

# PHILOSOPHICAL TRANSACTIONS.

## I. *The Monoclinic Double Sulphates Containing Ammonium.* *Completion of the Double Sulphate Series.*

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IN this communication are described the five remaining double sulphates of the series  $R_2M(SO_4)_2 \cdot 6H_2O$ , in which R is ammonium and M is nickel, cobalt, manganese, copper, and cadmium. The ammonium salts, in which M is magnesium, zinc, and iron, have been described in two previous communications,\*† in the latter of which (that concerning ammonium ferrous sulphate) a number of general questions concerning the whole series were also discussed. The present contribution completes the author's work, commenced in the year 1890, on the double sulphates of this important monoclinic series, in all 31 salts, of which the R bases have been potassium, rubidium, caesium, ammonium, and thallium. Excluding thallium—of which only the zinc double sulphate has been included, the other double salts containing thallium not having yet been obtained in crystals of the perfection necessary for detailed accurate work of the character regarded as essential by the author—the four bases, potassium, rubidium, caesium, and ammonium should give rise, with the eight several dyad bases above enumerated, to 32 double sulphates. All these have been obtained in excellent crystals, and fully described, with the two exceptions of potassium manganese and potassium cadmium sulphates, which, for some as yet undiscovered reason, are incapable of preparation. Yet so thoroughly are the relations between the various salts, and the rules governing the replacement of any one alkali base by any other, now understood, that it has been found possible to predict the constants of the two missing salts. Of the isomorphous double selenates, nine salts (including thallium zinc selenate) containing magnesium and zinc as M metals have already been described by the author, and it is intended that the remaining double selenates, those containing the other dyad metals, shall form the subject of the author's next communication.

\* 'Journ. Chem. Soc., Trans.,' 1905, vol. 87, p. 1123.

† 'Roy. Soc. Proc.,' A, 1913, vol. 88, p. 361.

*Ammonium Nickel Sulphate,  $(\text{NH}_4)_2 \text{Ni} (\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ .**Morphology.*

The first measurements of the crystals of this salt were made 60 years ago by MARIGNAC,\* and the salt was included four years later by MURMANN and ROTTER† in their comprehensive crystallographic investigation. The forms observed in both investigations were the same as those given in the list below, except  $a\{100\}$  and  $o\{111\}$ , and the values observed for the principal angles will be found quoted in the two last columns of the table of angles.

*Crystal System.*—Monoclinic. Class No. 5, holohedral-prismatic.

*Ratios of Axes.*— $a:b:c = 0.7373:1:0.5000$ . Values of MURMANN and ROTTER,  $0.7370:1:0.5032$ .

*Axial Angle.*— $\beta = 106^\circ 57'$ . Value of MURMANN and ROTTER,  $107^\circ 4'$ .

*Forms Observed.*— $a\{100\}$ ,  $b\{010\}$ ,  $c\{001\}$ ,  $p\{110\}$ ,  $p'\{120\}$ ,  $q\{011\}$ ,  $r'\{201\}$ ,  $o\{111\}$ ,  $o'\{\bar{1}11\}$ .

*Habit.*—Short prismatic parallel  $p\{110\}$ , or more or less tabular parallel to a pair of faces of this prism (developed more than the other pair), or parallel to  $c\{001\}$ .

Ten excellent small and perfectly transparent crystals of this magnificent bluish emerald-green salt were measured, selected from six different crops. The results are shown in the accompanying table of angles.

The crystals were of the two types illustrated in figs. 1 and 2.

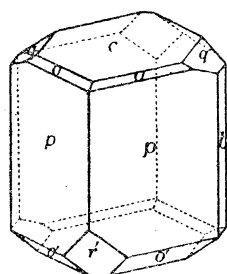


Fig. 1.

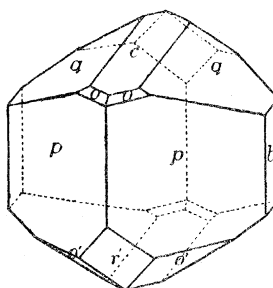


Fig. 2.

The characteristic of the first type is the predominance of the primary prism  $p\{110\}$  and the basal plane  $c\{001\}$ , with smaller faces of the clinopinakoid  $b\{010\}$ , the clinodome  $q\{011\}$ , the form  $r'\{201\}$ , and the two hemipyramids  $o\{111\}$  and  $o'\{\bar{1}11\}$ . The whole of the faces of the two latter forms were never found on any one crystal, and usually only one or two such faces were present. The form  $r'\{201\}$  was also very subsidiary, and on many crystals only one of the two faces was present.

\* 'Mém. Soc. Phys. Genève,' 1885, vol. 14, p. 247.

† 'Sitz. Ber. Akad. Wiss. Wien,' 1859, vol. 34, p. 158.

## INTERFACIAL Angles of Ammonium Nickel Sulphate.

Angle.	No. of measure- ments.	Limits.	Mean observed.	Calcu- lated.	Diff.	Values of	
						M. & R.	MARIGNAC.
$\left\{ \begin{array}{l} ac = (100):(001) \\ as = (100):(101) \\ sc = (101):(001) \end{array} \right.$	1 — —	— — —	73 4 — —	73 3 44 35 28 28	1 — —	72 56 — —	— — —
$\left\{ \begin{array}{l} cr' = (001):(201) \\ cs' = (001):(\bar{1}01) \\ s'r' = (101):(201) \end{array} \right.$	8 — —	64 56- 65 6 — —	65 2 — —	65 5 39 1 26 4	3 — —	— — —	64 0 — —
$\left\{ \begin{array}{l} r'a = (201):(\bar{1}00) \\ r'c = (201):(00\bar{1}) \end{array} \right.$	1 8	— 114 52-115 4	41 47 114 58	41 52 114 55	5 3	— —	— —
$\left\{ \begin{array}{l} ap = (100):(110) \\ pp' = (110):(120) \\ p'b = (120):(010) \end{array} \right.$	— 1 1	— — —	— 19 26 35 18	35 11 19 28 35 21	— 2 3	— — —	— — —
$\left\{ \begin{array}{l} pp''' = (110):(130) \\ p'''b = (130):(010) \\ pb = (110):(010) \\ pp = (110):(\bar{1}\bar{1}0) \end{array} \right.$	— — 28 16	— — 54 39- 54 58 70 8- 70 39	— — 54 49 70 22	29 31 25 18 * 70 22	— — — 0	— — 54 50 70 20	— — — 70 40
$\left\{ \begin{array}{l} cq = (001):(011) \\ qb = (011):(010) \end{array} \right.$	31 35	25 23- 25 45 64 17- 64 40	25 34 64 26	* 64 26	— 0	25 37 64 24	25 10 —
$\left\{ \begin{array}{l} ao = (100):(111) \\ oq = (111):(011) \\ aq = (100):(011) \\ qo' = (011):(\bar{1}\bar{1}1) \\ o'a = (\bar{1}\bar{1}1):(\bar{1}00) \end{array} \right.$	— 1 — 1 —	— — — — —	— 26 56 — 35 13 —	47 46 26 59 74 45 35 8 70 7	— 3 — 5 —	— — — — —	— — — 32 30 —
$\left\{ \begin{array}{l} co = (001):(111) \\ op = (111):(110) \\ cp = (001):(110) \\ po' = (110):(11\bar{1}) \\ o'c = (11\bar{1}):(00\bar{1}) \end{array} \right.$	3 3 38 19 19	33 57- 34 0 42 9- 42 15 76 1- 76 25 58 28- 58 50 44 59- 45 19	33 58 42 12 76 13 58 37 45 9	33 58 42 15 * 58 39 45 8	0 3 — 2 1	— — 76 7 58 29 45 4	— — 77 0 — 44 0
$\left\{ \begin{array}{l} bn = (010):(121) \\ no = (121):(111) \\ bo = (010):(111) \\ os = (111):(101) \end{array} \right.$	— — 2 —	— — 70 38- 70 39 —	— — 70 39 —	54 57 15 43 70 40 19 20	— — 1 —	— — — —	— — — —
$\left\{ \begin{array}{l} bo' = (010):(\bar{1}\bar{1}1) \\ o's' = (\bar{1}\bar{1}1):(\bar{1}01) \\ o'o' = (\bar{1}\bar{1}1):(\bar{1}\bar{1}1) \end{array} \right.$	7 — 3	65 3- 65 10 — -49 44- 49 50	65 7 — 49 47	65 8 24 52 49 44	1 — 3	— — —	— — 50 30
$\left\{ \begin{array}{l} sq = (101):(011) \\ qp = (011):(\bar{1}\bar{1}0) \\ ps = (\bar{1}\bar{1}0):(\bar{1}01) \\ pq = (\bar{1}\bar{1}0):(0\bar{1}\bar{1}) \end{array} \right.$	— 32 — 33	— 87 51- 88 14 — 91 44- 92 9	— 88 6 — 91 55	37 32 88 4 54 24 91 56	— 2 — 1	— — — —	— — — —
$\left\{ \begin{array}{l} s'q = (\bar{1}01):(011) \\ qn = (011):(121) \\ np = (121):(110) \\ qp = (011):(110) \\ ps' = (110):(\bar{1}01) \\ pq = (110):(0\bar{1}\bar{1}) \end{array} \right.$	— — — 35 — 36	— — — 62 14- 62 32 — 117 23-117 44	— — — 62 24 — 117 36	45 30 26 15 36 8 62 23 72 7 117 37	— — — 1 — 1	— — — — — —	— — — — — —
$\left\{ \begin{array}{l} r'o' = (201):(\bar{1}\bar{1}1) \\ o'p = (\bar{1}\bar{1}1):(110) \\ pr' = (110):(20\bar{1}) \end{array} \right.$	11 15 19	35 21- 35 33 91 52- 92 10 52 24- 52 49	35 26 92 3 52 34	35 25 92 5 52 30	1 2 4	35 28 — 52 24	— — 52 30
Total number of measurements .	407						

In type 2, the  $q\{011\}$  faces were larger, and the  $c\{001\}$  faces relatively smaller and often reduced to narrow strips. The  $r'\{201\}$  faces were also somewhat more prominent, and more of the faces of  $o\{111\}$  and  $o'\{\bar{1}11\}$  were developed.

The  $c$  and  $p$  faces in many crops were affected by striation, but those crystals selected for measurement were wonderfully free from this defect, and several of the crystals measured were practically perfect, yielding brilliant single images of the signal throughout, offering no trace of ambiguity as to the position of the faces. The contact face (that parallel to the bottom of the crystallising vessel) was either  $c$  or  $p$ .

The next table affords a comparison of the axial angles and axial ratios of the four salts containing nickel. The axial angle of the ammonium salt is almost identical with that of the caesium salt. The values of the axial ratios of the ammonium salt clearly indicate the existence of isomorphism between this salt and the three salts containing the alkali metals.

COMPARISON of the Axial Angles and Axial Ratios.

	Axial angle.	Axial ratios.
	$\beta$ .	$a : b : c$
Potassium nickel sulphate . .	$105^\circ 0'$	$0.7379 : 1 : 0.5020$
Rubidium " " . .	$106^\circ 3'$	$0.7350 : 1 : 0.5022$
Ammonium " " . .	$106^\circ 57'$	$0.7373 : 1 : 0.5000$
Caesium " " . .	$107^\circ 2'$	$0.7270 : 1 : 0.4984$

The next table affords a comparison of the morphological angles of the four salts.

COMPARISON of the Interfacial Angles.

Angle.	KNi sulphate.	RbNi sulphate.	CsNi sulphate.	AmNi sulphate.
	$^\circ \quad '$	$^\circ \quad '$	$^\circ \quad '$	$^\circ \quad '$
$\left\{ \begin{array}{l} ac = (100):(001) \\ as = (100):(101) \\ sc = (101):(001) \end{array} \right.$	$\left\{ \begin{array}{l} 75 \ 0 \\ 45 \ 48 \\ 29 \ 12 \end{array} \right.$	$\left\{ \begin{array}{l} 73 \ 57 \\ 45 \ 4 \\ 28 \ 53 \end{array} \right.$	$\left\{ \begin{array}{l} 72 \ 58 \\ 44 \ 21 \\ 28 \ 37 \end{array} \right.$	$\left\{ \begin{array}{l} 73 \ 3 \\ 44 \ 35 \\ 28 \ 28 \end{array} \right.$
$\left\{ \begin{array}{l} cr' = (001):(201) \\ cs' = (001):(\bar{1}01) \end{array} \right.$	$\left\{ \begin{array}{l} 63 \ 44 \\ 38 \ 33 \end{array} \right.$	$\left\{ \begin{array}{l} 64 \ 36 \\ 38 \ 57 \end{array} \right.$	$\left\{ \begin{array}{l} 65 \ 28 \\ 39 \ 22 \end{array} \right.$	$\left\{ \begin{array}{l} 65 \ 5 \\ 39 \ 1 \end{array} \right.$
$\left\{ \begin{array}{l} s'r' = (\bar{1}01):(201) \\ r'a = (201):(100) \end{array} \right.$	$\left\{ \begin{array}{l} 25 \ 11 \\ 41 \ 16 \end{array} \right.$	$\left\{ \begin{array}{l} 25 \ 39 \\ 41 \ 27 \end{array} \right.$	$\left\{ \begin{array}{l} 26 \ 6 \\ 41 \ 34 \end{array} \right.$	$\left\{ \begin{array}{l} 26 \ 4 \\ 41 \ 52 \end{array} \right.$
$\left\{ \begin{array}{l} ap = (100):(110) \\ pp' = (110):(120) \\ p'b = (120):(010) \\ pb = (110):(010) \end{array} \right.$	$\left\{ \begin{array}{l} 35 \ 29 \\ 19 \ 28 \\ 35 \ 3 \\ 54 \ 31 \end{array} \right.$	$\left\{ \begin{array}{l} 35 \ 17 \\ 19 \ 28 \\ 35 \ 15 \\ 54 \ 43 \end{array} \right.$	$\left\{ \begin{array}{l} 34 \ 48 \\ 19 \ 28 \\ 35 \ 44 \\ 55 \ 12 \end{array} \right.$	$\left\{ \begin{array}{l} 35 \ 11 \\ 19 \ 28 \\ 35 \ 21 \\ 54 \ 49 \end{array} \right.$
$\left\{ \begin{array}{l} cq = (001):(011) \\ qb = (011):(010) \end{array} \right.$	$\left\{ \begin{array}{l} 25 \ 52 \\ 64 \ 8 \end{array} \right.$	$\left\{ \begin{array}{l} 25 \ 44 \\ 64 \ 16 \end{array} \right.$	$\left\{ \begin{array}{l} 25 \ 28 \\ 64 \ 32 \end{array} \right.$	$\left\{ \begin{array}{l} 25 \ 34 \\ 64 \ 26 \end{array} \right.$



## COMPARISON of the Interfacial Angles (continued).

Angle.	KNi sulphate.	RbNi sulphate.	CsNi sulphate.	AmNi sulphate.
	° /	° /	° /	° /
$\left\{ \begin{array}{l} ao = (100):(111) \\ oq = (111):(011) \\ aq = (100):(011) \\ qo' = (011):(\bar{1}11) \\ o'a = (\bar{1}11):(\bar{1}00) \end{array} \right.$	$\begin{array}{l} 48\ 59 \\ 27\ 33 \\ 76\ 32 \\ 34\ 46 \\ 68\ 42 \end{array}$	$\begin{array}{l} 48\ 16 \\ 27\ 19 \\ 75\ 35 \\ 35\ 5 \\ 69\ 20 \end{array}$	$\begin{array}{l} 47\ 32 \\ 27\ 8 \\ 74\ 40 \\ 35\ 31 \\ 69\ 49 \end{array}$	$\begin{array}{l} 47\ 46 \\ 26\ 59 \\ 74\ 45 \\ 35\ 8 \\ 70\ 7 \end{array}$
$\left\{ \begin{array}{l} co = (001):(111) \\ op = (111):(\bar{1}10) \\ cp = (001):(\bar{1}10) \\ po' = (110):(\bar{1}1\bar{1}) \\ o'c = (\bar{1}1\bar{1}):(00\bar{1}) \end{array} \right.$	$\begin{array}{l} 34\ 46 \\ 43\ 4 \\ 77\ 50 \\ 57\ 26 \\ 44\ 44 \end{array}$	$\begin{array}{l} 34\ 25 \\ 42\ 32 \\ 76\ 57 \\ 57\ 57 \\ 45\ 6 \end{array}$	$\begin{array}{l} 34\ 0 \\ 42\ 5 \\ 76\ 5 \\ 58\ 31 \\ 45\ 24 \end{array}$	$\begin{array}{l} 33\ 58 \\ 42\ 15 \\ 76\ 13 \\ 58\ 39 \\ 45\ 8 \end{array}$
$\left\{ \begin{array}{l} bo = (010):(111) \\ os = (111):(\bar{1}01) \end{array} \right.$	$\begin{array}{l} 70\ 12 \\ 19\ 48 \end{array}$	$\begin{array}{l} 70\ 25 \\ 19\ 35 \end{array}$	$\begin{array}{l} 70\ 48 \\ 19\ 12 \end{array}$	$\begin{array}{l} 70\ 40 \\ 19\ 20 \end{array}$
$\left\{ \begin{array}{l} bo' = (010):(\bar{1}11) \\ o's' = (\bar{1}11):(\bar{1}01) \end{array} \right.$	$\begin{array}{l} 65\ 17 \\ 24\ 43 \end{array}$	$\begin{array}{l} 65\ 11 \\ 24\ 49 \end{array}$	$\begin{array}{l} 65\ 15 \\ 24\ 45 \end{array}$	$\begin{array}{l} 65\ 8 \\ 24\ 52 \end{array}$
$\left\{ \begin{array}{l} sq = (101):(011) \\ qp = (011):(\bar{1}10) \\ ps = (\bar{1}10):(\bar{1}0\bar{1}) \end{array} \right.$	$\begin{array}{l} 38\ 13 \\ 86\ 22 \\ 55\ 25 \end{array}$	$\begin{array}{l} 37\ 56 \\ 87\ 17 \\ 54\ 47 \end{array}$	$\begin{array}{l} 37\ 35 \\ 88\ 23 \\ 54\ 2 \end{array}$	$\begin{array}{l} 37\ 32 \\ 88\ 4 \\ 54\ 24 \end{array}$
$\left\{ \begin{array}{l} s'q = (\bar{1}01):(011) \\ qp = (011):(\bar{1}10) \\ ps' = (110):(\bar{1}0\bar{1}) \end{array} \right.$	$\begin{array}{l} 45\ 17 \\ 63\ 43 \\ 71\ 0 \end{array}$	$\begin{array}{l} 45\ 32 \\ 63\ 0 \\ 71\ 28 \end{array}$	$\begin{array}{l} 45\ 44 \\ 62\ 27 \\ 71\ 49 \end{array}$	$\begin{array}{l} 45\ 30 \\ 62\ 23 \\ 72\ 7 \end{array}$
$\left\{ \begin{array}{l} r'o' = (\bar{2}01):(\bar{1}11) \\ o'p = (\bar{1}11):(\bar{1}10) \\ pr' = (110):(20\bar{1}) \end{array} \right.$	$\begin{array}{l} 34\ 43 \\ 93\ 1 \\ 52\ 16 \end{array}$	$\begin{array}{l} 35\ 6 \\ 92\ 38 \\ 52\ 16 \end{array}$	$\begin{array}{l} 35\ 22 \\ 92\ 32 \\ 52\ 6 \end{array}$	$\begin{array}{l} 35\ 25 \\ 92\ 5 \\ 52\ 30 \end{array}$

The average and maximum changes of angle for the various replacements of one alkali base by another are given in the small table which follows.

## DOUBLE Sulphates containing Nickel.

Replacement.	Average change.	Maximum change.
	/	° /
K by Rb . . . . .	27	63 = 1 3
K by Cs . . . . .	54	122 = 2 2
K by NH <sub>4</sub> . . . . .	49	117 = 1 57

The average and maximum changes of angle when potassium is replaced by ammonium are very nearly the same as occur when potassium is replaced by caesium, and are twice as great as when potassium is replaced by rubidium.

Of the 36 angles compared, 33 show differences on replacing potassium by ammonium in the same direction as when rubidium or caesium are introduced instead of potassium, the only three exceptions being when the differences are very minute. In 32 of the 33 cases the changes are greater than when rubidium is introduced, and in 11 cases they exceed the effect produced by introducing caesium for potassium.

*Cleavage.*—There is a good cleavage parallel to  $r'\{201\}$ , as usual in this series. Also a good cleavage was found parallel to  $b\{010\}$ .

#### Volume.

*Relative Density.*—Five determinations of specific gravity by the immersion method, using methylene iodide and benzene as the immersion liquid, gave the following results:—

I.	Density for $18^{\circ}9/4^{\circ}$	. . .	1.9240	For $20^{\circ}/4^{\circ}$	. . .	1.9238
II.	„ $19^{\circ}4/4^{\circ}$	. . .	1.9238	„ $20^{\circ}/4^{\circ}$	. . .	1.9237
III.	„ $18^{\circ}8/4^{\circ}$	. . .	1.9228	„ $20^{\circ}/4^{\circ}$	. . .	1.9226
IV.	„ $18^{\circ}2/4^{\circ}$	. . .	1.9222	„ $20^{\circ}/4^{\circ}$	. . .	1.9219
V.	„ $19^{\circ}1/4^{\circ}$	. . .	1.9219	„ $20^{\circ}/4^{\circ}$	. . .	1.9217
						Mean . . . 1.9227

The value accepted for  $20^{\circ}/4^{\circ}$  is therefore **1.923**.

PERROT\* obtained the value 1.92 (three individual values 1.920, 1.920, and 1.927).

*Molecular Volume.*— $\frac{M}{d} = \frac{392.12}{1.923} = 203.91$ . PERROT gives 205.

*Molecular Distance Ratios (topic axial ratios).*—

$$\chi : \psi : \omega = 6.1426 : 8.3312 : 4.1656.$$

*Redeterminations of Densities of Potassium, Rubidium, and Caesium Nickel Sulphates.*—These were carried out in order to render all results involving the molecular volumes of the four salts strictly comparable, the same immersion liquid being used under like conditions.

In earlier density determinations made with these salts the pyknometer method was employed.

#### Potassium Nickel Sulphate, $K_2Ni(SO_4)_2 \cdot 6H_2O$ .

I.	Density for $19^{\circ}0/4^{\circ}$	. . .	2.2363	For $20^{\circ}/4^{\circ}$	. . .	2.2361
II.	„ $17^{\circ}7/4^{\circ}$	. . .	2.2378	„ $20^{\circ}/4^{\circ}$	. . .	2.2373
III.	„ $18^{\circ}1/4^{\circ}$	. . .	2.2357	„ $20^{\circ}/4^{\circ}$	. . .	2.2353
IV.	„ $19^{\circ}6/4^{\circ}$	. . .	2.2374	„ $20^{\circ}/4^{\circ}$	. . .	2.2373
						Mean . . . 2.2365

The value accepted for  $20^{\circ}/4^{\circ}$  is **2.237**.

\* 'Arch. des Sciences phys. et nat., Genève,' 1891, 23. 'Dissertation, Genève,' 1890, 47.

*Rubidium Nickel Sulphate*,  $\text{Rb}_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ .

I.	Density for $17^\circ 8/4^\circ$	. . .	2.5857	For $20^\circ/4^\circ$	. . .	2.5851
II.	„ $17^\circ 2/4^\circ$	. . .	2.5854	„ $20^\circ/4^\circ$	. . .	2.5847
III.	„ $17^\circ 5/4^\circ$	. . .	2.5867	„ $20^\circ/4^\circ$	. . .	2.5861
IV.	„ $17^\circ 6/4^\circ$	. . .	2.5886	„ $20^\circ/4^\circ$	. . .	2.5880
						Mean . . . 2.5860

The value accepted for  $20^\circ/4^\circ$  is **2.586**.

*Cesium Nickel Sulphate*,  $\text{Cs}_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ .

I.	Density for $19^\circ 1/4^\circ$	. . .	2.8720	For $20^\circ/4^\circ$	. . .	2.8717
II.	„ $18^\circ 0/4^\circ$	. . .	2.8753	„ $20^\circ/4^\circ$	. . .	2.8747
III.	„ $19^\circ 2/4^\circ$	. . .	2.8706	„ $20^\circ/4^\circ$	. . .	2.8704
IV.	„ $19^\circ 6/4^\circ$	. . .	2.8730	„ $20^\circ/4^\circ$	. . .	2.8729
						Mean . . . 2.8724

The value accepted for  $20^\circ/4^\circ$  is **2.872**.

The former pyknometer values obtained for the three salts were respectively 2.233, 2.583, and 2.865. The higher values now obtained are doubtless very near the truth, the error of the pyknometer method being on the side of lowness, due to inevitable mother-liquor inclusions, whereas the immersion method affords the result for the most cavity-free crystal.

