Quantitative Spectrometric Studies of Ammonium and of Potassium Cupric Chloride Dihydrate $(NH_4)_2CuCl_4 \cdot 2H_2O$ and $K_2CuCl_4 \cdot 2H_2O$.

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(With 3 figures.)

Two different determinations have been made of the atomic arrangement in crystals of $(NH_4)_2CuCl_4 \cdot 2\,H_2O$. Both are in qualitative agreement with the available photographic data and it has seemed important to ascertain whether a series of quantitative spectrometric measurements would lead to a satisfactory choice between them.

The essential difference between the two arrangements lies in the position of the chlorine atoms. Both are developed from the holohedral tetragonal space group D_{4h}^{14} and have atoms of their two molecule cells in the following special positions[1]):

Cu: (a) $000;\ \frac{1}{2}\frac{1}{2}\frac{1}{2}$
NH_4 or K: (d) $0\frac{1}{2}\frac{1}{4};\ 0\frac{1}{2}\frac{3}{4};\ \frac{1}{2}0\frac{3}{4};\ \frac{1}{2}0\frac{1}{4}$
O of H_2O: (e) $00w;\ 00\bar{w};\ \frac{1}{2}, \frac{1}{2}, w+\frac{1}{2};\ \frac{1}{2}, \frac{1}{2}, \frac{1}{2}-w.$

In one arrangement[2]), hereafter designated as A, the chlorine atoms are at:

Cl: (f) $uu0;\ \bar{u}\bar{u}0;\ \frac{1}{2}-u, u+\frac{1}{2}, \frac{1}{2};\ u+\frac{1}{2}, \frac{1}{2}-u, \frac{1}{2}$
and (g) $vv\frac{1}{2};\ \bar{v}\bar{v}\frac{1}{2};\ \frac{1}{2}-v, v+\frac{1}{2}, 0;\ v+\frac{1}{2}, \frac{1}{2}-v, 0,$

with $u = 0.217$, $v = 0.221$ and w (for O) $= 0.32$.

In the other[3]) grouping, C, the chlorine atoms are at:

Cl: (j) $uuz;\ uu\bar{z};\ \bar{u}\bar{u}z;\ \bar{u}\bar{u}\bar{z}$
$u+\frac{1}{2}, \frac{1}{2}-u, \frac{1}{2}-z;\ u+\frac{1}{2}, \frac{1}{2}-u, z+\frac{1}{2};\ \frac{1}{2}-u, u+\frac{1}{2}, z+\frac{1}{2};\ \frac{1}{2}-u, u+\frac{1}{2}, \frac{1}{2}-z,$

with $u = 0.275$, $z = 0.255$ and w (for O) $= 0.36$.

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1) R. W. G. Wyckoff, The Analytical Expression of the Results of the Theory of Space Groups, 2nd Ed. (Washington 1930) p. 97.

2) S. B. Hendricks and R. G. Dickinson, J. Am. chem. Soc. **49**, 2149. 1927.

3) L. Chrobak, Bull. Acad. polonaise Sci. Lettres **1929** A, 361.

The quantitative data of this paper indicate that the water oxygen parameter w has been chosen too great in both suggested groupings. In subsequent calculations, including comparisons with these original structures, w will accordingly have values around 0.25.

In the following study spectrometric measurements have been made of the intensities of the simplest powder reflections of the two salts $(NH_4)_2CuCl_4 \cdot 2\,H_2O$ and $K_2CuCl_4 \cdot 2\,H_2O$. These intensities were used to correct series of single crystal reflections for extinction. Fourier series with coefficients based on these intensities have then been evaluated for the possible arrangements and comparisons have finally been made between observed intensities and those predicted by the atomic positions derived from the Fourier summations.

The dimensions of the two molecule units of the two substances have been taken as:

Crystal	a_0	c_0
$(NH_4)_2CuCl_4 \cdot 2\,H_2O$	7.58 Å	7.95 Å
$K_2CuCl_4 \cdot 2\,H_2O$	7.45	7.88

Measurements of $(NH_4)_2CuCl_4 \cdot 2\,H_2O$.

