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VI. *Monoclinic Double Selenates of the Nickel Group.*

By A. E. H. Tutton, *D.Sc.*, *M.A.*, *F.R.S.*

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This communication deals with the four double selenates of the series $R_2M(SeO_4)_2 . 6H_2O$, in which M is nickel and R is potassium, rubidium, cæsium, and ammonium. Potassium nickel selenate and ammonium nickel selenate only have been previously investigated, and to a very limited extent, by vom Rath and Topsøe and Christiansen; rubidium nickel selenate and cæsium nickel selenate do not appear to have formed the subject of either goniometrical or physical investigation.

Great care has been taken with the preparation of the four double salts in a state of purity. The solutions in pure water from which the crystals were deposited contained in each case the two simple constituent salts in exactly equal molecular proportions. Good crystallised specimens of potassium selenate and ammonium selenate were already in the author's possession, and the selenates of cæsium and rubidium were prepared by dissolving the pure carbonates of the two metals in the exact quantity of pure selenic acid, all trace of carbonic acid being removed by boiling. The nickel selenate was prepared in the four cases separately, by dissolving in pure water the quantity of nickel sulphate corresponding molecularly to the amount of the alkali selenate to be used in the preparation of the double salt, and adding a very slight excess of caustic potash solution (freshly prepared from the weighed quantity of solid potash) in order to precipitate all the nickel as nickelous hydrate. After warming, so as to complete the precipitation, the liquid was allowed to stand until the precipitate had settled, when it was washed with a large volume of water, six times by decantation and six further times on the filter. The nickelous hydrate was then dissolved in the calculated amount of selenic acid, the filtered solution of nickel selenate was added to the alkali selenate solution, and the whole allowed to crystallise in successive crops by spontaneous evaporation, with all the precautions indicated on p. 9 of the author's 'Crystallography and Practical Crystal Measurement.'

Potassium Nickel Selenate $K_2Ni(SeO_4)_2 . 6H_2O$.

Morphology.

Some crystals of this salt were measured in the year 1862 by vom Rath.* They were of a very simple character, comprising only four forms, and it is somewhat

* 'Pogg. Ann. der Phys.' (1862), vol. 115, p. 484, and vol. 116, p. 363.

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singular that even in the very numerous (over 30) crops prepared in the course of the work now described no other than these same four forms have been observed on this member of the great monoclinic series.

The crystals are bright green in colour.

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

Ratios of Axes.—

$a : b : c = 0{\cdot}7467 : 1 : 0{\cdot}5059$. Values of VOM RATH, $0{\cdot}7453 : 1 : 0{\cdot}5060$.

Axial Angle.—$\beta = 104° 27'$. Value of VOM RATH, $104° 53'$.

Forms Observed.—$c\{001\}$, $p\{110\}$, $q\{011\}$, and $r'\{\bar{2}01\}$.

Habit.—Tabular parallel to $c\{001\}$, to short prismatic parallel to $p\{110\}$. A common intermediate type is shown in fig. 1.

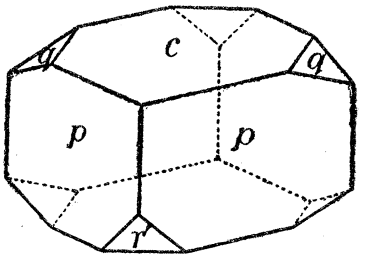

Fig. 1.

Eleven small crystals were measured, selected from four different crops. Greater difficulty than usual was experienced in obtaining crystals free from serious striation of the $p\{110\}$ and $c\{001\}$ faces, and a very large number of crops were grown, from two entirely distinct preparations, before satisfactory small crystals were produced. The striation affects the values of the angles pp and cp particularly, rendering pp $(= 2ap)$ considerably too large, pp $(= 2bp)$ conversely too small to the same extent (possibly as much as five minutes), and cp to a less degree ($2'$ or $3'$) too large. This fact was established by measuring a number of crystals affected by the striation and comparing the results with those derived from the perfect crystals used in the measurements recorded in the table, which represent the true value of the angles. The unusual prevalence of such striation of the p and c faces is also responsible for the more than usual discrepancy between the observed and calculated values of the angle cr', in cases like that of the salt under consideration, in which the r' faces were perfect (yielding brilliant single images of the signal) and in which the c faces, when adjusted for the measurement of this orthozone, gave also indubitably placed images, all the images of the bundle coalescing for this zone in the same vertical line.

The faces of $q\{011\}$ were usually relatively much smaller than those of the basal pinakoid $c\{001\}$, as shown in fig. 1, and the faces of $r'\{\bar{2}01\}$ were usually also small, although generally somewhat larger than the q faces. Occasionally, in particular crops, the q faces were relatively larger and the c faces correspondingly less.

Of the only four forms observed, $c\{001\}$ and $p\{110\}$ thus usually largely predominate and determine the habit.

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Interfacial Angles of Potassium Nickel Selenate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.	Values of vom Rath.
		° ′ ° ′	° ′	° ′	′	° ′
$ac = (100):(001)$	—	—	—	75 33	—	75 7
$as = (100):(101)$	—	—	—	46 15	—	—
$sc = (101):(001)$	—	—	—	29 18	—	—
$cr' = (001):(\bar{2}01)$	20	63 20– 63 28	63 24	63 13	11	63 35
$cs' = (001):(\bar{1}01)$	—	—	—	38 16	—	—
$s'r' = (\bar{1}01):(\bar{2}01)$	—	—	—	24 57	—	—
$r'a = (\bar{2}01):(\bar{1}00)$	—	—	—	41 14	—	—
$r'c = (\bar{2}01):(00\bar{1})$	20	116 32–116 41	116 36	116 47	11	—
$ap = (100):(110)$	—	—	—	35 54	—	—
$pp' = (110):(120)$	—	—	—	19 28	—	—
$p'b = (120):(010)$	—	—	—	34 38	—	—
$pp''' = (110):(130)$	—	—	—	29 22	—	—
$p'''b = (130):(010)$	—	—	—	24 44	—	—
$pb = (110):(010)$	—	—	—	54 6	—	—
$pp = (110):(1\bar{1}0)$	22	71 41– 71 58	71 48	*	—	71 32
$pp = (110):(\bar{1}10)$	22	108 0–108 24	108 12	108 12	0	—
$cq = (001):(011)$	42	25 54– 26 17	26 6	26 6	0	26 0
$qb = (011):(010)$	—	—	—	63 54	—	—
$qq = (011):(01\bar{1})$	18	127 46–127 53	127 48	*	—	—
$ao = (100):(111)$	—	—	—	49 30	—	—
$oq = (111):(011)$	—	—	—	27 33	—	—
$aq = (100):(011)$	—	—	—	77 3	—	—
$qo' = (011):(\bar{1}11)$	—	—	—	34 26	—	—
$o'a = (\bar{1}11):(\bar{1}00)$	—	—	—	68 31	—	—
$co = (001):(111)$	—	—	—	35 0	—	—
$op = (111):(110)$	—	—	—	43 20	—	—
$cp = (001):(\bar{1}10)$	38	78 12– 78 28	78 20	*	—	77 58
$po' = (110):(11\bar{1})$	—	—	—	57 7	—	—
$o'c = (11\bar{1}):(00\bar{1})$	—	—	—	44 33	—	—
$pc = (110):(00\bar{1})$	38	101 29–101 47	101 40	101 40	0	—
$bn = (010):(121)$	—	—	—	53 50	—	—
$no = (121):(111)$	—	—	—	16 6	—	—
$bo = (010):(111)$	—	—	—	69 56	—	—
$os = (111):(101)$	—	—	—	20 4	—	—
$bo' = (010):(\bar{1}11)$	—	—	—	65 10	—	—
$o's' = (\bar{1}11):(\bar{1}01)$	—	—	—	24 50	—	—
$sq = (101):(011)$	—	—	—	38 27	—	—
$qp = (011):(\bar{1}10)$	28	85 23– 85 44	85 35	85 37	2	86 7
$ps = (\bar{1}10):(\bar{1}0\bar{1})$	—	—	—	55 56	—	—
$pq = (\bar{1}10):(0\bar{1}\bar{1})$	28	94 13– 94 38	94 25	94 23	2	—
$s'q = (\bar{1}01):(011)$	—	—	—	45 10	—	—
$qn = (011):(121)$	—	—	—	26 52	—	—
$np = (121):(110)$	—	—	—	37 3	—	—
$qp = (011):(110)$	31	63 45– 64 5	63 55	63 55	0	63 36
$ps' = (110):(10\bar{1})$	—	—	—	70 55	—	—
$pq = (110):(0\bar{1}\bar{1})$	31	115 57–116 12	116 5	116 5	0	—
$r'o' = (\bar{2}01):(\bar{1}11)$	—	—	—	34 38	—	—
$o'p = (\bar{1}11):(110)$	—	—	—	92 54	—	—
$pr' = (110):(20\bar{1})$	38	52 10– 52 30	52 22	52 28	6	52 25
$r'p = (\bar{2}01):(110)$	38	127 32–127 52	127 39	127 32	7	—
Total number of measurements.	414					

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The values of the principal angles measured by VOM RATH are quoted in the last column of the table of angles.