In the next table the volume constants of the four nickel-containing salts are compared. It shows that the molecular volume and topic axial ratios of the ammonium salt are close to those of the rubidium salt; the molecular volume is half a unit higher, the  $\chi$  and  $\psi$  ratios are also slightly higher and the  $\omega$  ratio very slightly lower.

## VOLUME Constants of the Nickel Group.

Salt.	Molecular weight.	Specific gravity.	Molecular volume.	Topic axial ratios.
KNi sulphate . .	433.96	2.237	193.99	$\chi : \psi : \omega$ 6.0170 : 8.1542 : 4.0934
RbNi „ . .	526.06	2.586	203.43	6.1065 : 8.3081 : 4.1723
$\text{NH}_4\text{Ni}$ „ . .	392.12	1.923	203.91	6.1426 : 8.3312 : 4.1656
CsNi „ . .	620.06	2.872	215.90	6.2097 : 8.5416 : 4.2572

*Optics.*

*Orientation of the Optical Ellipsoid.*—The plane of the optic axes is the symmetry plane  $b\{010\}$ . The double refraction is of positive sign, so that the first median line corresponds to the refractive index  $\gamma$  and the second median line to  $\alpha$ .

Extinction determinations with two sections parallel to the symmetry plane afforded the following results:—

*Inclination of 2M.L. from normal to  $c\{001\}$ .*

Plate 1. . . . .	11° 28'	Plate 2. . . . .	12° 2'
Mean . . . . .	11° 45'		

The direction is behind the normal, towards the vertical axis  $c$ .

MURMANN and ROTTER found for this angle 10° 58', and SENARMONT 12° 1'.

As the axial angle  $ac$  is 73° 3', this 2M.L. extinction direction is 5° 12' in front of the vertical axis  $c$ , and the first median line is 11° 45' from the inclined axis  $a$ , both extinction directions in the symmetry plane thus lying in the obtuse axial angle  $ac$ .

The next table shows the positions of the  $\alpha$  extinction direction in all four nickel salts, and fig. 3 illustrates them graphically.

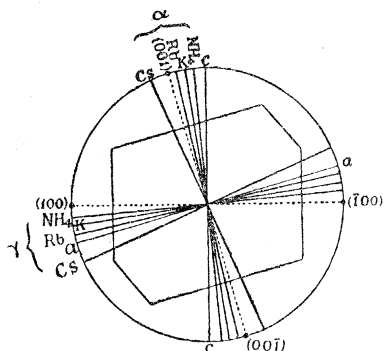


Fig. 3.

*Inclinations of  $\alpha$  extinctions of Ni salts in front of axis  $c$ .*

(2M.L. for Am, K, and Rb salts, 1M.L. for Cs salt.)

AmNi Sulphate	5° 12'	RbNi Sulphate	12° 38'
KNi	8° 42'	CsNi	24° 7'

The position of the ammonium salt ellipsoid is such that its  $\alpha$  axis lies nearest to the  $c$  axis, and the ellipsoid rotates as the potassium, rubidium, and caesium salts are successively reached, further and further from this position, the rotation following the order of the atomic weights of the three alkali metals.

*Refractive Indices.*—Six 60°-prisms were ground by means of the author's cutting and grinding goniometer,\* each to afford two indices directly, and the results are

\* A new crystal-grinding goniometer on the Goldschmidt two-circle principle has recently been described by F. E. WRIGHT ('Journ. Washington Acad. of Sciences,' 1915, 5, 35). In its description a mere passing mention is made of the very efficient instrument which the author (TUTTON) described in the year 1899 ('Phil. Trans. Roy. Soc.,' A, 1899, 192, 457; 'Zeitschr. für Kryst.,' 1899, 31, 458; 'Crystallography and Practical Crystal Measurement,' 1911, p. 682), and which has been used in all his investigations during the past 16 years, over a thousand section-plates and prisms having been most accurately prepared with its aid, truly orientated and plane surfaced. This instrument is capable of achieving all that the new Wright instrument is described as accomplishing, and much more besides. The use of a second circle cannot add to rigidity, and the author infinitely prefers the most rigid one-circle principle. After 16 years of hard service the author's cutting and grinding goniometer is as efficient and accurate as when first constructed by Messrs. Troughton and Simms.

given in the next table. This is followed by another table, in which the refractive indices of the four nickel-containing salts are compared.

MURMANN and ROTTER obtained indirectly the values  $\alpha = 1.489$ ,  $\beta = 1.498$ , and  $\gamma = 1.508$  for the middle of the spectrum.

There is a considerable amount of absorption by this green salt at the red end of the spectrum, but the electric arc, used as a source of light with the author's spectroscopic monochromatic illuminator,\* affords ample light for the observations in Li and C light.

#### REFRACTIVE INDICES OF AMMONIUM NICKEL SULPHATE.

Light.	$\alpha$ .	$\beta$ .	$\gamma$ .
Li . . . . .	1.4916	1.4975	1.5046
C. . . . .	1.4921	1.4980	1.5051
Na . . . . .	1.4949	1.5007	1.5081
Tl . . . . .	1.4976	1.5037	1.5110
Cd . . . . .	1.4993	1.5052	1.5125
F. . . . .	1.5007	1.5069	1.5142
G. . . . .	1.5060	1.5123	1.5196

Mean of  $\alpha$ ,  $\beta$ , and  $\gamma$  for Na light = 1.5012.

$\alpha$  = Vibration direction parallel to second median line,  $5^\circ 12'$  in front of axis  $c$ .

$\beta$  = " " " symmetry axis  $b$ .

$\gamma$  = " " " first median line.

General Formula for the intermediate refractive index  $\beta$ , corrected to a vacuum (correction +0.0004):—

$$\beta = 1.4873 + \frac{472\ 952}{\lambda^2} + \frac{212\ 960\ 000\ 000}{\lambda^4} + \dots$$

The  $\alpha$  indices are also reproduced very closely by the formula if the constant 1.4873 is diminished by 0.0060, and the  $\gamma$  indices if the constant is increased by 0.0073.

Observations at  $70^\circ$  indicate that the refractive indices of ammonium nickel sulphate are diminished by about  $0.0018^\circ$  (for  $\alpha$ ) to  $0.0022^\circ$  (for  $\gamma$ ) for  $55^\circ$  rise of temperature.

The comparative table shows that the refractive indices of ammonium nickel sulphate are just slightly higher than those of the analogous rubidium salt, and not nearly so high as those of the caesium salt. This is also clearly apparent as regards the mean refractive index given at the foot of the table. As regards double refraction, the ammonium salt occupies a similar position between the rubidium and caesium salts and much nearer to the rubidium one; as this property of double refraction diminishes

\* 'Crystallography and Practical Crystal Measurement,' 1911, p. 698.

## COMPARISON of the Refractive Indices.

Index.	Light.	KNi sulphate	RbNi sulphate.	NH <sub>4</sub> Ni sulphate.	CsNi sulphate.
$\alpha$ . . . . .	Li. . . . .	1·4809	1·4868	1·4916	1·5061
	C . . . . .	1·4813	1·4872	1·4921	1·5065
	Na . . . . .	1·4836	1·4895	1·4949	1·5087
	Tl. . . . .	1·4860	1·4920	1·4976	1·5112
	F . . . . .	1·4889	1·4949	1·5007	1·5146
	G . . . . .	1·4933	1·4996	1·5060	1·5192
$\beta$ . . . . .	Li. . . . .	1·4889	1·4933	1·4975	1·5100
	C . . . . .	1·4893	1·4937	1·4980	1·5104
	Na . . . . .	1·4916	1·4961	1·5007	1·5129
	Tl. . . . .	1·4941	1·4987	1·5037	1·5154
	F . . . . .	1·4972	1·5017	1·5069	1·5187
	G . . . . .	1·5015	1·5062	1·5123	1·5235
$\gamma$ . . . . .	Li. . . . .	1·5022	1·5023	1·5046	1·5133
	C . . . . .	1·5026	1·5027	1·5051	1·5137
	Na . . . . .	1·5051	1·5052	1·5081	1·5162
	Tl. . . . .	1·5077	1·5078	1·5110	1·5189
	F . . . . .	1·5109	1·5110	1·5142	1·5221
	G . . . . .	1·5153	1·5156	1·5196	1·5266
Mean refractive index $\frac{1}{3}(\alpha + \beta + \gamma)$ for Na light		1·4934	1·4969	1·5012	1·5126
Double refraction, $\text{Na}_{\gamma-\alpha}$ . . . . .		0·0215	0·0157	0·0132	0·0075

with rise of atomic weight of the alkali metal, the value is less than that for the rubidium salt.

## AXIAL Ratios of the Optical Indicatrix.

	$\alpha$ : $\beta$ : $\gamma$	$\alpha$ : $\beta$ : $\gamma$
KNi sulphate . . .	0·9946 : 1 : 1·0091	0·9946 : 1 : 1·0091
RbNi „ . . .	0·9956 : 1 : 1·0061	0·9986 : 1·0030 : 1·0091
NH <sub>4</sub> Ni „ . . .	0·9961 : 1 : 1·0049	1·0022 : 1·0061 : 1·0111
CsNi „ . . .	0·9972 : 1 : 1·0022	1·0115 : 1·0143 : 1·0165

## AXIAL Ratios of the Optical Velocity Ellipsoid.

	a : b : c	a : b : c
KNi sulphate . . .	1·0054 : 1 : 0·9910	1·0054 : 1 : 0·9910
RbNi „ . . .	1·0044 : 1 : 0·9940	1·0014 : 0·9970 : 0·9910
NH <sub>4</sub> Ni „ . . .	1·0039 : 1 : 0·9951	0·9978 : 0·9939 : 0·9891
CsNi „ . . .	1·0028 : 1 : 0·9978	0·9887 : 0·9859 : 0·9838

*Axial Ratios of the Optical Ellipsoid.*—These have been calculated for ammonium nickel sulphate for either form of ellipsoid; the values are given in the accompanying table, and are compared with the values for the three analogous salts of the alkali

metals. The first series (on the left) shows the ratios when the  $\beta$ -axis of each salt is taken as 1, and the second (right hand) series when the  $\beta$ -axis of the potassium salt is taken = 1; this second series thus shows the effect on the optical ellipsoid of replacing one alkali base by another. In both series the position of the ammonium salt is between the rubidium and caesium salts, and much nearer to the former.

*Molecular Optical Constants.*—These have been calculated with the aid of the densities as determined by the immersion method, both for the ammonium salt now under discussion, and for the potassium, rubidium, and caesium salts, and the results are set forth comparatively in the next three tables.

The specific refraction and dispersion of ammonium nickel sulphate are considerably higher than those of the alkali-metal salts. The molecular dispersion is slightly higher than that of the caesium salt. The molecular refraction, whether calculated by the formula of LORENZ, or by that of GLADSTONE and DALE, is very close to (just higher than) that for the rubidium salt. The mean molecular refraction shows this very succinctly.

TABLE of Specific Refraction and Dispersion (LORENZ).

Sulphate.	Specific refraction, $\frac{n^2-1}{(n^2+2)d} = n$ .						Specific dispersion. $n_G - n_C$ .		
	For ray C (H $\alpha$ ).			For ray H $\gamma$ near G.					
	$\alpha$ .	$\beta$ .	$\gamma$ .	$\alpha$ .	$\beta$ .	$\gamma$ .	$\alpha$ .	$\beta$ .	$\gamma$ .
AmNi . . .	0.1509	0.1524	0.1543	0.1545	0.1561	0.1580	0.0036	0.0037	0.0037
KNi . . . .	0.1273	0.1290	0.1321	0.1300	0.1318	0.1349	0.0027	0.0028	0.0028
RbNi . . . .	0.1113	0.1125	0.1143	0.1137	0.1149	0.1167	0.0024	0.0024	0.0024
CsNi . . . .	0.1035	0.1042	0.1048	0.1057	0.1064	0.1070	0.0022	0.0022	0.0022

TABLE of Molecular Refraction and Dispersion (LORENZ).

Salt.	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = m$ .						Molecular dispersion. $m_G - m_C$ .		
	For ray C (H $\alpha$ ).			For ray H $\gamma$ near G.					
	$\alpha$ .	$\beta$ .	$\gamma$ .	$\alpha$ .	$\beta$ .	$\gamma$ .	$\alpha$ .	$\beta$ .	$\gamma$ .
KNi sulphate	55.23	56.00	57.31	56.41	57.20	58.53	1.18	1.20	1.22
RbNi „	58.53	59.19	60.10	59.79	60.46	61.40	1.26	1.27	1.30
AmNi „	59.17	59.77	60.49	60.58	61.22	61.95	1.41	1.45	1.46
CsNi „	64.20	64.61	64.97	65.55	66.00	66.34	1.35	1.39	1.37

## MOLECULAR Refraction (GLADSTONE and DALE).

Salt.	$\frac{n-1}{d}$ M for ray C.			Mean molecular refraction for ray C. $\frac{1}{3}(\alpha + \beta + \gamma)$ .
	$\alpha$ .	$\beta$ .	$\gamma$ .	
KNi sulphate . . . . .	93·37	94·92	97·50	95·26
RbNi „ . . . . .	99·11	100·43	102·26	100·60
AmNi „ . . . . .	100·34	101·55	103·00	101·63
CsNi „ . . . . .	109·35	110·19	110·91	110·15

*Optic Axial Angle.*—Three pairs of section plates were ground perpendicular to the first and second median lines. The optic axial angle is so large as to be invisible in air. The next table affords the results of the measurements of  $2H_a$  and  $2H_o$  in monobromonaphthalene, the interference figures in which are very well defined.

MURMANN and ROTTER obtained  $86^\circ 26'$  for the true angle  $2V_a$ , for the middle of the spectrum.

*Dispersion of the Median Lines.*—The inclined dispersion of the median lines is small. Measurements in toluene, the refractive index of which (1·4955) is slightly lower, and in benzene, which possesses a slightly higher index (1·5027), indicated that the dispersion is such that the first median line is nearer by 8 minutes to the axis  $\alpha$  for red C-hydrogen light than for greenish-blue F-hydrogen light.

*Ammonium Nickel Sulphate.*

## DETERMINATION of True Optic Axial Angle in Bromonaphthalene.

Light.	No. of plate perp. 1 M.L.	Observed $2H_a$ .	No. of plate perp. 2 M.L.	Observed $2H_o$ .	Calculated $2V_a$ .	Mean $2V_a$ .
		° ' .		° ' .	° ' .	° ' .
Li . . . . .	1	76 33	1a	82 35	86 23	86 27
	2	76 26	2a	82 18	86 28	
	3	76 32	3a	82 20	86 31	
C . . . . .	1	76 30	1a	82 31	86 24	86 28
	2	76 23	2a	82 13	86 28	
	3	76 29	3a	82 15	86 32	
Na . . . . .	1	76 8	1a	81 55	86 30	86 33
	2	76 7	2a	81 50	86 32	
	3	76 10	3a	81 45	86 36	
Tl . . . . .	1	75 51	1a	81 29	86 34	86 37
	2	75 50	2a	81 23	86 36	
	3	75 50	3a	81 19	86 40	
Cd . . . . .	1	75 42	1a	81 11	86 38	86 40
	2	75 39	2a	81 5	86 40	
	3	75 38	3a	81 0	86 42	
F . . . . .	1	75 33	1a	80 56	86 42	86 43
	2	75 27	2a	80 50	86 42	
	3	75 26	3a	80 45	86 44	



A comparison of the optic axial angles of the four salts containing nickel, instituted in the next table, shows that the angle for the ammonium salt is close to that of the caesium salt, being slightly lower than the latter. It has to be remembered that caesium nickel sulphate is (by exception in the series) of negative double refraction, so that the first median line is, in this case, the  $\alpha$  axis of the indicatrix ellipsoid, instead of (as usual in the series) the  $\gamma$  axis.

OPTIC Axial Angles  $2V_a$  of the Nickel Group.

	KNi sulphate.	RbNi sulphate.	AmNi sulphate.	CsNi sulphate.
Li . . . . .	75 21	82 5	86 27	87 15
C . . . . .	75 19	82 4	86 28	87 17
Na . . . . .	75 16	82 0	86 33	87 21
Tl . . . . .	75 13	81 56	86 37	87 29
F . . . . .	75 9	81 48	86 43	87 40

*Ammonium Cobalt Sulphate*  $(\text{NH}_4)_2 \text{Co} (\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ .*Morphology.*

The only crystallographic investigation of this salt hitherto made is that of MARIGNAC (*loc. cit.*). The values of the angles observed by him are quoted in the last column of the table of angles.

*Crystal System.*—Monoclinic. Class No. 5, holohedral-prismatic.

*Ratios of Axes.*—

$a : b : c = 0.7386 : 1 : 0.4975$ . Values of MARIGNAC,  $0.7392 : 1 : 0.4985$ .

*Axial Angle.*— $\beta = 107^\circ 2'$ . Value of MARIGNAC,  $106^\circ 56'$ .

*Forms Observed.*— $a \{100\}$ ,  $b \{010\}$ ,  $c \{001\}$ ,  $p \{110\}$ ,  $q \{011\}$ ,  $r' \{\bar{2}01\}$ ,  $o \{111\}$ ,  $o' \{\bar{1}\bar{1}1\}$ .

*Habit.*—Short prismatic parallel  $p \{110\}$ , often with narrower  $c$  faces and larger  $q$  faces than in the nickel salt; or more or less tabular parallel to a pair of faces of this prism  $p \{110\}$  predominatingly grown, or to  $c \{001\}$ .

This is one of the finest salts of the series, the crystals being of a ruby or red-currant red colour. The crystals of several of the numerous crops obtained were composed of completely transparent well-developed individuals, having absolutely plane faces yielding brilliant single images of the signal of unusual perfection. Ten superb crystals were measured, selected from five different crops. The results are shown in the table of angles. A typical crystal is shown in fig. 4, and fig. 2, representing a crystal of ammonium nickel sulphate, is equally typical of many crops of the cobalt analogue. Both are of the short prismatic type, but not infrequently

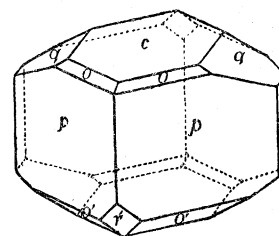


Fig. 4.

## INTERFACIAL Angles of Ammonium Cobalt Sulphate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.	Values of MARIIGNAC.
$\left\{ \begin{array}{l} ac = (100):(001) \\ as = (100):(101) \\ sc = (101):(001) \end{array} \right.$	—	° — °	—	72 58	—	73 4
$cr' = (001):(\bar{2}01)$	17	64 37- 64 59	64 52	64 46	6	64 48
$cs' = (001):(\bar{1}01)$	—	—	—	38 41	—	—
$s'r' = (\bar{1}01):(\bar{2}01)$	—	—	—	26 5	—	—
$r'a = (\bar{2}01):(\bar{1}00)$	—	—	—	42 16	—	—
$r'c = (\bar{2}01):(00\bar{1})$	16	115 2-115 21	115 8	115 14	6	—
$\left\{ \begin{array}{l} ap = (100):(110) \\ pp' = (110):(120) \\ p'b = (120):(010) \\ pp''' = (110):(130) \\ p'''b = (130):(010) \end{array} \right.$	—	—	—	35 14	—	—
$pb = (110):(010)$	40	54 38- 54 52	54 46	*	—	—
$pp = (110):(\bar{1}\bar{1}0)$	20	70 23- 70 33	70 28	70 28	0	70 32
$\left\{ \begin{array}{l} cq = (001):(011) \\ qb = (011):(010) \end{array} \right.$	31 33	25 12- 25 39 64 27- 64 52	25 26 64 34	* 64 34	— 0	25 15 —
$\left\{ \begin{array}{l} ao = (100):(111) \\ oq = (111):(011) \\ aq = (100):(011) \\ qo' = (011):(\bar{1}\bar{1}\bar{1}) \\ o'a = (\bar{1}\bar{1}\bar{1}):(\bar{1}00) \end{array} \right.$	— 4 1 5 1	— 26 41- 26 51 — 34 54- 35 6 —	— 26 47 74 29 35 2 70 33	47 52 26 47 74 39 34 57 70 24	— 0 10 5 9	— 26 47 — 34 55 —
$\left\{ \begin{array}{l} co = (001):(111) \\ op = (111):(110) \\ cp = (001):(110) \\ po' = (110):(\bar{1}\bar{1}\bar{1}) \\ o'c = (\bar{1}\bar{1}\bar{1}):(\bar{0}0\bar{1}) \end{array} \right.$	9 9 40 16 16	33 42- 33 52 42 18- 42 29 75 55- 76 24 58 40- 58 59 44 50- 45 25	33 46 42 22 76 9 58 52 44 57	33 45 42 24 * 58 56 44 55	1 2 — 4 2	33 40 — 76 14 — 44 54
$\left\{ \begin{array}{l} bn = (010):(121) \\ no = (121):(111) \\ bo = (010):(111) \\ os = (111):(101) \\ oo = (111):(\bar{1}\bar{1}\bar{1}) \end{array} \right.$	— — 7 — 1	— — 70 35- 70 46 — —	— — 70 41 — 38 38	55 1 15 42 70 43 19 17 38 34	— — 2 — 4	— — — — 38 39
$\left\{ \begin{array}{l} bo' = (010):(\bar{1}\bar{1}\bar{1}) \\ o's' = (\bar{1}\bar{1}\bar{1}):(\bar{1}01) \\ o'o' = (\bar{1}\bar{1}\bar{1}):(\bar{1}\bar{1}\bar{1}) \end{array} \right.$	7 — 1	65 6- 65 20 — —	65 10 — 49 42	65 11 24 49 49 38	1 — 4	— — 49 20
$\left\{ \begin{array}{l} sq = (101):(011) \\ qp = (011):(\bar{1}\bar{1}0) \\ ps = (\bar{1}\bar{1}0):(\bar{1}0\bar{1}) \\ pq = (\bar{1}\bar{1}0):(0\bar{1}\bar{1}) \end{array} \right.$	— 37 — 38	— 88 2- 88 29 — 91 27- 91 57	— 88 12 — 91 47	37 18 88 11 54 31 91 49	— 1 — 2	— — — —
$\left\{ \begin{array}{l} s'q = (\bar{1}01):(011) \\ qn = (011):(121) \\ np = (121):(110) \\ qp = (011):(110) \\ ps' = (110):(\bar{1}0\bar{1}) \\ pq = (110):(0\bar{1}\bar{1}) \end{array} \right.$	— — — 36 — 36	— — — 62 7- 62 28 — 117 29-117 52	— — — 62 21 — 117 40	45 11 26 6 36 15 62 21 72 28 117 39	— — — 0 — 1	— — — — — —
$\left\{ \begin{array}{l} r'o' = (\bar{2}01):(\bar{1}\bar{1}\bar{1}) \\ o'p = (\bar{1}\bar{1}\bar{1}):(\bar{1}\bar{1}0) \\ pr' = (110):(\bar{2}0\bar{1}) \end{array} \right.$	17 18 36	35 9- 35 37 91 44- 92 5 52 36- 52 52	35 21 91 54 52 43	35 23 91 48 52 49	2 6 6	35 28 — 52 40
Total number of measurements . .	492					

the prism is relatively longer than is shown in the two figures. In the great majority of crops prepared the type was that of fig. 4, or of the same elongated vertically, the faces of the basal plane  $c\{001\}$  predominating at the terminations. But in several of the crops the  $c$  faces were relatively narrower and the faces of  $q\{011\}$  proportionately larger, as shown in fig. 2. In all the crops the prism faces  $p\{110\}$  were always important, and indeed usually predominated. The two faces of the clinopinakoid  $b\{010\}$  were often well developed, although many crops showed these faces only as strips, and not uncommonly they were either entirely absent or mere lines. The faces of the orthopinakoid  $r'\{\bar{2}01\}$  were usually very subordinate, as shown in the figure. The two hemipyramids  $o\{111\}$  and  $o'\{\bar{1}11\}$  were usually represented by some of their faces, and the latter form often by all its faces, although small. The orthopinakoid  $a\{100\}$  was only very rarely developed to a measurable extent.

The next three tables compare the morphological constants of the four salts containing cobalt. The first of these shows that the axial angle  $\beta$  of ammonium cobalt sulphate is very close to that of caesium cobalt sulphate, and that the axial ratios of the ammonium salt are very clearly such as place that salt in the same isomorphous series as the three cobalt salts containing the alkali metals.

The angular comparisons instituted in the second table are supplemented by a further short table showing the average and maximum changes of angle which occur when potassium is replaced by the other three alkali bases. These changes are seen to be nearly the same for the ammonium and caesium replacements, and these again are twice as great as the average and maximum changes of angle when rubidium is introduced instead of potassium. A critical analysis of the comparative table of angles also shows that of the 36 angles compared 32 show changes, when ammonium replaces potassium, in the same direction as when the latter is replaced by the other two alkali metals, and the only four exceptions are in cases where the changes are very minute. Of the 32, 29 show larger changes than for the rubidium replacement, and 11 show even larger changes than for the caesium replacement.