Powder observations. The necessary crystals were obtained by the slow evaporation of a water solution containing ammonium chloride and cupric chloride in stoichiometric proportions. Selected clear specimens were thoroughly ground a few at a time until the dimensions of the largest particles present were less than 0.03 mm. During even the most careful grinding the powder became greener but after a few hours it reverted to a blue-green; this process perhaps corresponds to a temporary loss of some water of crystallization. To provide the sample for powder spectrometric measurements the seasoned powder was formed into a cake using very gentle pressure. The experimental apparatus and procedures for the spectrometric observations have been described[1]). All measurements have been made with the radiation from a copper target tube, operated at 5 M.A. and a constant high potential of 20 K.V., after filtration through nickel foil sufficiently thick to absorb all but a negligible amount of the K-β lines. In order to reduce as much as possible the preferred orientation which resulted from the presence of cleavage fragments in the powder the surface layer of the pressed sample was cautiously removed before use.

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[1]) R. W. G. Wyckoff, The Structure of Crystals, Rev. Ed. (New York 1931) Chap. VIII.

Table I.

Powder Spectrometric Data from $(NH_4)_2CuCl_4 \cdot 2\,H_2O$.

Indices	Observed Intensities	Observed F-values per cell	Calculated F's: $A_{1,2}$	Calculated F's: B	Calculated F's: C
			$w = 0.26$	$w = 0.25$	$w = 0.25$
			$u = 0.217$, $v = 0.221$ or $u = 0.283$, $v = 0.279$	$u = v = 0.218$ or 0.282	$u = 0.218$, $z = 0.248$ or $u = 0.282$, $z = 0.252$
111	0	0	1	0	2
002	210	102.4	95	85	135
120	87	39.0	41	42	42
112	93	43.0	45	45	36
121	99	32.2	38	39	40
022	289	89.8	104	104	77
220	346	142.6	176	174	174
122	68	33.0	36	37	37
013	56	43.8	43	37	36
131	0	0	2	0	1
222	97	66.0	68	67	81
004	[100]	153.0	148	149	149
040	73	97.8	121	119	119
224	91	95.2	115	115	110
			SD: 122	122	164
NaCl					
200	1012	20.2			
220	547	15.62			

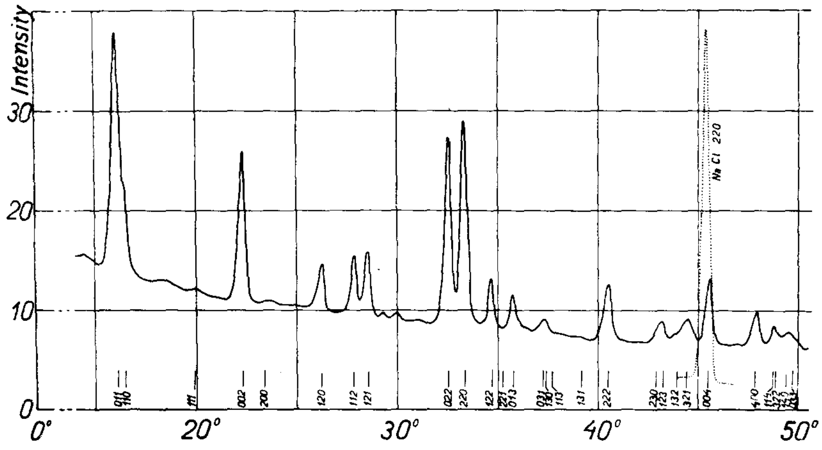

Fig. 1. A plot of the intensities of the observed powder reflections from $(NH_4)_2CuCl_2 \cdot 2\,H_2O$.

After a preliminary survey (Fig. 1), accurate intensity measurements were made of those reflections which were far enough apart to give separate peaks. Their absolute intensities found in the usual manner by comparison with a standard $NaCl$ sample [F (220, $NaCl$) = 15.62] are listed in Table I. For making these calculations the following absorption coefficients for $Cu\,K$ radiation, calculated after the method of Jönsson[1]), have been used: for $NaCl$, $\mu = 160.8$; for $(NH_4)_2CuCl_4 \cdot 2\,H_2O$, $\mu = 133.4$ ($\varrho = 2.007$); for $K_2CuCl_4 \cdot 2\,H_2O$ it is 221.2 ($\varrho = 2.41$).

