Electron Distribution in (NH4)2C2O4–H2O and the Structure of the Oxalate Group

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for 373.2°K, Eq. (2) predicts $P_K(=P) = 1.32 \times 10^{-5}$ mm, while the equations fitted to their experimental results by Edmondson and Egerton,[9] Mayer [18] and Neumann and Völker[19] give 1.82, 3.01 and 1.89×10^{-5}, respectively.

From Eq. (2), from the heat of fusion of potassium (575 cal.) and from the thermal data of Simon and Zeidler,[15] $\Delta E_0{}^0$ for the reaction $K(s) = K(g)$ is 22,230 cal.; while from Eq. (2), the entropy of gaseous monatomic potassium and the heat capacity data of Simon and Zeidler, $S^0{}_{298.1}$ for crystalline potassium is 14.60 cal./deg.— definitely *less* than the third law value, 15.2 cal./deg. The reason for this discrepancy is not immediately apparent, but it should be noted that the Neumann-Völker vapor pressure equation leads to a value of $S^0{}_{298.1}$ in agreement with the third law value, but is in definite disagreement with Fiock and Rodebush's results even when al-

lowance has been made for the molecule formation.

In the case of lithium, Hartmann and Schneider[20] have measured the vapor pressure in the range 1204°–1353°K (pressures of from 17 to 94 mm); after correcting their observed pressures for p_{Li_2} by means of Table II, the pressure of the lithium atoms can be represented (as a rule to better than one percent by the equation)

$$\log p_{Li} = 11.889 - 38,900/4.575T - 1.174 \log T. \quad (3)$$

The normal boiling points for the three alkalis and the partial pressures of atoms and molecules at the boiling point in the saturated vapors, predicted by Eqs. (1), (2) and (3) and Table II are:

	K	Na	Li
T_B	1030°	1162°	1599°
p_M	716 mm	658 mm	648 mm
p_{M_2}	44 mm	102 mm	112 mm

[18] Mayer, Zeits. f. Physik **67**, 240 (1931).
[19] Neumann and Völker, Zeits. f. physik. Chemie **A161**, 33 (1932).

[20] Hartmann and Schneider, Zeits. f. anorg. Chemie **180**, 275 (1929).

Electron Distribution in (NH4)2C2O4·H2O and the Structure of the Oxalate Group

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The electron distribution of $(NH_4)_2C_2O_4 \cdot H_2O$ projected on (001) was obtained by a Fourier analysis making use of quantitative intensity measurements of x-ray scattering from ($hk0$). This analysis combined with a determination of the atomic parameters perpendicular to (001) gave the complete structure. Separations of covalently linked atoms in the $C_2O_4{}^{--}$ group are C—C, 1.581±0.01A; C—O, 1.25±0.02A; and C—O, 1.23±0.02A with the angle O—C—O =129°±2°. In this compound the O—C—O parts of an oxalate group are in planes at an angle of 28° while in $H_2C_2O_4 \cdot 2H_2O$, α and β $H_2C_2O_4$ the parts are coplanar.

INTRODUCTION

THE crystal structures of a number of oxalates have been determined by the usual methods of analysis of x-ray diffraction data. In $H_2C_2O_4 \cdot 2H_2O$,[1] α $H_2C_2O_4$ and β $H_2C_2O_4$[2] the oxalate group apparently has a center of symmetry and thus the four oxygen atoms of the group must be coplanar but cannot be crystallographically equivalent. Atomic separations as

found for these compounds and for KHC_2O_4, $RbHC_2O_4$, $K_2C_2O_4 \cdot H_2O$, and $Rb_2C_2O_4 \cdot H_2O$ are C—C, 1.57 to 1.60A; C—O, 1.20 to 1.30A; and angle O—C—O, 125°–134°.[3] A more accurate determination of these values and a knowledge of the possible equivalence of the oxygen atoms can be obtained from a Fourier analysis of the electron distribution on a given plane.

[1] W. H. Zachariasen, Zeits. f. Krist. **89**, 442 (1934).
[2] S. B. Hendricks, Zeits. f. Krist. **91**, 48 (1935).