Cleavage.—There is a good cleavage parallel to $r'\{\bar{2}01\}$. The cleaved surfaces gave excellent signal images at exactly 180° from the r' face left on each fragment.

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	16°·3/4° . . .	2·5578	For 20°/4° . . .	2·5569
II.	,,	17°·1/4° . . .	2·5586	,, 20°/4° . . .	2·5579
III.	,,	17°·6/4° . . .	2·5618	,, 20°/4° . . .	2·5612
IV.	,,	17°·9/4° . . .	2·5619	,, 20°/4° . . .	2·5614
V.	,,	18°·2/4° . . .	2·5591	,, 20°/4° . . .	2·5586
				Mean . . .	2·5592

The value accepted for 20°/4° is therefore **2·559**.

VON GROTH (' Chemische Krystallographie,' vol. II, p. 545) quotes a value, 2·539, of TOPSØE and CHRISTIANSEN for the specific gravity of this salt ; the author is unable to find it in the 1874 memoir of these authors (which deals with the optics), but it is given by TOPSØE in his dissertation of 1870.*

Molecular Volume.— $\frac{M}{d} = \frac{527{\cdot}52}{2{\cdot}559} = 206{\cdot}14.$

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

$$\chi : \psi : \omega = 6{\cdot}1677 : 8{\cdot}2598 : 4{\cdot}1786.$$

Optics.

Orientation and Nature of the Optical Ellipsoid.—The plane of the optic axes is the plane of symmetry $b\{010\}$. The sign of the double refraction is positive. The first median line, therefore, corresponds to the refractive index γ and the second median line to the index α.

The orientation of the two median lines in the plane of symmetry was determined with two section-plates ground parallel to that plane with the aid of the cutting and grinding goniometer. The following results were obtained.

Extinction Direction in the Symmetry Plane.

Plate 1 . . . . 7° 15′, Plate 2 . . . . 7° 40′,
Mean . . . 7° 28′ with normal to $c\{001\}$.

The position of this extinction direction is behind the normal to $c\{001\}$, and it is

* 'Krystallogr.-kem. Unders. over de selensure Salte,' Copenhagen, 1870, p. 10.

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the second median line, the first median line being at 90° thereto, as shown in the accompanying fig. 2.

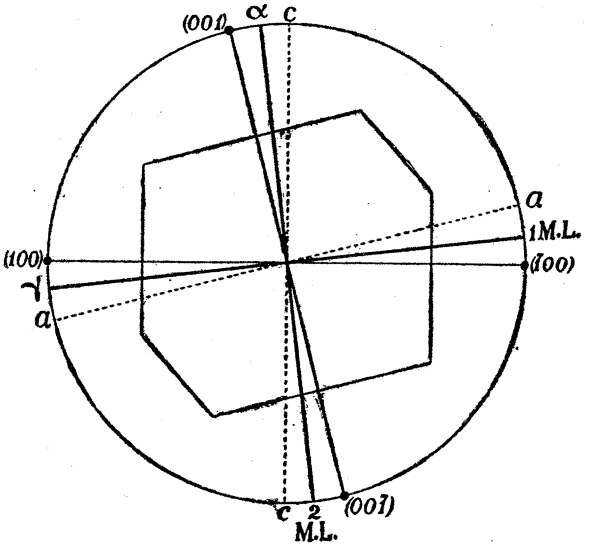

Fig. 2.

As the normal to $c\{001\}$ lies 14° 27′ in front of the vertical axis c (the morphological axial angle $ac = 75° 33'$), the second median line lies 6° 59′ in front of the vertical morphological axis c. The first median line lies to the same extent (6° 59′) below the normal to $a\{100\}$ and 7° 28′ above the inclined morphological axis a.

Very similar positions for the median lines were obtained by Topsøe and Christiansen,* that for the first median line being given as 6° 57′ above the axis a.

Optic Axial Angle.—Three excellent pairs of section-plates, perpendicular to the first (numbered 1, 2, 3) and second (numbered $1a$, $2a$, $3a$) median lines, were prepared, yielding perfect interference figures in convergent polarised light. They afforded the measurements of 2E (the apparent optic axial angle in air) and of $2H_a$ and $2H_o$ (the apparent acute and obtuse angles in monobromonaphthalene) recorded in the two following tables; the true optic axial angles calculated from $2H_a$ and $2H_o$ are given in the penultimate column, and the mean value of the true angle in the last column.

Apparent Optic Axial Angle in Air, 2E, of KNi Selenate.

Light.	Plate 1.	Plate 2.	Plate 3.	Mean 2E.
	° ′	° ′	° ′	° ′
Li	129 33	128 40	129 24	129 12
C	129 38	128 45	129 29	129 17
Na	130 16	129 36	130 17	130 3
Tl	131 14	130 26	131 2	130 54
Cd	131 35	130 50	131 34	131 20
F	132 6	131 16	131 55	131 46

* 'Ann. Chim. Phys.,' series 5, vol. 1, p. 82 (1874).

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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	66 7	1a	95 46	72 40	72 45
	2	66 13	2a	95 37	72 48	
	3	66 17	3a	95 45	72 48	
C	1	66 5	1a	95 42	72 40	72 45
	2	66 11	2a	95 34	72 48	
	3	66 15	3a	95 40	72 48	
Na	1	65 53	1a	95 18	72 42	72 48
	2	66 2	2a	95 9	72 52	
	3	66 0	3a	95 10	72 50	
Tl	1	65 41	1a	94 54	72 43	72 51
	2	65 46	2a	94 38	72 54	
	3	65 48	3a	94 34	72 57	
Cd	1	65 31	1a	94 35	72 44	72 53
	2	65 38	2a	94 20	72 56	
	3	65 39	3a	94 14	73 0	
F	1	65 20	1a	94 15	72 45	72 56
	2	65 31	2a	93 56	73 1	
	3	65 29	3a	93 51	73 2	

The values obtained by TOPSØE and CHRISTIANSEN* were, for 2E 129° 56′ and for $2V_a$ 72° 56′.

Dispersion of the Median Lines.—This is exceedingly small, namely, about 7′ only. The direction is such that the first median line is nearer to the axis a by 7′ for red C hydrogen light than for greenish blue F hydrogen light. It was determined by observations with the section-plates 2 and 3 immersed in monochlorbenzene, the refractive index of which, 1·5248 for D-light, is nearly identical with the mean index of the crystals.

Effect of Temperature on Optic Axial Angle.—The apparent optic axial angle in air 2E increases with rise of temperature. The amount of the increase was determined with section 3, and proved to be 3° 16′ for a rise of 50° (from 18° to 68°) of temperature.

Refractive Indices.—Six 60° prisms were prepared with the aid of the cutting and grinding goniometer, each to yield two of the three indices directly, the bisecting plane and refractive edge being parallel respectively to a principal plane and principal axis of the optical ellipsoid. Four different values for each index were thus obtained. The mean results are given in the accompanying table.

* 'Ann. Chim. Phys.,' series 5, vol. 1, p. 83 (1874).

