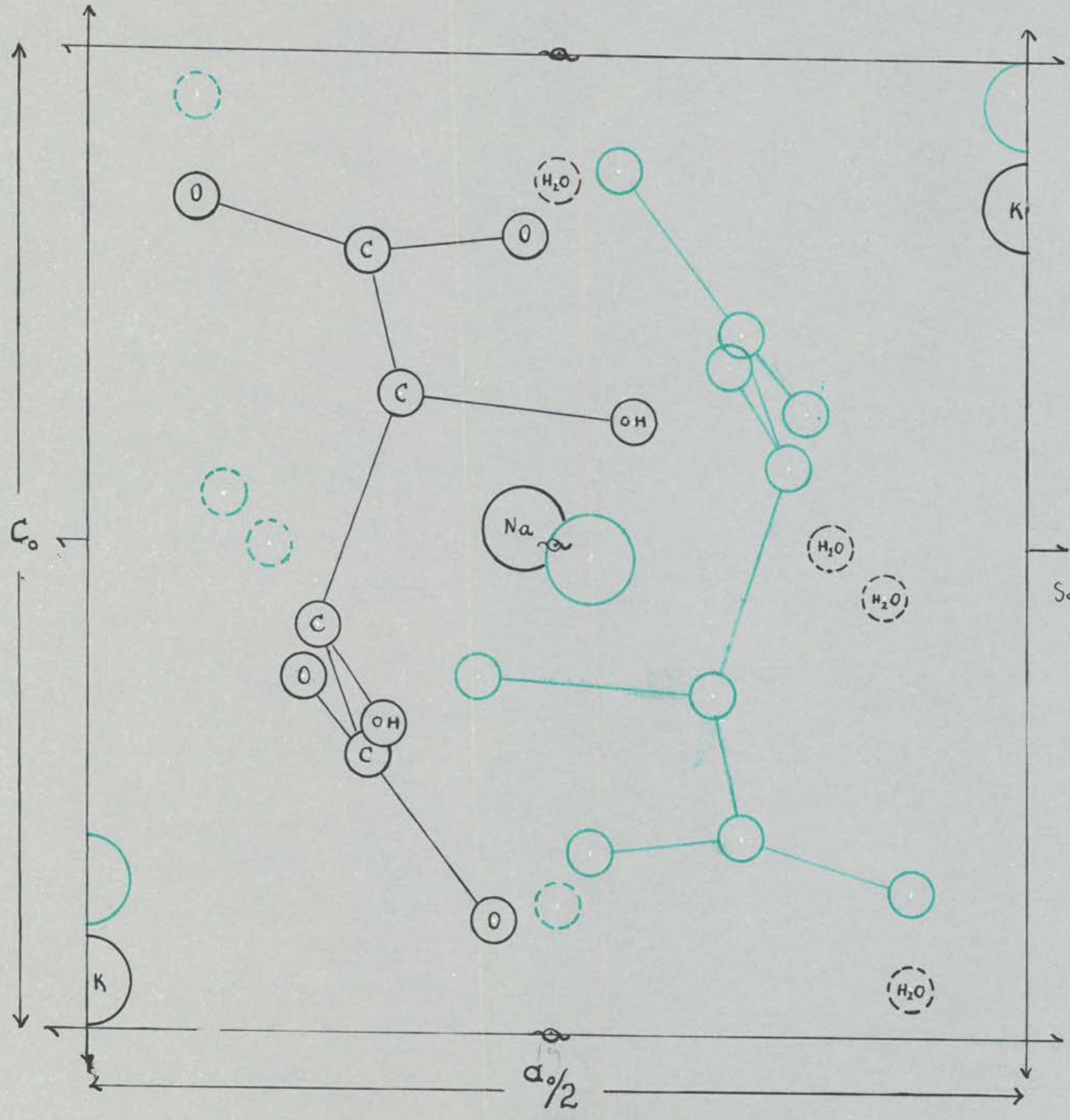


Figure 6.

Scale 1" ≡ 1 Å.

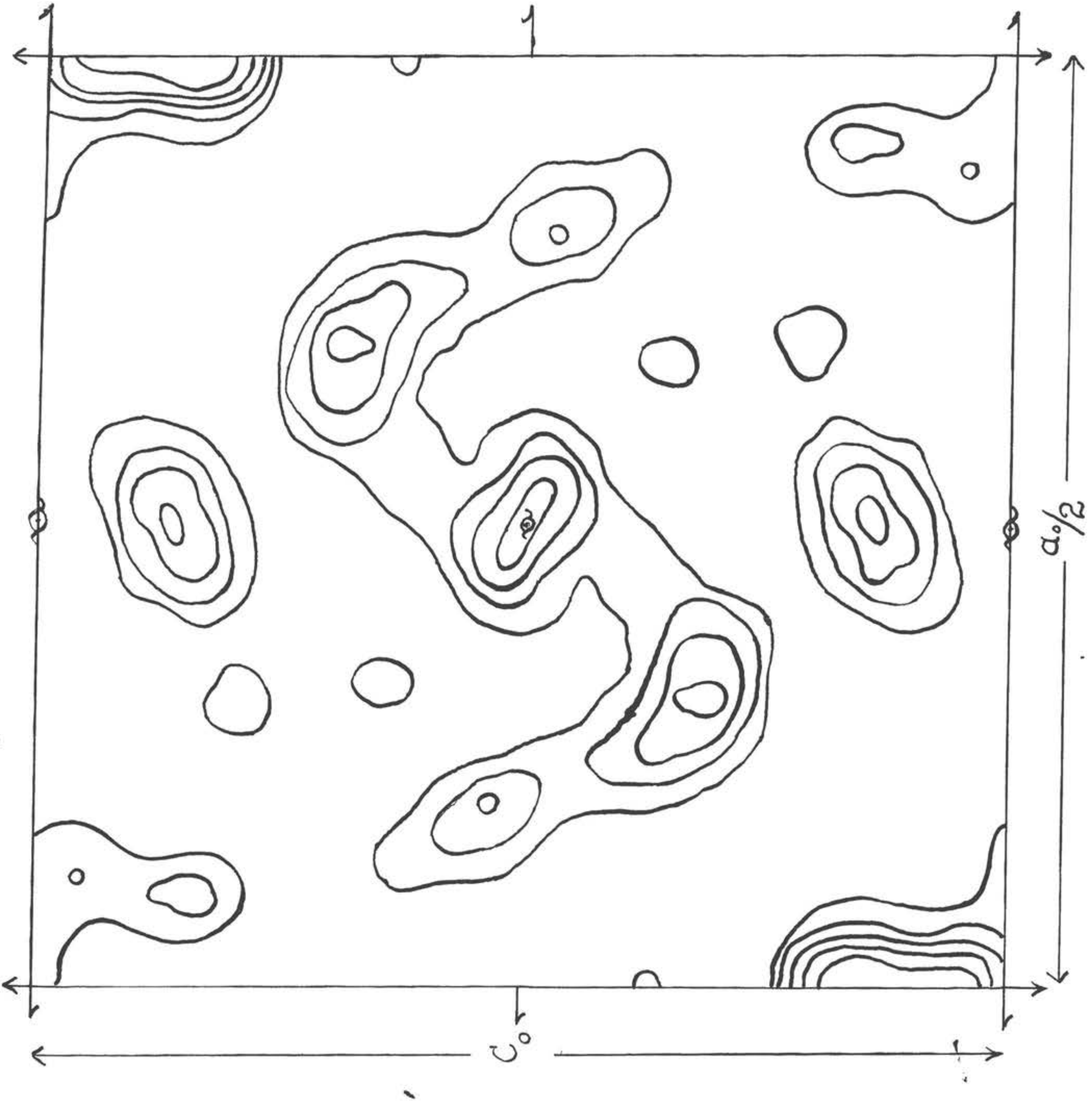

1
a₀/2
c₀

Figure 6.