[3] Note *X-rays in Theory and Experiment*, by A. H. Compton and S. K. Allison (New York, 1935), p. 444 *et seq.*, for a logical development of the subject.

W. L. Bragg[4] has shown that the electron density per unit area at any point (x, y) in a projection with a center of symmetry is given by

$$\sigma(x, y) = \frac{1}{AZ} \sum_{-\infty}^{\infty} n \sum_{-\infty}^{\infty} m F_{nm} \cos 2\pi(nx + mz),$$

where n and m are the indices of planes in a zone whose axis is normal to the plane of projection, F_{nm} is the structure amplitude of the scattered wave, A is the area of the plane of projection, and Z is the total number of electrons in the projected volume. To evaluate this series it is necessary to have values of F_{nm} for all planes of a zone and these can be derived from the measured intensities which are proportional to F_{nm}^2.[5] The signs of F_{nm}, however, are only to be found from an approximate analysis of the structure by the usual methods.

It is perhaps apparent that the plane selected for the projection should be one that gives the minimum overlapping of atoms and groups in the projection. Further, in the case of an oxalate group with a center of symmetry, the most desirable plane would be one that is parallel to the plane of the oxygen atoms. These conditions are best fulfilled by a projection of the structure of $(NH_4)_2C_2O_4 \cdot H_2O$ on (001). This compound, as it will develop, is of particular interest in that the oxalate group has a twofold axis rather than a center of symmetry and there is the possibility of formation of hydrogen bonds with the ammonium ion and the water molecule.

EXPERIMENTAL PROCEDURE AND APPROXIMATE ANALYSIS OF THE STRUCTURE PROJECTED

Previous work[6] on ammonium oxalate monohydrate led to the space group $P2_12_1$ with $2[(NH_4)_2C_2O_4 \cdot H_2O]$ in a unit of structure having $a = 8.06A$, $b = 10.34A$, $c = 3.82A$. We have verified the space group assignment and have found $a = 8.04A$, $b = 10.27A$, and $c = 3.82A$; the first two values being determined from high order reflections of the pinacoids and the last from a layer line photograph about the c axis.

Intensities of reflections for $(hk0)$ were measured for Mo $K\alpha$ radiation from a constant source

with an argon-filled ionization chamber; the ionization current being measured by an FP54 vacuum tube direct current amplifier. The sample of $(NH_4)_2C_2O_4 \cdot H_2O$ was a cylindrical one, 0.1 cm in radius (r), with its axis parallel to $(kh0)$ and it was illuminated through a narrow slit. The linear absorption coefficient (μ) measured with monochromatic Mo $K\alpha$ radiation is 1.42, and thus $\mu r = 0.14$. With this arrangement the maximum error that could be introduced into the intensity measurement due to varying absorption in the sample[7] would be less than one percent. These measurements were reduced to absolute values by comparison with the integrated reflection from (400) for Mo $K\alpha$ radiation on an extended face of NaCl, this being taken as 0.98×10^{-4} from the work of James and Firth.[8] The square of the structure amplitude, F_{nm}^2, was found according to the following expressions for a mosaic crystal:

$\rho_{nm} = \text{integrated reflection} = 2Qre^{-2\mu r}$

$$Q = \left(\frac{Ne^2}{mc^2} F_{nm}\right)^2 \lambda^3 \frac{1 + \cos^2 2\theta}{2 \sin 2\theta} = 2.19 \times 10^{-8} \theta F_{nm}^2,$$

where

$$\theta = \frac{1 + \cos^2 2\theta}{\sin 2\theta},$$

N is the number of scattering units per unit volume, and the other terms have their usual significance. μ was taken in the first analysis as the linear absorption coefficient since it was thought that a correction for extinction could best be based on a knowledge of the structure and the atomic scattering factors. In the end it appeared, however, that extinction must be quite small.