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REFRACTIVE Indices of Potassium Nickel Selenate.

Light.	α.	β.	γ.
Li	1·5142	1·5232	1·5387
C	1·5147	1·5237	1·5392
Na	1·5181	1·5272	1·5427
Tl	1·5212	1·5305	1·5464
Cd	1·5232	1·5325	1·5486
F	1·5251	1·5344	1·5507
G	1·5314	1·5407	1·5571

Mean of α, β, and γ for Na light = 1·5293.

α = Vibration direction parallel to second median line, 6° 59′ in front of axis c.
β = ,, ,, ,, ,, symmetry axis b.
γ = ,, ,, ,, ,, first median line, 7° 28′ above axis a.

Double refraction, $Na_{\gamma-\alpha} = 0·0246$.

General formula for β, corrected to a vacuum :—

$$\beta = 1·5043 + \frac{1\ 034\ 256}{\lambda^2} - \frac{7\ 821\ 960\ 000\ 000}{\lambda^4} + \ldots .$$

The α indices are equally well reproduced by the formula if the constant 1·5043 is diminished by 0·0092, and the γ indices if it is increased by 0·0156.

Observations at 70° indicated that the refractive indices of potassium nickel selenate diminish by about 0·0018 for a rise of 55° of temperature.

The values of TOPSØE and CHRISTIANSEN* for the refractive indices were : for β, line C 1·5207, line D 1·5248, line F 1·5315 ; the α and γ values were only obtained indirectly, and for line D only ; they are given as 1·5199 and 1·5339.

Axial Ratios of the Optical Ellipsoid.—These values work out as under :—

Indicatrix . . . . $\alpha : \beta : \gamma = 0·9940 : 1 : 1·0101$.
Velocity ellipsoid . . $\mathfrak{a} : \mathfrak{b} : \mathfrak{c} = 1·0060 : 1 : 0·9900$.

Molecular Optical Constants.—The values of these constants, calculated by both the formulæ of LORENZ and of GLADSTONE and DALE, are given in the next table.

	Axis of optical indicatrix	α.	β.	γ.
LORENZ	Specific refraction, $\frac{n^2-1}{(n^2+2)d} = \mathfrak{r}$ . . { C	0·1178	0·1195	0·1225
	{ G	0·1210	0·1227	0·1258
,,	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = \mathfrak{m}$. { C	62·14	63·04	64·60
	{ G	63·82	64·75	66·37
,,	Specific dispersion, $\mathfrak{r}_G - \mathfrak{r}_C$	0·0032	0·0032	0·0033
,,	Molecular dispersion, $\mathfrak{m}_G - \mathfrak{m}_C$	1·68	1·71	1·77
GLADSTONE	Molecular refraction, $\frac{n-1}{d} M$ C	106·10	107·96	111·10

Mean molecular refraction (GLADSTONE), $\frac{1}{3}(\alpha+\beta+\gamma) = 108·39$.

* 'Ann. Chim. Phys.,' series 5, vol. 1, p. 82 (1874).

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Rubidium Nickel Selenate, $Rb_2Ni(SeO_4)_2 . 6H_2O$.

Morphology.

The crystals of this salt do not appear to have been hitherto investigated. They are bright green in colour, resembling the potassium salt, but are somewhat richer in faces. About 20 crops were successively obtained, three of which were of special excellence for goniometrical purposes.

Ten small crystals were measured, selected from the three crops above mentioned, the crystals of which were most free from striation. The individuals measured were especially perfect, as will be obvious from the close agreement between the observed and calculated values in the accompanying table of angles representing the results of the measurements.

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

Ratios of Axes.—

$a : b : c = 0{\cdot}7395 : 1 : 0{\cdot}5031.$

Axial Angle.—$\beta = 105° 20'$.

Forms Observed.—$b\{010\}$, $c\{001\}$, $p\{110\}$, $q\{011\}$, $r'\{\bar{2}01\}$, and $o'\{\bar{1}11\}$.

Habit.—More or less tabular parallel to $c\{001\}$, the commonest type being represented in fig. 3; occasionally the tables become so thick as to affect a short prismatic habit parallel to $p\{110\}$.

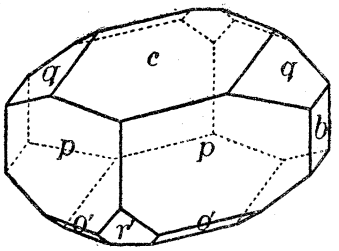

Fig. 3.

The $q\{011\}$ faces were relatively more prominent on the crystals of this salt, and the $c\{001\}$ faces correspondingly less so, than in the case of the crystals of the potassium salt. The c faces were generally, however, still to some extent the larger. The faces of the primary prism $p\{110\}$ were invariably predominant. Several of the crops consisted of crystals showing good little faces of the clino-pinakoid $b\{010\}$, and very narrow faces of $o'\{\bar{1}11\}$ on each side of the small faces of $r'\{\bar{2}01\}$, which latter were shown by most of the crystals of all the crops prepared.

Cleavage.—There is a good cleavage parallel to $r'\{\bar{2}01\}$. No trace of any other cleavage was observed.

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Interfacial Angles of Rubidium Nickel Selenate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.
		° ′ ° ′	° ′	° ′	′
$ac = (100):(001)$	—	—	—	74 40	—
$as = (100):(101)$	—	—	—	45 36	—
$sc = (101):(001)$	—	—	—	29 4	—
$cr' = (001):(\bar{2}01)$	12	63 50– 64 7	63 59	63 58	1
$cs' = (001):(\bar{1}01)$	—	—	—	38 38·5	—
$s'r' = (\bar{1}01):(\bar{2}01)$	—	—	—	25 19·5	—
$r'a = (\bar{2}01):(\bar{1}00)$	—	—	—	41 22	—
$r'c = (\bar{2}01):(00\bar{1})$	12	115 49–116 10	116 1	116 2	1
$ap = (100):(110)$	—	—	—	35 30·5	—
$pp' = (110):(120)$	—	—	—	19 28	—
$p'b = (120):(010)$	—	—	—	35 1·5	—
$pp''' = (110):(130)$	—	—	—	29 27	—
$p'''b = (130):(010)$	—	—	—	25 2·5	—
$pb = (110):(010)$	28	54 23– 54 35	54 29·5	*	—
$pp = (110):(1\bar{1}0)$	18	70 57– 71 4	71 1	71 1	0
$pp = (110):(\bar{1}10)$	18	108 51–109 9	108 59	108 59	0
$cq = (001):(011)$	23	25 46– 25 58	25 53	25 53	0
$qb = (011):(010)$	19	64 2– 64 14	64 7	*	—
$qq = (011):(01\bar{1})$	9	128 9–128 21	128 14	128 14	0
$ao = (100):(111)$	—	—	—	48 49	—
$oq = (111):(011)$	—	—	—	27 25	—
$aq = (100):(011)$	—	—	—	76 14	—
$qo' = (011):(\bar{1}11)$	—	—	—	34 50	—
$o'a = (\bar{1}11):(\bar{1}00)$	—	—	—	68 56	—
$co = (001):(111)$	—	—	—	34 40	—
$op = (111):(110)$	—	—	—	42 54	—
$cp = (001):(110)$	40	77 27– 77 39	77 34	*	—
$po' = (110):(11\bar{1})$	10	57 27– 57 44	57 31	57 34	3
$o'c = (11\bar{1}):(00\bar{1})$	10	44 33– 45 7	44 55	44 52	3
$pc = (110):(00\bar{1})$	40	102 17–102 34	102 26	102 26	0
$bn = (010):(121)$	—	—	—	54 18	—
$no = (121):(111)$	—	—	—	15 56	—
$bo = (010):(111)$	—	—	—	70 14	—
$os = (111):(101)$	—	—	—	19 46	—
$bo' = (010):(\bar{1}11)$	9	65 9– 65 14	65 11	65 12	1
$o's' = (\bar{1}11):(\bar{1}01)$	—	—	—	24 48	—
$o'o' = (\bar{1}11):(\bar{1}\bar{1}1)$	2	49 38– 49 40	49 39	49 36	3
$sq = (101):(011)$	—	—	—	38 9	—
$qp = (011):(\bar{1}10)$	17	86 31– 86 40	86 35	86 34	1
$ps = (\bar{1}10):(\bar{1}0\bar{1})$	—	—	—	55 17	—
$pq = (\bar{1}10):(0\bar{1}\bar{1})$	17	93 15– 93 33	93 25	93 26	1
$s'q = (\bar{1}01):(011)$	—	—	—	45 21	—
$qn = (011):(121)$	—	—	—	26 42	—
$np = (121):(110)$	—	—	—	36 44	—
$qp = (011):(110)$	18	63 12– 63 31	63 24	63 26	2
$ps' = (110):(10\bar{1})$	—	—	—	71 13	—
$pq = (110):(0\bar{1}\bar{1})$	18	116 27–116 43	116 35	116 34	1
$r'o' = (\bar{2}01):(\bar{1}11)$	6	34 40– 34 56	34 47	34 52	5
$o'p = (\bar{1}11):(110)$	6	92 45– 92 56	92 51	92 47·5	3·5
$pr' = (110):(20\bar{1})$	16	52 11– 52 28	52 20·5	52 20·5	0
$r'p = (\bar{2}01):(110)$	15	127 27–127 50	127 38	127 39·5	1·5
Total number of measurements.	363				