COMPARISON of the Axial Angles and Axial Ratios.

	Axial angle.	Axial ratios.
	$\beta$ .	$a : b : c$
Potassium cobalt sulphate . .	$104^{\circ} 55'$	$0.7404 : 1 : 0.5037$
Rubidium     "     "     . .	$106^{\circ} 1'$	$0.7391 : 1 : 0.5011$
Ammonium     "     "     . .	$107^{\circ} 2'$	$0.7386 : 1 : 0.4975$
Caesium     "     "     . .	$107^{\circ} 8'$	$0.7270 : 1 : 0.4968$

## COMPARISON of the Interfacial Angles.

Angle.	KCo sulphate.	RbCo sulphate.	CsCo sulphate.	AmCo sulphate.
	° ' /	° ' /	° ' /	° ' /
$\left\{ \begin{array}{l} ac = (100):(001) \\ as = (100):(101) \\ sc = (101):(001) \\ cr' = (001):(201) \\ cs' = (001):(\bar{1}01) \\ s'r' = (\bar{1}01):(201) \\ r'a = (201):(\bar{1}00) \end{array} \right.$	$\left\{ \begin{array}{l} 75 \ 5 \\ 45 \ 53 \\ 29 \ 12 \\ 63 \ 38 \\ 38 \ 29 \\ 25 \ 9 \\ 41 \ 17 \end{array} \right.$	$\left\{ \begin{array}{l} 73 \ 59 \\ 45 \ 11 \\ 28 \ 48 \\ 64 \ 24 \\ 38 \ 47 \\ 25 \ 37 \\ 41 \ 37 \end{array} \right.$	$\left\{ \begin{array}{l} 72 \ 52 \\ 44 \ 20 \\ 28 \ 32 \\ 65 \ 24 \\ 39 \ 15 \\ 26 \ 9 \\ 41 \ 44 \end{array} \right.$	$\left\{ \begin{array}{l} 72 \ 58 \\ 44 \ 43 \\ 28 \ 15 \\ 64 \ 46 \\ 38 \ 41 \\ 26 \ 5 \\ 42 \ 16 \end{array} \right.$
$\left\{ \begin{array}{l} ap = (100):(110) \\ pp' = (110):(120) \\ p'b = (120):(010) \\ pb = (110):(010) \end{array} \right.$	$\left\{ \begin{array}{l} 35 \ 37 \\ 19 \ 28 \\ 34 \ 55 \\ 54 \ 23 \end{array} \right.$	$\left\{ \begin{array}{l} 35 \ 21 \\ 19 \ 28 \\ 35 \ 11 \\ 54 \ 39 \end{array} \right.$	$\left\{ \begin{array}{l} 34 \ 48 \\ 19 \ 28 \\ 35 \ 44 \\ 55 \ 12 \end{array} \right.$	$\left\{ \begin{array}{l} 35 \ 14 \\ 19 \ 28 \\ 35 \ 18 \\ 54 \ 46 \end{array} \right.$
$\left\{ \begin{array}{l} eq = (001):(011) \\ qb = (011):(010) \end{array} \right.$	$\left\{ \begin{array}{l} 25 \ 55 \\ 64 \ 5 \end{array} \right.$	$\left\{ \begin{array}{l} 25 \ 43 \\ 64 \ 17 \end{array} \right.$	$\left\{ \begin{array}{l} 25 \ 24 \\ 64 \ 36 \end{array} \right.$	$\left\{ \begin{array}{l} 25 \ 26 \\ 64 \ 34 \end{array} \right.$
$\left\{ \begin{array}{l} ao = (100):(111) \\ oq = (111):(011) \\ aq = (100):(011) \\ qo' = (011):(\bar{1}11) \\ o'a = (\bar{1}11):(\bar{1}00) \end{array} \right.$	$\left\{ \begin{array}{l} 49 \ 6 \\ 27 \ 31 \\ 76 \ 37 \\ 34 \ 41 \\ 68 \ 42 \end{array} \right.$	$\left\{ \begin{array}{l} 48 \ 23 \\ 27 \ 13 \\ 75 \ 36 \\ 34 \ 59 \\ 69 \ 25 \end{array} \right.$	$\left\{ \begin{array}{l} 47 \ 30 \\ 27 \ 4 \\ 74 \ 34 \\ 35 \ 26 \\ 70 \ 0 \end{array} \right.$	$\left\{ \begin{array}{l} 47 \ 52 \\ 26 \ 47 \\ 74 \ 39 \\ 34 \ 57 \\ 70 \ 24 \end{array} \right.$
$\left\{ \begin{array}{l} co = (001):(111) \\ op = (111):(110) \\ cp = (001):(110) \\ po' = (110):(111) \\ o'c = (111):(00\bar{1}) \end{array} \right.$	$\left\{ \begin{array}{l} 34 \ 50 \\ 43 \ 5 \\ 77 \ 55 \\ 57 \ 22 \\ 44 \ 43 \end{array} \right.$	$\left\{ \begin{array}{l} 34 \ 20 \\ 42 \ 40 \\ 77 \ 0 \\ 58 \ 3 \\ 44 \ 57 \end{array} \right.$	$\left\{ \begin{array}{l} 33 \ 54 \\ 42 \ 6 \\ 76 \ 0 \\ 58 \ 42 \\ 45 \ 18 \end{array} \right.$	$\left\{ \begin{array}{l} 33 \ 45 \\ 42 \ 24 \\ 76 \ 9 \\ 58 \ 56 \\ 44 \ 55 \end{array} \right.$
$\left\{ \begin{array}{l} bo = (010):(111) \\ os = (111):(101) \end{array} \right.$	$\left\{ \begin{array}{l} 70 \ 7 \\ 19 \ 53 \end{array} \right.$	$\left\{ \begin{array}{l} 70 \ 26 \\ 19 \ 34 \end{array} \right.$	$\left\{ \begin{array}{l} 70 \ 52 \\ 19 \ 8 \end{array} \right.$	$\left\{ \begin{array}{l} 70 \ 43 \\ 19 \ 17 \end{array} \right.$
$\left\{ \begin{array}{l} bo' = (010):(\bar{1}11) \\ o's' = (\bar{1}11):(\bar{1}01) \end{array} \right.$	$\left\{ \begin{array}{l} 65 \ 13 \\ 24 \ 47 \end{array} \right.$	$\left\{ \begin{array}{l} 65 \ 12 \\ 24 \ 48 \end{array} \right.$	$\left\{ \begin{array}{l} 65 \ 17 \\ 24 \ 43 \end{array} \right.$	$\left\{ \begin{array}{l} 65 \ 11 \\ 24 \ 49 \end{array} \right.$
$\left\{ \begin{array}{l} sq = (101):(011) \\ qp = (011):(\bar{1}10) \\ ps = (\bar{1}10):(10\bar{1}) \end{array} \right.$	$\left\{ \begin{array}{l} 38 \ 16 \\ 86 \ 12 \\ 55 \ 32 \end{array} \right.$	$\left\{ \begin{array}{l} 37 \ 51 \\ 87 \ 14 \\ 54 \ 55 \end{array} \right.$	$\left\{ \begin{array}{l} 37 \ 29 \\ 88 \ 29 \\ 54 \ 2 \end{array} \right.$	$\left\{ \begin{array}{l} 37 \ 18 \\ 88 \ 11 \\ 54 \ 31 \end{array} \right.$
$\left\{ \begin{array}{l} s'q = (\bar{1}01):(011) \\ qp' = (011):(110) \\ ps' = (110):(10\bar{1}) \end{array} \right.$	$\left\{ \begin{array}{l} 45 \ 15 \\ 63 \ 43 \\ 71 \ 2 \end{array} \right.$	$\left\{ \begin{array}{l} 45 \ 23 \\ 63 \ 0 \\ 71 \ 37 \end{array} \right.$	$\left\{ \begin{array}{l} 45 \ 37 \\ 62 \ 24 \\ 71 \ 59 \end{array} \right.$	$\left\{ \begin{array}{l} 45 \ 11 \\ 62 \ 21 \\ 72 \ 28 \end{array} \right.$
$\left\{ \begin{array}{l} r'o' = (\bar{2}01):(\bar{1}11) \\ o'p = (\bar{1}11):(110) \\ pr' = (110):(20\bar{1}) \end{array} \right.$	$\left\{ \begin{array}{l} 34 \ 44 \\ 92 \ 55 \\ 52 \ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 35 \ 4 \\ 92 \ 30 \\ 52 \ 26 \end{array} \right.$	$\left\{ \begin{array}{l} 35 \ 22 \\ 92 \ 25 \\ 52 \ 13 \end{array} \right.$	$\left\{ \begin{array}{l} 35 \ 23 \\ 91 \ 48 \\ 52 \ 49 \end{array} \right.$

## DOUBLE Sulphates containing Cobalt.

Replacement.	Average change.	Maximum change.
K by Rb . . . . .	27	66 = 1 6
K by Cs . . . . .	56	137 = 2 17
K by NH <sub>4</sub> . . . . .	52	127 = 2 7

*Cleavage.*—The common cleavage of the series parallel  $r \{ \bar{2}01 \}$  is well developed in this salt. No trace of the  $b \{ 010 \}$  cleavage found on the nickel ammonium salt was discoverable on the cobalt salt.

*Volume.*

*Relative Density.*—Five determinations by the immersion method gave the following results :—

I. Density for $16^{\circ}8/4^{\circ}$	. . .	1.9000	For $20^{\circ}/4^{\circ}$	. . .	1.8994
II. „ $17^{\circ}4/4^{\circ}$	. . .	1.9006	„ $20^{\circ}/4^{\circ}$	. . .	1.9001
III. „ $16^{\circ}2/4^{\circ}$	. . .	1.9037	„ $20^{\circ}/4^{\circ}$	. . .	1.9030
IV. „ $16^{\circ}3/4^{\circ}$	. . .	1.9016	„ $20^{\circ}/4^{\circ}$	. . .	1.9009
V. „ $16^{\circ}8/4^{\circ}$	. . .	1.9014	„ $20^{\circ}/4^{\circ}$	. . .	1.9008
					<hr/>
Mean . . .					1.9008

The value accepted for  $20^{\circ}/4^{\circ}$  is **1.901**.

PERROT (*loc. cit.*) records three determinations of the density of this salt, the values obtained being 1.895, 1.892, and 1.862, and gives as his accepted mean 1.88.

*Molecular Volume.*— $\frac{M}{d} = \frac{392.37}{1.901} = 206.40$ . PERROT gives 210.

*Molecular Distance Ratios (topic axial ratios).*—

$$\chi : \psi : \omega = 6.1860 : 8.3753 : 4.1667.$$

*Redeterminations of Densities of Alkali-Metal-Cobalt Salts.*

*Potassium Cobalt Sulphate,  $K_2Co(SO_4)_2 \cdot 6H_2O$ .*

I. Density for $15^{\circ}3/4^{\circ}$	. . .	2.2196	For $20^{\circ}/4^{\circ}$	. . .	2.2186
II. „ $15^{\circ}1/4^{\circ}$	. . .	2.2203	„ $20^{\circ}/4^{\circ}$	. . .	2.2192
III. „ $15^{\circ}2/4^{\circ}$	. . .	2.2175	„ $20^{\circ}/4^{\circ}$	. . .	2.2164
IV. „ $15^{\circ}7/4^{\circ}$	. . .	2.2211	„ $20^{\circ}/4^{\circ}$	. . .	2.2201
V. „ $16^{\circ}9/4^{\circ}$	. . .	2.2213	„ $20^{\circ}/4^{\circ}$	. . .	2.2206
					<hr/>
Mean . . .					2.2190

The value accepted for  $20^{\circ}/4^{\circ}$  is **2.219**.

*Rubidium Cobalt Sulphate,  $Rb_2Co(SO_4)_2 \cdot 6H_2O$ .*

I. Density for $13^{\circ}6/4^{\circ}$	. . .	2.5676	For $20^{\circ}/4^{\circ}$	. . .	2.5660
II. „ $15^{\circ}1/4^{\circ}$	. . .	2.5679	„ $20^{\circ}/4^{\circ}$	. . .	2.5666
III. „ $15^{\circ}0/4^{\circ}$	. . .	2.5684	„ $20^{\circ}/4^{\circ}$	. . .	2.5671
IV. „ $15^{\circ}2/4^{\circ}$	. . .	2.5676	„ $20^{\circ}/4^{\circ}$	. . .	2.5664
					<hr/>
Mean . . .					2.5665

The value accepted for  $20^{\circ}/4^{\circ}$  is **2.567**.

*Cæsium Cobalt Sulphate*,  $\text{Cs}_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ .

I.	Density for $16^\circ 7/4^\circ$	. . .	2·8468	For $20^\circ/4^\circ$	. . .	2·8459
II.	„ $16^\circ 7/4^\circ$	. . .	2·8444	„ $20^\circ/4^\circ$	. . .	2·8435
III.	„ $17^\circ 7/4^\circ$	. . .	2·8439	„ $20^\circ/4^\circ$	. . .	2·8432
IV.	„ $18^\circ 1/4^\circ$	. . .	2·8436	„ $20^\circ/4^\circ$	. . .	2·8431
						Mean . . . 2·8439

The value accepted for  $20^\circ/4^\circ$  is 2·844.

The former pyknometer values for potassium, rubidium, and cæsium cobalt sulphates were 2·212, 2·557, and 2·837 respectively. The new values all being higher are certainly nearer the truth.

The next table affords a comparison of the volume constants of all four cobalt-containing salts.

## VOLUME Constants of the Cobalt Group.

Salt.	Molecular weight.	Specific gravity.	Molecular volume.	Topic axial ratios.
KCo sulphate . .	434·21	2·219	195·68	$\chi : \psi : \omega$ 6·0405 : 8·1583 : 4·1093
RbCo „ . .	526·31	2·567	205·03	6·1494 : 8·3201 : 4·1692
$\text{NH}_4\text{Co}$ „ . .	392·37	1·901	206·40	6·1860 : 8·3753 : 4·1667
CsCo „ . .	620·31	2·844	218·11	6·2386 : 8·5814 : 4·2632

It shows that the position of the ammonium salt as regards both molecular volume and topic axial ratios is close to that of the rubidium salt; the molecular volume and the ratios  $\chi$  and  $\psi$  are slightly higher, and the ratio  $\omega$  slightly lower.

*Optics.*

*Orientation of the Optical Ellipsoid.*—The symmetry plane  $b\{010\}$  is the plane of the optic axes. The double refraction is positive, the first median line corresponding to the refractive index  $\gamma$ , and the second median line to  $\alpha$ . Two section plates parallel to the symmetry plane afforded the following extinction angles:—

*Inclination of 2M.L. from normal to  $c\{001\}$ .*

Plate I. . . .	$10^\circ 38'$	Plate II. . . .	$10^\circ 48'$
Mean . . . .		$10^\circ 43'$	

The direction is behind the normal, towards axis  $c$ .

MURMANN and ROTTER obtained  $11^\circ 0'$  for this extinction angle, and SENARMONT gives it as  $12^\circ 0'$ .

As the axial angle  $ac = 72^\circ 58'$ , this extinction direction of the second median line is  $6^\circ 19'$  in front of the vertical axis  $c$ , and the first median line is  $10^\circ 43'$  above the axis  $a$ , both median lines being in the obtuse angle of the morphological axes  $ac$ . The positions of the optical ellipsoids of all four cobalt-containing salts are compared in the following table, and are graphically expressed in the accompanying fig. 5.

*Inclinations of  $\alpha$  Axis of Indicatrix (2M.L.) of the Cobalt Salts in front of Axis  $c$ .*

AmCo sulphate	$6^\circ 19'$
KCo	$10^\circ 5'$
RbCo	$16^\circ 1'$
CsCo	$26^\circ 8'$

The ammonium salt ellipsoid lies with its  $\alpha$  axis nearest the vertical axis  $c$ , and the ellipsoid rotates further away from this position as ammonium is replaced by potassium, rubidium, and caesium in turn, according to the order of the atomic weights of those alkali metals.

*Refractive Indices.*—The following table gives the results of measurements with six excellent  $60^\circ$ -prisms, each ground accurately to afford two indices directly, the prism edge and bisecting plane being parallel to a principal axis and principal plane of the indicatrix. There is considerable absorption in the green and blue parts of the spectrum, but the illumination of the images of the spectrometer slit for Tl, Cd and F light was quite adequate to ensure accuracy, using the electric arc with the monochromatic illuminator, as usual.

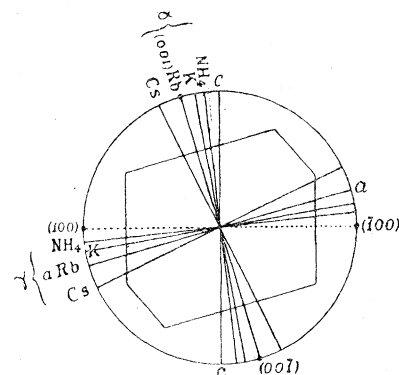


Fig. 5.

REFRACTIVE INDICES OF AMMONIUM COBALT SULPHATE.

Light.	$\alpha$ .	$\beta$ .	$\gamma$ .
Li . . . . .	1.4871	1.4922	1.5001
C . . . . .	1.4876	1.4927	1.5006
Na . . . . .	1.4902	1.4953	1.5032
Tl . . . . .	1.4930	1.4982	1.5060
Cd . . . . .	1.4946	1.4998	1.5076
F . . . . .	1.4964	1.5014	1.5094
G . . . . .	1.5018	1.5067	1.5148

Mean of  $\alpha$ ,  $\beta$ , and  $\gamma$  for Na light = 1.4962.

$\alpha$  = Vibration direction parallel to second median line,  $6^\circ 19'$  in front of axis  $c$ .

$\beta$  = " " " " symmetry axis  $b$ .

$\gamma$  = " " " " first median line.

MURMANN and ROTTER found indirectly for yellow light  $\alpha = 1.489$ ,  $\beta = 1.494$ , and  $\gamma = 1.501$ ; also  $\beta$  for red light = 1.492, and for green light = 1.497.

General Formula for  $\beta$ , corrected to a vacuum :—

$$\beta = 1.4826 + \frac{441\,773}{\lambda^2} + \frac{449\,400\,000\,000}{\lambda^4} + \dots$$

The index  $\alpha$  is reproduced also by the formula if the constant 1.4826 is diminished by 0.0051, and  $\gamma$  if it is increased by 0.0079.

Observations at 70° showed that the refractive indices of ammonium cobalt sulphate are diminished by about 0.0020 (for  $\alpha$ ) to 0.0025 (for  $\gamma$ ) by 55° rise of temperature.

In the next table the refractive indices of the four cobalt-containing salts are compared.

COMPARISON of the Refractive Indices.

Index.	Light.	KCo sulphate.	RbCo sulphate.	NH <sub>4</sub> Co sulphate.	CsCo sulphate.
$\alpha$ . . . . .	Li. . . . .	1.4780	1.4833	1.4871	1.5028
	C . . . . .	1.4784	1.4837	1.4876	1.5032
	Na . . . . .	1.4807	1.4859	1.4902	1.5057
	Tl. . . . .	1.4830	1.4882	1.4930	1.5079
	F . . . . .	1.4861	1.4910	1.4964	1.5112
	G . . . . .	1.4904	1.4954	1.5018	1.5159
$\beta$ . . . . .	Li. . . . .	1.4838	1.4889	1.4922	1.5057
	C . . . . .	1.4842	1.4893	1.4927	1.5061
	Na . . . . .	1.4865	1.4916	1.4953	1.5085
	Tl. . . . .	1.4889	1.4940	1.4982	1.5110
	F . . . . .	1.4919	1.4968	1.5014	1.5142
	G . . . . .	1.4961	1.5011	1.5067	1.5188
$\gamma$ . . . . .	Li. . . . .	1.4973	1.4985	1.5001	1.5102
	C . . . . .	1.4977	1.4989	1.5006	1.5106
	Na . . . . .	1.5004	1.5014	1.5032	1.5132
	Tl. . . . .	1.5028	1.5038	1.5060	1.5156
	F . . . . .	1.5059	1.5068	1.5094	1.5187
	G . . . . .	1.5105	1.5114	1.5148	1.5237
Mean refractive index $\frac{1}{3} (\alpha + \beta + \gamma)$ for Na light		1.4892	1.4930	1.4962	1.5091
Double refraction, $\text{Na}_{\gamma-\alpha}$ . . . . .		0.0197	0.0155	0.0130	0.0075

The refractive indices of the ammonium salt, which are concisely represented by the mean index given at the foot of the table, are slightly higher than those of the rubidium salt, and the double refraction is slightly less than that of the rubidium salt, the ammonium salt thus standing between the rubidium and caesium salts as regards both properties, and much nearer to the rubidium salt.



*Axial Ratios of the Optical Ellipsoid.*—These are given in the next table, both for the ammonium salt now described and for the three alkali-metal salts previously described. The comparison shows that the dimensions of the optical ellipsoid (either form) of the ammonium salt are also intermediate between those for the rubidium and caesium salts, and much nearer to those for the rubidium salt.

AXIAL Ratios of the Optical Indicatrix.

				$\alpha$	:	$\beta$	:	$\gamma$	$\alpha$	:	$\beta$	:	$\gamma$	
KCo	sulphate	.	.	.	0.9961	:	1	:	1.0094	0.9961	:	1	:	1.0094
RbCo	„	.	.	.	0.9962	:	1	:	1.0066	0.9996	:	1.0034	:	1.0100
NH <sub>4</sub> Co	„	.	.	.	0.9966	:	1	:	1.0053	1.0025	:	1.0059	:	1.0113
CsCo	„	.	.	.	0.9981	:	1	:	1.0031	1.0129	:	1.0148	:	1.0180

AXIAL Ratios of the Optical Velocity Ellipsoid.

				a	:	b	:	c	a	:	b	:	c	
KCo	sulphate	.	.	.	1.0039	:	1	:	0.9907	1.0039	:	1	:	0.9907
RbCo	„	.	.	.	1.0038	:	1	:	0.9935	1.0004	:	0.9966	:	0.9901
NH <sub>4</sub> Co	„	.	.	.	1.0034	:	1	:	0.9947	0.9975	:	0.9941	:	0.9889
CsCo	„	.	.	.	1.0019	:	1	:	0.9969	0.9872	:	0.9854	:	0.9823

*Molecular Optical Constants.*—These are given in the next three tables for all four salts of the cobalt group. The newly determined densities were employed in recalculating the values for the three alkali-metal salts. The specific refraction and dispersion of the ammonium salt are considerably higher than those of the three salts containing the alkali metals. The molecular dispersion of the ammonium salt is slightly higher than that of the caesium salt. The molecular refraction, either of LORENZ or GLADSTONE and DALE, is invariably just higher than that of the rubidium salt, a fact which is very clearly demonstrated by the mean molecular refraction given in the last column of the third table.

TABLE of Specific Refraction and Dispersion (LORENZ).

Sulphate.	Specific refraction, $\frac{n^2 - 1}{(n^2 + 2) d} = n$ .						Specific dispersion. $n_g - n_c$ .		
	For ray C (H $\alpha$ ).			For ray H $\gamma$ near G.					
	$\alpha$ .	$\beta$ .	$\gamma$ .	$\alpha$ .	$\beta$ .	$\gamma$ .	$\alpha$ .	$\beta$ .	$\gamma$ .
AmCo . . .	0.1515	0.1528	0.1549	0.1552	0.1565	0.1586	0.0037	0.0037	0.0037
KCo. . . .	0.1277	0.1290	0.1320	0.1304	0.1317	0.1349	0.0027	0.0027	0.0029
RbCo . . .	0.1144	0.1125	0.1144	0.1137	0.1148	0.1168	0.0023	0.0023	0.0024
CsCo. . . .	0.1040	0.1045	0.1053	0.1062	0.1067	0.1075	0.0022	0.0022	0.0022

TABLE of Molecular Refraction and Dispersion (LORENZ).

Salt.	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = m.$						Molecular dispersion. $m_G - m_C.$		
	For ray C (H $\alpha$ ).			For ray H $\gamma$ near G.					
	$\alpha.$	$\beta.$	$\gamma.$	$\alpha.$	$\beta.$	$\gamma.$	$\alpha.$	$\beta.$	$\gamma.$
KCo sulphate	55.43	56.00	57.33	56.61	57.17	58.57	1.18	1.17	1.24
RbCo     ,,	58.63	59.20	60.19	59.83	60.41	61.48	1.20	1.21	1.29
AmCo     ,,	59.43	59.95	60.77	60.89	61.40	62.22	1.46	1.45	1.45
CsCo     ,,	64.50	64.81	65.30	65.87	66.18	66.71	1.37	1.37	1.41

MOLECULAR Refraction (GLADSTONE and DALE).