Single crystal observations. To obtain suitable specimens for single crystal spectrometry, individual crystals several millimeters long were reduced to cylinders[2]) after being accurately mounted on goniometer heads. The orientation of each cylinder set on its thin glass rod in the spectrometer head was checked by making a spectrum photograph. The crystal cylinder having its [001] direction parallel to the axis of rotation was 3.0 mm. long by 0.46 mm. diameter; the one for the [100] zone was 3.5 mm. long and 0.31 mm. diameter.

For each of the measured zones, [001] and [100], the individual integrated intensities have been compared with the intensity of (040) chosen as standard. These intensities, recorded in Tables II and III, are averages of the intensities of all the symmetrically equivalent planes in the zone, e. g.: (022), ($0\bar{2}\bar{2}$), ($0\bar{2}2$), ($02\bar{2}$). It is interesting to note that with the present substances the differences between such single values are sometimes as great as 10% of the average value. Correction for secondary extinction was made by choosing such an extinction coefficient as would give most satisfactory agreement with a set of intensities obtained by multiplying the F^2 derived from the powder data by appropriate values of the geometrical factor $\frac{1 + \cos^2 2\,\theta}{\sin 2\,\theta}$ for single crystals.

The Fourier analysis. F-factors from these intensities provide coefficients for Fourier analyses of the distribution of scattering matter as projected[3]) on the XY and YZ planes. Two separate summations have been made in each direction, one giving the coefficients the signs they would have according to structure A, the other the signs required by C. Experimentally determined F-curves[2]) have been used in establishing these signs and for all other calculations of structure factors. In the case

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1) E. Jönsson, Uppsala Univers. Årsskrift (1928).

2) L. Chrobak, Bull. Acad. polonaise Sci. Lettres **1929** A, 497.

3) W. L. Bragg, Pr. Roy. Soc. (London) **123** A, 537. 1929.

4) R. W. G. Wyckoff, op. cit. p. 101.

Table II.

Intensities and Structure Factors of the [001] Zone Reflections from $(NH_4)_2CuCl_4 \cdot 2\,H_2O$.

Indices	Integrated Intensities		Observed F's	Calculated F's1)	
	Observed	Corrected	per cell	$A_{1,2,a}$	B or C $(u = 0.218)$
110	926	1064	39.7	49	49
020	0	0	0	11	1
120	490	526	35.9	−41	−42
220	3150	5635	135.0	176	174
130	225	232	29.4	30	28
230	178	183	28.5	27	27
400	1711	2250	107.3	121	119
140	530	573	55.3	54	55
330	600	655	60.3	57	58
240	32	32	13.9	9	10
340	221	228	40.2	−39	−41
150	282	294	46.2	51	42
250	18	18	11.9	−14	−14
440	645	709	77.2	76	75
350	6	6	7.3	−2	−4
600	62	63	23.9	17	19
160	360	379	59.0	−54	−55
260	373	394	61.3	59	57
450	89	90	29.5	23	23
360	263	273	52.0	43	44
170	15	15	12.2	10	10
550	428	455	67.4	58	59
460	64	65	25.4	15	17
270	6	6	7.7	4	3
370	288	300	53.3	46	47
			SD:	169	147

of the XY projections of the structure A the following pairs of chlorine positions are possible:

A (a) 1. $u = 0.217$, $v = 0.221$ (b) 1. $u = 0.279$, $v = 0.283$
2. $u = 0.221$, $v = 0.217$ 2. $u = 0.283$, $v = 0.279$

They lead to equal F's for the same plane $(hk0)$ except that for mixed indices the signs for the (a) pairs are opposite those for the (b) pairs.

The calculated projected electron densities, per Å^2, computed with a series of the usual form are recorded in Tables IV and V and plotted in

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1) Though for (b) structures the signs of many terms are different they lead to the same electron distributions.

Table III.

Intensities and Structure Factors of the [100] Zone Reflections from $(NH_4)_2CuCl_4 \cdot 2\,H_2O$.