Fourier projection of Rochelle Salt on (010). Projection of half cell shown. The black atoms are those lying in the far quarter of the unit cell, and correspond to the black atoms in figure 5. The green atoms are those in the near quarter.
Contours are drawn at 10, 50, 90, 130, 170; average background, about -40 and quite good.

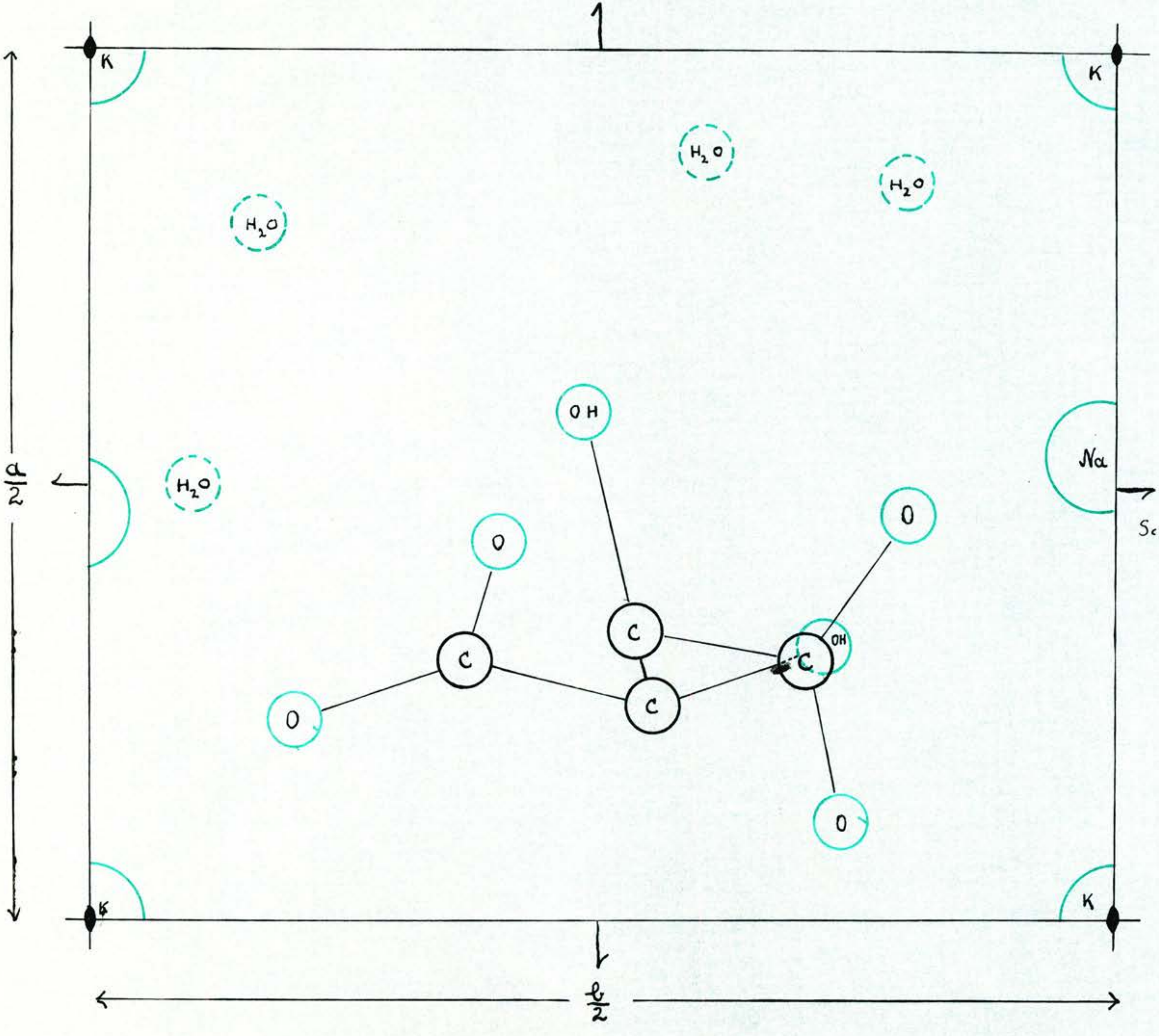


Figure 7.

Scale 1" ≡ 1 Å.