Salt.	$\frac{n-1}{d} M$ for ray C.			Mean molecular refraction for ray C. $\frac{1}{3}(\alpha + \beta + \gamma).$
	$\alpha.$	$\beta.$	$\gamma.$	
KCo sulphate. . . . .	93.61	94.75	97.35	95.24
RbCo „ . . . . .	99.17	100.32	102.29	100.59
AmCo „ . . . . .	100.64	101.70	103.33	101.89
CsCo „ . . . . .	109.75	110.39	111.37	110.50

*Optic Axial Angle.*—The results with three pairs of section-plates perpendicular to the first and second median lines are given in the two next tables. The angle in air, although very large, was just clearly visible in all three of the plates ground perpendicular to the first median line, but the absorption at the blue end of the spectrum prevented trustworthy observations being obtained beyond the wave-length of Tl light.

APPARENT Optic Axial Angle in Air, 2E, of AmCo Sulphate.

Light.	Plate 1.	Plate 2.	Plate 3.	Mean 2E.
	° ' ,	° ' ,	° ' ,	° ' ,
Li . . . . .	156 1	157 34	155 16	156 17
C. . . . .	156 20	157 51	155 34	156 35
Na . . . . .	158 32	159 52	157 29	158 38
Tl . . . . .	160 40	162 0	159 40	160 47

A determination of 2E at 70° with Plate 1 gave the value 153° 5' for sodium light, indicating that the optic axial angle in air diminishes with rise of temperature to the extent of 5½° for 55° of rise.

## DETERMINATION of True Optic Axial Angle in Bromonaphthalene.

Light.	No. of plate perp. 1 M.L.	Observed $2H_a$ .	No. of plate perp. 2 M.L.	Observed $2H_o$ .	Calculated $2V_a$ .	Mean $2V_a$ .
Li . . . . .	1	72 31	1a	85 46	81 59	82 1
	2	72 53	2a	85 51	82 12	
	3	72 29	3a	85 55	81 53	
C . . . . .	1	72 30	1a	85 43	82 0	82 2
	2	72 51	2a	85 46	82 13	
	3	72 27	3a	85 50	81 54	
Na . . . . .	1	72 18	1a	85 16	82 6	82 9
	2	72 43	2a	85 22	82 20	
	3	72 16	3a	85 22	82 2	
Tl . . . . .	1	72 9	1a	84 48	82 16	82 17
	2	72 35	2a	84 58	82 28	
	3	72 4	3a	84 57	82 8	
Cd . . . . .	1	72 3	1a	84 33	82 20	82 21
	2	72 29	2a	84 43	82 32	
	3	71 58	3a	84 42	82 12	
F . . . . .	1	71 56	1a	84 14	82 26	82 27
	2	72 22	2a	84 24	82 38	
	3	71 51	3a	84 23	82 17	

MURMANN and ROTTER obtained  $155^{\circ} 12'$  for  $2E$ , and  $81^{\circ} 39'$  for  $2V_a$  (no specific wave-length).

*Dispersion of the Median Lines.*—The inclined dispersion is very minute, and is such that the first median line is nearer to the axis  $a$  by about eight minutes for red C-hydrogen light than for green thallium light. The determinations were carried out with Plates 1, 2 and 3 immersed in toluene, the refractive index of which (1.4955) is almost identical with the mean refraction (1.4962) of ammonium cobalt sulphate.

OPTIC AXIAL ANGLES  $2V_a$  of the Cobalt Group.

	KCo sulphate.	RbCo sulphate.	CsCo sulphate.	AmCo sulphate.
Li . . . . .	68 38	75 15	81 42	82 1
C . . . . .	68 39	75 14	81 40	82 2
Na . . . . .	68 41	75 11	81 34	82 9
Tl . . . . .	68 44	75 8	81 29	82 17
F . . . . .	68 48	75 3	81 22	82 27

The last table comparing the optic axial angles of the four cobalt-containing salts shows that the angle of the ammonium salt is just slightly greater than that of the caesium salt. All four salts are positive.

*Ammonium Manganese Sulphate*,  $(\text{NH}_4)_2 \text{Mn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ .*Morphology.*

Crystals of this salt were measured by MURMANN and ROTTER (*loc. cit.*, p. 148), and also to some extent by GRAILICH\* and by SCACCHI†. The results of MURMANN and ROTTER are given in the next to the last column of the table of angles, and those of GRAILICH (G) and of SCACCHI (S) in the last column.

*Crystal System.*—Monoclinic. Class No. 5, holohedral-prismatic.

*Ratios of Axes.*— $a : b : c = 0.7400 : 1 : 0.4931$ . Values of MURMANN and ROTTER,  $0.7359 : 1 : 0.4972$ .

*Axial Angle.*— $\beta = 106^\circ 51'$ . Value of MURMANN and ROTTER,  $107^\circ 2'$ .

*Forms observed.*— $a \{100\}$ ,  $b \{010\}$ ,  $c \{001\}$ ,  $p \{110\}$ ,  $p' \{120\}$ ,  $p''' \{130\}$ ,  $q \{011\}$ ,  $r' \{210\}$ ,  $o \{111\}$ ,  $o' \{1\bar{1}1\}$ . MURMANN and ROTTER also found a minute face of  $n' \{1\bar{2}1\}$  on one crystal.

*Habit.*—Prismatic (primary prism  $p \{110\}$ ) parallel axis  $c$ . The prisms are sometimes fairly long, but more frequently short.

Ten good crystals were measured, obtained from five different crops. The results are given in the table of angles. The crystals were beautifully transparent in the crops retained for use, but some other crops showed an appreciable amount of turbidity. They are not quite colourless, a faint pink tint appearing to be an essential property of the salt which in the cases of truly transparent crystals renders them very beautiful, especially when a number are seen together against a white background. Great care is required in growing them for goniometrical purposes, as crops grown without the precautions indicated in the author's "Crystallography and Practical Crystal Measurement" (p. 9) show more facial irregularities than many other salts of this series.

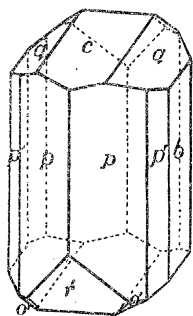


Fig. 6.

The primary prism  $p \{110\}$  is generally the largely predominating form, closely followed by the basal plane  $c \{001\}$ , as shown in fig. 1. Often, however, the latter form  $c$  is less prominent, the faces of  $q \{011\}$  being relatively larger and the orthopinakoid  $r' \{210\}$  being exceptionally well developed, as shown in fig. 6. Occasionally crystals were also seen, and one was measured, having large  $b \{010\}$  faces. The hemipyramid faces  $o' \{1\bar{1}1\}$  (common) and  $o \{111\}$  (rarer) were usually somewhat distorted, rarely giving images of the signal so good as those derived from the faces of other forms. The prismatic form  $p' \{120\}$  was fairly common, appearing as a strip, but the prism  $p''' \{130\}$  was much more rarely developed. The orthopinakoid  $a \{100\}$  was only once seen, and was then merely a fine narrow strip affording an image too faint for absolute measurement. The face  $n' \{1\bar{2}1\}$  recorded by MURMANN

\* 'Krystallogr.-optische Untersuchungen, Preisschr. Wien,' 1858, 140.

† 'Il Giambattista-Vico, Giornale Scientifico,' Naples, 1857, fasc. 6, sep. 9.

## INTERFACIAL Angles of Ammonium Manganese Sulphate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.	Values of	
						M. & R.	G. & S.
$ac = (100):(001)$	—	—	—	73 9	—	72 58	71 42 G.
$as = (100):(101)$	—	—	—	45 1	—	—	—
$sc = (101):(001)$	—	—	—	28 8	—	—	—
$cr' = (001):(201)$	10	64 7- 64 25	64 15	64 19	4	64 18	—
$cs' = (001):(101)$	—	—	—	38 20	—	—	—
$s'r' = (\bar{1}01):(201)$	—	—	—	25 59	—	—	—
$r'a = (201):(\bar{1}00)$	—	—	—	42 32	—	42 6	—
$r'c = (201):(001)$	10	115 33-116 0	115 45	115 41	4	—	—
$ap = (100):(110)$	—	—	—	35 18	—	35 40	—
$pp' = (110):(120)$	8	19 17- 19 33	19 27	19 28	1	19 17	—
$p'b = (120):(010)$	2	35 8- 35 22	35 15	35 14	1	35 25	—
$pp''' = (110):(130)$	—	—	—	29 29	—	—	—
$p''b = (130):(010)$	1	—	25 19	25 13	6	25 45	—
$pb = (110):(010)$	40	54 36- 54 55	54 42	*	—	54 57	—
$pp = (110):(\bar{1}\bar{1}0)$	21	70 22- 70 47	70 35	70 36	1	70 16	{ 70 35 G. 70 32 S.
$cq = (001):(011)$	29	25 4- 25 33	25 16	*	—	24 35	{ 24 55 G. 25 13 S.
$qb = (011):(010)$	18	64 31- 64 48	64 44	64 44	0	—	—
$ao = (100):(111)$	—	—	—	48 8	—	—	—
$oq = (111):(011)$	—	—	—	26 40	—	—	—
$aq = (100):(011)$	—	—	—	74 48	—	—	—
$qo' = (011):(\bar{1}\bar{1}1)$	1	—	34 34	34 38	4	—	—
$o'a = (\bar{1}\bar{1}1):(\bar{1}00)$	—	—	—	70 34	—	—	—
$co = (001):(111)$	1	—	33 41	33 38	3	—	—
$op = (111):(110)$	1	—	42 40	42 41	1	—	—
$cp = (001):(110)$	40	76 13- 76 30	76 19	*	—	—	76 24 S.
$po' = (110):(\bar{1}\bar{1}1)$	21	58 49- 59 24	59 4	59 10	6	—	—
$o'c = (\bar{1}\bar{1}1):(00\bar{1})$	20	44 27- 44 52	44 38	44 31	7	—	—
$bn = (010):(121)$	—	—	—	55 6	—	—	—
$no = (121):(111)$	—	—	—	15 40	—	—	—
$bo = (010):(111)$	—	—	—	70 46	—	—	—
$os = (111):(101)$	—	—	—	19 14	—	—	—
$bo' = (010):(\bar{1}\bar{1}1)$	1	—	65 16	65 21	5	—	—
$o's' = (\bar{1}\bar{1}1):(\bar{1}01)$	—	—	—	24 39	—	—	—
$o'o' = (\bar{1}\bar{1}1):(\bar{1}\bar{1}1)$	1	—	49 25	49 18	7	—	—
$sq = (101):(011)$	—	—	—	37 6	—	—	—
$qp = (011):(\bar{1}\bar{1}0)$	24	87 57- 88 28	88 9	88 8	1	—	—
$ps = (110):(\bar{1}01)$	—	—	—	54 46	—	—	—
$pq = (\bar{1}\bar{1}0):(0\bar{1}\bar{1})$	24	91 40- 92 4	91 50	91 52	2	—	—
$s'q = (\bar{1}01):(011)$	—	—	—	44 49	—	—	—
$qn = (011):(121)$	—	—	—	26 3	—	—	—
$np = (121):(110)$	—	—	—	36 31	—	—	—
$qp = (011):(110)$	25	62 24- 62 42	62 33	62 34	1	—	—
$ps' = (110):(\bar{1}0\bar{1})$	—	—	—	72 37	—	—	—
$pq = (110):(0\bar{1}\bar{1})$	24	117 23-117 41	117 28	117 26	2	—	—
$r'o' = (201):(\bar{1}\bar{1}1)$	11	34 51- 35 24	35 7	35 13	6	35 25	—
$o'p = (\bar{1}\bar{1}1):(110)$	16	91 34- 92 5	91 50	91 45	5	91 47	—
$pr' = (110):(20\bar{1})$	24	52 52- 53 26	53 6	53 2	4	52 22	—
Total number of measurements .	373						

and ROTTER was never seen on this salt, although the author has observed it on other salts of the series.

In the next three tables the morphological constants of the three salts containing manganese are compared. From the first table it will be observed that the axial angle  $\beta$  of the ammonium salt is fairly near to that of the caesium salt, and that the axial ratios of the ammonium and rubidium salts are also close to each other; the values for the ammonium salt clearly indicate the propriety of including this salt in this isomorphous series of double salts.

The impossibility of preparing potassium manganese sulphate renders as complete a comparison as usual of the interfacial angles of a group impossible; but the angles of the ammonium salt are very obviously related to those of the rubidium and caesium salts in a manner similar to that which has been observed in the other groups investigated, where the complete set of four salts has been obtained. Like the axial ratios, the angles indicate clearly that the ammonium salt does belong to the same series as the rubidium and caesium salts.

*Cleavage.*—There is an excellent cleavage parallel to the orthopinakoid  $r'\{\bar{2}01\}$ , and also a fairly good cleavage parallel to the clinopinakoid  $b\{010\}$ .

COMPARISON of the Axial Angles and Axial Ratios.

	Axial angle.	Axial ratios.
	$\beta$ .	$a : b : c$
Rubidium manganese sulphate .	$105^\circ 57'$	$0.7382 : 1 : 0.4950$
Ammonium     "     "     .	$106^\circ 51'$	$0.7400 : 1 : 0.4931$
Cæsium       "     "     .	$107^\circ 7'$	$0.7274 : 1 : 0.4913$

COMPARISON of the Interfacial Angles.

Angle.	RbMn sulphate.	CsMn sulphate.	AmMn sulphate.
$\left\{ \begin{array}{l} ac = (100) : (001) \\ as = (100) : (101) \\ sc = (101) : (001) \\ cr' = (001) : (201) \\ cs' = (001) : (\bar{1}01) \\ s'r' = (\bar{1}01) : (201) \\ r'a = (201) : (\bar{1}00) \end{array} \right.$	$\left\{ \begin{array}{l} 74 \ 3 \\ 45 \ 27 \\ 28 \ 36 \\ 63 \ 58 \\ 38 \ 23 \\ 25 \ 35 \\ 41 \ 59 \end{array} \right.$	$\left\{ \begin{array}{l} 72 \ 53 \\ 44 \ 37 \\ 28 \ 16 \\ 64 \ 55 \\ 38 \ 48 \\ 26 \ 7 \\ 42 \ 12 \end{array} \right.$	$\left\{ \begin{array}{l} 73 \ 9 \\ 45 \ 1 \\ 28 \ 8 \\ 64 \ 19 \\ 38 \ 20 \\ 25 \ 59 \\ 42 \ 32 \end{array} \right.$
$\left\{ \begin{array}{l} ap = (100) : (110) \\ pp' = (110) : (120) \\ p'b = (120) : (010) \\ pb = (110) : (010) \end{array} \right.$	$\left\{ \begin{array}{l} 35 \ 20 \\ 19 \ 28 \\ 35 \ 12 \\ 54 \ 40 \end{array} \right.$	$\left\{ \begin{array}{l} 34 \ 51 \\ 19 \ 28 \\ 35 \ 41 \\ 55 \ 9 \end{array} \right.$	$\left\{ \begin{array}{l} 35 \ 18 \\ 19 \ 28 \\ 35 \ 14 \\ 54 \ 42 \end{array} \right.$
$\left\{ \begin{array}{l} cq = (001) : (011) \\ qb = (011) : (010) \end{array} \right.$	$\left\{ \begin{array}{l} 25 \ 30 \\ 64 \ 30 \end{array} \right.$	$\left\{ \begin{array}{l} 25 \ 11 \\ 64 \ 49 \end{array} \right.$	$\left\{ \begin{array}{l} 25 \ 16 \\ 64 \ 44 \end{array} \right.$

## COMPARISON of the Interfacial Angles (continued).

Angle.	RbMn sulphate.	CsMn sulphate.	AmMn sulphate.
$\left\{ \begin{array}{l} ao = (100) : (111) \\ oq = (111) : (011) \\ aq = (100) : (011) \\ qo' = (011) : (\bar{1}11) \\ o'a = (\bar{1}11) : (100) \end{array} \right.$	$\left\{ \begin{array}{l} 48 \ 34 \\ 27 \ 4 \\ 75 \ 38 \\ 34 \ 40 \\ 69 \ 42 \end{array} \right.$	$\left\{ \begin{array}{l} 47 \ 43 \\ 26 \ 50 \\ 74 \ 33 \\ 35 \ 5 \\ 70 \ 22 \end{array} \right.$	$\left\{ \begin{array}{l} 48 \ 8 \\ 26 \ 40 \\ 74 \ 48 \\ 34 \ 38 \\ 70 \ 34 \end{array} \right.$
$\left\{ \begin{array}{l} co = (001) : (111) \\ op = (111) : (110) \\ cp = (001) : (110) \\ po' = (110) : (\bar{1}11) \\ o'c = (\bar{1}11) : (001) \end{array} \right.$	$\left\{ \begin{array}{l} 34 \ 6 \\ 42 \ 57 \\ 77 \ 3 \\ 58 \ 25 \\ 44 \ 32 \end{array} \right.$	$\left\{ \begin{array}{l} 33 \ 38 \\ 42 \ 23 \\ 76 \ 1 \\ 59 \ 8 \\ 44 \ 51 \end{array} \right.$	$\left\{ \begin{array}{l} 33 \ 38 \\ 42 \ 41 \\ 76 \ 19 \\ 59 \ 10 \\ 44 \ 31 \end{array} \right.$
$\left\{ \begin{array}{l} bo = (010) : (111) \\ os = (111) : (101) \end{array} \right.$	$\left\{ \begin{array}{l} 70 \ 34 \\ 19 \ 26 \end{array} \right.$	$\left\{ \begin{array}{l} 70 \ 58 \\ 19 \ 2 \end{array} \right.$	$\left\{ \begin{array}{l} 70 \ 46 \\ 19 \ 14 \end{array} \right.$
$\left\{ \begin{array}{l} bo' = (010) : (\bar{1}11) \\ o's' = (\bar{1}11) : (101) \end{array} \right.$	$\left\{ \begin{array}{l} 65 \ 25 \\ 24 \ 35 \end{array} \right.$	$\left\{ \begin{array}{l} 65 \ 27 \\ 24 \ 33 \end{array} \right.$	$\left\{ \begin{array}{l} 65 \ 21 \\ 24 \ 39 \end{array} \right.$
$\left\{ \begin{array}{l} sq = (101) : (011) \\ qp = (011) : (\bar{1}10) \\ ps = (\bar{1}10) : (101) \end{array} \right.$	$\left\{ \begin{array}{l} 37 \ 35 \\ 87 \ 20 \\ 55 \ 5 \end{array} \right.$	$\left\{ \begin{array}{l} 37 \ 9 \\ 88 \ 36 \\ 54 \ 15 \end{array} \right.$	$\left\{ \begin{array}{l} 37 \ 6 \\ 88 \ 8 \\ 54 \ 46 \end{array} \right.$
$\left\{ \begin{array}{l} s'q = (\bar{1}01) : (011) \\ qp = (011) : (110) \\ ps' = (\bar{1}10) : (101) \end{array} \right.$	$\left\{ \begin{array}{l} 44 \ 58 \\ 63 \ 10 \\ 71 \ 52 \end{array} \right.$	$\left\{ \begin{array}{l} 45 \ 9 \\ 62 \ 30 \\ 72 \ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 44 \ 49 \\ 62 \ 34 \\ 72 \ 37 \end{array} \right.$
$\left\{ \begin{array}{l} r'o' = (\bar{2}01) : (\bar{1}11) \\ o'p = (\bar{1}11) : (110) \\ pr' = (110) : (201) \end{array} \right.$	$\left\{ \begin{array}{l} 34 \ 54 \\ 92 \ 26 \\ 52 \ 40 \end{array} \right.$	$\left\{ \begin{array}{l} 35 \ 14 \\ 92 \ 13 \\ 52 \ 33 \end{array} \right.$	$\left\{ \begin{array}{l} 35 \ 13 \\ 91 \ 45 \\ 53 \ 2 \end{array} \right.$

## Volume.

*Relative Density.*—Five determinations by the immersion method yielded the following results :—

I. Density for $16^{\circ}2/4^{\circ}$	. . . 1.8324	For $20^{\circ}/4^{\circ}$	. . . 1.8317
II. „ $15^{\circ}7/4^{\circ}$	. . . 1.8300	„ $20^{\circ}/4^{\circ}$	. . . 1.8292
III. „ $16^{\circ}1/4^{\circ}$	. . . 1.8319	„ $20^{\circ}/4^{\circ}$	. . . 1.8312
IV. „ $17^{\circ}6/4^{\circ}$	. . . 1.8312	„ $20^{\circ}/4^{\circ}$	. . . 1.8308
V. „ $17^{\circ}3/4^{\circ}$	. . . 1.8329	„ $20^{\circ}/4^{\circ}$	. . . 1.8324

Mean . . . 1.8311

Accepted value for  $20^{\circ}/4^{\circ}$ , **1.831**.

A determination by SCHROEDER\* gave the density 1.825.

*Molecular Volume.*— $\frac{M}{d} = \frac{388.42}{1.831} = 212.13$ .

\* 'Journ. für Prakt. Chemie,' 1879, [2], 19, 266.

*Molecular Distance Ratios (topic axial ratios).—*

$$\chi : \psi : \omega = 6.2670 : 8.4690 : 4.1761.$$

*Redeterminations of Densities of Rubidium and Cæsium Manganese Sulphates.**Rubidium Manganese Sulphate,  $\text{Rb}_2\text{Mn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ .*

I.	Density for $14^\circ 9/4^\circ$	. . .	2.4617	For $20^\circ/4^\circ$	. . .	2.4605
II.	„ $16^\circ 5/4^\circ$	. . .	2.4613	„ $20^\circ/4^\circ$	. . .	2.4604
III.	„ $16^\circ 1/4^\circ$	. . .	2.4607	„ $20^\circ/4^\circ$	. . .	2.4597
IV.	„ $16^\circ 6/4^\circ$	. . .	2.4622	„ $20^\circ/4^\circ$	. . .	2.4614
						Mean . . . 2.4605

Accepted value for  $20^\circ/4^\circ$ , **2.461**. Former pyknometer value 2.459.

*Cæsium Manganese Sulphate,  $\text{Cs}_2\text{Mn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ .*

I.	Density for $18^\circ 9/4^\circ$	. . .	2.7397	For $20^\circ/4^\circ$	. . .	2.7394
II.	„ $19^\circ 3/4^\circ$	. . .	2.7420	„ $20^\circ/4^\circ$	. . .	2.7418
III.	„ $19^\circ 7/4^\circ$	. . .	2.7409	„ $20^\circ/4^\circ$	. . .	2.7408
IV.	„ $17^\circ 2/4^\circ$	. . .	2.7373	„ $20^\circ/4^\circ$	. . .	2.7365
						Mean . . . 2.7396

Accepted value for  $20^\circ/4^\circ$ , **2.740**. Former pyknometer value 2.738.

The next table affords a comparison of the volume constants of the three salts, employing the new densities.

**VOLUME Constants of the Manganese Group.**

Salt.	Molecular weight.	Specific gravity.	Molecular volume.	Topic axial ratios.
RbMn sulphate . .	522.36	2.461	212.26	$\chi : \psi : \omega$ 6.2404 : 8.4536 : 4.1846
$\text{NH}_4\text{Mn}$ „ . .	388.42	1.831	212.13	6.2670 : 8.4690 : 4.1761
CsMn „ . .	616.36	2.740	224.95	6.3286 : 8.7004 : 4.2745

From this table it will be apparent that the molecular volume and topic axial ratios of ammonium manganese sulphate are very close to the values of these constants for the rubidium salt. The molecular volume and the ratio  $\omega$  are very slightly lower, and the ratios  $\chi$  and  $\psi$  slightly higher.

*Optics.*

*Orientation of the Optical Ellipsoid.*—The symmetry plane  $b\{010\}$  is the plane of the optic axes, and the sign of double refraction is positive. The first median line is the axis  $\gamma$  of the optical indicatrix, and the second median line corresponds to the  $\alpha$  refractive index.



A pair of section-plates parallel to the symmetry plane afforded the following angles for the extinction direction corresponding to the second median line :—

*Inclination of 2M.L. from normal to  $c$  {001}.*

Plate 1 . . .	9° 24'	Plate 2 . . .	9° 6'
Mean . . .	9° 15'		

The direction is behind the normal. As the axial angle  $ac = 73^\circ 9'$  this extinction direction is  $7^\circ 36'$  in front of the vertical axis  $c$ , and the first median line extinction is  $9^\circ 15'$  above the axis  $a$ , both axes of the optical indicatrix which lie in the symmetry plane being thus in the obtuse angle of the morphological axes  $ac$ . MURMANN and ROTTER found the two extinctions  $8^\circ 36'$  in front of  $c$ , and  $8^\circ 26'$  above  $a$ . In the next table the positions of the optical indicatrix of the three manganese salts are compared, and in fig. 7 they are graphically illustrated.

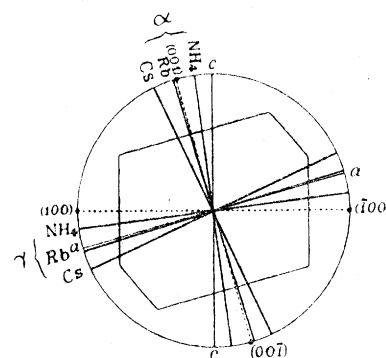


Fig. 7.