Indices	Integrated Intensities		Observed	Calculated F's			
	Observed	Corrected	F's	A_{1a}	A_{2a}	B	C
				$w = 0.26$		$w = 0.25$	
						$u = v = 0.218$	$u = 0.218$ $z = 0.248$
011	1225	1479	46.2	46	43	46	47
002	3229	5893	109.8	95	95	95	—135
020	0	0	0	11	11	1	1
022	1836	2471	88.2	—104	—104	—104	77
013	505	544	43.8	43	40	37	36
031	193	198	27.1	32	37	36	35
004	2904	4894	153.0	148	148	149	149
040	1711	2250	107.3	121	121	119	119
033	115	117	25.1	31	36	31	32
024	4	4	4.8	—11	—11	—10	—10
042	428	455	51.9	54	54	52	—52
015	163	167	33.7	24	22	27	28
051	172	176	35.7	28	23	26	27
044	776	871	84.3	90	90	90	91
035	64	65	23.3	18	22	24	22
006	475	509	65.9	68	68	67	—59
053	106	108	30.5	28	24	24	22
060	47	47	20.7	17	17	19	19
026	182	187	41.4	—50	—50	—51	61
062	11	11	10.2	—18	—18	—16	27
017	53	53	23.0	24	23	20	19
055	78	79	28.1	19	15	20	22
046	157	161	40.1	46	46	44	—31
071	32	32	17.9	18	20	19	18
064	30	30	17.3	10	10	12	12
037	25	25	15.7	19	23	18	21
073	24	24	15.1	18	19	17	19
008	547	592	74.8	77	77	78	77
			SD:	165	198	151	195

Figs. 2 and 3. On account of symmetry only one eighth of the cell projections need be given. The XY projection indicates chlorine parameters which are equal: $u = v = 0.218$ or 0.282. This variation of structure A will be designated as B. It is striking that both the A (including B) and C structures give acceptable electron distributions through these summations. Since their calculated structure factors also agree about

Table IV.

Electron Densities Projected upon the *XY*-Plane as Calculated from a Fourier Analysis of the (*hk*0) Reflections of $(NH_4)_2CuCl_4 \cdot 2\,H_2O$ [signs according to parameters *a*].

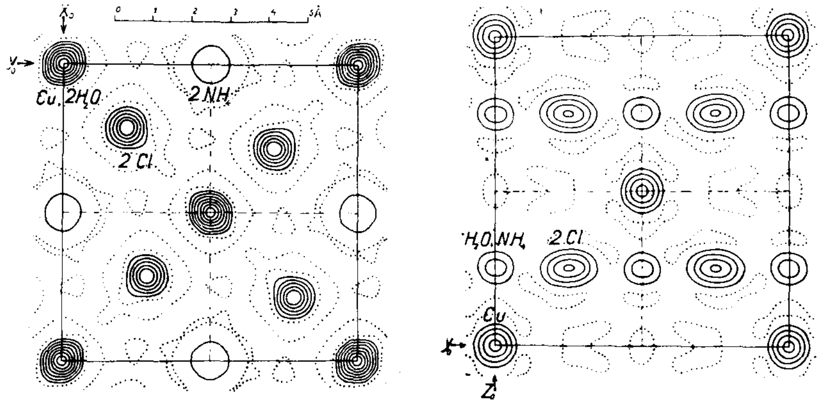
x ↓ \ *y* →	0	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50
0	73.0	34.1	—5.8	1.4	2.2	—0.3	4.5	0.3	3.3	11.5	12.5
0.05		8.5	—2.9	9.0	4.9	2.5	7.6	1.4	0.4	8.6	11.5
0.10			4.0	1.7	—4.9	—4.1	1.5	3.3	0.9	1.5	3.3
0.15				—4.3	11.8	11.3	—2.0	3.9	6.3	—0.6	0.3
0.20					51.4	38.5	—1.9	—2.2	6.1	0.6	4.5
0.25						28.5	0.4	—1.0	4.1	—2.6	—0.3
0.30							0.6	1.4	4.9	1.5	2.2
0.35								—1.1	2.8	2.4	1.4
0.40									0.3	—1.8	—5.8
0.45										19.6	34.1
0.50											73.0

Table V.