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Volume.

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

I.	Density for	16°·9/4° . . .	2·8579	For 20°/4° . . .	2·8570
II.	,,	17°·3/4° . . .	2·8577	,, 20°/4° . . .	2·8569
III.	,,	17°·3/4° . . .	2·8551	,, 20°/4° . . .	2·8543
IV.	,,	18°·9/4° . . .	2·8556	,, 20°/4° . . .	2·8553
				Mean . . .	2·8559

Accepted value for 20°/4°, **2·856**. This appears to be the first determination of the specific gravity of rubidium nickel selenate.

Molecular Volume.— $\frac{M}{d} = \frac{619{\cdot}62}{2{\cdot}856} = 216{\cdot}96.$

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

$$\chi : \psi : \omega = 6{\cdot}2533 : 8{\cdot}4561 : 4{\cdot}2542.$$

Optics.

Orientation and Nature of Optical Ellipsoid.—The plane of the optic axes is the symmetry plane $b\{010\}$. The double refraction is of positive sign, the first median line corresponding to the refractive index λ and the second median line to α.

Extinction determinations with two section-plates parallel to the symmetry plane afforded the following indications of the direction of one of the two principal axes of the optical ellipsoid (the median lines) lying in that plane.

Extinction Direction in the Symmetry Plane.

Plate 1 . . . . 5° 34′, Plate 2 . . . . 5° 8′,

Mean . . . 5° 21′ with normal to $c\{001\}$.

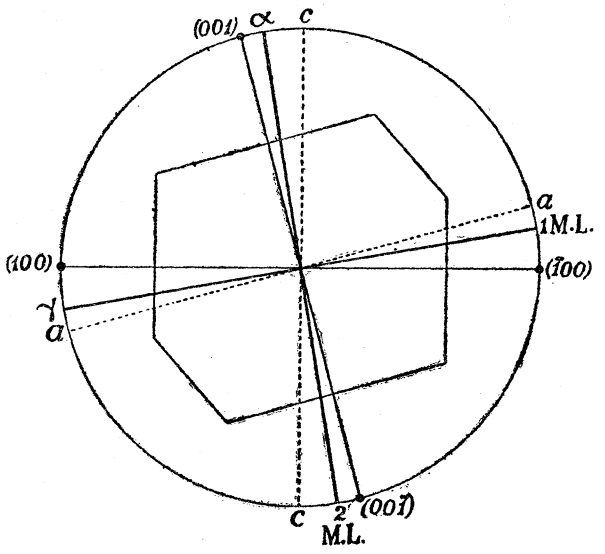

Fig. 4.

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This direction is behind the normal to the basal plane $c_1\{001\}$, towards the vertical morphological axis c, and it is the second median line. Fig. 4 will make the position clear. As the morphological axial angle ac is 74° 40′, and the angle between the normal to $c\{001\}$ and the vertical axis c is consequently 15° 20′, the second median line lies 9° 59′ in front of the vertical axis c, in the obtuse angle of the morphological axes a and c. The first median line lies 5° 21′ above the inclined morphological axis a, also in the obtuse angle ac, and 9° 59′ below the normal to $a\{100\}$.

Optic Axial Angle.—Three excellent pairs of section-plates were ground perpendicular to the first (1, 2, 3) and second ($1a$, $2a$, $3a$), median lines, and they afforded good interference figures in monobromonaphthalene, from which the measurements of the acute and obtuse angles $2H_a$ and $2H_o$ and the calculated results for the true angle $2V_a$ recorded in the accompanying table were derived. The apparent optic axial angle in air 2E is so large that it is not possible to measure it, the interference brushes and innermost rings disappearing before the brushes can be brought quite to the cross-wires of the polarising goniometer.

Rubidium Nickel Selenate.

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	74 36	$1a$	87 37	82 24	
	2	74 38	$2a$	87 52	82 18	82 23
	3	74 53	$3a$	87 53	82 27	
C	1	74 33	$1a$	87 36	82 22	
	2	74 36	$2a$	87 50	82 17	82 22
	3	74 50	$3a$	87 51	82 26	
Na	1	74 14	$1a$	87 29	82 14	
	2	74 19	$2a$	87 30	82 16	82 13
	3	74 14	$3a$	87 38	82 9	
Tl	1	73 52	$1a$	87 21	82 4	
	2	73 58	$2a$	87 9	82 13	82 7
	3	73 47	$3a$	87 14	82 4	
Cd	1	73 36	$1a$	87 12	81 58	
	2	73 36	$2a$	86 55	82 7	82 3
	3	73 33	$3a$	87 0	82 2	
F	1	73 23	$1a$	87 5	81 52	
	2	73 22	$2a$	86 39	82 5	81 58
	3	73 18	$3a$	86 46	81 59	

Dispersion of the Median Lines.—The median lines show practically no dispersion. Section 1 showed 3′ in one direction and section 3 showed 2′ in the other direction,

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while section 2 exhibited no measurable amount of dispersion. The section-plates were immersed during these observations in methyl salicylate, the refractive index of which liquid (1·5363) is not far from the mean index of the crystals.

Refractive Indices.—Six 60°-prisms were employed, ground so that each afforded directly two indices, α and β, or β and γ, or α and γ, the refracting edge not only being parallel to a principal axis of the optical ellipsoid, but the bisecting plane being also parallel to a principal plane of the ellipsoid. The mean results for the four independent values of each index thus obtained are given in the accompanying table.

Refractive Indices of Rubidium Nickel Selenate.

Light.	α.	β.	γ.
Li	1·5161	1·5253	1·5351
C	1·5166	1·5258	1·5356
Na	1·5198	1·5291	1·5390
Tl	1·5231	1·5325	1·5424
Cd	1·5248	1·5342	1·5443
F	1·5268	1·5362	1·5466
G	1·5335	1·5429	1·5534

Mean of α, β, and γ for Na light = 1·5293.

α = Vibration direction parallel to second median line, 9° 59′ in front of axis c.
β = „ „ „ „ symmetry axis b.
γ = „ „ „ „ first median line, 5° 21′ above axis a.

Double refraction, $Na_{\gamma-\alpha} = 0{\cdot}0192$.

General formula for β, corrected to a vacuum :—

$$\beta = 1{\cdot}5103 + \frac{760\,688}{\lambda^2} - \frac{3\,270\,190\,000\,000}{\lambda^4} + \ldots .$$

The α indices are also reproduced by the formula if the constant 1·5103 is diminished by 0·0093, and the γ indices if it is increased by 0·0099.

Observations at 70° indicated that the refractive indices diminished with rise of temperature, to the extent of 0·0017 for 55° rise of temperature.