*Inclinations of  $\alpha$  Axis of Indicatrix (2M.L.) of the Manganese Salts in front of Axis  $c$ .*

AmMn sulphate	7° 36'
RbMn	16° 57'
CsMn	25° 27'

Although the potassium salt is missing, the relations of the indicatrices of the ammonium, rubidium, and caesium manganese salts are similar to what has been observed in groups which are complete, the ammonium salt indicatrix standing with its  $\alpha$ -axis nearest to the vertical axis of the crystal  $c$ .

*Refractive Indices.*—The results with six prisms, each ground so as to afford directly two indices, are given in the accompanying table.

REFRACTIVE INDICES OF AMMONIUM MANGANESE SULPHATE.

Light.	$\alpha$ .	$\beta$ .	$\gamma$ .
Li . . . . .	1.4770	1.4810	1.4882
C . . . . .	1.4775	1.4815	1.4887
Na . . . . .	1.4801	1.4840	1.4913
Tl . . . . .	1.4827	1.4865	1.4940
Cd . . . . .	1.4842	1.4881	1.4956
F . . . . .	1.4858	1.4897	1.4971
G . . . . .	1.4912	1.4951	1.5025

Mean of  $\alpha$ ,  $\beta$ , and  $\gamma$  for Na light = 1.4851.

$\alpha$  = Vibration direction parallel to second median line,  $7^\circ 36'$  in front of axis  $c$ .

$\beta$  = " " " " symmetry axis  $b$ .

$\gamma$  = " " " " first median line.

MURMANN and ROTTER obtained for  $\beta$  in red light 1.482, in yellow light 1.484, and in green light 1.485.

General Formula for  $\beta$ , corrected to a vacuum :—

$$\beta = 1.4691 + \frac{633\,924}{\lambda^2} - \frac{3\,568\,840\,000\,000}{\lambda^4} + \dots$$

The index  $\alpha$  is also reproduced by the formula if the constant 1.4691 is diminished by 0.0039, and the  $\gamma$  index if the constant is increased by 0.0073.

Observations at 70° showed that the refractive indices of ammonium manganese sulphate diminish by about 0.0019 (for  $\alpha$ ) to 0.0021 (for  $\gamma$ ) for 55° rise of temperature.

In the next table the refractive indices of the three salts containing manganese are compared.

COMPARISON of the Refractive Indices.

Index.	Light.	RbMn sulphate.	NH <sub>4</sub> Mn sulphate.	CsMn sulphate.
$\alpha$ . . . . .	Li. . . . .	1.4741	1.4770	1.4918
	C . . . . .	1.4745	1.4775	1.4922
	Na . . . . .	1.4767	1.4801	1.4946
	Tl. . . . .	1.4791	1.4827	1.4972
	F . . . . .	1.4821	1.4858	1.5003
	G . . . . .	1.4864	1.4912	1.5046
$\beta$ . . . . .	Li. . . . .	1.4781	1.4810	1.4936
	C . . . . .	1.4785	1.4815	1.4940
	Na . . . . .	1.4807	1.4840	1.4966
	Tl. . . . .	1.4831	1.4865	1.4991
	F . . . . .	1.4860	1.4897	1.5022
	G . . . . .	1.4907	1.4951	1.5066
$\gamma$ . . . . .	Li. . . . .	1.4880	1.4882	1.4995
	C . . . . .	1.4884	1.4887	1.4999
	Na . . . . .	1.4907	1.4913	1.5025
	Tl. . . . .	1.4933	1.4940	1.5051
	F . . . . .	1.4965	1.4971	1.5083
	G . . . . .	1.5015	1.5025	1.5129
Mean refractive index $\frac{1}{3}(\alpha + \beta + \gamma)$ for Na light		1.4827	1.4851	1.4979
Double refraction, $\text{Na}_{\gamma-\alpha}$ . . . . .		0.0140	0.0112	0.0079

The position of the ammonium salt as regards refractive indices is precisely similar to that in the nickel and cobalt groups already dealt with, namely, just beyond that of the rubidium salt, the indices of which are only very slightly lower. The ammonium salt also occupies an intermediate position between the rubidium and

cæsium salts as regards double refraction, the value being slightly nearer to that of the rubidium salt.

*Axial Ratios of the Optical Ellipsoid.*—These are given in the next table, and compared with the corresponding values for rubidium and cæsium manganese sulphates.

		AXIAL Ratios of					
		Optical Indicatrix.			Optical Velocity Ellipsoid.		
		$\alpha$	$:\beta:$	$\gamma$	$a$	$b:$	$c$
RbMn	sulphate . . .	0.9973	: 1 :	1.0067	1.0027	: 1 :	0.9933
NH <sub>4</sub> Mn	„ . . .	0.9974	: 1 :	1.0049	1.0026	: 1 :	0.9951
CsMn	„ . . .	0.9987	: 1 :	1.0039	1.0013	: 1 :	0.9961

The values when  $\beta$  for the same salt = 1 show a similar arrangement as in the groups previously described, with the ammonium salt intermediate between the rubidium and cæsium salts. The potassium salt not existing, the values cannot be calculated on the basis of  $\beta_{K \text{ salt}} = 1$ .

*Molecular Optical Constants.*—These are given in the following three tables, and compared with the analogous values for the rubidium and cæsium salts, using the newly determined values of the densities of the latter salts in the calculations for these salts. The specific refraction and dispersion of the ammonium salt again stand out prominently higher than those of the alkali-metal salts, and the molecular dispersion of ammonium manganese sulphate is slightly higher than that of the cæsium salt. The molecular refraction, calculated by either formula, of the ammonium salt is just slightly higher than that of the rubidium salt, the relationship being very concisely expressed by the mean molecular refraction shown at the conclusion of the third table.

TABLE of Specific Refraction and Dispersion (LORENZ).

Sulphate.	Specific refraction, $\frac{n^2-1}{(n^2+2)d} = n$ .						Specific dispersion, $n_G - n_C$ .		
	For ray C(H $\alpha$ ).			For ray H $\gamma$ near G.					
	$\alpha$ .	$\beta$ .	$\gamma$ .	$\alpha$ .	$\beta$ .	$\gamma$ .	$\alpha$ .	$\beta$ .	$\gamma$ .
AmMn . . .	0.1545	0.1556	0.1576	0.1582	0.1593	0.1613	0.0037	0.0037	0.0037
RbMn . . .	0.1143	0.1151	0.1172	0.1167	0.1176	0.1198	0.0024	0.0025	0.0026
CsMn . . .	0.1059	0.1062	0.1073	0.1082	0.1085	0.1097	0.0023	0.0023	0.0024

TABLE of Molecular Refraction and Dispersion (LORENZ).

Salt.	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = m.$						Molecular dispersion, $m_G - m_C.$		
	For ray C (Hz).			For ray H $\gamma$ near G.					
	$\alpha.$	$\beta.$	$\gamma.$	$\alpha.$	$\beta.$	$\gamma.$	$\alpha.$	$\beta.$	$\gamma.$
RbMn sulphate	59·70	60·13	61·19	60·98	61·44	62·59	1·28	1·31	1·40
AmMn       ,,	59·99	60·42	61·20	61·46	61·87	62·66	1·47	1·45	1·46
CsMn       ,,	65·29	65·48	66·15	66·67	66·90	67·60	1·38	1·42	1·45

MOLECULAR Refraction (GLADSTONE and DALE).

Salt.	$\frac{n-1}{d} M$ for ray C.			Mean molecular refraction for ray C. $\frac{1}{3}(\alpha + \beta + \gamma).$
	$\alpha.$	$\beta.$	$\gamma.$	
RbMn sulphate . . . . .	100·72	101·56	103·65	101·98
AmMn „ . . . . .	101·29	102·14	103·67	102·37
CsMn „ . . . . .	110·72	111·12	112·45	111·43

*Optic Axial Angle.*—The determinations with three pairs of excellent section-plates are given in the two following tables.

APPARENT Optic Axial Angle in Air, 2E, of AmMn Sulphate.

Light.	Plate 1.	Plate 2.	Plate 3.	Mean 2E.
Li . . . . .	115 46	115 22	114 57	115 22
C . . . . .	115 58	115 31	115 6	115 32
Na . . . . .	116 51	116 8	116 9	116 23
Tl . . . . .	117 18	116 53	116 50	117 0
Cd . . . . .	117 43	117 2	116 59	117 15
F . . . . .	118 5	117 25	117 10	117 33

## DETERMINATION of True Optic Axial Angle in Bromonaphthalene.

Light.	No. of plate perp. 1 M.L.	Observed 2H <sub>a</sub> .	No. of plate perp. 2 M.L.	Observed 2H <sub>a</sub> .	Calculated 2V <sub>a</sub> .	Mean 2V <sub>a</sub> .
Li . . . . .	1	61 34	1a	94 26	69 47	69 45
	2	61 34	2a	94 29	69 45	
	3	61 29	3a	94 24	69 44	
C . . . . .	1	61 31	1a	94 21	69 47	69 46
	2	61 32	2a	94 25	69 46	
	3	61 28	3a	94 20	69 45	
Na . . . . .	1	61 18	1a	93 52	69 48	69 49
	2	61 22	2a	94 0	69 48	
	3	61 21	3a	93 53	69 51	
Tl . . . . .	1	61 9	1a	93 27	69 53	69 54
	2	61 13	2a	93 25	69 57	
	3	61 8	3a	93 26	69 53	
Cd . . . . .	1	61 0	1a	92 58	69 58	70 0
	2	61 5	2a	92 59	70 2	
	3	61 3	3a	92 58	70 1	
F . . . . .	1	60 50	1a	92 38	70 0	70 2
	2	60 54	2a	92 38	70 3	
	3	60 54	3a	92 37	70 3	

MURMANN and ROTTER obtained for 2E 114° 45', and for 2V<sub>a</sub> 69° 9' (no wave-length specified).

A determination of 2E at 70° with Plate 2 showed that the optic axial angle in air diminishes by about 4° for 55° rise of temperature.

*Dispersion of the Median Lines.*—The inclined dispersion is again small in ammonium manganese sulphate, the first median line lying nearer by 10' only to the axis *a* for red lithium light than for greenish-blue F light. The determination was carried out by immersion of the Plates 1, 2, and 3 in toluene.

The optic axial angle of ammonium manganese sulphate is shown in the following comparative table to be slightly larger than that of the rubidium salt.

OPTIC Axial Angles 2V<sub>a</sub> of the Manganese Group.

	AmMn sulphate.	RbMn sulphate.	CsMn sulphate.
Li . . . . .	69 45	67 10	60 10
C . . . . .	69 46	67 8	60 7
Na . . . . .	69 49	67 5	59 57
Tl . . . . .	69 54	67 1	59 46
F . . . . .	70 2	66 55	59 28

*Ammonium Copper Sulphate*,  $(\text{NH}_4)_2 \text{Cu} (\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ .*Morphology.*

Crystals of this salt were measured in the year 1835 by MILLER,\* who observed the forms  $a$ ,  $c$ ,  $p$ ,  $q$ ,  $r'$ , and  $o'$ , of those enumerated in the list of forms given below. MURMANN and ROTTER included the salt in their optical investigation of 1859 (*loc. cit.*, p. 170), and observed the further forms  $b$  and  $p'$ ; but they did not record any accurate measurements of the crystal angles. MILLER's values are quoted in the last column of the table of angles now given.

*Crystal System.*—Monoclinic Class No. 5, holohedral-prismatic.

*Ratios of Axes.*—

$a : b : c = 0.7463 : 1 : 0.5066$ . Values of MILLER,  $0.7433 : 1 : 0.4838$ .

*Axial Angle.*— $\beta = 106^\circ 9'$ . Value of MILLER,  $106^\circ 6'$ .

*Forms observed.*— $a \{100\}$ ,  $b \{010\}$ ,  $c \{001\}$ ,  $p \{110\}$ ,  $p' \{120\}$ ,  $p''' \{130\}$ ,  $q \{011\}$ ,  $r' \{\bar{2}01\}$ ,  $o \{111\}$ ,  $o' \{\bar{1}11\}$ .

*Habit.*—Short prismatic parallel to  $p \{110\}$ , or tabular parallel to  $c \{001\}$ .

Eleven perfectly transparent crystals were measured of this beautiful pale blue salt, selected from seven different crops. They were of the two types shown in figs. 8 and 9, and of intermediate types.

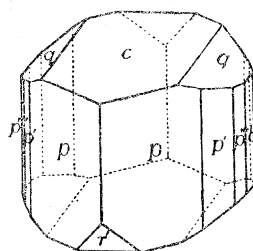


Fig. 8.

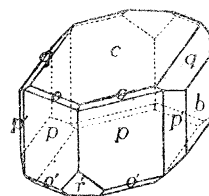


Fig. 9.

Many crystals of the numerous crops prepared were very simple, exhibiting only the forms  $c \{001\}$ ,  $p \{110\}$ ,  $q \{011\}$ , and  $r' \{\bar{2}01\}$ . On numerous others small or narrow representatives of the other forms mentioned in the list of forms were present. On a good number of the crystals of the crops from which individuals were selected for measurement there were well developed faces of the clinopinakoid  $b \{010\}$ , the rarer prisms  $p' \{120\}$  and  $p''' \{130\}$ , and the hemipyramids  $o \{111\}$  and  $o' \{\bar{1}11\}$ . Traces only of the orthopinakoid  $a \{100\}$  were observed, no measurements being possible. The variation of the length of the faces of the prism zone causes the variation of habit from prismatic along  $p \{110\}$  to tabular parallel to  $c \{001\}$ . Both these forms showed striation in many of the crops prepared, but the crops used were composed of crystals exhibiting this property at a minimum, and several of the measured crystals were quite free from striation. The face in contact with the bottom of the crystallising vessel had been either  $p$  or  $c$ .

\* 'Phil. Mag.' 1835, [3], 6, 105; 'Pogg. Ann. der Phy.', 1835, 36, 477.

## INTERFACIAL Angles of Ammonium Copper Sulphate.

Angle.	No. of measure- ments.	Limits.	Mean observed.	Calcu- lated.	Diff.	Values of MILLER.
$\left\{ \begin{array}{l} ac = (100):(001) \\ as = (100):(101) \\ sc = (101):(001) \end{array} \right.$	—	—	—	73 51 45 5 28 46	—	73 54 — —
$\left\{ \begin{array}{l} cr' = (001):(201) \\ cs' = (001):(101) \end{array} \right.$	6	64 37- 64 42	64 38	64 33 38 51	5	64 54 —
$\left\{ \begin{array}{l} sr' = (101):(201) \\ r'a = (201):(100) \end{array} \right.$	—	—	—	25 42 41 36	—	— —
$r'c = (201):(001)$	3	115 17-115 23	115 22	115 27	5	—
$\left\{ \begin{array}{l} ap = (100):(110) \\ pp' = (110):(120) \end{array} \right.$	—	—	—	35 38 19 26	—	— —
$\left\{ \begin{array}{l} pb = (120):(010) \\ p'p''' = (120):(130) \end{array} \right.$	3 2	19 26- 19 26 34 42- 35 1	19 26 34 52	19 28 34 54	2	— —
$\left\{ \begin{array}{l} pp''' = (110):(130) \\ p'''b = (130):(010) \end{array} \right.$	1 1	—	9 53 29 24	9 58 29 26	5 2	— —
$\left\{ \begin{array}{l} pb = (110):(010) \\ pp = (110):(110) \end{array} \right.$	24 19	54 8- 54 37 71 4- 71 27	54 22 71 16	* 71 16	—	— 71 4
$\left\{ \begin{array}{l} cq = (001):(011) \\ qb = (011):(010) \end{array} \right.$	29 29	25 34- 26 16 63 40- 64 27	25 57 64 3	* 64 3	— 0	26 10 —
$\left\{ \begin{array}{l} ao = (100):(111) \\ oq = (111):(011) \end{array} \right.$	— 1	—	— 27 8	48 21 27 10	— 2	— —
$\left\{ \begin{array}{l} aq = (100):(011) \\ qo' = (011):(111) \end{array} \right.$	— 1	—	— 34 59	75 31 34 54	— 5	— —
$o'a = (111):(100)$	—	—	—	69 35	—	69 11
$\left\{ \begin{array}{l} co = (001):(111) \\ op = (111):(110) \end{array} \right.$	4 5	34 12- 34 32 42 21- 42 29	34 26 42 27	34 24 42 32	2 5	— —
$\left\{ \begin{array}{l} cp = (001):(110) \\ po' = (110):(111) \end{array} \right.$	40 1	76 41- 77 12 —	76 56 57 52	* 57 59	— 7	— —
$o'c = (111):(001)$	1	—	45 12	45 5	7	45 31
$\left\{ \begin{array}{l} bn = (010):(121) \\ no = (121):(111) \end{array} \right.$	— —	—	—	54 21 15 55	—	— —
$\left\{ \begin{array}{l} bo = (010):(111) \\ os = (111):(101) \end{array} \right.$	1 —	—	70 17 —	70 16 19 44	1	— —
$\left\{ \begin{array}{l} bo' = (010):(111) \\ o's' = (111):(101) \end{array} \right.$	1 —	—	64 57 —	64 57 25 3	0	— —
$\left\{ \begin{array}{l} o'o' = (111):(111) \\ sq = (101):(011) \end{array} \right.$	— —	—	—	50 6 37 59	—	— —
$\left\{ \begin{array}{l} qp = (011):(110) \\ ps = (110):(101) \end{array} \right.$	17 —	86 38- 87 23 —	87 4 —	87 2 54 59	2	— —
$pq = (110):(011)$	16	92 40- 93 7	92 56	92 58	2	—
$\left\{ \begin{array}{l} s'q = (101):(011) \\ qn = (011):(121) \end{array} \right.$	— —	—	—	45 33 26 26	—	— —
$\left\{ \begin{array}{l} np = (121):(110) \\ qp = (011):(110) \end{array} \right.$	— 21	— 62 32- 62 57	— 62 44	36 18 62 44	— 0	— —
$\left\{ \begin{array}{l} ps' = (110):(101) \\ pq = (110):(011) \end{array} \right.$	— 20	— 117 0-117 32	— 117 16	71 43 117 16	— 0	— —
$\left\{ \begin{array}{l} r'o' = (201):(111) \\ op = (111):(110) \end{array} \right.$	1 1	—	35 12 92 16	35 16 92 9	4 7	— —
$pr' = (110):(201)$	7	52 23- 52 42	52 31	52 35	4	—
Total number of measurements . .	256					

In the three following tables the morphological constants of the four salts containing copper are compared. The first shows that the axial angles of the ammonium and caesium copper salts are almost identical, and that the axial ratios are such as place the ammonium salt indubitably in the same isomorphous series with the alkali-metal salts.

COMPARISON of the Axial Angles and Axial Ratios.

	Axial angle.	Axial ratios.
	$\beta$ .	$a : b : c$
Potassium copper sulphate . .	$104^{\circ} 28'$	$0.7490 : 1 : 0.5088$
Rubidium " " . .	$105^{\circ} 18'$	$0.7490 : 1 : 0.5029$
Ammonium " " . .	$106^{\circ} 9'$	$0.7463 : 1 : 0.5066$
Cæsium " " . .	$106^{\circ} 10'$	$0.7429 : 1 : 0.4946$

COMPARISON of the Interfacial Angles.

Angle.	KCu sulphate.	RbCu sulphate.	CsCu sulphate.	AmCu sulphate.
	$^{\circ} \quad '$	$^{\circ} \quad '$	$^{\circ} \quad '$	$^{\circ} \quad '$
$\left\{ \begin{array}{l} ac = (100) : (001) \\ as = (100) : (101) \\ sc = (101) : (001) \end{array} \right.$	$\begin{array}{l} 75 \ 32 \\ 46 \ 11 \\ 29 \ 21 \end{array}$	$\begin{array}{l} 74 \ 42 \\ 45 \ 53 \\ 28 \ 49 \end{array}$	$\begin{array}{l} 73 \ 50 \\ 45 \ 29 \\ 28 \ 21 \end{array}$	$\begin{array}{l} 73 \ 51 \\ 45 \ 5 \\ 28 \ 46 \end{array}$
$\left\{ \begin{array}{l} cr' = (001) : (201) \\ cs' = (001) : (101) \\ s'r' = (101) : (201) \end{array} \right.$	$\begin{array}{l} 63 \ 19 \\ 38 \ 22 \\ 24 \ 57 \end{array}$	$\begin{array}{l} 63 \ 30 \\ 38 \ 12 \\ 25 \ 18 \end{array}$	$\begin{array}{l} 63 \ 50 \\ 38 \ 9 \\ 25 \ 41 \end{array}$	$\begin{array}{l} 64 \ 33 \\ 38 \ 51 \\ 25 \ 42 \end{array}$
$r'a = (201) : (100)$	$41 \ 9$	$41 \ 48$	$42 \ 20$	$41 \ 36$
$\left\{ \begin{array}{l} ap = (100) : (110) \\ pp' = (110) : (120) \\ p'b = (120) : (010) \end{array} \right.$	$\begin{array}{l} 35 \ 59 \\ 19 \ 28 \\ 34 \ 33 \end{array}$	$\begin{array}{l} 35 \ 52 \\ 19 \ 28 \\ 34 \ 40 \end{array}$	$\begin{array}{l} 35 \ 30 \\ 19 \ 28 \\ 35 \ 2 \end{array}$	$\begin{array}{l} 35 \ 38 \\ 19 \ 28 \\ 34 \ 54 \end{array}$
$\left\{ \begin{array}{l} p'p'' = (120) : (130) \\ p''b = (130) : (010) \\ pb = (110) : (010) \end{array} \right.$	$\begin{array}{l} 9 \ 54 \\ 24 \ 39 \\ 54 \ 1 \end{array}$	$\begin{array}{l} 9 \ 55 \\ 24 \ 45 \\ 54 \ 8 \end{array}$	$\begin{array}{l} 9 \ 59 \\ 25 \ 3 \\ 54 \ 30 \end{array}$	$\begin{array}{l} 9 \ 58 \\ 24 \ 56 \\ 54 \ 22 \end{array}$
$\left\{ \begin{array}{l} cq = (001) : (011) \\ qb = (011) : (010) \end{array} \right.$	$\begin{array}{l} 26 \ 11 \\ 63 \ 49 \end{array}$	$\begin{array}{l} 25 \ 54 \\ 64 \ 6 \end{array}$	$\begin{array}{l} 25 \ 24 \\ 64 \ 36 \end{array}$	$\begin{array}{l} 25 \ 57 \\ 64 \ 3 \end{array}$
$\left\{ \begin{array}{l} ao = (100) : (111) \\ oq = (111) : (011) \\ aq = (100) : (011) \end{array} \right.$	$\begin{array}{l} 49 \ 28 \\ 27 \ 35 \\ 77 \ 3 \end{array}$	$\begin{array}{l} 49 \ 5 \\ 27 \ 11 \\ 76 \ 16 \end{array}$	$\begin{array}{l} 48 \ 36 \\ 26 \ 50 \\ 75 \ 26 \end{array}$	$\begin{array}{l} 48 \ 21 \\ 27 \ 10 \\ 75 \ 31 \end{array}$
$\left\{ \begin{array}{l} qo' = (011) : (111) \\ o'a = (111) : (100) \end{array} \right.$	$\begin{array}{l} 34 \ 30 \\ 68 \ 27 \end{array}$	$\begin{array}{l} 34 \ 24 \\ 69 \ 20 \end{array}$	$\begin{array}{l} 34 \ 28 \\ 70 \ 6 \end{array}$	$\begin{array}{l} 34 \ 54 \\ 69 \ 35 \end{array}$
$\left\{ \begin{array}{l} co = (001) : (111) \\ op = (111) : (110) \\ cp = (001) : (110) \end{array} \right.$	$\begin{array}{l} 35 \ 6 \\ 43 \ 14 \\ 78 \ 20 \end{array}$	$\begin{array}{l} 34 \ 31 \\ 43 \ 8 \\ 77 \ 39 \end{array}$	$\begin{array}{l} 33 \ 55 \\ 42 \ 59 \\ 76 \ 54 \end{array}$	$\begin{array}{l} 34 \ 24 \\ 42 \ 32 \\ 76 \ 56 \end{array}$
$\left\{ \begin{array}{l} po' = (110) : (11\bar{1}) \\ o'c = (11\bar{1}) : (00\bar{1}) \end{array} \right.$	$\begin{array}{l} 56 \ 58 \\ 44 \ 42 \end{array}$	$\begin{array}{l} 57 \ 50 \\ 44 \ 31 \end{array}$	$\begin{array}{l} 58 \ 44 \\ 44 \ 22 \end{array}$	$\begin{array}{l} 57 \ 59 \\ 45 \ 5 \end{array}$



## COMPARISON of the Interfacial Angles (continued).

Angle.	KCu sulphate.	RbCu sulphate.	CsCu sulphate.	AmCu sulphate.
	° ' "	° ' "	° ' "	° ' "
$\left\{ \begin{array}{l} bo = (010):(111) \\ os = (111):(101) \end{array} \right.$	69 50 20 10	70 8 19 52	70 34 19 26	70 16 19 44
$\left\{ \begin{array}{l} bo' = (010):(\bar{1}11) \\ o's' = (\bar{1}11):(\bar{1}01) \end{array} \right.$	65 3 24 57	65 8 24 52	65 22 24 38	64 57 25 3
$\left\{ \begin{array}{l} sq = (101):(011) \\ qp = (011):(\bar{1}10) \\ ps = (\bar{1}10):(\bar{1}0\bar{1}) \end{array} \right.$	38 32 85 32 55 56	37 59 86 22 55 39	37 21 87 27 55 12	37 59 87 2 54 59
$\left\{ \begin{array}{l} s'q = (\bar{1}01):(011) \\ qp = (011):(110) \\ ps' = (110):(10\bar{1}) \end{array} \right.$	45 17 63 51 70 52	45 1 63 22 71 37	44 44 63 0 72 16	45 33 62 44 71 43
$\left\{ \begin{array}{l} r'o' = (201):(\bar{1}11) \\ o'p = (\bar{1}11):(110) \\ pr' = (110):(20\bar{1}) \end{array} \right.$	34 43 92 49 52 28	34 53 92 17 52 50	35 1 91 59 53 0	35 16 92 9 52 35

Of the 38 angles compared in the second table, 32 show a change of angle, on passing from the potassium salt to the ammonium salt, in the same direction as is observed when rubidium or caesium replaces potassium. Of these 32 cases, 27 show larger changes than for the rubidium replacement, and 10 even larger ones than for the caesium replacement.