The general positions of the space group $P2_12_1$ are

$$xyz; \quad 1/2 + x, \quad 1/2 - y, \quad \bar{z},$$
$$\bar{x}\bar{y}z; \quad 1/2 - x, \quad 1/2 + y, \quad \bar{z},$$

which lead to special positions on the twofold axes, $00Z$, $1/2\ 1/2\ \bar{Z}$; and $1/2\ 0\ Z$; $0\ 1/2\ \bar{Z}$. Because of interatomic distance requirements the oxalate groups must be at one of these sets and the H_2O molecules at the other, say $1/2\ 0\ Z$; $0\ 1/2\ \bar{Z}$. The NH_4, C, O_1 and O_2 atoms are in sets of general positions, thus giving thirteen parameters defining the structure.

[4] W. L. Bragg, Proc. Roy. Soc. A123, 537 (1929).
[5] W. L. Bragg, Zeits. f. Krist. 69, 118 (1928).
[6] J. F. Wood, Proc. Univ. of Durham Phil. Soc. 7, 111 (1928).
[7] F. C. Blake, Rev. Mod. Phys. 5, 169 (1933).
[8] James and Firth, Proc. Roy. Soc. A117, 62 (1927).

TABLE I. *Observed and calculated values of the structure amplitudes (F) for (hk0) of $(NH_4)_2C_2O_4 \cdot H_2O \cdot Mo\ K\alpha$.*

$h\backslash k$	0	1	2	3	4	5	6	7	8	9	10
0 obs			25.2		27.0		11.2		11.8		11.8
calc			18.5		30.6		8.0		6.7		$\overline{10.0}$
1 obs		23.5	15.5	13.4	28.9	21.6	17.4	11.5	0.0	13.1	12.2
calc		18.4	$\overline{10.0}$	$\overline{10.1}$	33.2	$\overline{13.8}$	11.9	7.9	$\overline{0.4}$	$\overline{11.7}$	$\overline{7.5}$
2 obs	3.2	12.6	0.0	29.9	19.4	36.1	21.9	6.4	18.4	14.8	9.9
calc	6.0	10.1	$\overline{3.1}$	$\overline{25.5}$	12.0	44.6	13.3	$\overline{6.7}$	13.2	$\overline{7.2}$	7.2
3 obs		32.5	29.7	15.2	6.7	0.0	13.3	12.2	9.4	6.6	10.6
calc		$\overline{38.6}$	$\overline{33.8}$	$\overline{9.9}$	$\overline{3.6}$	1.4	$\overline{10.3}$	$\overline{9.1}$	$\overline{6.9}$	7.0	$\overline{6.0}$
4 obs	29.4	8.3	25.2	25.1	10.9	14.5	0.0	12.3	10.6	(3.3)	(9.4)
calc	$\overline{21.6}$	$\overline{2.6}$	25.8	$\overline{23.9}$	8.1	$\overline{9.5}$	0.5	$\overline{9.3}$	$\overline{6.5}$	$\overline{2.0}$	5.7
5 obs		10.2	8.0	0.0	(3.8)	(5.7)	(3.0)	23.5	0.0		
calc		$\overline{5.8}$	9.1	1.1	$\overline{3.8}$	3.3	$\overline{2.0}$	$\overline{19.8}$	$\overline{1.4}$		
6 obs	7.7	8.2	6.8	22.0	0.0	(2.8)	0.0	8.6	0.0	(7.3)	
calc	$\overline{4.5}$	4.8	5.3	19.0	0.4	$\overline{3.7}$	2.6	7.7	0.2	3.5	
7 obs		13.8	15.5	16.6	$\overline{0.0}$	(6.6)	(7.8)	(7.2)	(3.8)		
calc		$\overline{9.8}$	10.0	$\overline{12.0}$	$\overline{1.5}$	$\overline{4.2}$	2.6	3.4	2.5		
8 obs	8.2	0.0	(7.5)						7.8		
calc	7.8	$\overline{1.6}$	$\overline{2.1}$						5.8		
10 obs	16.5	0.0	(7.1)								
calc	8.2	$\overline{1.0}$	4.4								

Parenthetical values are visually estimated from an equatorial zone (hk0) Weissenberg photograph.   Bars indicate negative values.