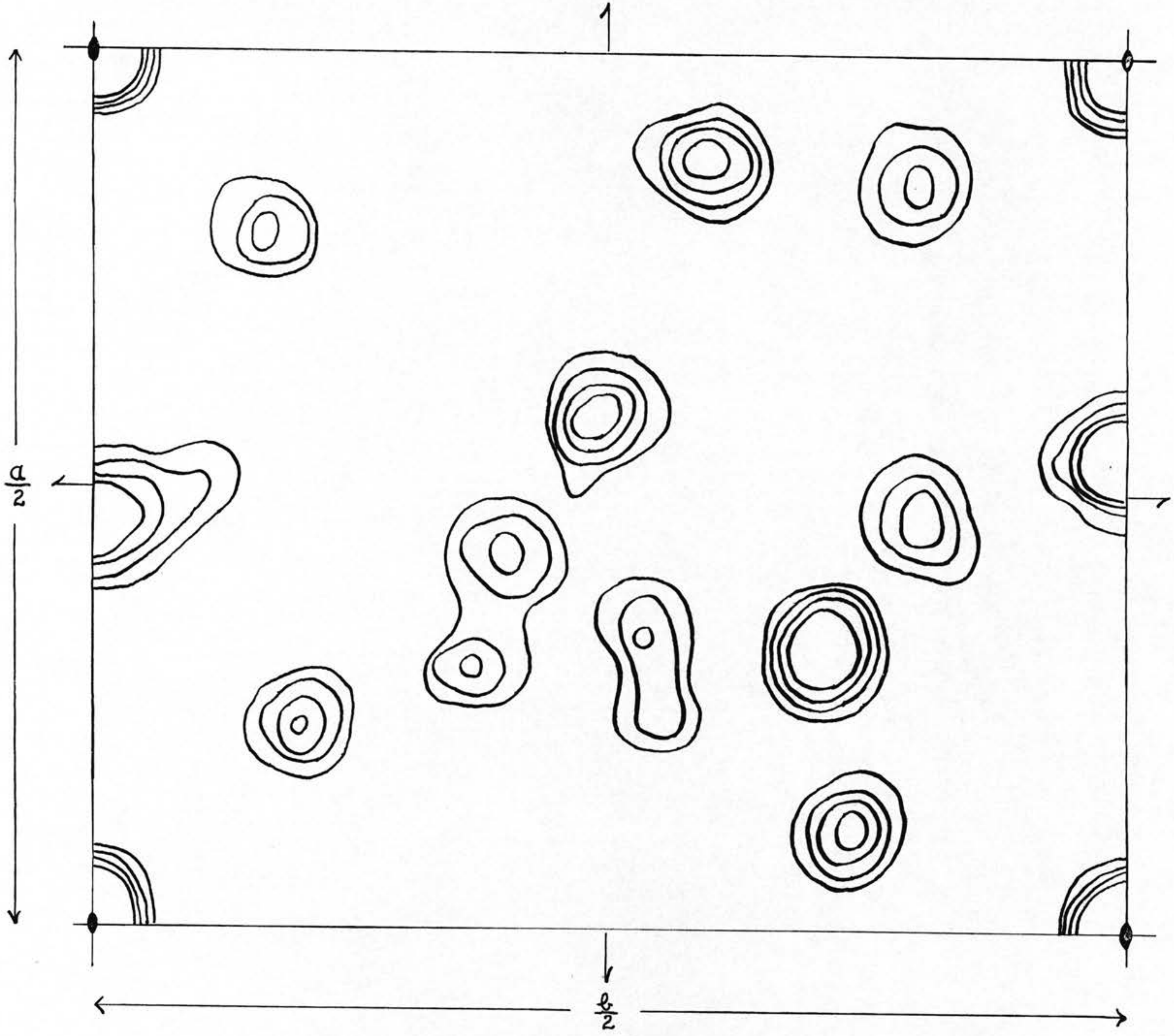

$\frac{a}{2}$
$\frac{b}{2}$

Figure 7.

Fourier projection of Rochelle Salt on (001). Projection of quarter cell shown, corresponding to the black atoms in the two previous diagrams.

Contours are drawn at 50, 100, 150, and 200.

Background rather variable, averag~~e~~ing about -40.

Figure 8.

Scale 2" ≡ 1Å

Figure 8.

Superimposition of a-axis Fourier projection and Rochelle Salt and section of three-dimensional Patterson synthesis of the Ammonium salt, at $x = \frac{1}{2}a_0$. Both have been drawn as though the salts possessed the same unit cell dimensions. The co-ordinate system of the Patterson section has been altered so that it corresponds directly to the co-ordinate system of the Fourier projection. This has been done by drawing the Fourier projection to double the scale of the Patterson, and plotting the latter so that a point (YZ) in the Patterson becomes (yz), where

$$y = \pm \tfrac{1}{2}(\tfrac{1}{2} - Y)$$

$$z = \pm \tfrac{1}{2}Z, \qquad \text{(see p. 42)}$$

The unique quarter of the Fourier Projection is shown in green along with the unique quarter of the Patterson section in red. The latter has been repeated four times.

It is obvious that the Patterson section indicates atomic sites very close to those indicated by the Fourier projection in spite of the fact that the two series were obtained from independent data. Contours in the Patterson section have been drawn at 0, 40, 80, 120, 160.

The Fourier projection is not identical with the a-axis projection shown before, It is one of the

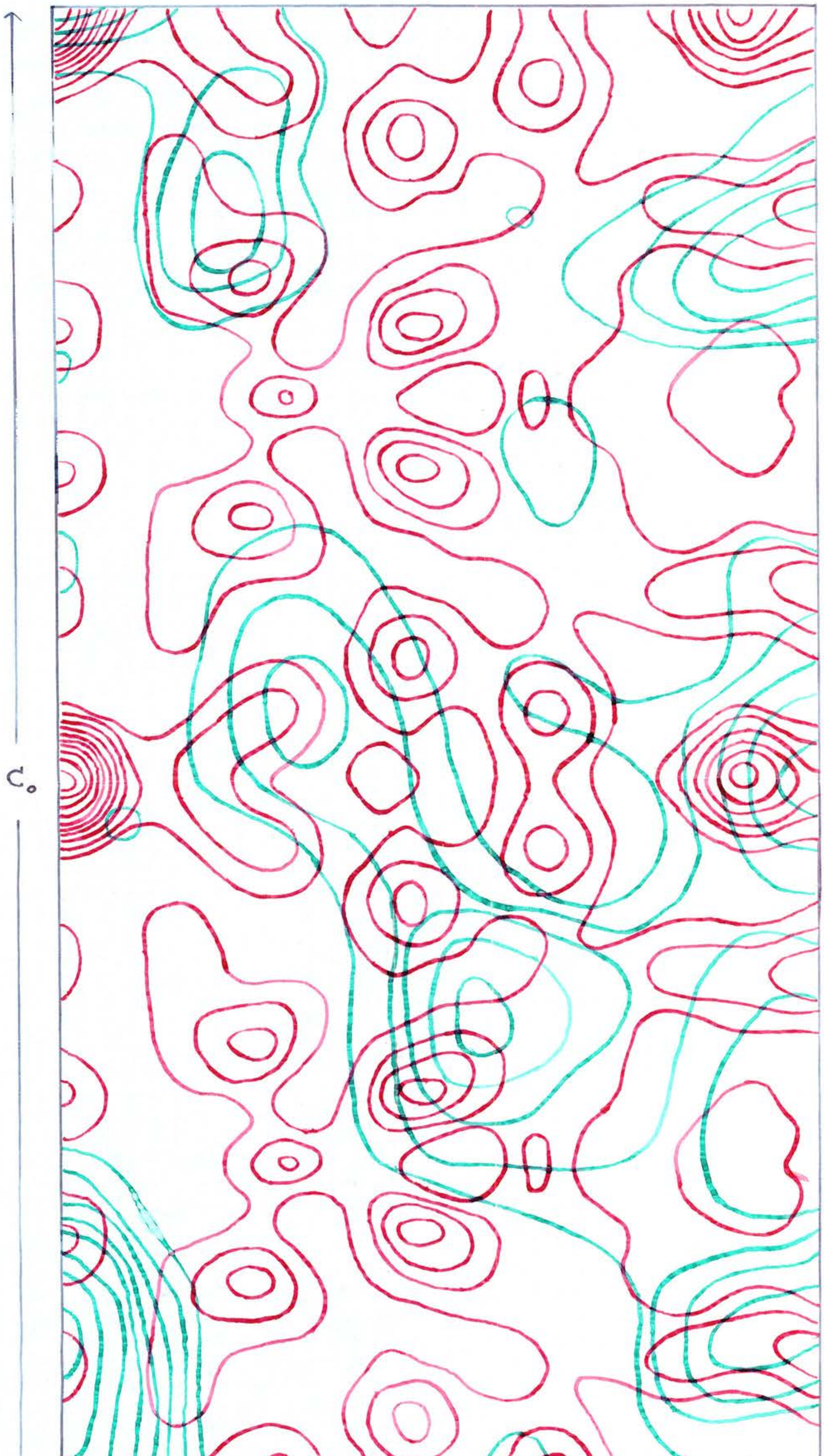


Figure 9.