## DOUBLE Sulphates containing Copper.

Replacement.	Average change.	Maximum change.
	' "	' ' "
K by Rb . . . . .	22	53
K by Cs . . . . .	47	115 = 1 55
K by NH <sub>4</sub> . . . . .	39	101 = 1 41

The third small table shows that the average and maximum change of angle for the ammonium replacement is nearly as much as for the caesium replacement, both being twice as much approximately as for the replacement of potassium by rubidium.

*Cleavage.*—The cleavage common to the series, parallel to  $r'\{\bar{2}01\}$ , is developed, but is not very facile. There is quite a good cleavage parallel to  $b\{010\}$ , and in this salt this cleavage is undoubtedly the better one of the two. The fact was confirmed on several crystals of different crops, and excellent images of the signal were obtained from the cleaved surfaces, at exactly 90 degrees from  $c$  faces subsisting on the fragments

*Volume.*

*Relative Density.*—Four determinations by the immersion method yielded the following values :—

I. Density for 13°·8/4° . . .	1·9267	For 20°/4° . . .	1·9255
II. „ 13°·3/4° . . .	1·9268	„ 20°/4° . . .	1·9255
III. „ 13°·6/4° . . .	1·9273	„ 20°/4° . . .	1·9261
IV. „ 13°·6/4° . . .	1·9270	„ 20°/4° . . .	1·9258
			<hr/>
Mean . . .			1·9257

Accepted value for 20°/4°, **1·926**. This appears to be the first determination of the specific gravity of ammonium copper sulphate.

*Molecular Volume.*— $\frac{M}{d} = \frac{396·92}{1·926} = 206·08$ .

*Molecular Distance Ratios (topic axial ratios).*—

$$\chi : \psi : \omega = 6·1786 : 8·2790 : 4·1942.$$

*Redeterminations of Densities of Alkali-metal Copper Sulphates.**Potassium Copper Sulphate, K<sub>2</sub>Cu (SO<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O.*

The crystals for this determination were freshly prepared for the purpose, as this salt is the most difficult of all the potassium salts of the series to obtain in crystals free from turbidity and efflorescence. The crystals employed were almost perfectly clear, and were used immediately after removal from the mother liquor.

I. Density for 14°·5/4° . . .	2·2336	For 20°/4° . . .	2·2324
II. „ 15°·5/4° . . .	2·2335	„ 20°/4° . . .	2·2325
III. „ 15°·8/4° . . .	2·2329	„ 20°/4° . . .	2·2320
IV. „ 15°·9/4° . . .	2·2351	„ 20°/4° . . .	2·2342
			<hr/>
Mean . . .			2·2328

Accepted value for 20°/4°, **2·233**.

*Rubidium Copper Sulphate, Rb<sub>2</sub>Cu (SO<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O.*

I. Density for 16°·7/4° . . .	2·5761	For 20°/4° . . .	2·5753
II. „ 16°·8/4° . . .	2·5752	„ 20°/4° . . .	2·5744
III. „ 16°·1/4° . . .	2·5751	„ 20°/4° . . .	2·5741
IV. „ 16°·2/4° . . .	2·5726	„ 20°/4° . . .	2·5716
			<hr/>
Mean . . .			2·5739

Accepted value for 20°/4°, **2·574**.

*Cæsium Copper Sulphate*,  $\text{Cs}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ .

I. Density for $19^\circ 8/4^\circ$	. . .	2.8605	For $20^\circ/4^\circ$	. . .	2.8604
II. „ $17^\circ 2/4^\circ$	. . .	2.8570	„ $20^\circ/4^\circ$	. . .	2.8562
III. „ $17^\circ 2/4^\circ$	. . .	2.8591	„ $20^\circ/4^\circ$	. . .	2.8583
IV. „ $17^\circ 3/4^\circ$	. . .	2.8586	„ $20^\circ/4^\circ$	. . .	2.8578
					Mean . . . 2.8582

Accepted value for  $20^\circ/4^\circ$ , **2.858**.

The former pyknometer values for potassium, rubidium, and cæsium copper sulphates were 2.224, 2.570, and 2.854 respectively. There is every reason for confidence that the new values now given are nearer the truth.

The next table presents the whole of the volume constants of the four copper-containing salts in comparative form. It shows that the molecular volume of the ammonium salt is almost identical with that of the rubidium salt, and in this case very slightly lower. As regards topic axial ratios, the  $\chi$  and  $\psi$  values are slightly lower, and the  $\omega$  value somewhat higher, than the corresponding values for the rubidium salt.

## VOLUME Constants of the Copper Group.

Salt.	Molecular weight.	Specific gravity.	Molecular volume.	Topic axial ratios.
KCu sulphate . .	438.76	2.233	196.49	$\chi : \psi : \omega$ 6.0709 : 8.1053 : 4.1240
RbCu „ . .	530.86	2.574	206.24	6.2017 : 8.2800 : 4.1640
$\text{NH}_4\text{Cu}$ „ . .	396.92	1.926	206.08	6.1786 : 8.2790 : 4.1942
CsCu „ . .	624.86	2.858	218.64	6.3332 : 8.5249 : 4.2164

*Optics.*

*Orientation of the Optical Ellipsoid.*—The plane of the optic axes is the symmetry plane  $b\{010\}$ , as usual throughout the series; but the double refraction is by exception of negative sign, the first median line corresponding to the refractive index and axis of indicatrix  $\alpha$ , and the second median line to  $\gamma$ . A pair of section-plates ground parallel to the symmetry plane  $b\{010\}$  afforded the following extinction angles:—

*Inclination of 1st M.L. from normal to  $c\{001\}$ .*

Plate 1 . . .	$2^\circ 26'$	Plate 2 . . .	$2^\circ 50'$
Mean . . .		$2^\circ 38'$	

The direction is (by exception in the series) in front of the normal, away from the axis  $c$ . MURMANN and ROTTER observed the same fact and found the angle from the normal  $2^\circ 33'$ .

As the axial angle  $ac = 73^\circ 51'$ , this direction, which is that of the first and not the second median line (the double refraction being negative), is  $18^\circ 47'$  from (in front of) the vertical axis  $c$ , and the other extinction in the symmetry plane is  $2^\circ 38'$  from (below) the axis  $a$ . The two mutually perpendicular extinction directions in the symmetry plane are thus not both in the obtuse angle of the morphological axes  $ac$  (as is the case in other groups than the copper group). The positions of the four optical ellipsoids of the copper group of salts are given in the next table, and expressed in fig. 10.

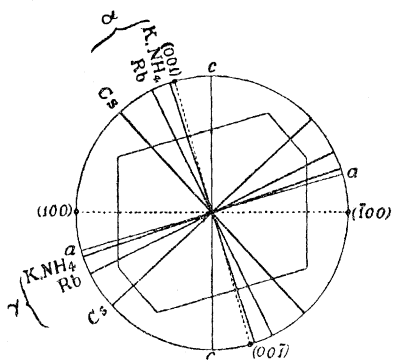


Fig. 10.

*Inclinations of  $\alpha$ -Extinctions of the Copper Salt in front of Axis  $c$ .*

(1M.L. in Am salt and 2M.L. in other three salts).

AmCu sulphate	$18^\circ 47'$	RbCu sulphate	$26^\circ 28'$
KCu	„ $18^\circ 33'$	CsCu	„ $42^\circ 57'$

In this case of the copper group the ellipsoid of the ammonium salt is almost identically situated with the potassium salt, whereas in other groups it has not been inclined so much as the potassium salt from the vertical position. The whole of the positions of the ellipsoid (as indicated by its  $\alpha$ -axis) for the four copper salts are considerably further forward than in the other groups.

*Refractive Indices.*—The next table gives the results of the refractive index determinations, carried out with six excellent  $60^\circ$ -prisms, each ground so as to afford two indices directly.

REFRACTIVE Indices of Ammonium Copper Sulphate.

Light.	$\alpha$ .	$\beta$ .	$\gamma$ .
Li . . . . .	1.4878	1.4972	1.5020
C . . . . .	1.4883	1.4977	1.5025
Na . . . . .	1.4910	1.5007	1.5054
Tl . . . . .	1.4938	1.5035	1.5083
Cd . . . . .	1.4954	1.5052	1.5099
F . . . . .	1.4971	1.5067	1.5116
G . . . . .	1.5024	1.5121	1.5171

Mean of  $\alpha$ ,  $\beta$ , and  $\gamma$  for Na light = 1.4990.

$\alpha$  = Vibration direction parallel to first median line,  $18^\circ 47'$  in front of axis  $c$ .

$\beta$  = „ „ „ symmetry axis  $b$ .

$\gamma$  = „ „ „ second median line.

MURMANN and ROTTER obtained indirectly values for the  $\beta$  index varying from 1.494 for red light to 1.502 for blue light.

General Formula for  $\beta$  (corrected to a vacuum):—

$$\beta = 1.4809 + \frac{904\,205}{\lambda^2} - \frac{7\,045\,250\,000\,000}{\lambda^4} + \dots$$

The  $\alpha$  indices are also reproduced by the formula if the constant 1.4809 is diminished by 0.0096, and the  $\gamma$  indices if it is increased by 0.0048.

Observations at 70° indicated that for 55° rise of temperature the refractive indices are diminished by about 0.0027 for  $\gamma$ , but only by 0.0005 for  $\alpha$ , and by an intermediate amount for  $\beta$ , the  $\beta$  index approaching nearer to the midway position between the  $\alpha$  and  $\gamma$  indices.

The refractive indices of the four salts containing copper are compared in the next table.

COMPARISON of the Refractive Indices.

Index.	Light.	KCu sulphate.	RbCu sulphate.	NH <sub>4</sub> Cu sulphate.	CsCu sulphate.
$\alpha$ . . . . .	Li. . . . .	1.4807	1.4858	1.4878	1.5017
	C . . . . .	1.4811	1.4862	1.4883	1.5021
	Na . . . . .	1.4836	1.4886	1.4910	1.5048
	Tl. . . . .	1.4861	1.4912	1.4938	1.5074
	F . . . . .	1.4893	1.4943	1.4971	1.5108
	G . . . . .	1.4944	1.4991	1.5024	1.5159
$\beta$ . . . . .	Li. . . . .	1.4834	1.4878	1.4972	1.5032
	C . . . . .	1.4838	1.4882	1.4977	1.5036
	Na . . . . .	1.4864	1.4906	1.5007	1.5061
	Tl. . . . .	1.4889	1.4933	1.5035	1.5089
	F . . . . .	1.4922	1.4966	1.5067	1.5123
	G . . . . .	1.4975	1.5013	1.5121	1.5174
$\gamma$ . . . . .	Li. . . . .	1.4990	1.5007	1.5020	1.5122
	C . . . . .	1.4994	1.5011	1.5025	1.5126
	Na . . . . .	1.5020	1.5036	1.5054	1.5153
	Tl. . . . .	1.5047	1.5064	1.5083	1.5180
	F . . . . .	1.5081	1.5098	1.5116	1.5216
	G . . . . .	1.5134	1.5148	1.5171	1.5266
Mean refractive index $\frac{1}{3}(\alpha + \beta + \gamma)$ for Na light		1.4907	1.4943	1.4990	1.5087
Double refraction, $\text{Na}_{\gamma-\alpha}$ . . . . .		0.0184	0.0150	0.0144	0.0105

It will be clear from this table that the refractive indices of ammonium copper sulphate are slightly higher than those of rubidium copper sulphate; the mean refractive index at the foot of the table shows this well. The double refraction is also only slightly different from (beyond) that of the rubidium salt, being slightly less, this property being a diminishing one while refractive index is an increasing property as the alkali-metal series is ascended.

*Axial Ratios of the Optical Ellipsoid.*—The calculated values of these ratios, both for the ammonium salt now described and for the analogous salts of the alkali metals previously studied, are collated comparatively in the next table.

AXIAL Ratios of the Optical Indicatrix.

		$\alpha$	$\beta$	$\gamma$	$\alpha$	$\beta$	$\gamma$
KCu	sulphate . . .	0·9981	: 1	: 1·0105	0·9981	: 1	: 1·0105
RbCu	„ . . .	0·9987	: 1	: 1·0087	1·0015	: 1·0028	: 1·0116
NH <sub>4</sub> Cu	„ . . .	0·9936	: 1	: 1·0031	1·0031	: 1·0096	: 1·0128
CsCu	„ . . .	0·9991	: 1	: 1·0061	1·0124	: 1·0132	: 1·0194

AXIAL Ratios of the Optical Velocity Ellipsoid.

		$a$	$b$	$c$	$a$	$b$	$c$
KCu	sulphate . . .	1·0019	: 1	: 0·9896	1·0019	: 1	: 0·9896
RbCu	„ . . .	1·0013	: 1	: 0·9914	0·9985	: 0·9972	: 0·9886
NH <sub>4</sub> Cu	„ . . .	1·0065	: 1	: 0·9969	0·9969	: 0·9905	: 0·9874
CsCu	„ . . .	1·0009	: 1	: 0·9939	0·9878	: 0·9869	: 0·9809

Here again, as regards the absolute dimensions of the optical ellipsoid along its three axial directions, as indicated by the right-hand series of ratios, the ammonium salt stands just beyond the rubidium salt. In the left-hand series, in which the  $\beta$  axis of each salt is the reference dimension for that salt, the copper group shows its individuality in the fact that the ratios for the ammonium salt are the lowest or highest, instead of, as in the other groups, being intermediate between the values for the rubidium and caesium salts.

*Molecular Optical Constants.*—These are set forth in the next three tables, for all four salts, the new values now given for the densities having been employed in recalculating the values for the three salts containing the alkali metals.

The specific refraction and dispersion of the ammonium salt stand out prominently higher than those of the three alkali-metal salts. The molecular dispersion for the ammonium salt is not, in this group by exception, the highest, but stands below, yet nearest to, that for the caesium salt.

TABLE of Specific Refraction and Dispersion (LORENZ).

Sulphate.	Specific refraction, $\frac{n^2 - 1}{(n^2 + 2) d} = n.$						Specific dispersion. $n_G - n_C.$		
	For ray C (H $\alpha$ ).			For ray H $\gamma$ near G.			$\alpha.$	$\beta.$	$\gamma.$
	$\alpha.$	$\beta.$	$\gamma.$	$\alpha.$	$\beta.$	$\gamma.$			
AmCu . . .	0·1497	0·1521	0·1534	0·1533	0·1558	0·1571	0·0036	0·0037	0·0037
KCu . . .	0·1275	0·1281	0·1316	0·1305	0·1312	0·1347	0·0030	0·0031	0·0031
RbCu . . .	0·1116	0·1120	0·1145	0·1141	0·1145	0·1171	0·0025	0·0025	0·0026
CsCu . . .	0·1033	0·1035	0·1051	0·1057	0·1059	0·1075	0·0024	0·0024	0·0024

TABLE of Molecular Refraction and Dispersion (LORENZ).

Salt.	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = m.$						Molecular dispersion, $m_G - m_C.$		
	For ray C (H $\alpha$ ).			For ray H $\gamma$ near G.					
	$\alpha.$	$\beta.$	$\gamma.$	$\alpha.$	$\beta.$	$\gamma.$	$\alpha.$	$\beta.$	$\gamma.$
KCu sulphate	55.93	56.20	57.73	57.24	57.55	59.09	1.31	1.35	1.36
RbCu     ,,	59.23	59.44	60.77	60.57	60.79	62.17	1.34	1.35	1.40
AmCu     ,,	59.41	60.38	60.87	60.86	61.85	62.35	1.45	1.47	1.48
CsCu     ,,	64.53	64.70	65.67	66.02	66.19	67.18	1.49	1.49	1.51

MOLECULAR Refraction (GLADSTONE and DALE).

Salt.	$\frac{n-1}{d} M$ for ray C.			Mean molecular refraction for ray C. $\frac{1}{3}(\alpha + \beta + \gamma).$
	$\alpha.$	$\beta.$	$\gamma.$	
KCu sulphate . . . . .	94.53	95.06	98.13	95.91
RbCu „ . . . . .	100.27	100.69	103.35	101.44
AmCu „ . . . . .	100.63	102.57	103.56	102.25
CsCu „ . . . . .	109.78	110.11	112.07	110.65

As regards the important property of molecular refraction the copper group shows the same relation as the other groups, namely, that the values for the ammonium salt are slightly higher than those for the rubidium salt, as is well expressed in the last column of the third table by the mean molecular refraction.

. *Optic Axial Angle*.—Three pairs of section plates, parallel to the first and second median lines, afforded the following results:—

APPARENT Optic Axial Angle in Air, 2E, of AmCu Sulphate.

Light.	Plate 1.	Plate 2.	Plate 3.	Mean 2E.
	° /	° /	° /	° /
Li . . . . .	116 41	115 45	116 20	116 15
C . . . . .	116 20	115 27	116 0	115 56
Na . . . . .	115 18	113 43	114 46	114 36
Tl . . . . .	114 19	112 50	113 40	113 36
Cd . . . . .	113 32	112 0	113 9	112 54
F . . . . .	113 12	111 30	112 45	112 29

A determination with Plate 3 at temperatures up to  $65^\circ$  indicated that  $2E$  increases rapidly on rise of temperature, a fact which accords with the alteration of the refractive indices by rise of temperature.

For Na light the angle at the ordinary temperature,  $15^\circ$ , was  $114^\circ 46'$ , at  $40^\circ$  it had increased to  $131^\circ 15'$ , at  $45^\circ$  to  $136^\circ$ , at  $50^\circ$  to  $138^\circ$ , at  $55^\circ$  to  $143^\circ$ , and at  $65^\circ$  to  $158^\circ 20'$ . The angle thus increases by  $44^\circ$  for  $50^\circ$  rise of temperature.

#### DETERMINATION of True Optic Axial Angle in Bromonaphthalene.

Light.	No. of plate perp. 1 M.L.	Observed $2H_a$ .	No. of plate perp. 2 M.L.	Observed $2H_o$ .	Calculated $2V_a$ .	Mean $2V_a$ .
		° ' "		° ' "	° ' "	° ' "
Li . . . . .	1	61 56	1a	96 31	69 11	69 1
	2	61 25	2a	96 30	68 47	
	3	61 45	3a	96 25	69 5	
C . . . . .	1	61 52	1a	96 30	69 8	68 57
	2	61 23	2a	96 30	68 46	
	3	61 35	3a	96 25	68 57	
Na. . . . .	1	61 3	1a	96 26	68 32	68 31
	2	60 50	2a	96 30	68 20	
	3	60 50	3a	96 25	68 22	
Tl . . . . .	1	60 4	1a	96 21	67 46	67 40
	2	59 58	2a	96 30	67 38	
	3	59 52	3a	96 25	67 35	
Cd. . . . .	1	59 42	1a	96 18	67 30	67 16
	2	59 18	2a	96 30	67 6	
	3	59 24	3a	96 25	67 13	
F . . . . .	1	59 18	1a	96 14	67 12	66 55
	2	58 45	2a	96 30	66 39	
	3	59 0	3a	96 25	66 53	

Section 1a showed clear although minute dispersion, but Sections 2a and 3a showed no trace of dispersion, the brushes in white light being sharply black without trace of coloured borders.

MURMANN and ROTTER found by indirect observation  $121^\circ 39'$  for  $2E$ , and  $71^\circ 21'$  for  $2V_a$ .

*Dispersion of the Median Lines.*—The inclined dispersion is very minute. Measurements in toluene indicated that the first median line lies nearer to the axis  $c$  for red Li light by  $7'$  (mean of  $4'$ ,  $10'$ , and  $6'$ ) than for greenish-blue F light.

In the next table the optic axial angles of the four copper salts are compared. The ammonium salt is seen to display an essential difference from the alkali-metal salts as regards optic axial angle.



OPTIC Axial Angles  $2V_a$  of the Copper Group.

	AmCu sulphate.	KCu sulphate.	RbCu sulphate.	CsCu sulphate.
	°   '   ''	°   '   ''	°   '   ''	°   '   ''
Li . . . . .	69 1	46 1	44 26	43 6
C . . . . .	68 57	46 6	44 29	43 9
Na . . . . .	68 31	46 32	44 42	43 24
Tl . . . . .	67 40	47 0	44 57	43 40
F . . . . .	66 55	47 33	45 15	44 3

*Ammonium Cadmium Sulphate*,  $(\text{NH}_4)_2 \text{Cd} (\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ .

This salt is not included in the investigations of MURMANN and ROTTER, but a few measurements of the crystals are given by RAMMELSBERG,\* and these values are appended in the last column of the table of angles given on next page. All the forms given in the list of "forms observed" below were also observed by RAMMELSBERG.

*Crystal System*.—Monoclinic. Class No. 5, holohedral-prismatic.

*Ratios of Axes*.—

$a : b : c = 0.7364 : 1 : 0.4931$ . Values of RAMMELSBERG,  $0.7431 : 1 : 0.4945$ .

*Axial Angle*.— $\beta = 106^\circ 41'$ . Value of RAMMELSBERG,  $107^\circ 23'$ .

*Forms observed*.— $a \{100\}$ ,  $b \{010\}$ ,  $c \{001\}$ ,  $p \{110\}$ ,  $p' \{120\}$ ,  $p''' \{130\}$ ,  $q \{011\}$ ,  $r' \{201\}$ ,  $o \{111\}$ ,  $o' \{\bar{1}11\}$ .

*Habit*.—Prismatic parallel to the axis  $c$ , sometimes fairly long as in fig. 11, but more frequently short and almost tabular parallel to  $c \{001\}$  as in fig. 12.

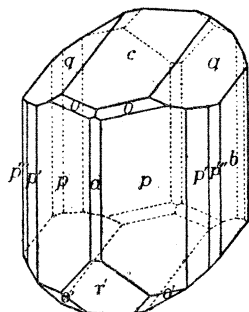


Fig. 11.

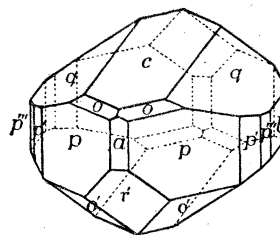


Fig. 12.

The crystals of this salt are exceptionally rich in faces, practically all the ten crystals measured exhibiting all the forms enumerated in the above list. They are less transparent than those of the other salts, being a translucent white. For this reason their optical investigation has presented considerable difficulty, and for the purpose of

\* 'Handb. der Krystall.-phys. Chemie,' Leipzig, 1881, 1, 460.