In deriving the approximate projection on (001) it was assumed that the oxalate group has a coplanar arrangement of atoms of the configuration previously found. It would then follow that this plane is parallel to (001) and this is supported by the cleavage parallel to that direction and c as the direction of vibration of the slow ray. The high polarizability of the NH_4^+ ion makes impossible further use of the optical data in the structure analysis.[9] To find the projection on (001) it is necessary to find the parameters of the ammonium group and the orientation of the oxalate group, which requires two parameters in both the a and b directions. The approximately normal intensities for reflections from (10.0.0) and (0.10.0) (note Table I) suggest that the majority of the atoms scatter in phase from these planes. This fact, the intensities from other orders of the pinacoids, and the absence of (220) require the following approximate parameters:

X_C, 0.095; X_{O_1}, 0.21; X_{O_2}, 0.11; X_{NH_4}, 0.40; Y_C, 0.03; Y_{O_1}, -0.05; Y_{O_2}, 0.145; Y_{NH_4}, 0.24.

The above parameter values were used in calculating the signs of $F_{(hk0)}$, use being made of assumed scattering curves for the various atoms and groups as follows: NH_4^+ as in NH_4Cl,[10]

O and C as in urea[11] and water below $\sin \theta/\lambda = 0.20$ similar to NH_4^+ and above that value similar to O. A Fourier analysis was made using these signs and the resulting improved parameters were used in a final calculation of the signs and values of $F_{(hk0)}$ listed in Table I, as well as in the final Fourier analysis. It is to be emphasized that the final analysis does not depend upon arbitrary assumptions used in deriving the approximate structure.

The method suggested by Beevers and Lipson[12] was used for summing the double Fourier series and this greatly shortened the labor involved. Projected electron densities were calculated for values of x and y by steps of 0.02 save in the region near atomic centers where the interval was reduced to 0.01. Final values on the open scale are listed in Table II and the resulting contour map is shown as Fig. 1. The final parameters were taken as the average values for the centers of the contour areas and they are listed in Table III. The variation in these as determined from various contours did not exceed 0.001. An arbitrary splitting of the projection into areas per atom led to the results shown in Table III. The projected number of electrons exceeds that required by a neutral water molecule and is less than that required

[9] S. B. Hendricks, Zeits. f. Krist. (A) **91**, 290 (1935).
[10] Wyckoff and Armstrong, Zeits. f. Krist. **72**, 324 (1929–30).
[11] Wyckoff, Zeits. f. Krist. **81**, 108 (1932). The carbon data are combined with Bernal's results from graphite.
[12] Beevers and Lipson, Phil. Mag. **17**, 855 (1934).

TABLE II. *Calculated values of the projected electron density (σ) on (001) for $(NH_4)_2C_2O_4 \cdot H_2O$.*