Axial Ratios of the Optical Ellipsoid.—The values for the optical indicatrix and optical velocity ellipsoid are respectively as follows :—

$$\alpha : \beta : \gamma = 0{\cdot}9939 : 1 : 1{\cdot}0065.$$

$$\mathfrak{a} : \mathfrak{b} : \mathfrak{c} = 1{\cdot}0061 : 1 : 0{\cdot}9936.$$

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Molecular Optical Constants.—The values of the LORENZ and the GLADSTONE and DALE constants are given in the accompanying table.

	Axis of optical indicatrix . . .	α.	β.	γ.
LORENZ	Specific refraction, $\frac{n^2-1}{(n^2+2)d} = \mathfrak{n}$ . . { C	0·1059	0·1074	0·1091
	{ G	0·1088	0·1104	0·1121
,,	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = \mathfrak{m}$. { C	65·59	66·57	67·61
	{ G	67·39	68·38	69·47
,,	Specific dispersion, $\mathfrak{n}_G - \mathfrak{n}_C$	0·0029	0·0030	0·0030
,,	Molecular dispersion, $\mathfrak{m}_G - \mathfrak{m}_C$	1·80	1·81	1·86
GLADSTONE	Molecular refraction, $\frac{n-1}{d} M$ C	112·08	114·07	116·20

Mean molecular refraction (GLADSTONE), $\frac{1}{3}(\alpha+\beta+\gamma) = 114{\cdot}12$.

Cæsium Nickel Selenate, $Cs_2Ni(SeO_4)_2 . 6H_2O$.

Morphology.

No previous measurements or description of this salt appear to have been made. It forms bright emerald green crystals of perfect transparency, possessing faces of high reflecting power. About thirty crops were prepared, derived from two distinct preparations.

Twelve small crystals, in several cases no larger than a pin's head, were measured, selected from four different crops.

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

Ratios of Axes.—$a : b : c = 0{\cdot}7288 : 1 : 0{\cdot}4993$.

Axial Angle.—$\beta = 106° 11'$.

Forms Observed.—$a\{100\}$, $b\{010\}$, $c\{001\}$, $p\{110\}$, $q\{011\}$, $r'\{\bar{2}01\}$, and $o'\{\bar{1}11\}$.

Habit.—Very characteristic. Prismatic parallel to the inclined axis a, the prism being formed by the broad and elongated faces of $q\{011\}$ and the narrower elongated faces of the basal plane $c\{001\}$, as shown in fig. 5.

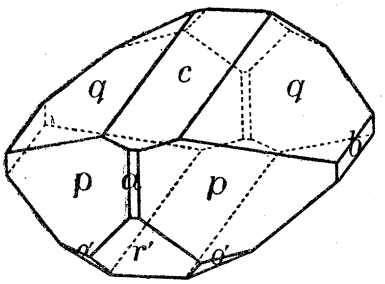

Fig. 5.

The facial development and planeness, in the cases of the measured crystals, were exceptionally perfect, the signal reflections being so sharp and true that in the cases

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Interfacial Angles of Cæsium Nickel Selenate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.
$ac = (100):(001)$	—	—	—	73 49	—
$as = (100):(101)$	—	—	—	44 51	—
$sc = (101):(001)$	—	—	—	28 58	—
$cr' = (001):(\bar{2}01)$	14	64 42– 65 4	64 54	64 54	0
$cs' = (001):(\bar{1}01)$	—	—	—	39 11	—
$s'r' = (\bar{1}01):(\bar{2}01)$	—	—	—	25 43	—
$r'a = (\bar{2}01):(\bar{1}00)$	—	—	—	41 17	—
$r'c = (\bar{2}01):(00\bar{1})$	14	114 55–115 19	115 5	115 6	1
$ap = (100):(110)$	—	—	—	34 58	—
$pp' = (110):(120)$	—	—	—	19 28	—
$p'b = (120):(010)$	—	—	—	35 34	—
$pp''' = (110):(130)$	—	—	—	29 33	—
$p'''b = (130):(010)$	—	—	—	25 29	—
$pb = (110):(010)$	48	54 58– 55 6	55 2	*	—
$pp = (110):(1\bar{1}0)$	26	69 50– 70 0	69 56	69 56	0
$cq = (001):(011)$	48	25 33– 25 44	25 37	25 37	0
$qb = (011):(010)$	48	64 17– 64 29	64 23	*	—
$ao = (100):(111)$	—	—	—	48 2	—
$oq = (111):(011)$	—	—	—	27 25	—
$aq = (100):(011)$	—	—	—	75 27	—
$qo' = (011):(\bar{1}11)$	1	—	35 18	35 19	1
$o'a = (\bar{1}11):(\bar{1}00)$	—	—	—	69 14	—
$co = (001):(111)$	—	—	—	34 23	—
$op = (111):(110)$	—	—	—	42 25	—
$cp = (001):(110)$	40	76 41– 76 56	76 48	*	—
$po' = (110):(11\bar{1})$	8	57 55– 58 4	58 0	58 0	0
$o'c = (11\bar{1}):(00\bar{1})$	10	45 2– 45 21	45 12	45 12	0
$bn = (010):(121)$	—	—	—	54 51	—
$no = (121):(111)$	—	—	—	15 45	—
$bo = (010):(111)$	—	—	—	70 36	—
$os = (111):(101)$	—	—	—	19 24	—
$bo' = (010):(\bar{1}11)$	9	65 12– 65 26	65 18	65 19	1
$o's' = (\bar{1}11):(\bar{1}01)$	—	—	—	24 41	—
$o'o' = (\bar{1}11):(\bar{1}\bar{1}1)$	1	—	49 23	49 22	1
$sq = (101):(011)$	—	—	—	37 55	—
$qp = (011):(\bar{1}10)$	40	87 32– 87 43	87 37	87 36	1
$ps = (\bar{1}10):(\bar{1}0\bar{1})$	—	—	—	54 29	—
$pq = (\bar{1}10):(0\bar{1}\bar{1})$	40	92 18– 92 28	92 23	92 24	1
$s'q = (\bar{1}01):(011)$	—	—	—	45 39	—
$qn = (011):(121)$	—	—	—	26 37	—
$np = (121):(110)$	—	—	—	36 24	—
$qp = (011):(110)$	40	62 54– 63 5	63 0	63 1	1
$ps' = (110):(10\bar{1})$	—	—	—	71 20	—
$pq = (110):(0\bar{1}\bar{1})$	40	116 56–117 6	117 0	116 59	1
$r'o' = (\bar{2}01):(\bar{1}11)$	10	34 51– 35 14	35 5	35 4	1
$o'p = (\bar{1}11):(110)$	12	92 48– 93 6	92 54	92 57	3
$pr' = (110):(20\bar{1})$	23	51 50– 52 10	52 1	51 59	2
Total number of measurements . .	472				

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of practically all the measured angles the agreement between the observed and calculated values lies within two minutes, as will be seen from the table. The habit defined above is essentially characteristic of the salt, the vast majority of the crystals in all the 30 crops grown consisting of crystals of this type. Usually also only the forms $q\{011\}$ and $c\{001\}$, forming the prism, and smaller faces of $p\{110\}$, forming the ends, are visible. Closer inspection, however, reveals small faces of $r'\{\bar{2}01\}$, still more minute ones of $o'\{\bar{1}11\}$, and occasionally traces of the primary orthopinakoid $a\{100\}$, at the ends; while the sharper long edges of the prism $q\{011\}$ are blunted by long but very narrow faces, often mere lines, of the clinopinakoid $b\{010\}$. The signal images from the q and p faces were wonderfully sharply defined and perfect on all the crystals measured, and on most of these crystals, selected for their perfection, the other faces just referred to were somewhat more prominently developed than usual, and gave excellent reflections.

Some larger crystals were obtained in several of the crops which were somewhat tabular parallel to $c\{001\}$, owing to the faces of the basal plane being more extensively developed; the faces of $r'\{\bar{2}01\}$ were also frequently relatively larger on these crystals.

Cleavage.—A good cleavage is developed parallel to $r'\{\bar{2}01\}$. There is no facility for cleavage parallel to any other direction.

Volume.