## INTERFACIAL Angles of Ammonium Cadmium Sulphate.

Angle.	No. of measure- ments.	Limits.	Mean observed.	Calcu- lated.	Diff.	Values of RAMMELS- BERG.
$\left\{ \begin{array}{l} ac = (100):(001) \\ as = (100):(101) \\ sc = (101):(001) \end{array} \right.$	16	73 5- 73 28	73 16	73 19	3	72 37
$\left\{ \begin{array}{l} cr' = (001):(201) \\ cs' = (001):(101) \\ sr' = (101):(201) \end{array} \right.$	18	64 8- 64 29	64 22	64 18	4	64 50
$\left\{ \begin{array}{l} r'a = (201):(100) \\ ap = (100):(110) \\ pp' = (110):(120) \end{array} \right.$	15	42 11- 42 25	42 19	42 23	4	—
$\left\{ \begin{array}{l} p'b = (120):(010) \\ p'p''' = (120):(130) \\ pp''' = (110):(130) \end{array} \right.$	21	35 3- 35 24	35 13	35 14	1	—
$\left\{ \begin{array}{l} p'''b = (130):(010) \\ pb = (110):(010) \\ pp = (110):(110) \end{array} \right.$	21	19 10- 19 37	19 24	19 28	4	19 28
$\left\{ \begin{array}{l} cq = (001):(011) \\ qb = (011):(010) \end{array} \right.$	21	35 9- 35 34	35 23	35 18	5	—
$\left\{ \begin{array}{l} ao = (100):(111) \\ oq = (111):(011) \\ aq = (100):(011) \end{array} \right.$	13	9 52- 10 17	10 5	10 2	3	—
$\left\{ \begin{array}{l} qo' = (011):(111) \\ o'a = (111):(100) \end{array} \right.$	16	29 16- 29 46	29 29	29 30	1	29 30
$\left\{ \begin{array}{l} co = (001):(111) \\ qp = (111):(110) \\ cp = (001):(110) \end{array} \right.$	18	25 7- 25 27	25 17	25 16	1	—
$\left\{ \begin{array}{l} po' = (110):(111) \\ o'c = (111):(001) \end{array} \right.$	26	54 36- 54 57	54 46	*	—	—
$\left\{ \begin{array}{l} bn = (010):(121) \\ no = (121):(111) \\ bo = (010):(111) \end{array} \right.$	17	70 18- 70 37	70 26	70 28	2	70 36
$\left\{ \begin{array}{l} os = (111):(101) \\ oo = (111):(111) \end{array} \right.$	32	25 4- 25 26	25 17	25 17	0	25 11
$\left\{ \begin{array}{l} bo' = (010):(111) \\ o's' = (111):(101) \\ o'o' = (111):(111) \end{array} \right.$	31	64 32- 64 54	64 43	*	—	—
$\left\{ \begin{array}{l} sq = (101):(011) \\ qp = (011):(110) \\ ps = (110):(101) \end{array} \right.$	14	48 1- 48 25	48 10	48 12	2	—
$\left\{ \begin{array}{l} pq = (110):(011) \\ s'q = (101):(011) \\ qn = (011):(121) \end{array} \right.$	19	26 33- 27 1	26 47	26 45	2	—
$\left\{ \begin{array}{l} np = (121):(110) \\ qp = (011):(110) \\ ps' = (110):(101) \end{array} \right.$	23	74 36- 75 11	74 55	74 57	2	74 45
$\left\{ \begin{array}{l} pq = (110):(011) \\ ps' = (110):(101) \\ pr' = (110):(201) \end{array} \right.$	24	34 36- 34 57	34 47	34 43	4	34 35
$\left\{ \begin{array}{l} r'o' = (201):(111) \\ o'p = (111):(110) \\ pr' = (110):(201) \end{array} \right.$	21	70 0- 70 28	70 16	70 20	4	—
$\left\{ \begin{array}{l} co = (001):(111) \\ qp = (111):(110) \\ cp = (001):(110) \end{array} \right.$	27	33 25- 33 56	33 42	33 43	1	33 30
$\left\{ \begin{array}{l} po' = (110):(111) \\ o'c = (111):(001) \end{array} \right.$	25	42 30- 42 58	42 44	42 43	1	—
$\left\{ \begin{array}{l} bn = (010):(121) \\ no = (121):(111) \\ bo = (010):(111) \end{array} \right.$	35	76 18- 76 43	76 26	*	—	—
$\left\{ \begin{array}{l} os = (111):(101) \\ oo = (111):(111) \end{array} \right.$	32	58 40- 59 5	58 53	59 0	7	59 39
$\left\{ \begin{array}{l} sq = (101):(011) \\ qp = (011):(110) \\ ps = (110):(101) \end{array} \right.$	33	44 25- 44 57	44 41	44 34	7	44 42
$\left\{ \begin{array}{l} pq = (110):(011) \\ s'q = (101):(011) \\ qn = (011):(121) \end{array} \right.$	—	—	—	55 4	—	—
$\left\{ \begin{array}{l} np = (121):(110) \\ qp = (011):(110) \\ ps' = (110):(101) \end{array} \right.$	—	—	—	15 41	—	—
$\left\{ \begin{array}{l} pq = (110):(011) \\ s'q = (101):(011) \\ qn = (011):(121) \end{array} \right.$	19	70 31- 70 55	70 46	70 45	1	—
$\left\{ \begin{array}{l} np = (121):(110) \\ qp = (011):(110) \\ ps' = (110):(101) \end{array} \right.$	—	—	—	19 15	—	—
$\left\{ \begin{array}{l} pq = (110):(011) \\ s'q = (101):(011) \\ qn = (011):(121) \end{array} \right.$	8	38 14- 38 38	38 28	38 30	2	—
$\left\{ \begin{array}{l} np = (121):(110) \\ qp = (011):(110) \\ ps' = (110):(101) \end{array} \right.$	29	65 11- 65 30	65 24	65 23	1	—
$\left\{ \begin{array}{l} pq = (110):(011) \\ s'q = (101):(011) \\ qn = (011):(121) \end{array} \right.$	—	—	—	24 37	—	—
$\left\{ \begin{array}{l} np = (121):(110) \\ qp = (011):(110) \\ ps' = (110):(101) \end{array} \right.$	13	49 0- 49 20	49 12	49 14	2	—
$\left\{ \begin{array}{l} pq = (110):(011) \\ s'q = (101):(011) \\ qn = (011):(121) \end{array} \right.$	28	87 54- 88 8	88 2	88 2	0	—
$\left\{ \begin{array}{l} np = (121):(110) \\ qp = (011):(110) \\ ps' = (110):(101) \end{array} \right.$	—	—	—	54 47	—	—
$\left\{ \begin{array}{l} pq = (110):(011) \\ s'q = (101):(011) \\ qn = (011):(121) \end{array} \right.$	26	91 50- 92 7	91 58	91 58	0	—
$\left\{ \begin{array}{l} np = (121):(110) \\ qp = (011):(110) \\ ps' = (110):(101) \end{array} \right.$	—	—	—	44 52	—	—
$\left\{ \begin{array}{l} pq = (110):(011) \\ s'q = (101):(011) \\ qn = (011):(121) \end{array} \right.$	—	—	—	26 9	—	—
$\left\{ \begin{array}{l} np = (121):(110) \\ qp = (011):(110) \\ ps' = (110):(101) \end{array} \right.$	31	62 31- 62 59	62 42	62 43	1	—
$\left\{ \begin{array}{l} pq = (110):(011) \\ s'q = (101):(011) \\ qn = (011):(121) \end{array} \right.$	—	—	—	72 25	—	—
$\left\{ \begin{array}{l} np = (121):(110) \\ qp = (011):(110) \\ ps' = (110):(101) \end{array} \right.$	30	117 4- 117 30	117 17	117 17	0	—
$\left\{ \begin{array}{l} pq = (110):(011) \\ s'q = (101):(011) \\ qn = (011):(121) \end{array} \right.$	30	34 45- 35 24	35 6	35 9	3	—
$\left\{ \begin{array}{l} np = (121):(110) \\ qp = (011):(110) \\ ps' = (110):(101) \end{array} \right.$	28	91 52- 92 17	92 3	91 58	5	—
$\left\{ \begin{array}{l} pq = (110):(011) \\ s'q = (101):(011) \\ qn = (011):(121) \end{array} \right.$	30	52 37- 52 58	52 49	52 53	4	—
Total number of measurements . .	790					

density determinations the crystals have had to be freshly prepared and used very soon after removal from the mother liquor. Their goniometrical measurement, however, has offered no difficulty.

The relative development of the faces is frequently so different from the main types illustrated in figs. 11 and 12, that it is not always easy to recognise the various faces immediately. The ten small crystals measured were selected from the two best crops of a very large number prepared. They afforded very satisfactory goniometrical results (see accompanying table of angles) in all cases but those involving the faces of  $o'\{\bar{1}11\}$  in the zone  $[cpo']$ ; for when this zone was adjusted these faces invariably showed multiple images of the signal, due to more or less striation, so that the mean measured values of the angles  $po'$  and  $o'c$  differed rather more than usual from the calculated values.

The rarer forms common to this monoclinic series of double salts are exceptionally well developed on the crystals of cadmium ammonium sulphate; for instance, the faces of  $a\{100\}$ ,  $o\{111\}$ ,  $p'\{120\}$ , and  $p'''\{130\}$  have been frequently observed quite large. Moreover, single faces of the commoner forms  $b\{010\}$  and  $r'\{\bar{2}01\}$  are occasionally found phenomenally developed; thus several crystals were found roughly hemispherical, the large flat base being a particularly large and perfectly plane  $b$ -face, while others were found with a similarly predominatingly developed  $r'$ -face.

The morphological constants of the three cadmium-containing salts are compared in the next two tables. As already explained, potassium cadmium sulphate with  $6H_2O$  has so far resisted all attempts at preparation. The first table shows that the axial ratios of the ammonium cadmium salt are very close to those of the rubidium cadmium salt. The axial angle  $\beta$  of the ammonium salt is not far removed from that of the caesium salt, but is not so close as in all the other groups investigated. The morphological angles of the ammonium salt are shown in the second table to be related to those of the rubidium and caesium salts in a very similar manner to what has been shown to occur in the other groups, for which it has been possible to effect a complete comparison and to determine the differences in angle of all three salts from the potassium salt. They indicate conclusively that the ammonium salt belongs to the same isomorphous series as the rubidium and caesium salts containing cadmium.

COMPARISON of the Axial Angles and Axial Ratios.

	Axial angle.	Axial ratios.
	$\beta.$	$a : b : c$
Rubidium cadmium sulphate .	$105^\circ 53'$	$0.7346 : 1 : 0.4931$
Ammonium       "       " .	$106^\circ 41'$	$0.7364 : 1 : 0.4931$
Cæsium         "       " .	$107^\circ 11'$	$0.7259 : 1 : 0.4906$

## COMPARISON of the Interfacial Angles.

Angle.	RbCd sulphate.	CsCd sulphate.	AmCd sulphate.
$\left\{ \begin{array}{l} ac = (100) : (001) \\ as = (100) : (101) \\ sc = (101) : (001) \\ cr' = (001) : (201) \\ cs' = (001) : (\bar{1}01) \\ s'r' = (\bar{1}01) : (201) \\ r'a = (201) : (\bar{1}00) \end{array} \right.$	$\begin{array}{l} 74 \ 7 \\ 45 \ 29 \\ 28 \ 38 \\ 63 \ 56 \\ 38 \ 22 \\ 25 \ 34 \\ 41 \ 57 \end{array}$	$\begin{array}{l} 72 \ 49 \\ 44 \ 31 \\ 28 \ 18 \\ 65 \ 5 \\ 38 \ 54 \\ 26 \ 11 \\ 42 \ 6 \end{array}$	$\begin{array}{l} 73 \ 19 \\ 45 \ 5 \\ 28 \ 14 \\ 64 \ 18 \\ 38 \ 23 \\ 25 \ 55 \\ 42 \ 23 \end{array}$
$\left\{ \begin{array}{l} ap = (100) : (110) \\ pp' = (110) : (120) \\ p'b = (120) : (010) \\ pb = (110) : (010) \end{array} \right.$	$\begin{array}{l} 35 \ 14 \\ 19 \ 28 \\ 35 \ 18 \\ 54 \ 46 \end{array}$	$\begin{array}{l} 34 \ 44 \\ 19 \ 28 \\ 35 \ 48 \\ 55 \ 16 \end{array}$	$\begin{array}{l} 35 \ 14 \\ 19 \ 28 \\ 35 \ 18 \\ 54 \ 46 \end{array}$
$\left\{ \begin{array}{l} cq = (001) : (011) \\ qb = (011) : (010) \end{array} \right.$	$\begin{array}{l} 25 \ 24 \\ 64 \ 36 \end{array}$	$\begin{array}{l} 25 \ 8 \\ 64 \ 52 \end{array}$	$\begin{array}{l} 25 \ 17 \\ 64 \ 43 \end{array}$
$\left\{ \begin{array}{l} ao = (100) : (111) \\ oq = (111) : (011) \\ aq = (100) : (011) \\ qo' = (011) : (\bar{1}11) \\ o'a = (\bar{1}11) : (\bar{1}00) \end{array} \right.$	$\begin{array}{l} 48 \ 35 \\ 27 \ 6 \\ 75 \ 41 \\ 34 \ 41 \\ 69 \ 38 \end{array}$	$\begin{array}{l} 47 \ 37 \\ 26 \ 52 \\ 74 \ 29 \\ 35 \ 11 \\ 70 \ 20 \end{array}$	$\begin{array}{l} 48 \ 12 \\ 26 \ 45 \\ 74 \ 57 \\ 34 \ 43 \\ 70 \ 20 \end{array}$
$\left\{ \begin{array}{l} co = (001) : (111) \\ op = (111) : (110) \\ cp = (001) : (110) \\ po' = (110) : (111) \\ o'c = (111) : (001) \end{array} \right.$	$\begin{array}{l} 34 \ 6 \\ 42 \ 59 \\ 77 \ 5 \\ 58 \ 26 \\ 44 \ 29 \end{array}$	$\begin{array}{l} 33 \ 38 \\ 42 \ 19 \\ 75 \ 57 \\ 59 \ 8 \\ 44 \ 55 \end{array}$	$\begin{array}{l} 33 \ 43 \\ 42 \ 43 \\ 76 \ 26 \\ 59 \ 0 \\ 44 \ 34 \end{array}$
$\left\{ \begin{array}{l} bo = (010) : (111) \\ os = (111) : (101) \end{array} \right.$	$\begin{array}{l} 70 \ 38 \\ 19 \ 22 \end{array}$	$\begin{array}{l} 71 \ 1 \\ 18 \ 59 \end{array}$	$\begin{array}{l} 70 \ 45 \\ 19 \ 15 \end{array}$
$\left\{ \begin{array}{l} bo' = (010) : (\bar{1}11) \\ o's' = (\bar{1}11) : (\bar{1}01) \end{array} \right.$	$\begin{array}{l} 65 \ 30 \\ 24 \ 30 \end{array}$	$\begin{array}{l} 65 \ 30 \\ 24 \ 30 \end{array}$	$\begin{array}{l} 65 \ 23 \\ 24 \ 37 \end{array}$
$\left\{ \begin{array}{l} sq = (101) : (011) \\ qp = (011) : (\bar{1}10) \\ ps = (\bar{1}10) : (\bar{1}01) \end{array} \right.$	$\begin{array}{l} 37 \ 33 \\ 87 \ 23 \\ 55 \ 4 \end{array}$	$\begin{array}{l} 37 \ 9 \\ 88 \ 43 \\ 54 \ 8 \end{array}$	$\begin{array}{l} 37 \ 11 \\ 88 \ 2 \\ 54 \ 47 \end{array}$
$\left\{ \begin{array}{l} s'q = (\bar{1}01) : (011) \\ qp = (011) : (110) \\ ps' = (110) : (101) \end{array} \right.$	$\begin{array}{l} 44 \ 54 \\ 63 \ 18 \\ 71 \ 48 \end{array}$	$\begin{array}{l} 45 \ 12 \\ 62 \ 30 \\ 72 \ 18 \end{array}$	$\begin{array}{l} 44 \ 52 \\ 62 \ 43 \\ 72 \ 25 \end{array}$
$\left\{ \begin{array}{l} r'o' = (\bar{2}01) : (\bar{1}11) \\ o'p = (\bar{1}11) : (110) \\ pr' = (110) : (201) \end{array} \right.$	$\begin{array}{l} 34 \ 50 \\ 92 \ 35 \\ 52 \ 35 \end{array}$	$\begin{array}{l} 35 \ 15 \\ 92 \ 19 \\ 52 \ 26 \end{array}$	$\begin{array}{l} 35 \ 9 \\ 91 \ 58 \\ 52 \ 53 \end{array}$

*Cleavage.*—A fairly good cleavage parallel to  $r'\{\bar{2}01\}$  is developed in the crystals of ammonium cadmium sulphate. No trace of cleavage parallel to  $b\{010\}$  was discovered.

*Volume.*

*Relative Density.*—Four determinations by the immersion method gave the following results :—

I.	Density for	13°·6/4°	. . .	2·0613	For	20°/4°	. . .	2·0600
II.	„	14°·2/4°	. . .	2·0620	„	20°/4°	. . .	2·0608
III.	„	13°·9/4°	. . .	2·0623	„	20°/4°	. . .	2·0610
IV.	„	13°·5/4°	. . .	2·0631	„	20°/4°	. . .	2·0618
								<hr/>
Mean . . .								2·0609

Accepted value for 20°/4°, **2·061**.

*Molecular Volume.*— $\frac{M}{d} = \frac{445·42}{2·061} = 216·12$ .

*Molecular Distance Ratios (topic axial ratios).*—

$$\chi : \psi : \omega = 6·2838 : 8·5332 : 4·2078.$$

*Redeterminations of Densities of Rubidium and Cesium Cadmium Sulphates.*

*Rubidium Cadmium Sulphate, Rb<sub>2</sub> Cd (SO<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O.*

I.	Density for	15°·6/4°	. . .	2·6963	For	20°/4°	. . .	2·6951	
II.	„	15°·8/4°	. . .	2·6976	„	20°/4°	. . .	2·6965	
III.	„	15°·3/4°	. . .	2·6984	„	20°/4°	. . .	2·6972	
IV.	„	15°·0/4°	. . .	2·6942	„	20°/4°	. . .	2·6928	
V.	„	16°·0/4°	. . .	2·6946	„	20°/4°	. . .	2·6935	
								<hr/>	
								Mean . . .	2·6950

Accepted value for 20°/4°, **2·695**.

*Cesium Cadmium Sulphate, Cs<sub>2</sub> Cd (SO<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O.*

I.	Density for	14°·8/4°	. . .	2·9582	For	20°/4°	. . .	2·9568
II.	„	15°·6/4°	. . .	2·9572	„	20°/4°	. . .	2·9560
III.	„	14°·8/4°	. . .	2·9567	„	20°/4°	. . .	2·9553
IV.	„	14°·7/4°	. . .	2·9593	„	20°/4°	. . .	2·9578
								<hr/>
Mean . . .								2·9565

Accepted value for 20°/4°, **2·957**.

The former values for the pycnometer method were 2·672 for the rubidium salt, and 2·955 for the cesium salt.

As was fully described in the communication describing the work on rubidium cadmium sulphate,\* special difficulties were found in carrying out density determina-

\* 'Journ. Chem. Soc., Trans.,' 1896, 69, 445.

tions of this salt by the pyknometer method, owing to rapid efflorescence, which was greatly accelerated by powdering and necessitated rapid working and weighing while covered with carbon tetrachloride, the pyknometer liquid. The immersion method is free from the powdering difficulty, and it is only necessary to use freshly grown crystals, and to preserve them under benzene until the moment of dropping them into the immersion liquid mixture of methylene iodide and benzene. This was done in the cases of the five determinations now recorded, and the result, 2.695, is much higher than the former pyknometer one, and can be accepted with confidence.

#### VOLUME Constants of the Cadmium Group.

Salt.	Molecular weight.	Specific gravity.	Molecular volume.	Topic axial ratios.
RbCd sulphate . . .	579.36	2.695	214.98	$\chi : \psi : \omega$ 6.2539 : 8.5133 : 4.1980
NH <sub>4</sub> Cd „ . .	445.42	2.061	216.12	6.2838 : 8.5332 : 4.2078
CsCd „ . .	673.36	2.957	227.72	6.3497 : 8.7472 : 4.2914

The comparative table of the volume constants shows that the ammonium cadmium salt occupies a position just beyond that of the rubidium cadmium salt, the molecular volume and all three topic axial ratios being slightly higher.

#### Optics.

No optical investigation of this salt appears to have been hitherto undertaken. It is a matter of some difficulty, as ground surfaces of the crystals effloresce with great rapidity; also the use of warm wax on the crystal holder for cementing purposes is precluded, as rise of temperature provokes instant opacity from loss of water of crystallisation. By careful rapid work, however, the use of a special wax, and immediately covering ground surfaces with very thin truly plane glass plates cemented by hard balsam in benzene, all these difficulties were eventually overcome.

*Orientation of Optical Ellipsoid.*—The optic axes lie in the symmetry plane  $b\{010\}$  and the sign of the double refraction is positive. The first median line corresponds to the axis  $\gamma$  of the optical indicatrix and the second median line to  $\alpha$ .

A pair of section-plates parallel to the symmetry plane afforded the extinction angles:—

*Inclination of 2M.L. from normal to  $c\{001\}$ .*

Plate 1 . . .	5° 8'	Plate 2 . . .	5° 20'
Mean . . .	5° 14'.		

The direction is behind the normal. As the axial angle  $ac = 73^\circ 19'$  this extinction direction, the second median line, is  $11^\circ 27'$  from and in front of the vertical axis  $c$ ; and the other extinction in the symmetry plane, the first median line, is  $5^\circ 14'$  from and above the axis  $a$ , both median lines thus lying in the obtuse angle of the morphological axes  $ac$ .

The positions of the optical indicatrix for the three cadmium salts are compared in the next table, and illustrated in fig. 13.

*Inclinations of  $\alpha$ -Axis of the Indicatrix (2M.L.) of the Cadmium Salts in front of Axis  $c$ .*

AmCd sulphate	$11^\circ 27'$
RbCd	$15^\circ 53'$
CsCd	$26^\circ 56'$

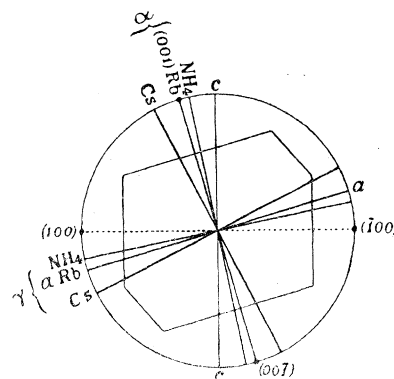


Fig. 13.

The order of these positions of the indicatrix for the three salts is similar to what has been observed in the other groups, in which the potassium salt also has been able to be compared.

*Refractive Indices.*—Determinations with six prisms, each ground to yield two indices directly, gave the results summarised in the accompanying table.

#### REFRACTIVE INDICES OF AMMONIUM CADMIUM SULPHATE.

Light.	$\alpha$ .	$\beta$ .	$\gamma$ .
Li . . . . .	1.4816	1.4855	1.4927
C . . . . .	1.4821	1.4860	1.4932
Na . . . . .	1.4847	1.4887	1.4959
Tl . . . . .	1.4875	1.4915	1.4987
Cd . . . . .	1.4891	1.4931	1.5003
F . . . . .	1.4907	1.4947	1.5019
G . . . . .	1.4961	1.5001	1.5073

Mean of  $\alpha$ ,  $\beta$ , and  $\gamma$  for Na light = 1.4898.

$\alpha$  = Vibration direction parallel to second median line,  $11^\circ 27'$  in front of axis  $c$ .

$\beta$  = " " " " symmetry axis  $b$ .

$\gamma$  = " " " " first median line.

General formula for  $\beta$ , corrected to a vacuum :—

$$\beta = 1.4736 + \frac{605\,763}{\lambda^2} - \frac{2\,351\,170\,000\,000}{\lambda^4} + \dots$$

The  $\alpha$  indices are equally well reproduced by the formula if the constant 1.4736 is diminished by 0.0040, and the  $\gamma$  indices if it is increased by 0.0072.

Observations at higher temperatures were precluded on account of decomposition and opacity due to loss of water of crystallisation.

In the next table the refractive indices of the three cadmium-containing salts are compared.

COMPARISON of the Refractive Indices.

Index.	Light.	RbCd sulphate.	NH <sub>4</sub> Cd sulphate.	CsCd sulphate.
$\alpha$ . . . . .	Li. . . . .	1.4773	1.4816	1.4947
	C . . . . .	1.4777	1.4821	1.4951
	Na . . . . .	1.4798	1.4847	1.4975
	Tl. . . . .	1.4823	1.4875	1.5000
	F . . . . .	1.4856	1.4907	1.5033
	G . . . . .	1.4906	1.4961	1.5081
$\beta$ . . . . .	Li. . . . .	1.4820	1.4855	1.4972
	C . . . . .	1.4824	1.4860	1.4976
	Na . . . . .	1.4848	1.4887	1.5000
	Tl. . . . .	1.4872	1.4915	1.5026
	F . . . . .	1.4905	1.4947	1.5058
	G . . . . .	1.4955	1.5001	1.5106
$\gamma$ . . . . .	Li. . . . .	1.4919	1.4927	1.5034
	C . . . . .	1.4923	1.4932	1.5038
	Na . . . . .	1.4948	1.4959	1.5062
	Tl. . . . .	1.4972	1.4987	1.5088
	F . . . . .	1.5097	1.5019	1.5123
	G . . . . .	1.5061	1.5073	1.5172
Mean refractive index $\frac{1}{3}(\alpha + \beta + \gamma)$ for Na light		1.4865	1.4898	1.5012
Double refraction, $\text{Na}_{\gamma-\alpha}$ . . . . .		0.0150	0.0112	0.0087

The refractive indices of the ammonium cadmium salt are just slightly higher than those of the rubidium cadmium salt, the relationship being best expressed by the mean index given at the foot of the table. The double refraction of the ammonium salt is also intermediate between the values for the rubidium and caesium salts, but in this case nearer to the caesium salt.