x\y	0.00	0.02	0.04	0.06	0.08	0.10	0.12	0.14	0.16	0.18	0.20	0.22	0.24
0.00	2.00	1.69	1.11	0.92	1.27	1.70	1.69	1.38	1.20	1.33	1.49	1.41	1.29
0.02	2.11	2.00	1.36	0.94	1.06	1.44	1.61	1.33	0.96	0.97	1.18	1.16	1.00
0.04	2.60	2.85	2.27	1.43	1.06	1.32	1.70	1.79	1.48	1.14	0.86	0.91	0.73
0.06	3.51	4.37	3.89	2.52	1.59	1.79	2.79	3.35	2.86	2.07	1.13	0.79	0.67
0.08	4.39	5.79	5.38	3.53	2.51	2.79	4.59	5.73	4.96	2.96	1.30	0.75	0.84
0.10	4.56	6.07	5.62	3.64	2.42	3.63	6.27	7.86	6.70	3.80	1.38	0.73	1.17
0.12	3.46	4.80	4.38	2.65	1.89	3.63	6.79	8.60	7.20	3.82	1.13	0.51	1.28
0.14	2.22	2.84	2.55	1.45	1.20	3.04	6.03	7.63	6.30	3.11	0.52	0.07	0.98
0.16	1.66	1.38	1.27	0.90	1.03	2.52	4.48	5.49	4.46	2.11	0.15	0.00	0.61
0.18	1.97	0.93	0.96	1.05	1.40	2.06	2.87	3.24	2.62	1.27	0.22	0.00	0.43
0.20	2.34	0.99	1.03	1.58	1.92	1.76	1.70	1.59	1.30	0.86	0.60	0.59	0.71
0.22	2.05	0.86	1.00	1.56	1.80	1.48	1.10	0.88	0.86	0.96	1.07	1.17	1.11
0.24	1.36	0.61	0.79	1.30	1.47	1.30	1.10	1.06	1.13	1.24	1.43	1.49	1.39
0.26	0.84	0.68	0.93	1.22	1.36	1.41	1.53	1.71	1.69	1.55	1.45	1.40	1.33
0.28	0.86	1.06	1.40	1.54	1.58	1.64	1.96	2.19	2.13	1.75	1.44	1.28	1.23
0.30	1.01	1.35	1.75	1.78	1.62	1.71	1.95	2.16	2.11	1.74	1.60	1.62	1.52
0.32	1.02	1.29	1.59	1.64	1.47	1.47	1.55	1.54	1.47	1.63	2.15	2.67	2.57
0.34	0.94	1.03	1.21	1.12	1.07	1.16	1.19	1.05	1.10	1.74	3.10	4.26	4.28
0.36	1.06	1.08	1.18	1.05	1.06	1.19	1.19	0.93	0.97	2.08	4.22	5.83	5.94
0.38	1.40	1.39	1.32	1.19	1.12	1.42	1.45	1.19	1.32	2.64	4.94	6.81	6.69
0.40	1.74	1.73	1.45	1.07	1.03	1.31	1.50	1.33	1.48	2.73	4.98	6.49	6.27
0.42	2.20	2.12	1.43	0.68	0.51	0.81	1.13	1.13	1.21	2.30	4.07	5.15	4.83
0.44	3.37	3.01	1.64	0.33	0.00	0.25	0.68	0.75	0.80	1.52	2.77	3.57	3.27
0.46	5.49	4.74	2.60	0.57	−0.24	0.09	0.54	0.77	0.43	0.88	1.77	2.31	2.03
0.48	7.76	6.64	3.89	1.29	0.24	0.36	0.68	0.58	0.33	0.67	1.19	1.56	1.57