Scale 2" ≡ 1Å.

earliest obtained syntheses. Its similarity to the final synthesis is a measure of the great power of the method used in its derivation.

Figure 9

Superimposition of b-axis Fourier projection of Rochelle Salt and section of three dimensional Patterson synthesis of the Ammonium salt, at $y = \frac{1}{2}b_0$. This diagram has been treated in the same manner as figure 8. The agreement is again very close. The Fourier projection shown was obtained at an early stage in the work.

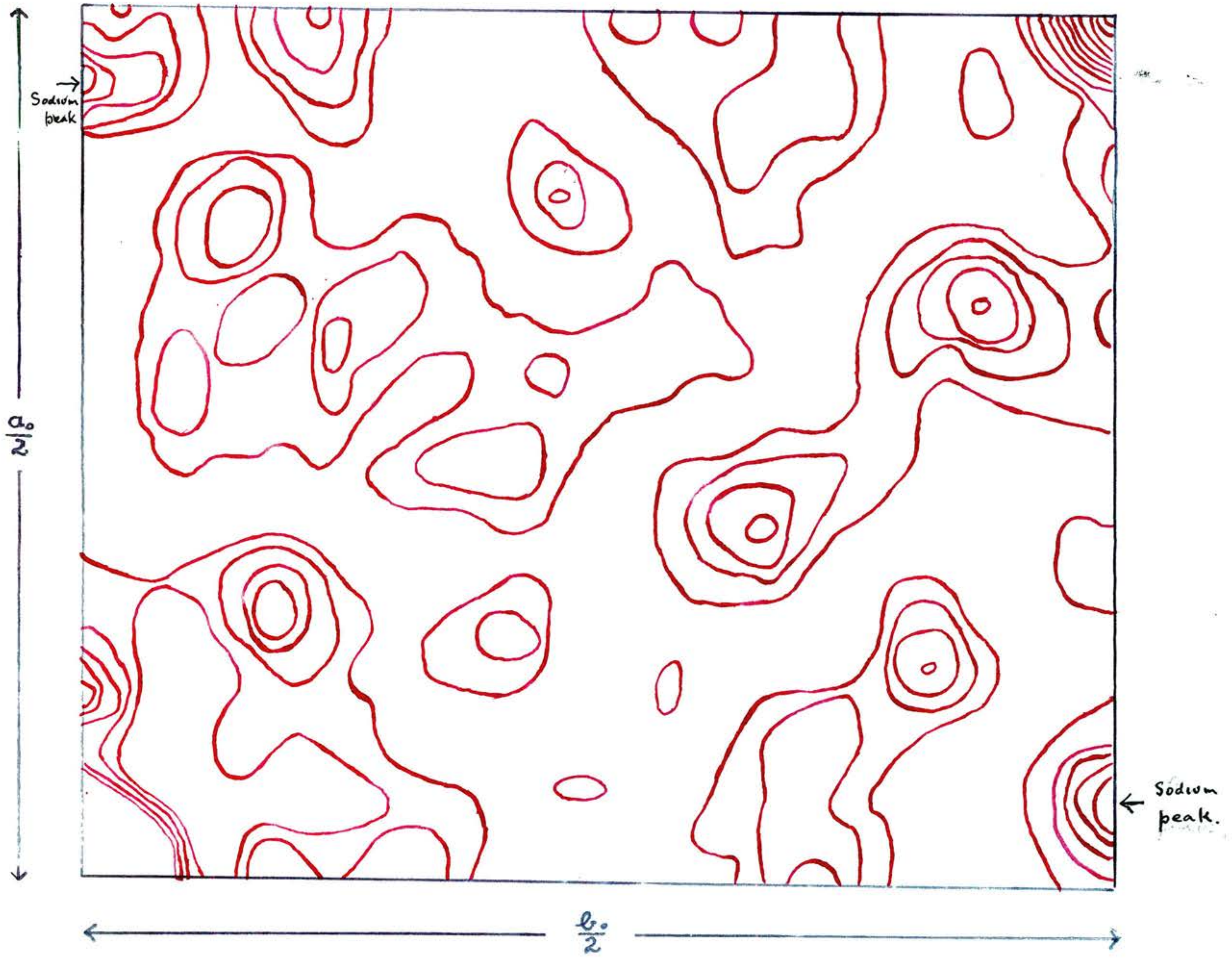


Figure 10.

Figure 10.

Section of three dimensional synthesis at $z = 0$. This section verifies beautifully the sodium position which had been indicated previously by the Fourier projections.

In these Patterson sections the Ammonium-Ammonium vectors do not show up at all well. This may be due to a very rapid fall in the atomic f with increasing sin θ.

DESCRIPTION OF THE STRUCTURE.

The potassium atoms occupy the two sets of twofold positions given in the table on p. 47. The sodium atoms occupy the general positions (23 $\overline{01}$ 52) and (as shown in figure 11) this gives an arrangement of positive ions lying rather closely together in sheets perpendicular to the b-axis. The remaining atomic positions are listed on p. 47, and the projection of the complete unit cell on the (001) plane is shown in figure 11. In this figure the atoms are numbered to correspond to the table of parameters and the z co-ordinates are given alongside the circles representing the atoms. Interatomic distances in Å are also inserted.