Electron Densities Projected upon the *YZ*- (or *XZ*) Plane as Calculated from a Fourier Analysis of the (0*kl*) Reflections of $(NH_4)_2CuCl_4 \cdot 2\,H_2O$.

y ↓	*z* →	0	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50
0	*A*, *B*	49.8	21.2	—3.2	2.0	10.6	20.2	10.6	1.7	0.8	—0.8	1.3
	C	44.4	21.6	—0.1	—1.0	10.3	25.5	10.2	—1.4	3.8	—0.4	—4.1
0.05	*A*, *B*	26.7	9.1	—1.3	2.7	5.3	13.2	4.6	1.0	2.7	1.2	3.7
	C	24.7	9.3	—0.1	1.6	5.1	15.1	4.4	—0.2	3.9	1.8	1.7
0.10	*A*, *B*	1.0	—2.7	2.6	2.7	—2.0	4.4	0.9	0.9	3.1	0.5	2.9
	C	3.5	—2.5	1.6	3.7	—2.2	2.0	0.1	2.0	2.1	0.7	5.3
0.15	*A*, *B*	11.4	6.0	2.6	1.3	—1.2	3.4	—0.1	2.2	0.9	0.3	7.5
	C	5.4	3.2	2.7	1.2	1.6	9.4	2.8	2.1	1.0	—2.5	1.3
0.20	*A*, *B*	32.9	13.6	—1.6	1.5	1.6	1.4	—0.9	2.6	0.0	10.5	27.7
	C	4.0	1.9	1.4	—1.2	13.3	30.3	10.8	—0.1	2.8	—1.2	—1.2
0.25	*A*, *B*	41.0	17.2	—1.6	2.2	—0.1	—1.4	—0.1	2.2	—1.6	17.2	41.0
	C	—1.4	—0.1	2.2	—1.6	17.2	41.0	17.2	—1.6	2.2	—0.1	—1.4

equally well with observations on all the measured planes, it is obvious that the quantitative data of this paper do not lead to a unique selection between structures for $(NH_4)_2CuCl_4 \cdot 2\,H_2O$.



a b

Fig. 2. A map of the electron densities of $(NH_4)_2CuCl_4 \cdot 2H_2O$ projected upon the XY and the YZ-planes if the signs of F are chosen according to structure A_{1a}.

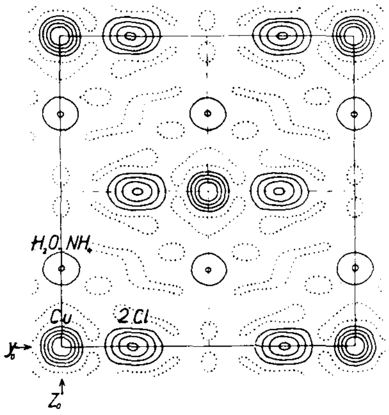


Fig. 3. A map of the electron density of $(NH_4)_2CuCl_4 \cdot 2H_2O$ projected upon the YZ-plane if the signs of F are chosen according to structure C. The XY projection is the same as that of Fig. 2.

Measurements of $K_2CuCl_4 \cdot 2H_2O$.

Powder and single crystal spectrometric data similar to those already described for the ammonium salt were obtained and analyzed for $K_2CuCl_4 \cdot 2\,H_2O$. Fourier summations were made of projections upon

Table VI.

Powder Spectrometric Data from $K_2CuCl_4 \cdot 2\,H_2O$.

Indices	Observed		Calculated F's
	Intensities	F-values	for B
011	293	44.8	44
110	26	19.4	17
111	0	0	0
002	101	73.2	63
200	21	25.0	33
120	51	31.1	39
112	265	75.2	74
121	96	33.0	39
022	464	117.7	133
220	408	160.9	202
122	50	29.3	34
013	67	49.4	41
131	0	0	0
222	33	40.0	39
132	69	44.9	51
321	38	33.8	31
004	157	197.5	178
240	6	23.7	37
332	22	47.5	75
224	145	124.5	144
611	6	24.3	21
NaCl			SD: 200
220	799	15.62	

the XY and upon the YZ planes using the corrected single crystal intensities as the basis for calculating coefficients and employing the signs dictated by calculations of structure factors for arrangements A and C. The observed powder intensities are recorded in Table VI; single crystal reflections before and after correction using the powder data in the manner previously outlined are listed in Tables VII and VIII.