x\y	0.26	0.28	0.30	0.32	0.34	0.36	0.38	0.40	0.42	0.44	0.46	0.48	0.50
0.00	1.25	1.30	1.11	0.75	0.54	0.64	0.75	0.59	0.64	1.83	4.49	7.45	8.75
0.02	0.97	1.09	1.12	0.94	0.62	0.47	0.48	0.52	0.88	1.79	3.93	6.51	7.76
0.04	0.70	0.84	1.11	1.07	0.72	0.34	0.12	0.26	0.47	1.17	2.55	4.50	5.49
0.06	0.67	0.72	0.93	1.34	0.88	0.53	0.36	0.34	0.51	0.85	1.64	2.67	3.37
0.08	0.97	0.88	0.82	0.96	1.10	1.02	0.86	0.81	0.86	1.31	1.27	1.77	2.20
0.10	1.44	1.05	0.67	0.84	1.27	1.48	1.39	1.17	1.19	1.25	1.37	1.53	1.74
0.12	1.65	1.28	0.59	0.58	1.26	1.56	1.40	1.09	1.07	1.27	1.28	1.36	1.40
0.14	1.48	1.13	0.63	0.71	1.21	1.37	1.01	0.71	0.83	1.21	1.33	1.16	1.06
0.16	1.02	0.94	0.76	0.89	1.23	1.20	0.71	0.51	0.81	1.26	1.27	1.10	0.94
0.18	0.77	0.76	0.82	1.20	1.36	1.13	0.69	0.60	1.00	1.42	1.40	1.13	1.02
0.20	0.62	0.71	0.93	1.24	1.36	1.10	0.78	0.87	1.23	1.50	1.38	1.05	1.01
0.22	0.97	0.83	0.88	1.06	1.02	1.03	0.90	0.96	1.53	1.77	1.53	1.02	0.86
0.24	1.24	0.96	0.86	0.86	0.70	0.54	0.64	1.44	2.30	2.82	2.50	1.64	0.84
0.26	1.22	1.03	0.95	0.85	0.59	0.37	0.79	2.06	3.81	4.95	4.54	2.98	1.36
0.28	1.15	1.11	1.17	1.08	0.71	0.33	0.83	2.86	5.47	7.18	6.73	4.48	2.05
0.30	1.26	1.15	1.29	1.38	0.99	0.49	0.96	3.13	6.23	8.22	7.67	5.10	2.34
0.32	1.93	1.32	1.32	1.45	1.35	0.66	0.90	2.74	5.65	7.25	6.63	4.17	1.97
0.34	3.07	1.75	1.25	1.40	1.35	0.87	1.26	1.44	3.84	4.82	4.23	2.72	1.66
0.36	4.11	2.17	1.23	1.28	1.44	1.15	0.96	1.47	2.33	3.43	2.09	1.80	2.22
0.38	4.71	2.39	1.27	1.36	1.51	1.52	1.18	1.29	1.58	1.40	1.17	1.84	3.46
0.40	4.37	2.36	1.44	1.47	1.60	1.16	1.14	1.29	1.37	1.16	1.13	2.27	4.56
0.42	3.42	2.03	1.58	1.66	1.54	1.07	0.93	1.22	1.39	1.28	1.39	2.45	4.39
0.44	2.41	1.73	1.68	1.79	1.52	0.88	0.79	1.02	1.33	1.31	1.34	2.15	3.51
0.46	1.75	1.57	1.90	2.00	1.33	1.20	1.05	1.35	1.33	1.21	1.22	1.79	2.60
0.48	1.44	1.54	1.83	1.70	1.25	1.38	1.50	1.63	1.38	0.94	1.10	1.64	2.11

for carbon, while the other values correspond to O_1^-, O_2 and NH_4^+. These particular values depend upon choice of area but it is to be noted that the value of σ is greater for O_1 than for O_2 and that this would be more pronounced if the area of O_2 were increased or that of O_1 decreased. The oxygen atoms thus apparently have neither equivalent surroundings nor similar electron distributions.

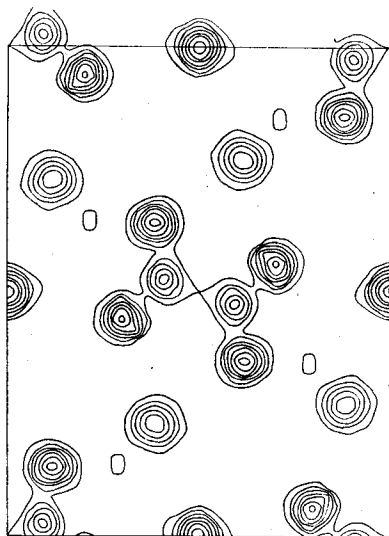Values of $F_{(hk0)}$ calculated using the above

FIG. 1. The approximate electron distribution of $(NH_4)_2C_2O_4 \cdot H_2O$ projected on (001), with a contour interval of 1 electron/A^2, the lowest contour being 2.

TABLE III. *Parameter values and electron counts for* $(NH_4)_2C_2O_4 \cdot H_2O$.

| ATOM | PARAMETERS | | | ELECTRON COUNT | | |
	x	y	z	Area, A^2	Av. σ (001)	No. of Electrons
C	0.092	0.027	0.07	2.25	2.218	5.0
O_1	0.200	−0.056	0.14	5.00	1.870	9.3
O_2	0.118	0.142	0.00	4.58	1.763	8.1
NH_4	0.386	0.228	0.43	5.70	1.763	10.1
H_2O			−0.20	6.32	1.740	11.0

parameters and the indicated atomic scattering curves are listed in Table I. The agreement is not perfect, a major part of the discrepancy undoubtedly being due to the use of the particular scattering curves. All absent reflections, however, are in close agreement and these are particularly sensitive for testing the possible correctness of a structure. Agreement between calculated and observed values of $F_{(hk0)}$ for strong reflections indicates the absence of extinction.