The sodium atom has around it a co-ordination group of six; two oxygens and one hydroxyl from the tartrate groups, and three water molecules. The sodium-oxygen distances average 2.39 Å, which is sufficiently close to the accepted values. (Sum of Na and O radii from Internationale Tabellen II p. 611, is 2.32 Å.) The potassium atom on (00 00 05) has a co-ordination group of four. This consists of two oxygens from tartrate groups and two water molecules. The other potassium atom touches two oxygens and two

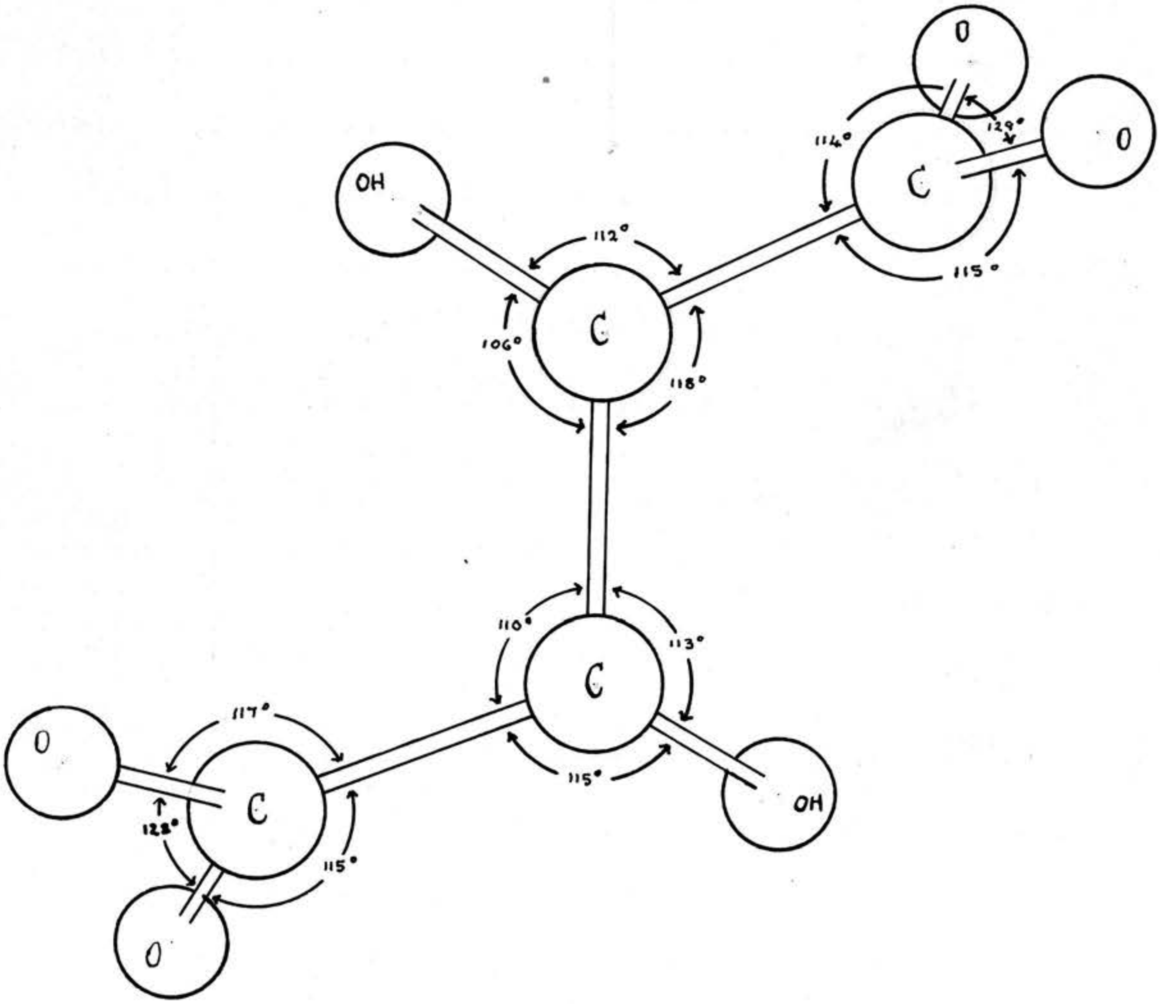


Figure 12.

Perspective drawing of tartrate molecule. Carbon atoms lie in plane of paper. The C(OH)-COO groups are practically plane and inclined at 60° to the carbon plane.

hydroxyls from tartrate groups, and four water molecules, thus having a co-ordination of eight. The interatomic distances are given in figure 11.

The tartrate molecule has its chain of carbon atoms almost exactly in a plane. Figure 12 is a perspective drawing of the molecule, the carbon atoms being in the plane of the paper. The C(OH)-COO groups constituting each half of the molecule are also practically plane groups inclined at approximately 60° to the plane of the carbon atoms. The C-C distances found are 1.58, 1.53, 1.52 Å, while the C-O distances are 1.36, 1.32, 1.22, and 1.15 Å. The C-OH distances seem to be rather longer viz. 1.40 and 1.51 Å. All the final atomic positions were chosen from the Fourier maps without manipulation with a view to obtaining good interatomic distances. These values may therefore be taken as independent determinations. They are not regarded as being very accurate, but the mean C-C and C-O separations are good supporting evidence for the usually accepted values. The measurements are summarised in the following table.

Mean C-C separation	1.54 Å
" C-O "	1.26 Å
" C-OH "	1.46 Å

Water molecule 7 (figure 11) is 2.75 Å from a potassium atom, 2.39 Å from a sodium atom, 2.73 Å from a hydroxyl group, and 2.96 Å from an oxygen atom, and apart from neighbouring atoms in the same co-ordination group it makes no other close approaches. The four bonds described have an approximately tetrahedral distribution, in agreement with the Bernal-Fowler model outlined in the introduction.

Water molecule 8 can also be given four bonds although these are not so regular as in the previous case. These bonds are; to a potassium atom, 3.07 Å, to a sodium atom, 2.34 Å, to an oxygen atom, 2.67 Å, and to a hydroxyl group, 3.14 Å. If the latter bond be disregarded the water molecule may be regarded as being of the planar type also mentioned in the introduction. This water molecule is not resolved from other atoms in any of the three Fourier projections so it is probably the least accurately located atom in the structure.

Both the water molecules 9 and 10 may be fitted into the tetrahedral theory, but the nature of the bonds involved raises an interesting point which will be considered later, concerning the anomalous dielectric properties of Rochelle Salt. Molecule 9 has a distance of 3.01 Å to a potassium atom and distances of 2.83 and 3.07 Å to oxygen atoms 4 and 2 respectively. It is distant 2.86 Å from water molecule 10 and 3.20 Å from the hydroxyl group 6 (in the unit cell c_0 removed) This final distance was neglected in order to fit the molecule into the tetrahedral theory.

Water molecule 10 has, in addition to the bond to 9, bonds to the sodium atom (2.31 Å), to the oxygen atom 1 (2.56 Å), and to the hydroxyl group 6 (2.99 Å).

DISCUSSION.

It is conventional to describe bonds as being directed from positive to negative regions of the structure. In figure 11 the arrow heads indicate the direction of the bonds. Each water molecule must have two incoming and two outgoing bonds if it is to conform to the Bernal-Fowler model.

It was shown in the last section that water molecules 9 and 10 may be ascribed a tetrahedral disposition of bonds. Molecule 9 touches a potassium atom, molecule 10, and two oxygen atoms of the tartrate molecule. The latter two atoms are regarded as negative regions, belonging as they do to the anion of the salt. The bonds involved are therefore outgoing from molecule 9. The fourth bond from 10 must be incoming.