Electron densities resulting from the Fourier summations are collected in Tables IX and X. It is evident that with this potassium salt, as with $(NH_4)_2CuCl_4 \cdot 2\,H_2O$, projections based on both structures A and C give "humps" indicative in density of real atoms. The best possible evaluation of atomic positions from these projections leads to the following coordinates:

From the projection based on structure C:

C_{1a}: $u = 0.220$, $z = 0.248$ (C_{1b}: $u = 0.280$, $z = 0.252$)

(and C_{2a}: $u = 0.220$, $z = 0.252$ C_{2b}: $u = 0.280$, $z = 0.248$).

Table VII.
Intensities and Structure Factors of the [001] Zone Reflections from $K_2CuCl_4 \cdot 2\,H_2O$.

Indices	Integrated Intensities		Observed F's	Calculated F's	
	Observed	Corrected		$A_{1,\,2.\,a}$	B or C
110	256	261	19.8	18	17
200	304	312	26.2	36	33
120	504	525	36.2	—45	39
220	5144	8741	170.0	198	202
130	16	16	7.8	3	1
230	184	187	29.1	28	26
400	3264	4417	152.1	143	150
140	568	595	57.1	58	52
330	168	170	31.1	32	25
240	224	228	37.5	44	37
340	224	228	40.7	—41	39
150	56	56	20.4	14	11
250	32	32	16.1	—13	14
440	1256	1396	109.6	97	104
350	48	48	20.7	—35	28
600	208	212	44.2	52	41
160	392	405	61.5	—57	53
260	872	937	95.2	76	86
450	112	113	33.2	20	23
360	288	295	54.2	43	43
550	224	228	47.6	38	31
170	8	8	8.9	—16	14
460	184	187	42.9	46	38
270	24	24	15.3	1	5
				SD: 198	173

From the projection based on structure A:

B_a: $u = v = 0.220$ (B_b: $u = v = 0.280$)

The structure factors calculated from these arrangements and from the original A structure:

A_{1a}: $u = 0.213$, $v = 0.217$

are compared with observation in Tables VII and VIII.

Examination of electron densities and structure factors makes it evident (1) that structure C gives several serious conflicts with experiment; (2) that the agreement provided by A is fair but definitely inferior to that furnished by the Fourier parameters which constitute structure B. With them the agreement though not perfect is sufficiently good so that

Table VIII.

Intensities and Structure Factors of the [100] Zone Reflections from $K_2CuCl_4 \cdot 2\,H_2O$.

Indices	Integrated Intensities		Observed	Calculated F's		
	Observed	Corrected	F's	A_{1a}	B	$C_{1a,\,1b}$
011	1048	1144	40.9	46	44	44
002	1216	1347	52.7	63	63	−167
020	544	569	35.4	36	33	33
022	2960	3878	111.3	−130	−133	49
013	680	719	50.7	42	41	40
031	416	430	40.3	32	34	34
004	3808	5476	162.8	178	178	178
040	3264	4417	152.1	143	150	150
033	280	286	39.6	31	34	35
024	216	220	35.6	20	18	19
042	344	354	46.3	18	25	−83
015	344	354	49.4	24	23	24
051	384	396	54.3	27	25	26
044	2032	2427	141.9	113	119	119
035	176	179	38.9	18	20	18
006	424	439	61.6	40	40	−85
053	272	278	49.4	27	25	23
060	280	286	51.4	52	41	41
026	808	864	89.4	−75	−77	35
062	280	286	52.5	−35	−46	4
017	168	170	41.2	24	23	22
055	216	220	46.9	19	17	20
046	208	212	46.0	17	22	−57
071	88	89	29.7	18	18	18
064	216	220	46.7	42	32	32
037	88	89	29.4	19	21	23
073	72	72	26.0	18	18	20
008	1784	2081	139.3	101	101	101
			SD:	455	441	669

there can be no reasonable doubt that they approximate the correct atomic arrangement. The discrepancies that remain between structure B and the experimentally observed intensities of reflection are probably the consequence of several factors. Some are undoubtedly due to inaccuracies and especially to the necessary extrapolations in the atomic F-factors used; some are an expression of the impossibility of making completely satisfactory corrections for extinction; and some may arise because the Fourier summations have too few terms to define with precision the true atomic positions. Data which have been accumulated on other crystals in this laboratory suggest that this last consideration is an important one.