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

I.	Density for 16°·2/4° . . .	3·1137	For 20°/4° . . .	3·1125
II.	,, 16°·3/4° . . .	3·1130	,, 20°/4° . . .	3·1118
III.	,, 16°·6/4° . . .	3·1186	,, 20°/4° . . .	3·1175
IV.	,, 17°·0/4° . . .	3·1149	,, 20°/4° . . .	3·1140
V.	,, 17°·1/4° . . .	3·1134	,, 20°/4° . . .	3·1125
			Mean . . .	3·1137

The value accepted for 20°/4° is **3·114.**

The specific gravity of cæsium nickel selenate does not appear to have been previously determined.

Molecular Volume.—$\frac{M}{d} = \frac{713{\cdot}62}{3{\cdot}114} = 229{\cdot}17.$

Molecular Distance Ratios (topic axial ratios).—

$$\chi : \psi : \omega = 6{\cdot}3317 : 8{\cdot}6878 : 4{\cdot}3378.$$

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Optics.

Nature and Orientation of the Optical Ellipsoid.—The plane of the optic axes is the symmetry plane $b\{010\}$, as usual for this series of double salts. But the sign of the double refraction is by exception negative, as was also found to be the case with cæsium nickel sulphate. Extinction determinations made with two section-plates ground parallel to the symmetry plane afforded the following values:—

Extinction Direction in the Symmetry Plane.

Plate 1 . . . . $0^\circ\ 55'$, Plate 2 . . . . $0^\circ\ 24'$,
Mean . . $0^\circ\ 40'$ in front of normal to $c\{001\}$.

This direction, nearly normal to the basal plane, is in this salt by exception the first median line, instead of the second median line as is usual in the series; it corresponds, however, as usual, to the refractive index α, while the other extinction at right angles to it in the symmetry plane corresponds to γ and is the second median line. This will be clear from fig. 6.

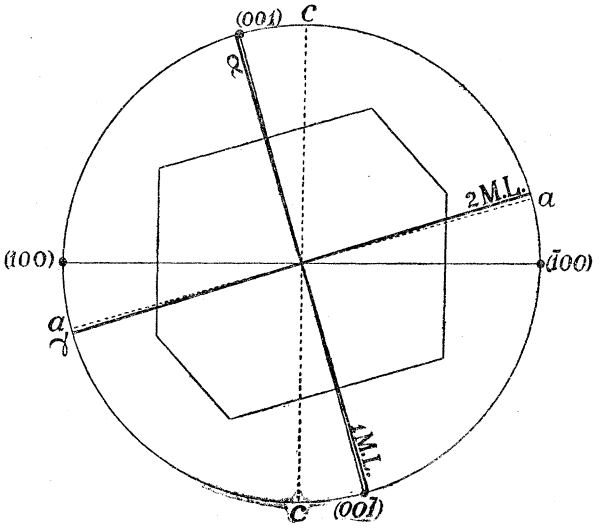

Fig. 6.

As the morphological axial angle ac is $73^\circ\ 49'$, and the angle between the normal to $c\{001\}$ and the vertical axis c is consequently $16^\circ\ 11'$, the first median line lies $16^\circ\ 51'$ in front of the vertical axis c in the obtuse axial angle ac. The second median line lies $0^\circ\ 40'$ below the inclined axis a in the acute morphological axial angle ac.

Optic Axial Angle.—Three section-plates, 1, 2, and 3, were ground perpendicular to the first median line, and three others, $1a$, $2a$, and $3a$, perpendicular to the second median line. The optic axial angle is so large that 2E, the apparent angle in air, is

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not measurable. The apparent acute and obtuse angles, $2H_a$ and $2H_o$, are readily measurable in bromonaphthalene, and the results of the measurements, together with the calculated values of the true optic axial angle $2V_a$ derived therefrom, are given in the accompanying table.

Cæsium Nickel Selenate.

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 15	1*a*	89 14	82 38	
	2	75 50	2*a*	89 2	82 28	82 41
	3	76 15	3*a*	88 35	82 58	
C	1	76 13	1*a*	89 8	82 40	
	2	75 49	2*a*	88 57	82 30	82 43
	3	76 14	3*a*	88 30	83 0	
Na	1	76 7	1*a*	88 4	83 8	
	2	75 45	2*a*	88 1	82 56	83 8
	3	76 9	3*a*	87 45	83 20	
Tl	1	76 1	1*a*	87 12	83 32	
	2	75 40	2*a*	87 4	83 22	83 28
	3	76 3	3*a*	87 17	83 30	
Cd	1	75 57	1*a*	86 55	83 38	
	2	75 35	2*a*	86 49	83 27	83 37
	3	75 59	3*a*	86 42	83 46	
F	1	75 53	1*a*	86 42	83 42	
	2	75 29	2*a*	86 28	83 34	83 43
	3	75 49	3*a*	86 20	83 52	

Dispersion of the Median Lines.—The dispersion of the two median lines in the symmetry plane is such that the first median line lies about 10′ nearer to the vertical axis *c* for greenish blue F light than for red C light. The determinations were made with sections 1 and 3 immersed in oil of anis, the refractive index of which liquid (1·5540) is not far removed from that of the crystal; the actual amounts observed with the two sections were respectively 12′ and 8′.

Refractive Indices.—Six 60°-prisms were ground, each with its bisecting plane parallel to a principal plane of the optical ellipsoid and its refracting edge parallel to one of the principal axes of the ellipsoid, so as to yield two refractive indices directly; the directions were so chosen that each of the three indices α, β and γ, was afforded by four different prisms. The results were very concordant, and the final mean values are recorded in the next table.

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REFRACTIVE Indices of Cæsium Nickel Selenate.

Light.	α.	β.	γ.
Li	1·5358	1·5412	1·5451
C	1·5363	1·5417	1·5456
Na	1·5395	1·5450	1·5489
Tl	1·5428	1·5483	1·5526
Cd	1·5447	1·5504	1·5547
F	1·5467	1·5525	1·5568
G	1·5533	1·5589	1·5631

Mean of α, β, and γ for Na light = 1·5445.

α = Vibration direction parallel to first median line, 16° 51′ in front of axis c.
β = ,, ,, ,, ,, symmetry axis b.
γ = ,, ,, ,, ,, second median line, 0° 40′ below axis a.

Double refraction, $Na_{\gamma-\alpha} = 0{\cdot}0094$.

General formula for the intermediate refractive index β, corrected to a vacuum (correction + 0·0004) :—

$$\beta = 1{\cdot}5252 + \frac{837\,474}{\lambda^2} - \frac{4\,729{\cdot}540\,000\,000}{\lambda^4} + \ldots.$$

The α indices are also reproduced very closely by the formula if the constant 1·5252 is diminished by 0·0055, and the γ indices if the constant is increased by 0·0040.

Observations at 70° showed that the refractive indices of cæsium nickel selenate are diminished by 0·0013 for α, 0·0016 for β, and 0·0018 for γ for 55° rise of temperature.

Axial Ratios of the Optical Ellipsoid.—The calculated values for both the optical indicatrix and the optical velocity ellipsoid are given below :—

$$\alpha : \beta : \gamma = 0{\cdot}9964 : 1 : 1{\cdot}0025.$$
$$\mathfrak{a} : \mathfrak{b} : \mathfrak{c} = 1{\cdot}0036 : 1 : 0{\cdot}9975.$$

Molecular Optical Constants.—These work out as under :—

	Axis of optical indicatrix . . .	α.	β.	γ.
LORENZ	Specific refraction, $\frac{n^2-1}{(n^2+2)d} = \mathfrak{r}$ . . { C	0·1002	0·1010	0·1016
	{ G	0·1028	0·1037	0·1043
,,	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = \mathfrak{m}$. { C	71·49	72·09	72·52
	{ G	73·37	73·98	74·44
,,	Specific dispersion, $\mathfrak{r}_G - \mathfrak{r}_C$	0·0026	0·0027	0·0027
,,	Molecular dispersion, $\mathfrak{m}_G - \mathfrak{m}_C$	1·88	1·89	1·92
GLADSTONE	Molecular refraction, $\frac{n-1}{d} M$ C	122·90	124·14	125·03

Mean molecular refraction (GLADSTONE), $\frac{1}{3}(\alpha+\beta+\gamma) = 124{\cdot}02$.