In this projection the separation of the atoms in a $C_2O_4^{--}$ group are C−C, 1.581A; O_1−C, 1.216A; and O_2−C, 1.200A with the angle O−C−O=124°. Since the oxalate group has a twofold axis the projected separation of the carbon atoms is their true separation while the O−C distances and the angle O−C−O are minimum values.

COMPLETE STRUCTURE ANALYSIS AND DISCUSSION

In order to complete the structure analysis it is necessary to determine the parameters along the *c* axis, the normal to the plane of the Fourier analysis. Trial and error methods can safely be used at least in determining the geometry of the oxalate group. *The observed intensities* (004)*a.*, (014)*m.w.*, (034)*m. cannot be explained if the atoms of the C_2O_4 group are coplanar.* Systematic

consideration of the intensities of (00*l*) and (0*kl*) leads to the parameters listed in Table III. Agreement between intensities estimated visually from a Weissenberg photograph and calculated values of $F_{(0kl)}/f_0$ are listed in Table IV; the assumption being made that $f_{NH_4}=f_0=f_{H_2O}=2f_C$, where f_i is the scattering power. These parameter values are probably accurate to 0.01 for the atoms of the $C_2O_4^{--}$ group and 0.03 for NH_4^+ and H_2O. Distances within the oxalate group are thus found to be: C−C=1.581±0.01A; O_1−C=1.25±0.02A; and O_2−C=1.23±0.02A with the angle, O−C−O=129°±2°. Measurements on other oxalates mentioned in the introduction agree with these values within limits of experimental error; this being particularly true for $H_2C_2O_4 \cdot 2H_2O$ as analyzed by Zachariasen who found C−C=1.59±0.07A; O−C=1.25±0.05A and the angle O−C−O =126°±3°. The angle between the O−C−O plane and (001) is 14° and thus the angle between the two O−C−O planes of an oxalate group is 28°, this being diagrammatically shown in Fig. 2.

Arrangements of atoms surrounding NH_4^+ ions and water molecules are diagrammatically shown in Fig. 2. Water molecules are tetra-

TABLE IV. *Estimated intensities of reflection for* (0*kl*), *Cu Kα radiation, of* $(NH_4)_2C_2O_4 \cdot H_2O$ *and calculated values of* F/f_0.

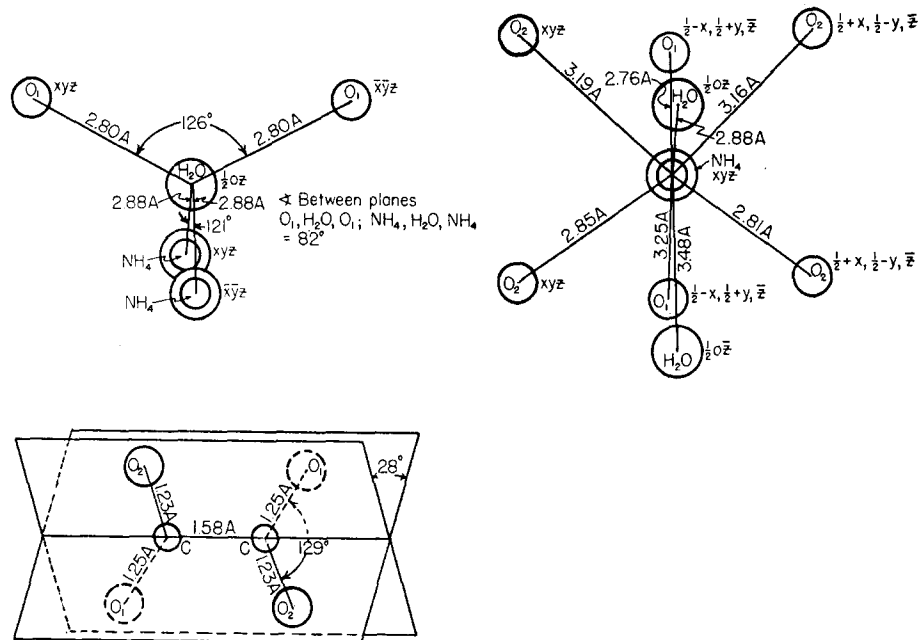| k/l	1	2	3	4
0	1.4, s.	1.3, m. s.	$\overline{0.4}$, a.	0.0, a.
1	0.5, m.	1.0, m.-m.s.	1.3, m.-m.s.	0.7, w.
2	1.8, v.s.	1.0, m.	1.0, m.w.	0.5, v.w.
3	0.0, a.	0.9, m.	0.5, w.	1.7, m.
4	$\overline{1.0}$, m.s.	0.7, w.	1.5, m.-m.s.	1.0, m.w.-w.
5	0.2, a.	0.7, w.	1.1, m.	0.2, a.
6	1.5, m.s.	0.1, v.w.	0.6, a.	
7	$\overline{1.3}$, m.	$\overline{0.3}$, a.		
8	$\overline{0.2}$, a.	0.7, v.w.		
9	$\overline{0.8}$, v.w.	$\overline{1.8}$, m.s.		
10	$\overline{1.1}$, w.	$\overline{1.4}$, m.w.		