Molecule 10 has therefore an incoming bond from the sodium atom and an outgoing bond to 9. It touches the hydroxyl group 6 and the oxygen atom 1. One of these must be incoming. If the bond from oxygen atom 1 be regarded as incoming we obtain at once a simple explanation of the anomalous dielectric properties of Rochelle Salt.

Oxygen atom 1 is behaving as a negative atom to the sodium and potassium atoms but as a positive atom to molecule 10. i.e. it is strongly polarised. The positive direction of the bonds is thus 1 to 10, 10 to 9, 9 to 2. However, if the polarization of atom 1 can be transferred to atom 2 within the same molecule the positive direction may now go 2 to 9, 9 to 10, 10 to 1. Such a change requires the water molecules 9 and 10 to interchange a positive and negative bond. i.e. in each case one of the hydrogen nuclei within the molecule shifts to one of the tetrahedral negative areas.
This chain of atoms 1-2-9-10-1-2-9-10- etc. extends along the direction of the a-axis, and is outlined in red in figure 11. It is in the direction of the a-axis that the anomalies are observed.

Normally the crystal is as a whole unpolarised, but if a field is applied in a direction parallel to a, all the molecules in the 1-2-9-10- chains will arrange themselves so that the directions of the bonds will be the same as the direction of the field. Such an effect accounts for the abnormally large values of the dielectric constant, since unit cells in strings parallel to a, mutually assist in their own polarization. It also accounts for the saturation and hysteresis effect, since there must be a limit to such a process, and when complete, there will be a tendency to retain the configuration, again because of mutual assistance.

When the Rochelle Salt crystal is polarised the symmetry is lowered to monoclinic, as Jaffe[9] pointed out. The polarity of the crystal will depend at any instant on its electrical history, and Rochelle Salt might well, as he says "consist(s) of regions having a spontaneous electric moment analogous to the Weiss regions in ferromagnetic metals ...... Regions of opposite polarity are in general not balanced, thus giving rise to a polarity of the crystal as a whole." He concludes that Rochelle Salt is monoclinic between the Curie points but at these temperatures inversion occurs between monoclinic and orthorhombic symmetry. Within the Curie range the symmetry is only pseudo-orthorhombic.

Certainly, the changes described above only involve bond directions and positions of hydrogen nuclei, so that the inversion cannot be detected by x-rays. This was shown by Warren and Krutter and others,[11,10,12] in a study of the effect of temperature on the crystal structure of Rochelle Salt above and below the Curie points. In the present work powder photographs were taken at -30 and +18°C but no difference could be detected.

In a paper summarising much of the theoretical work on Rochelle Salt Mueller[13] (1940) gives an account of measurements on the angle between the b- and c-axes as a function of temperature. Above 25°C he finds that it is constant, but variation occurs between 0° and 25°C. At 0°C the angle between the +b and +c axes had diminished by 3' 45", and by 3' at 10°C.

This certainly lends support to Jaffe's conclusions.

An effect which is commonly found in dielectric phenomena is the falling off of the dielectric constant with increase in the frequency of the applied alternating field. Rochelle Salt exhibits this effect to a marked degree, as was shown by Zeleny and Valasek.[14] This is generally attributed to the inability of molecular or atomic oscillations to keep in step with the higher frequencies. In the particular case of Rochelle Salt it may be due to the inability of the hydrogen nuclei of the water molecules 9 and 10 to oscillate with the higher frequencies.

Evans[15] has shown that when Ammonium is substituted for Potassium in increasing proportions in mixed crystals, the dielectric constant falls to normal values. This may be due to the breaking of certain bonds vital to the existence of the polarising chain in the structure. The bond 2-9 is already 3.07 Å long and this is probably near the limit; it is thus likely that it would not take much in the nature of environmental changes to alter the arrangements of bonds.

The upper Curie point is probably to be accounted for in a similar way, by the expansion of the lattice, involving the breaking of some of the contacts 2-9, 9-10, 10-1. The lower Curie point might correspond to a similar breaking of bonds or to the freezing of atomic or sub-atomic changes.

Further accurate intensity work on the potassium and ammonium salts, and the investigation of the latter by Fourier methods would enable these ideas to be tested rigorously. It is to be hoped that this work will be done at some more favourable time.

Comparison of Calculated and Observed F's.

In the following tables the F's (observed) have been multiplied by a constant factor in order to facilitate comparison. The numerical agreement is not perfect, but the general trend is very similar in observed and calculated F's. This is the most one could expect using a system of rapid visual estimation of intensities, which in effect only arranges the intensities in order of magnitude.

The atomic F's used in the calculations were those quoted by James and Brindley[16]. Sin 2πhx etc. were taken only to one place of decimals.

There is a suggestion of a systematic discrepancy in the (hk0) list. When a negative calculated F in the h, k, both even class is encountered it is usually rather smaller than one would expect. (They occur very seldom because of the high positive potassium contribution.) Examples are :- (2 4), (6 2), (6 10), (10 6). This suggests that in the calculation either the potassium contribution is being overestimated or the oxygen contribution underestimated, since the negative contribution is largely due to the oxygen atoms.

F(hk0)

$$F_{calc.} = \begin{cases} 10\,\Sigma f \cos hx \cos ky & (h+k \text{ even}) \\ \overline{10}\,\Sigma f \sin hx \sin ky & (h+k \text{ odd}) \end{cases}$$

summed over the unique atoms of the unit cell.

h	k	sinθ	F_{calc}	$\lvert F_{obs}\rvert$ ×7
0	2	.107	+? $\overline{72}$	35
1	2	.124	52	77
2	0	.127	$\overline{148}$	133
2	1	.138	$\overline{180}$	119
2	2	.166	119	98
1	3	.172	+? $\overline{10}$	0
3	1	.197	+? $\overline{6}$	0
2	3	.205	$\overline{9}$	49
0	4	.214	115	112
3	2	.217	103	70
1	4	.223	$\overline{59}$	63
2	4	.248	$\overline{27}$	84
3	3	.248	86	70
4	0	.253	147	147
4	1	.258	154	189
4	2	.274	228	224
1	5	.275	+$\overline{49}$	56
3	4	.290	$\overline{128}$	168
2	5	.296	136	154
4	3	.300	50	63
0	6	.321	50	70
5	1	.321	+? $\overline{4}$	0
1	6	.327	$\overline{164}$	154
3	5	.327	$\overline{37}$	98
4	4	.331	297	217
5	2	.334	41	119
2	6	.345	100	105
5	3	.354	+$\overline{79}$	84
4	5	.368	$\overline{19}$	0
3	6	.372	102	112
6	0	.379	$\overline{82}$	35
1	7	.379	$\overline{63}$	84
5	4	.381	28	35
6	1	.383	63	70
6	2	.394	$\overline{15}$	91
2	7	.397	$\overline{9}$	0
4	6	.408	178	203
6	3	.412	$\overline{83}$	91
5	5	.414	+$\overline{116}$	133
3	7	.419	$\overline{32}$	0
0	8	.427	196	266
1	8	.432	11	42
6	4	.435	90	119
2	8	.446	59	56
7	1	.446	$\overline{35}$	112
5	6	.450	$\overline{88}$	49
4	7	.451	39	56
7	2	.455	108	154
6	5	.464	24	56
3	8	.467	21	63
7	3	.471	$\overline{26}$	0
1	9	.485	26	63
5	7	.489	5	56
7	4	.491	30	0
4	8	.496	117	133
6	6	.496	157	168
2	9	.497	$\overline{78}$	105
8	0	.510	142	119
3	9	.510	12	42
7	5	.510	$\overline{110}$	161
8	1	.510	$\overline{83}$	119
8	2	.517	209	245
5	8	.530	$\overline{74}$	84
6	7	.530	$\overline{12}$	35
8	3	.531	? 1	0
0	10	.535	210	196
1	10	.540	35	84
4	9	.540	$\overline{112}$	126
7	6	.540	9	42
8	4	.549	130	126
2	10	.550	100	84
3	10	.560	82	77
5	9	.570	$\overline{32}$	0
6	8	.570	119	77
8	5	.572	8	0
9	1	.572	61	49
9	2	.579	$\overline{16}$	0
7	7	.580	$\overline{30}$	42
1	11	.590	122	98
4	10	.590	70	119
9	3	.592	23	0
8	6	.599	76	91