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Ammonium Nickel Selenate $(NH_4)_2\,Ni\,(SeO_4)_2\,.\,6H_2O$.

Morphology.

The crystals of ammonium nickel selenate were goniometrically investigated by Topsøe* in the year 1870, and as regards their optics were included, like the potassium salt, by Topsøe and Christiansen† in their well-known research of 1874.

The crystals are bright green in colour, very like the potassium salt, but more generally perfectly transparent.

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

Ratios of Axes.—$a : b : c = 0{\cdot}7395 : 1 : 0{\cdot}5048$. Values of Topsøe, $0{\cdot}7378 : 1 : 0{\cdot}5042$.

Axial Angle.—$\beta = 106^\circ\ 17'$. Value of Topsøe, $106^\circ\ 19'$.

Forms Observed.—$b\,\{010\}$, $c\,\{001\}$, $p\,\{110\}$, $p'\{120\}$, $q\,\{011\}$, $r'\{\bar{2}01\}$, and $o'\{\bar{1}11\}$. The same forms, and no others, were observed by Topsøe.

Habit.—More or less tabular parallel to $c\,\{001\}$, as shown in fig. 7.

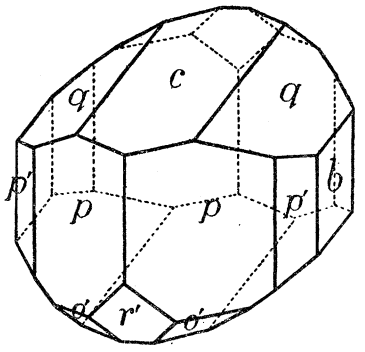

Fig. 7.

Eleven small crystals belonging to five different crops were measured, the crops being selected from the thirty or more prepared for their greater freedom from striation. The results are given in the accompanying table of angles.

A large proportion of the crystals showed no other forms than $c\,\{001\}$, $q\,\{011\}$, $p\,\{110\}$, and $r'\{\bar{2}01\}$. Certain crops, however, exhibited characteristically in addition excellent little faces of the clinopinakoid $b\,\{010\}$, with occasional development of the prism $p'\{120\}$ as a fairly broad face, and of the hemipyramid $o'\{\bar{1}11\}$ as narrow faces blunting the pc edges. The faces of $q\,\{011\}$ were particularly well formed, usually affording single sharp images of the signal. The b faces and r' faces were also similarly excellent when present. The faces of $c\,\{001\}$ and $p\,\{110\}$, however, were generally much striated. The measured crystals were selected on account of their exceptional freedom from this defect.

* 'Kryst.-kem. Unders. o. d. selens. Salte, Dissertation,' Copenhagen, 1870, p. 39.

† 'Ann. Chim. Phys.' (1874), series 5, vol. 1, p. 81.

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Interfacial Angles of Ammonium Nickel Selenate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.	Values of Topsøe.
		° ′ ° ′	° ′	° ′	′	° ′
ac = (100) : (001)	—	—	—	73 43	—	73 41
as = (100) : (101)	—	—	—	44 56	—	—
sc = (101) : (001)	—	—	—	28 47	—	—
cr' = (001) : ($\bar{2}$01)	17	64 42– 64 52	64 46	64 46	0	64 50
cs' = (001) : ($\bar{1}$01)	—	—	—	39 0	—	—
$s'r'$ = ($\bar{1}$01) : ($\bar{2}$01)	—	—	—	25 46	—	—
$r'a$ = ($\bar{2}$01) : ($\bar{1}$00)	—	—	—	41 31	—	—
$r'c$ = ($\bar{2}$01) : (00$\bar{1}$)	17	115 8–115 18	115 13	115 14	1	—
ap = (100) : (110)	—	—	—	35 22	—	—
pp' = (110) : (120)	2	19 20– 19 34	19 27	19 28	1	19 25
$p'b$ = (120) : (010)	2	35 7– 35 11	35 9	35 10	1	—
pp''' = (110) : (130)	—	—	—	29 29	—	—
$p'''b$ = (130) : (010)	—	—	—	25 9	—	—
pb = (110) : (010)	40	54 25– 54 48	54 38	*	—	—
pp = (110) : (1$\bar{1}$0)	15	70 36– 70 58	70 45	70 44	1	70 36
cq = (001) : (011)	42	25 44– 25 57	25 51	25 51	0	25 49
qb = (011) : (010)	44	64 4– 64 16	64 9	*	—	—
ao = (100) : (111)	—	—	—	48 10	—	—
oq = (111) : (011)	—	—	—	27 13	—	—
aq = (100) : (011)	—	—	—	75 23	—	—
qo' = (011) : ($\bar{1}$11)	—	—	—	35 7	—	—
$o'a$ = ($\bar{1}$11) : ($\bar{1}$00)	—	—	—	69 30	—	—
co = (001) : (111)	—	—	—	34 22	—	—
op = (111) : (110)	—	—	—	42 25	—	—
cp = (001) : (110)	42	76 37– 76 55	76 47	*	—	76 51
po' = (110) : (11$\bar{1}$)	11	57 52– 58 5	57 57	58 0	3	58 5
$o'c$ = (11$\bar{1}$) : (00$\bar{1}$)	11	45 8– 45 21	45 15	45 13	2	45 4
pc = (110) : (00$\bar{1}$)	32	103 7–103 24	103 13	103 13	0	—
bn = (010) : (121)	—	—	—	54 31	—	—
no = (121) : (111)	—	—	—	15 52	—	—
bo = (010) : (111)	—	—	—	70 23	—	—
os = (111) : (101)	—	—	—	19 37	—	—
bo' = (010) : ($\bar{1}$11)	12	65 0– 65 10	65 5	65 2	3	—
$o's'$ = ($\bar{1}$11) : ($\bar{1}$01)	—	—	—	24 58	—	—
$o'o'$ = ($\bar{1}$11) : ($\bar{1}\bar{1}$1)	6	49 46– 49 56	49 51	49 56	5	—
sq = (101) : (011)	—	—	—	37 56	—	—
qp = (011) : ($\bar{1}$10)	33	87 10– 87 29	87 17	87 20	3	87 23
ps = ($\bar{1}$10) : ($\bar{1}$0$\bar{1}$)	—	—	—	54 44	—	—
pq = ($\bar{1}$10) : (0$\bar{1}\bar{1}$)	38	92 31– 92 54	92 43	92 40	3	—
$s'q$ = ($\bar{1}$01) : (011)	—	—	—	45 37	—	—
qn = (011) : (121)	—	—	—	26 28	—	—
np = (121) : (110)	—	—	—	36 16	—	—
qp = (011) : (110)	41	62 32– 62 49	62 41	62 44	3	62 44
ps' = (110) : (10$\bar{1}$)	—	—	—	71 39	—	—
pq = (110) : (0$\bar{1}\bar{1}$)	41	117 11–117 29	117 19	117 16	3	—
$r'o'$ = ($\bar{2}$01) : ($\bar{1}$11)	11	35 7– 35 22	35 15	35 16	1	—
$o'p$ = ($\bar{1}$11) : (110)	10	92 10– 92 27	92 17	92 22	5	—
pr' = (110) : (20$\bar{1}$)	22	52 10– 52 36	52 25	52 22	3	52 26
Total number of measurements . .	489					

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Cleavage.—The cleavage common to the series, parallel to $r'\{\bar{2}01\}$, is very well developed in this salt. There is also a feeble and very imperfect cleavage parallel to $b\{010\}$; it is not so distinct, however, as in several other ammonium salts of the series (ammonium magnesium, ammonium nickel, ammonium manganese, and ammonium copper sulphates).

Volume.

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

I.	Density for	18°·3/4° . . .	2·2422	For 20°/4° . . .	2·2418
II.	,,	18°·7/4° . . .	2·2445	,, 20°/4° . . .	2·2442
III.	,,	18°·9/4° . . .	2·2443	,, 20°/4° . . .	2·2441
IV.	,,	18°·9/4° . . .	2·2435	,, 20°/4° . . .	2·2433
				Mean . . .	2·2434

Accepted value for 20°/4°, **2·243**.