*Axial Ratios of the Optical Ellipsoid.*—The values of these ratios are compared in the next table. The potassium salt not being available for comparison, only the ratios on the basis of the  $\beta$  value of each salt = 1 are possible.

		AXIAL Ratios of		
		Optical Indicatrix		
		$\alpha$	$\beta$	$\gamma$
		Optical Velocity Ellipsoid.		
		a	b	c
RbCd sulphate	. . .	0.9966	1	1.0067
NH <sub>4</sub> Cd	„ . . .	0.9973	1	1.0048
CsCd	„ . . .	0.9983	1	1.0041



The values for the ammonium salt are intermediate between those for the rubidium and caesium salts.

*Molecular Optical Constants.*—The next three tables set forth these constants for all three salts of the cadmium group in comparative form. In recalculating the values for the rubidium and caesium salts the new values for the densities now determined by the immersion method were employed. From the tables it may be deduced that the specific refraction and dispersion of the ammonium salt stand out prominently higher than those of the rubidium and caesium salts; the molecular dispersion of the ammonium salt also slightly exceeds that of caesium cadmium sulphate. As regards the most important molecular refraction, all the values for the ammonium salt, including the mean molecular refraction, are just slightly higher than the corresponding values for the rubidium salt. It is immaterial whether the formula of LORENZ or that of GLADSTONE and DALE is employed.

TABLE of Specific Refraction and Dispersion (LORENZ).

Sulphate.	Specific refraction, $\frac{n^2 - 1}{(n^2 + 2) d} = n$ .						Specific dispersion. $n_G - n_C$ .		
	For ray C (H $\alpha$ ).			For ray H $\gamma$ near G.					
	$\alpha$ .	$\beta$ .	$\gamma$ .	$\alpha$ .	$\beta$ .	$\gamma$ .	$\alpha$ .	$\beta$ .	$\gamma$ .
AmCd . . .	0.1383	0.1393	0.1411	0.1418	0.1427	0.1445	0.0035	0.0034	0.0034
RbCd . . .	0.1050	0.1058	0.1077	0.1074	0.1083	0.1103	0.0024	0.0025	0.0026
CsCd . . .	0.0986	0.0991	0.1001	0.1008	0.1012	0.1023	0.0022	0.0021	0.0022

TABLE of Molecular Refraction and Dispersion (LORENZ).

Salt.	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = m$ .						Molecular dispersion. $m_G - m_C$ .		
	For ray C (H $\alpha$ ).			For ray H $\gamma$ near G.					
	$\alpha$ .	$\beta$ .	$\gamma$ .	$\alpha$ .	$\beta$ .	$\gamma$ .	$\alpha$ .	$\beta$ .	$\gamma$ .
RbCd sulphate	60.82	61.32	62.40	62.22	62.75	63.88	1.40	1.43	1.48
AmCd     ,,	61.62	62.05	62.83	63.14	63.57	64.35	1.52	1.52	1.52
CsCd     ,,	66.42	66.70	67.41	67.89	68.17	68.92	1.47	1.47	1.51

## MOLECULAR Refraction (GLADSTONE and DALE).

Salt.	$\frac{n-1}{d}$ M for ray C.			Mean molecular refraction for ray C. $\frac{1}{3}(\alpha + \beta + \gamma)$ .
	$\alpha$ .	$\beta$ .	$\gamma$ .	
RbCd sulphate . . . . .	102.70	103.71	105.83	104.08
AmCd „ . . . . .	104.19	105.03	106.59	105.27
CsCd „ . . . . .	112.74	113.31	114.73	113.59

*Optic Axial Angle.*—Three pairs of section-plates perpendicular to the two median lines were, after much trouble, obtained by grinding, which were adequately transparent to enable a complete series of measurements to be obtained of 2H $\alpha$  and 2H $\delta$  in bromonaphthalene, and the measurement in two cases of 2E for the most brilliant sodium light wave-length. Observations of the dispersion of the median lines between Li and F light were also successfully carried out. The results are shown in the next two tables.

APPARENT Optic Axial Angle in Air, 2E, of AmCd Sulphate for Sodium Light.

Plate 1 . . .	124° 33'	Plate 2 . . .	124° 31'
Mean 2E . . .	124° 32'		

## DETERMINATION of True Optic Axial Angle in Bromonaphthalene.

Light.	No. of plate perp. 1 M.L.	Observed 2H $\alpha$ .	No. of plate perp. 2 M.L.	Observed 2H $\delta$ .	Calculated 2V $\alpha$ .	Mean 2V $\alpha$ .
Li . . . . .	1	64 29	1a	92 48	72 46	72 45
	2	64 27	2a	92 57	72 40	
	3	64 32	3a	92 44	72 50	
C . . . . .	1	64 28	1a	92 43	72 47	72 46
	2	64 25	2a	92 53	72 41	
	3	64 30	3a	92 38	72 51	
Na . . . . .	1	64 16	1a	92 18	72 50	72 51
	2	64 11	2a	92 20	72 45	
	3	64 16	3a	91 58	72 58	
Tl . . . . .	1	64 0	1a	91 43	72 53	72 56
	2	63 57	2a	91 46	72 50	
	3	64 2	3a	91 22	73 4	
Cd . . . . .	1	63 48	1a	91 22	72 54	72 58
	2	63 50	2a	91 23	72 54	
	3	63 54	3a	91 4	73 7	
F . . . . .	1	63 35	1a	90 58	72 56	73 1
	2	63 40	2a	91 3	72 57	
	3	63 44	3a	90 40	73 10	

*Dispersion of the Median Lines.*—The inclined dispersion is very minute. From observations in toluene with sections 1 and 2 it was ascertained that the first median line lies 8' nearer to the axis  $a$  for Li red light than for greenish-blue F light.

In the next table the optic axial angles of the three cadmium salts are compared.

OPTIC Axial Angles  $2V_a$  of the Cadmium Group.

	AmCd sulphate.	RbCd sulphate.	CsCd sulphate.
	° /	° /	° /
Li . . . . .	72 45	72 20	68 4
C . . . . .	72 46	72 21	68 2
Na . . . . .	72 51	72 26	67 53
Tl . . . . .	72 56	72 31	67 44
F . . . . .	73 1	72 37	67 28

It will be observed that the optic axial angle of the ammonium cadmium salt is only very slightly larger than that of the rubidium cadmium salt.

#### *Summary of Conclusions.*

The results of this investigation of the five remaining ammonium salts of the double sulphate series are perfectly in line with and fully confirm those already derived, in two former communications, from a study of three other ammonium salts of the series. The chief conclusion is that the close similarity of the crystal angles, the axial ratios, the volume constants, and the optical constants of these ammonium salts clearly entitles them to places in the monoclinic isomorphous series  $R_2M(SO_4)_2 \cdot 6H_2O$ , R being represented by the  $NH_4$  radicle; but that they are not so definitely related, "eutropic" as it has been termed, as are those salts of the series in which R is potassium, rubidium, or caesium. Now interchange of these R-metals has been shown to exert a comparatively great and dominating effect on the properties of the crystals, progressively with their atomic weights, while change of the M-metal only produces slight change. But this law of progression of the crystallographic properties, both morphological and physical, with the atomic weight of the alkali metal R, which law is the essence of "eutropism," cannot apply as regards ammonium; for we are here dealing with a radicle group of elements,  $NH_4$ , and not with three simple interchangeable elements of the same family group of MENDELEEFF'S table, definitely progressive in atomic weight and in all the properties which accompany atomic weight. Yet the group  $NH_4$  possesses the singular power of chemically replacing these alkali metals in their salts, as also does the metal thallium, which is well known to be of a different nature to the three alkali metals potassium rubidium, and caesium. It has now been shown that the replacement occurs in thes

two non-eutropic cases with surprisingly slight alteration of the morphology of the crystals, the change, in fact, being almost *nil* when rubidium is the alkali metal replaced by either ammonium or thallium. While no clear rule like that of eutropic progression can apply as regards ammonium (or thallium), there are still very definite relationships which have been established as the result of the research now completed, which can best be stated separately for the various properties.

*Crystal Angles.*—The monoclinic axial angle  $\beta$  of the ammonium salt of any group (set of salts containing the same M-metal) is usually very close to that of the caesium salt of the same group. In six of the eight groups, those in which all four salts (of  $\text{NH}_4$ , K, Rb, and Cs) are capable of existence, the difference is less than  $10'$ , and in three cases it does not exceed  $2'$ . The change in this important angle when K is replaced by Rb is usually about a degree, and when Cs replaces K about 2 degrees, the latter being almost exactly twice the former, the angular changes corresponding to the two changes in atomic weight, 46 and 93. The maximum changes observed for the two replacements were  $1^\circ 12'$  and  $2^\circ 20'$ , in the iron group, the  $\text{NH}_4$  replacement in this group causing  $2^\circ 18'$  of change.

In all the six complete groups 32 to 34 out of 36 different interfacial angles compared (all in which the differences are beyond the range of experimental error) show a change of angle on replacing K by  $\text{NH}_4$  in the same direction as if Rb or Cs were introduced instead. The average and maximum amounts of the change when  $\text{NH}_4$  replaces K are approximately the same as when K is replaced by Cs, and this amount is twice as great as when Rb replaces K; for the average and maximum changes of angles are directly proportional to the change of atomic weight when one alkali metal is substituted for another. (K = 38.85 when H = 1, Rb = 84.9, and Cs = 131.9, and  $\frac{38.85 + 131.9}{2} = 85.4$ ; also Rb-K = 46, and Cs-Rb = 47.) The

maximum change of angle observed for the replacement of K by Cs occurs in the magnesium group, and is  $2^\circ 25'$ ; the replacement of K by  $\text{NH}_4$  in the same group provokes a change of nearly the same amount,  $2^\circ 18'$ , while the change for the replacement of K by Rb is exactly half the value for the Cs replacement, namely,  $1^\circ 12'$ . This direct proportionality of the average and maximum change of angle to the change in atomic weight of the alkali metal is one of the most striking and important of all the facts brought to light by this prolonged investigation, and is rendered the more important by the large amounts of these changes. It is also interesting to note that the change (strictly proportional to that in atomic weight) in the most important of the angles, the axial angle  $\beta$ , between the primary orthopinakoid  $a\{100\}$  and basal plane  $c\{001\}$ , is so large as to be nearly equal to the maximum, and in several groups this angle is actually itself the angle of maximum change. These conclusions are, therefore, far away from any possible experimental error, which at the highest estimate could not exceed  $5'$  and probably does not exceed  $3'$ .

*Axial Ratios.*—The ratios of the morphological axes of any ammonium salt of the series are very close to those of the alkali-metal salts of the same group, and usually lie within the limits of the latter. They thus afford very strong evidence of the isomorphism of the ammonium salts with the alkali-metal salts of the group and series.

*Cleavage.*—The crystals of the whole series of salts show cleavage parallel to the orthopinakoid  $r'\{201\}$ . Four of the ammonium salts, those of the Mg, Ni, Mn, and Cu groups, show in addition a good cleavage parallel to the symmetry plane  $b\{010\}$ , and in ammonium copper sulphate this cleavage is the more perfect of the two. The introduction of the  $\text{NH}_4$  radicle in place of an alkali metal thus appears to affect the cleavage. A similar effect was observed in the simple rhombic sulphates of ammonium and the alkali metals; but in this case it took the form of the suppression in ammonium sulphate of one ( $b\{010\}$ , the more perfect cleavage) of the two cleavages (parallel to  $b\{010\}$  and  $c\{001\}$ ) common to the sulphates of K, Rb, and Cs.

*Density and Molecular Volume.*—The density of the ammonium salt is the lowest in every group. The molecular volume of the ammonium salt, however, is nearly identical with that of the rubidium salt of the same group; on the average it is just slightly higher, the differences varying from 1.6 above to 0.16 below the value for the rubidium salt. The average difference of molecular volume, for the whole of the double sulphate series, between a K and a Rb salt is 9.55 units, between a K and a  $\text{NH}_4$  salt 10.41 units, and between a K and a Cs salt 22.23 units. The change of molecular volume with change of the alkali metal thus follows the order of the atomic weights of the alkali metals, and the absolute amounts are a higher function of the atomic weight than direct proportionality. The two following tables will render these facts clear.

RELATIVE Densities Compared.

M metal.	Density of K salt.	Difference between K and Rb salts.	Density of Rb salt.	Difference between K and $\text{NH}_4$ salts.	Density of $\text{NH}_4$ salt.	Difference between Rb and Cs salts.	Density of Cs salt.	Difference between K and Cs salts.
Ni	2.237	0.349	2.586	-0.314	1.923	0.286	2.872	0.635
Co	2.219	0.348	2.567	-0.318	1.901	0.277	2.844	0.625
Mn	—	—	2.461	—	1.831	0.279	2.740	—
Cu	2.233	0.341	2.574	-0.307	1.926	0.284	2.858	0.625
Cd	—	—	2.695	—	2.061	0.262	2.957	—
Mg	2.034	0.352	2.386	-0.311	1.723	0.290	2.676	0.642
Zn	2.246	0.345	2.591	-0.314	1.932	0.284	2.875	0.629
Fe	2.177	0.341	2.518	-0.313	1.864	0.278	2.796	0.619

## MOLECULAR VOLUMES COMPARED.

M metal.	Molecular volume of K salt.	Difference between K and Rb salts.	Molecular volume of Rb salt.	Difference between K and NH <sub>4</sub> salts.	Molecular volume of NH <sub>4</sub> salt.	Difference between Rb and Cs salts.	Molecular volume of Cs salt.	Difference between K and Cs salts.
Ni	193·99	9·44	203·43	9·92	203·91	12·47	215·90	21·91
Co	195·68	9·35	205·03	10·72	206·40	13·08	218·11	22·43
Mn	—	—	212·26	—	212·13	12·69	224·95	—
Cu	196·49	9·75	206·24	9·59	206·08	12·40	218·64	22·15
Cd	—	—	214·98	—	216·12	12·74	227·72	—
Mg	196·58	9·60	206·18	11·20	207·78	12·78	218·96	22·38
Zn	196·16	9·42	205·58	10·22	206·38	12·39	217·97	21·81
Fe	198·05	9·76	207·81	10·81	208·86	12·96	220·77	22·72
Mean . . .		9·55	Mean . . .	10·41	Mean . . .	12·69	Mean . . .	22·23

*Molecular Distance Ratios (topic axial ratios).*—When considered comparatively for the different salts these represent directionally in the crystal the same changes as are represented in total alteration of volume by the comparison of the molecular volumes. The ratios may be regarded as expressing the relative dimensions in space of the unit cells of the space-lattice of the crystal structure, the volume of the cell being expressed by the molecular volume. In the zinc and cadmium groups all three ratios of the ammonium salt are slightly greater than those of the rubidium salt; in the magnesium, iron, manganese, nickel and cobalt groups  $\chi$  and  $\psi$  are slightly greater and  $\omega$  slightly less, and in the copper group  $\chi$  and  $\psi$  are slightly less and  $\omega$  slightly greater. Thus, on the average, just as for the molecular volume, the spatial axial ratios of the ammonium salt are slightly greater than for the intermediate rubidium salt. It will be observed that these results include, and are in agreement with, those previously published for the magnesium, zinc, and iron groups.

It may now, therefore, be stated definitely for the whole series of double sulphates, without exception, that the replacement of potassium by ammonium ( $K_2$  by  $2NH_4$ ) is accompanied by scarcely more change of volume, or change in the directional dimensions of the unit cell of the space-lattice, than when potassium is replaced by rubidium ( $K_2$  by  $Rb_2$ ), and by only half the change of volume which ensues on the replacement of potassium by caesium ( $K_2$  by  $Cs_2$ ). Regarded in another light, the replacement of the two atoms of rubidium by the ten atoms of the two ammonium  $NH_4$  radicle-groups is accompanied by scarcely any appreciable change in the structural dimensions, either molecular volume or topic axial ratios (volume or directional extension).

*Orientation of the Optical Ellipsoid.*—Throughout the series the optical ellipsoid rotates about the symmetry axis  $b$ , which is in all cases the intermediate  $\beta$  axis of the

ellipsoid, on replacing potassium successively by rubidium and caesium, the positions following the order of the atomic weights of the alkali metals. The  $\alpha$  axis of the ellipsoid is nearest to the vertical axis  $c$  of the crystal, and the approximation is closest, among the alkali-metal salts, for the potassium salt. It is even closer, except in the copper group, for the ammonium salt, the potassium salt coming next, then the rubidium salt and the caesium salt at such angles as accord with the order of the atomic weights, but with a higher function than mere direct proportion to atomic weight. In the copper group the ammonium and potassium salts exhibit optical ellipsoids almost identically situated, with the  $\alpha$  axis inclined  $18\frac{3}{4}^\circ$  from the vertical axis  $c$ , the positions of the ellipsoids of the rubidium and caesium salts still following the rule of progression.

*Refractive Indices.*—In all the eight groups the refractive indices, including the mean index, of the ammonium salt are very close to those of the rubidium salt (which are always intermediate between those for the K and Cs salts), and usually very slightly higher. The double refraction of the ammonium salt also lies intermediate between the values for the corresponding rubidium and caesium salts, the situation varying in the different groups on either side of the half-way position; on the average it lies nearer to the value for the rubidium salt. As regards the axial ratios (the directional dimensions) of the optical ellipsoid, the values for the ammonium salt of any group are intermediate between the values for the rubidium and caesium salts of the same group, and much nearer to the rubidium salt values.

*Molecular Optical Constants.*—In specific refraction and dispersion the ammonium salt of every group is distinguished by values much higher than those for the alkali-metal salts of the same group. As regards the important property of molecular refraction, in every group of the series the value for the ammonium salt, whether calculated by the LORENZ or the GLADSTONE and DALE formula, is very close to and just slightly higher than the value for the rubidium salt, which itself is intermediate between the values for the potassium and caesium salts, in accordance with the law of progression with the atomic weight of the alkali metal. The molecular dispersion of the ammonium salt is nearest to the value for the corresponding caesium salt, in four groups being just lower than the latter, and in the other four groups just higher; for high dispersion is a characteristic property in which the ammonium salts exhibit the constitutional difference of the  $\text{NH}_4$  radicle from the alkali metals which form the other R-bases in the isomorphous salts of the series.

*Optic Axial Angle.*—No definite rule can be traced from a comparison of the optic axial angles of the ammonium salts with those of the salts containing the alkali metals; these latter salts show a progressive change in optic axial angle with change of atomic weight of the alkali metal.

*Final Conclusion.*—The work now described on the remaining five double sulphates containing ammonium confirms and emphasises the two main conclusions derived from the study of the three ammonium salts already described, which may be

stated as follows:—(1) These ammonium salts are truly isomorphous with the similarly constituted potassium, rubidium, and caesium salts of the generic formula  $R_2M(SO_4)_2 \cdot 6H_2O$ , but are not eutropic with them; the potassium, rubidium, and caesium salts alone form the exclusive eutropic series, in which the crystallographic (morphological and physical) properties obey the law of progression with the atomic weight of the alkali metal, which has been established in the previous communications concerning those salts. This law is particularly well illustrated by the fact, to which no exceptions have been observed, that the average change of angle between the crystal faces, and also the maximum change of interfacial angle (which usually occurs for the all-important monoclinic axial angle between the primary faces, and exceeds between a K and a Cs salt two whole degrees), are directly proportional to the change in atomic weight, when any one alkali metal is replaced by another.

(2) The dimensions of the space-lattice of any ammonium salt of the series are nearly identical with those of the intermediate alkali metal salt, that containing rubidium as the R-metal; so that the two atoms of rubidium are replaced by the ten atoms of the two  $NH_4$  radicle-groups without appreciably altering the crystallographic structural dimensions.

To these may be added the following third general conclusion, which has been substantiated as regards thallium in a former communication\*:—(3) The salts of this series in which R is thallium resemble the ammonium salts closely, in truly belonging to the isomorphous series, but not to the more exclusive eutropic series formed by the salts of potassium, rubidium, and caesium. Like the ammonium salts, the thallium salts also closely resemble the rubidium salts, but the thallium salts are distinguished optically, by their transcendent refractive power, both their refractive indices and their molecular refraction being far higher than for any other salts of the whole isomorphous series.

An interesting memoir has recently appeared by F. M. JAEGER† on the crystallised ethylsulphates of the rare earths,  $R_2'''(SO_4 \cdot C_2H_5)_6 + 18H_2O$  in which R is Yt, Ce, La, Nd, Pr, Sm, Eu, Dys, Gd, Er, Thu, and NYb. JAEGER finds that the crystalline forms of these salts are so extremely close to each other that the differences fall within the limits of experimental error. He concludes, therefore, that they are rigorously identical, oscillating about a mean form in a manner entirely accidental. The rare earths, forming a group to themselves, and differing so little (especially in their sub-groups) in the values of their atomic weights, present an altogether different order of problem to the comparison of K, Rb, and Cs compounds. The series of rare earths belong to the central groups of the periodic system, in which the electro-positive property is at its minimum, and the chemical characters are so remarkably alike that extraordinary processes and refinement of method

\* 'Roy. Soc. Proc.' A, 1909, 83, 211.

† 'Recueil des Trav. Chim. des Pays-Bas,' 1914, 33, 343.



are necessary in order to separate their compounds from each other. Extreme closeness of the crystallographic characters of their crystallised salts is, therefore, precisely what one would expect to find. The very opposite is the case for the alkali metals, which latter were chosen expressly by the author (TUTTON) as belonging to the first group of the periodic system, exhibiting the electro-positive property at its maximum, while at the same time showing large differences (46 between K and Rb and 47 between Rb and Cs) in atomic weight. Moreover, the crystal system of the ethylsulphates of the rare earths is the hexagonal, and a comprehensive comparison of the author's results on the rhombic (simple sulphates and selenates) and monoclinic (double sulphates and selenates) series has shown that the system of crystallisation has a preponderating effect on the angular differences, the latter being the smaller the higher the degree of symmetry. It might have been expected, *a priori*, that the monoclinic pair, say,  $\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Cs}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  would give closer angular values than the more symmetric rhombic pair, for example,  $\text{K}_2\text{SO}_4$  and  $\text{Cs}_2\text{SO}_4$ , since there is a common "dead weight"; but experience proves the contrary, thus emphasising the effect of difference of system. Now the hexagonal is a higher system in degree of symmetry than the rhombic, and the angular differences (which the author found very small yet clear and unmistakeable in the rhombic sulphates and selenates, although not so large as those shown in the monoclinic double salts) to be expected in the hexagonal system, other factors remaining the same, are still smaller, and might easily fall within the limits  $2'-3'$  or thereabouts. JAEGER has, in fact, realised such a series, and his results are precisely what the author (TUTTON) would have expected. It cannot be emphasised too strongly (*a*) that the author's tables of angles of the whole 31 double sulphates, the 9 double selenates yet investigated, and the whole 10 simple sulphates and selenates, show a general correspondence of mean and calculated values within  $2'$  for the rhombic simple salts and at most  $5'$  (probably only  $3'$ ) for the monoclinic double salts, and that the constants given by the author for each individual salt can certainly be relied on within these narrow limits; and (*b*) that the deductions made by the author, such as the important one regarding the observed progression with the atomic weight of the alkali metal, are unquestionably valid, since the angular differences in question between the salts under comparison are far and away greater than these small limits of possible error, indeed in the maximum amounting to  $2\frac{1}{2}^\circ$ .

The author has no doubt of the probable accuracy of the work of JAEGER, the results agreeing perfectly with the author's expectations from the high symmetry displayed. The contribution is, moreover, a very welcome one at the present juncture. But if JAEGER's deduction, as the author understands it, is that literally the axial ratio  $a:c$  of his hexagonal salts is rigorously the same for all the salts, the minute differences being considered only chance variations from this mean form, then the author must hold that this view is not a reasonable conclusion, and that it cannot be accepted; it could in any case only be possibly true at some definite

temperature. There can be no doubt, however, that each salt has its own particular crystallographic angular values, and that there are real although very minute angular differences between the crystals of the various salts of the series, in accordance with the law of HAÜY, which the author (TUTTON) considers he has fully substantiated. This law provides that, except when the symmetry imposes identity of crystal angles (as in the cubic system and the  $90^\circ$ ,  $45^\circ$ ,  $60^\circ$ , and  $30^\circ$  angles of the tetragonal and hexagonal systems), every substance is characterised by its own specific crystalline form, the cases of isomorphism being only close resemblances within the limits of identity of symmetry.

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