h	k	sinθ	$F_{calc.}$	×7 $\lvert F_{obs}\rvert$
2	11	.600	$\overline{20}$	0
9	4	.608	$\overline{37}$	0
6	9	.610	20	84
7	8	.610	24	35
3	11	.620	$\overline{112}$	98
5	10	.620	$\overline{37}$	0
8	7	.629	37	0
9	5	.629	20	0
10	0	.630	? $\overline{7}$	0
10	1	.635	$\overline{20}$	49
0	12	.640	96	119
4	11	.640	41	63
10	2	.642	78	49
8	9	.648	$\overline{62}$	70
1	12	.650	$\overline{26}$	77
6	10	.650	$\overline{35}$	70
7	9	.650	$\overline{36}$	63
9	6	.653	$\overline{14}$	0
10	3	.653	$\overline{40}$	0
2	12	.655	60	0
5	11	.660	21	0
8	8	.662	57	91
10	4	.668	121	112
3	12	.670	$\overline{47}$	70
9	7	.681	133	147
1	13	.685	$\overline{78}$	147
10	5	.687	$\overline{12}$	0
4	12	.690	67	91
7	10	.690	4	0
11	1	.698	$\overline{47}$	84
6	11	.700	$\overline{12}$	0
11	2	.704	$\overline{99}$	105
2	13	.705	24	70
10	6	.709	$\overline{16}$	56
5	12	.710	137	147
9	8	.712	$\overline{3}$	0
11	3	.714	$\overline{24}$	77
3	13	.720	71	898
11	4	.728	20	0
7	11	.730	10	0
10	7	.735	9	63
8	10	.735	107	119

h	k	sinθ	$F_{calc.}$	×7 $\lvert F_{obs}\rvert$
4	13	.740	5	0
6	12	.740	66	56
0	14	.745	92	84
9	9	.745	33	0
11	5	.745	$\overline{107}$	77
1	14	.750	33	105
12	0	.760	103	49
2	14	.760	77	63
5	13	.760	20	0
12	1	.761	45	0
10	8	.764	70	63
11	6	.766	62	63
12	2	.769	130	98
3	14	.770	$\overline{66}$	63
8	11	.775	76	70
12	3	.776	56	0
7	12	.780	$\overline{18}$	56
9	10	.781	15	0
12	4	.789	30	0
4	14	.790	63	63
6	13	.790	25	70
11	7	.790	$\overline{1}$	0
10	9	.795	99	91
1	15	.800	$\overline{38}$	0
12	5	.805	?- 33	112
2	15	.810	11	0
5	14	.810	$\overline{10}$	0
8	12	.817	113	105
11	8	.817	51	49
9	11	.818	$\overline{37}$	91
3	15	.820	$\overline{16}$	63
7	13	.820	$\overline{19}$	77
12	6	.824	89	105
13	1	.824	23	0
10	10	.828	102	77
13	2	.829	$\overline{13}$	0
13	3	.838	43	0
6	14	.840	102	91
4	15	.840	41	49
11	9	.946	$\overline{2}$	49
13	4	.849	$\overline{30}$	0
0	16	.855	61	70
1	16	.855	24	70
9	12	.858	$\overline{53}$	0
8	13	.859	-? 15	0

h	k	sinθ	F_{cal}	×7 $\lvert F_{obs}\rvert$
2	16	.860	65	56
5	15	.860	91	56
10	11	.863	$\overline{71}$	49
13	5	.866	87	63
3	16	.870	6	0
7	14	.870	14	0
11	10	.877	$\overline{33}$	0
6	15	.880	$\overline{7}$	0
14	1	.887	$\overline{40}$	0
14	0	.887	117	84
4	16	.890	122	98
14	2	.892	27	0
9	13	.898	26	0
14	3	.900	38	42
10	12	.901	131	91
14	4	.911	64	0
14	5	.926	27	0
6	16	.930	79	70
14	6	.942	104	84
15	1	.950	30	0

F(h0l)

$$F_{calc} = \begin{cases} 10\Sigma f \cos 2\pi hx.\ \cos 2\pi lz & \text{(h even)} \\ 10\Sigma f \cos 2\pi hx.\ \sin 2\pi lz & \text{(h odd)} \end{cases}$$

summed over the unique atoms in the unit cell.

h	l	sinθ	F_{calc}	×7 $\|F_{obs}\|$
0	1	.124	$\overline{66}$	70
2	0	.127	$\overline{148}$	133
1	1	.139	84	70
2	1	.177	176	161
3	1	.225	$\overline{40}$	84
0	2	.249	123	112
4	0	.253	147	147
1	2	.257	$\overline{31}$	28
2	2	.280	89	91
4	1	.280	261	273
3	2	.312	186	196
5	1	.336	89	112
4	2	.354	71	91
0	3	.374	$\overline{159}$	98
6	0	.379	$\overline{72}$	35
1	3	.380	27	35
2	3	.395	53	56
6	1	.396	101	98
5	2	.400	123	112
3	3	.419	9	42
4	3	.450	$\overline{160}$	231
7	1	.451	132	182
6	2	.451	$\overline{139}$	203
5	3	.488	83	112
0	4	.499	$\overline{101}$	112
1	4	.504	67	105
7	2	.505	56	35
8	0	.510	142	119
2	4	.515	26	63
8	1	.517	14	0
6	3	.531	171	154
3	4	.534	$\overline{65}$	119
8	2	.550	21	35
4	4	.559	$\overline{56}$	63
7	3	.577	82	84
9	1	.578	110	119
5	4	.590	51	35
9	2	.619	120	77