Table IX.

Electron Densities Projected upon the XY-Plane as Calculated from a Fourier Analysis of the ($hk0$) Reflections of $K_2CuCl_4 \cdot 2H_2O$ [signs according to parameters a].

y → x ↓	0	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50
0	74.0	38.2	—5.6	0.2	8.4	—1.5	—5.9	—4.4	—2.9	30.5	60.2
0.05		12.4	—3.3	6.0	7.1	2.1	8.4	5.9	—4.3	12.2	30.5
0.10			4.5	1.8	—5.6	—4.4	1.5	3.6	—1.0	—4.2	—2.9
0.15				—2.7	9.7	12.7	—2.8	—2.2	8.4	3.9	—4.4
0.20					48.1	43.7	4.6	—3.1	7.8	1.5	—5.9
0.25						33.8	1.7	—1.9	3.2	—4.0	—1.5
0.30							—5.3	0.3	5.0	3.5	8.4
0.35								2.9	2.8	—0.8	0.2
0.40									—1.2	—2.0	—5.6
0.45										25.6	38.2
0.50											74.0

Table X.

Electron Densities Projected upon the YZ- (or XZ) Plane as Calculated from a Fourier Analysis of the ($0kl$) Reflections of $K_2CuCl_4 \cdot 2\,H_2O$.

y ↓	z →	0	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50
0	A, B	68.5	25.8	—8.3	—0.3	20.5	46.1	21.1	—1.2	1.9	—3.3	—4.7
	C	82.6	35.3	—5.8	—2.7	10.9	31.9	11.6	—3.6	4.3	6.3	9.5
0.05	A, B	33.0	8.1	—2.8	2.1	7.2	25.7	6.6	—1.5	6.6	2.3	2.0
	C	41.2	10.6	—4.4	3.8	4.7	17.5	4.1	0.1	5.0	4.8	10.2
0.10	A, B	—6.4	—9.4	5.7	4.8	—7.6	3.3	—3.7	1.3	7.7	0.4	2.7
	C	—1.3	—10.5	2.0	8.4	—6.5	—1.8	—2.6	5.0	4.0	—0.7	7.8
0.15	A, B	7.9	1.4	3.5	5.5	—1.3	6.3	0.6	6.3	1.3	—5.1	5.3
	C	7.6	4.5	6.6	2.4	—4.4	6.6	—2.4	3.2	4.6	—2.1	5.0
0.20	A, B	37.4	10.4	—3.9	4.8	3.4	3.0	—1.1	7.0	—0.7	7.2	31.7
	C	5.8	2.7	4.4	—3.4	11.0	34.5	6.5	—1.1	7.4	—0.5	0.1
0.25	A, B	49.2	16.2	—3.0	5.4	—2.9	—5.6	—2.9	5.4	—3.0	16.2	49.2
	C	—5.6	—2.9	5.4	—3.0	16.2	49.2	16.2	—3.0	5.4	—2.9	—5.6

When, as in the present instance, we are dealing with several structures which give almost equally good agreement with observed intensities, it has proved instructive to sum the differences between observation and calculation for all the reflections in a zone and to obtain an index which is the ratio of this sum to the sum of all the F-values in the zone. Such summations for the structures which have been considered for $(NH_4)_2CuCl_4 \cdot 2\,H_2O$ and for $K_2CuCl_4 \cdot 2\,H_2O$ are listed in the tables.

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Summary.

Powder and single crystal spectrometric measurements have been made of $(NH_4)_2CuCl_4 \cdot 2\,H_2O$ and of $K_2CuCl_4 \cdot 2\,H_2O$. With these data Fourier analyses have been made of the distribution of scattering matter in projections upon the XY and YZ planes, assuming as approximately correct each of the two previously suggested atomic arrangements for these crystals. No certain distinction can be drawn between these two possibilities for the ammonium salt, either from electron distribution maps or from a comparison between calculated and observed structure factors. In the case of the potassium compound, however, both criteria indicate that the atomic arrangement designated as B, which differs appreciably from the previous structure A only in the positions of the water molecules, is very close to correct.

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