FIG. 2. The configuration of the oxalate group and the atomic surroundings of the water molecule and the ammonium ion in $(NH_4)_2C_2O_4 \cdot H_2O$.

hedrally surrounded by two NH_4^+ ions and two oxygen atoms, (O_1), having the higher value of σ. The minimum distances of approach $NH_4 - H_2O$ and $H_2O - O_1$ considerably exceed the value of 2.55A required for hydrogen bond formation, but the tetrahedral arrangement is in agreement with Bernal's and Fowler's[13] model of the water molecule. Ammonium ions too are tetrahedrally surrounded by two sets of oxygen atoms as shown in the figure. Interatomic distances for one set are near 2.80A and for the other near 3.20A.

The observation that the planes of the $O - C - O$ parts of the $C_2O_4^{--}$ group are at an angle of 28° to one another is particularly interesting since the group is a plane one in $H_2C_2O_4 \cdot 2H_2O$ and α and β $H_2C_2O_4$. Indeed it is the first instance yet encountered in crystal structure analysis where a group has different configurations in various salts. However, such a result is neither improbable nor unexpected due to the possibility of rotation about the $C - C$ single bond. The effect is similar to that which leads to the optical activity of diphenyl derivatives[14] as brought about by the steric effects of appropriate groups.

The separation of the carbon atoms in the $C_2O_4^{--}$ group, namely $1.58 \pm 0.01A$, considerably exceeds the value 1.54A found for the carbon to carbon distance in other aliphatic compounds that have been studied. This is possibly a result of repulsion between the negatively charged $(-CO_2^-)$ parts of the group.

Several comments should be made relative to previous work on oxalates. Structure analyses of $K_2C_2O_4 \cdot H_2O$, $Rb_2C_2O_4 \cdot H_2O$, KHC_2O_4 and $RbHC_2O_4$ were based on the assumption that the atoms of the $C_2O_4^{--}$ group were coplanar. Reconsideration of the data from the first two compounds shows that the CO_2 parts of a C_2O_4 group might be displaced by as much as 10° from a coplanar arrangement, the angle being $0° \pm 10°$. This does not seem to be probable for the other two salts but it is perhaps the factor that prevented a successful analysis of the structure of $NaHC_2O_4 \cdot H_2O$. Such a rotation of the CO_2 parts of the $C_2O_4^{--}$ group in ammonium oxalate monohydrate partially accounts for the departure of its optical properties from values predicted on the basis of a coplanar $C_2O_4^{--}$ group.

We are indebted to Lola S. Deming for aid in summing the various Fourier series.

[13] Bernal and Fowler, J. Chem. Phys. 1, 515 (1933).
[14] See for instance R. Adams and H. C. Yuan, Chem. Rev. 12, 261 (1933).