h	l	sinθ	F_{calc}	×7 $\|F_{obs}\|$
0	5	.624	$\overline{58}$	35
6	4	.626	$\overline{29}$	56
8	3	.626	$\overline{72}$	112
1	5	.627	$\overline{36}$	63
10	0	.630	7	0
2	5	.637	44	112
10	1	.640	$\overline{27}$	0
3	5	.652	20	77
7	4	.665	$\overline{7}$	0
4	5	.673	$\overline{10}$	0
10	2	.675	4	56
9	3	.678	147	91
5	5	.698	$\overline{8}$	0
11	1	.702	21	56
8	4	.709	$\overline{20}$	56
6	5	.729	28	0
10	3	.731	$\overline{1}$	0
11	2	.735	169	91
0	6	.749	126	112
1	6	.752	12	0
9	4	.755	46	0
12	0	.760	103	49
2	6	.760	$\overline{40}$	0
7	5	.764	65	0
12	1	.765	49	0
3	6	.773	41	70
11	3	.787	53	0
4	6	.790	51	70
12	2	.796	9	0
8	5	.801	$\overline{1}$	0
10	4	.803	$\overline{17}$	91
5	6	.812	$\overline{13}$	0
13	1	.828	49	0
6	6	.839	4	0
9	5	.842	$\overline{47}$	98
12	3	.844	$\overline{37}$	0
11	4	.853	$\overline{26}$	56
13	2	.856	66	77
7	6	.869	$\overline{42}$	35

h	l	$\sin\theta$	F_{calc}	×7 $\lvert F_{obs}\rvert$
0	7	.874	$\overline{11}$	0
1	7	.876	$\overline{17}$	0
2	7	.882	36	70
14	0	.890	117	84
14	1	.890	72	49
3	7	.893	71	63
13	3	.900	$\overline{23}$	49
8	6	.902	18	0
12	4	.906	19	49
4	7	.909	21	0
9	6	.939	63	91
16	1	.953	40	63
13	4	.959	97	49
7	7	.978	108	84

F(0kl)

$$F_{calc} = \begin{cases} 10\ \Sigma\ f \cos 2\pi ky.\ \cos 2\pi lz & (k\ \text{even}) \\ 10\ \Sigma\ f \cos 2\pi ky.\ \sin 2\pi lz & (k\ \text{odd}) \end{cases}$$

summed over the unique atoms of the unit cell.

k	l	$\sin\theta$	F_{calc}	$\times 7$ $\lvert F_{obs} \rvert$
2	0	.106	$\overline{72}$	35
0	1	.124	$\overline{66}$	70
1	1	.135	27	28
2	1	.164	22	63
3	1	.203	$\overline{183}$	203
4	0	.212	115	112
4	1	.246	57	70
0	2	.250	123	112
1	2	.253	16	49
2	2	.271	161	147
5	1	.293	$\overline{86}$	98
3	2	.296	$\overline{165}$	175
6	0	.318	50	70
4	2	.327	165	224
6	1	.342	196	210
5	2	.364	$\overline{28}$	28
0	3	.376	$\overline{159}$	98
1	3	.380	$\overline{45}$	84
2	3	.391	$\overline{218}$	224
7	1	.392	$\overline{37}$	77
6	2	.405	13	0
3	3	.408	9	0
8	0	.426	196	266
4	3	.433	22	0
8	1	.445	$\overline{62}$	119
7	2	.448	51	42
5	3	.460	$\overline{30}$	0
6	3	.494	13	0
8	2	.496	23	28
9	1	.497	20	0
0	4	.501	$\overline{101}$	112
1	4	.505	62	77
2	4	.513	86	105
3	4	.527	150	189
7	3	.529	59	0
10	0	.532	210	196
9	2	.543	$\overline{74}$	42
4	4	.546	$\overline{1}$	0
10	1	.548	20	0
5	4	.568	132	168
8	3	.570	$\overline{64}$	0
10	2	.589	147	126
6	4	.596	67	98
11	1	.600	51	63
9	3	.611	18	0
7	4	.625	19	35
0	5	.628	$\overline{58}$	35
1	5	.630	10	0
2	5	.636	$\overline{63}$	63
11	2	.638	$\overline{44}$	0
12	0	.639	96	119
3	5	.648	117	119
12	1	.652	$\overline{74}$	91
10	3	.653	$\overline{74}$	98
8	4	.659	$\overline{31}$	56
4	5	.663	$\overline{35}$	42
5	5	.681	79	56
12	2	.687	54	63
9	4	.696	79	126
11	3	.697	16	0
6	5	.704	$\overline{61}$	63
13	1	.704	$\overline{49}$	49
7	5	.729	105	56
10	4	.733	32	56
13	2	.736	15	63
12	3	.742	$\overline{25}$	42
14	0	.744	92	84
0	6	.753	126	112
1	6	.754	141	112
14	1	.754	33	0
8	5	.759	36	42
2	6	.760	73	84
3	6	.770	125	91
11	4	.772	98	77

k	l	sinθ	F_{calc}	×7 $\lvert F_{obs}\rvert$
4	6	.782	$\overline{10}$	0
14	2	.785	53	42
13	3	.788	0	0
9	5	.791	$\overline{46}$	49
5	6	.798	$\overline{9}$	0
15	1	.808	$\overline{42}$	0
12	4	.813	60	63
6	6	.818	5	0
10	5	.824	$\overline{18}$	35
14	3	.834	$\overline{51}$	98
15	2	.837	19	70
7	6	.840	94	119
16	0	.851	61	70
13	4	.855	72	0
11	5	.859	22	49
8	6	.866	80	0
0	7	.879	$\overline{11}$	0
1	7	.880	$\overline{15}$	0
15	3	.883	39	42
2	7	.885	7	0

— ? —

Can add

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SUMMARY.

The isomorphous series of hydrates to which Rochelle Salt (Sodium Potassium Tartrate Tetrahydrate) belongs, has been investigated by x-ray methods. The evidence indicates that all the salts investigated have similar crystal structures.

The complete crystal structure of Rochelle Salt has been determined by Fourier and Patterson methods.

The tartrate molecule was found to lie approximately in three planes, the planes of each identical half of the molecule being inclined at 60° to the plane of the carbon atoms. The tartrate molecule is bonded directly and through the water molecules to the positive ions.

In order to make the water molecules conform to the customary tetrahedral model, it is necessary to suppose that one of the carboxyl groups of the tartrate molecule is a dipole. This supposition is used in an explanation of the anomalous dielectric properties of Rochelle Salt.

In conclusion, the author wishes to express appreciation of the advice and encouragement freely given by Dr. C. A. Beevers during the whole course of the work, and to make grateful acknowledgment of a grant from the Carnegie Trust which enabled the work to be carried out.

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