The value 2·228 was obtained by Topsøe.

Molecular Volume.—$\frac{M}{d} = \frac{485{\cdot}68}{2{\cdot}243} = 216{\cdot}53$.

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

$$\chi : \psi : \omega = 6{\cdot}2520 : 8{\cdot}4543 : 4{\cdot}2678.$$

Optics.

Nature and Orientation of the Optical Ellipsoid.—The optic axes lie in the symmetry plane $b\{010\}$. The sign of the double refraction is positive. Extinction determinations with two section-plates ground parallel to the symmetry plane yielded the following results:—

Extinction Direction in the Symmetry Plane.

Plate 1 . . . . 14° 18′ Plate 2 . . . . 14° 16′,
Mean . . . 14° 17′, behind the normal to $c\{001\}$.

This direction is the second median line, and corresponds to the refractive index α, the other extinction direction at right angles in the symmetry plane being the first median line and corresponding to the index γ. As the morphological axial angle $ac = 73° 43'$, and therefore the angle between the normal to $c\{001\}$ and the vertical axis $c = 16° 17'$, the second median line lies 2° 0′ in front of the vertical axis c, in the obtuse angle ac of the morphological axes a and c. The first median line also lies in

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the obtuse axial angle ac, 14° 17′ above the inclined axis a, and 2° 0′ below the normal to a {100}. These facts will be rendered clear by fig. 8.

Topsøe and Christiansen give the position of the first median line as 16° 54′ from the axis a and 89° 25′ from the axis c.

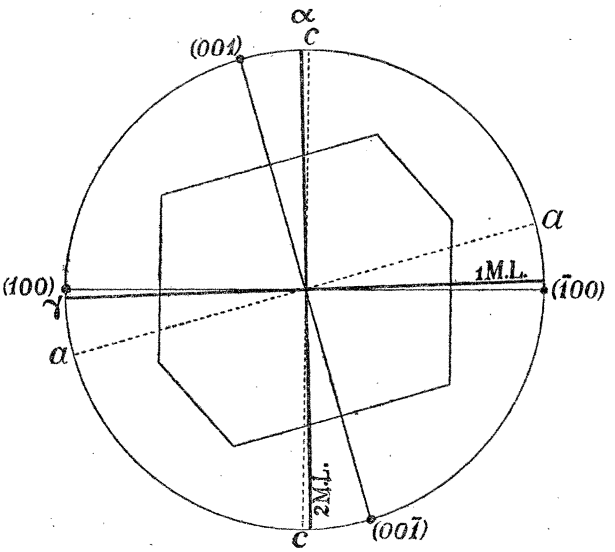

Fig. 8.

Optic Axial Angle.—Three section-plates perpendicular to the first median line, numbered 1, 2, 3, and three others labelled $1a$, $2a$, and $3a$, perpendicular to the second median line, were ground. The apparent optic axial angle in air, 2E, is too large for measurement, the brushes being not quite capable of being brought to the cross-wires; but excellent measurements were obtained for $2H_a$ and $2H_o$, the apparent acute and obtuse angles in bromonaphthalene. The results, together with the values of the true optic axial angle $2V_a$ calculated therefrom, are given in the accompanying table.

Ammonium Nickel Selenate.

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	78 43	1a	85 8	86 18	
	2	78 40	2a	85 2	86 20	86 19
	3	78 45	3a	85 6	86 20	
C	1	78 41	1a	85 5	86 18	
	2	78 38	2a	85 0	86 20	86 19
	3	78 43	3a	85 3	86 20	

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DETERMINATION of True Optic Axial Angle in Bromonaphthalene (continued).

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 $2V_a$.
		° ′		° ′	° ′	° ′
Na	1	78 21	1a	84 40	86 20	86 21
	2	78 21	2a	84 41	86 20	
	3	78 22	3a	84 39	86 22	
Tl	1	78 2	1a	84 17	86 22	86 24
	2	78 5	2a	84 13	86 25	
	3	78 5	3a	84 14	86 25	
Cd	1	77 50	1a	84 3	86 22	86 26
	2	77 56	2a	83 57	86 28	
	3	77 53	3a	83 54	86 28	
F	1	77 45	1a	83 45	86 28	86 29
	2	77 39	2a	83 38	86 29	
	3	77 39	3a	83 35	86 30	

TOPSØE and CHRISTIANSEN found 86° 14′ for $2V_a$.

Dispersion of the Median Lines.—Measurements with sections 1, 2, and 3 immersed in methyl salicylate, the refractive index of which (1·5363) is almost identical with the mean index of the crystals, indicated that the dispersion of the two mutually rectangular median lines lying in the symmetry plane is such, that the first median line lies nearer to the morphological axis a by about 12′ for red C light than for greenish blue F light.

Refractive Indices.—Six 60°-prisms were prepared as usual, to afford two indices each, α and β, β and γ, or α and γ, the bisecting plane being parallel to a principal plane, and the refractive edge parallel to one of the three principal axes, of the optical ellipsoid. The results are embodied in the accompanying table.

REFRACTIVE Indices of Ammonium Nickel Selenate.

Light.	α.	β.	γ.
Li	1·5246	1·5332	1·5419
C	1·5251	1·5337	1·5424
Na	1·5285	1·5370	1·5460
Tl	1·5320	1·5405	1·5496
Cd	1·5339	1·5425	1·5517
F.	1·5360	1·5447	1·5539
G.	1·5423	1·5510	1·5602

Mean of α, β, and γ for Na light = 1·5372.

α = Vibration direction parallel to second median line, 2° 0′ in front of vertical axis c.
β = ,, ,, ,, ,, symmetry axis b.
γ = ,, ,, ,, ,, first median line, 14° 17′ above inclined axis a.
Double refraction, $Na_{\gamma-\alpha}$ = 0·0175.

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General formula for β, corrected to a vacuum :—

$$\beta = 1{\cdot}5191 + \frac{690\,578}{\lambda^2} - \frac{1\,921\,310\,000\,000}{\lambda^4} + \ldots .$$

The α indices are equally well reproduced by the formula if the constant 1·5191 is diminished by 0·0086, and the γ indices if it is increased by 0·0090.

Observations at 70° indicated that the refractive indices of ammonium nickel selenate diminish by about 0·0020 for a rise of temperature of 55°.

Axial Ratios of the Optical Ellipsoid.—The calculated values for the two types of ellipsoid are as under :—

Indicatrix . . . . . $\alpha : \beta : \gamma = 0{\cdot}9945 : 1 : 1{\cdot}0059.$

Optical Velocity Ellipsoid . . $\mathfrak{a} : \mathfrak{b} : \mathfrak{c} = 1{\cdot}0055 : 1 : 0{\cdot}9942.$

Molecular Optical Constants.—These are given in the next table.

	Axis of optical indicatrix . . .	α.	β.	γ.
Lorenz	Specific refraction, $\frac{n^2-1}{(n^2+2)d} = \mathfrak{n}$ . . C	0·1366	0·1385	0·1404
	G	0·1404	0·1422	0·1442
,,	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = \mathfrak{m}$. C	66·37	67·27	68·19
	G	68·18	69·08	70·03
,,	Specific dispersion, $\mathfrak{n}_G - \mathfrak{n}_C$	0·0038	0·0037	0·0038
,,	Molecular dispersion, $\mathfrak{m}_G - \mathfrak{m}_C$	1·81	1·81	1·84
Gladstone	Molecular refraction, $\frac{n-1}{d}$ M C	113·70	115·56	117·45

Mean molecular refraction (Gladstone), $\frac{1}{3}(\alpha+\beta+\gamma) = 115{\cdot}57$.

Comparison of Results.

Habit.—The progression of habit which has been observed in all the other groups of double sulphates and double selenates of this large isomorphous series yet investigated (the work on the double sulphates having been completed by the author's last communication), is very clearly exhibited in this group of the double selenates containing nickel. The progression is characterised by the relative development of the faces of the forms $c\{001\}$ and $q\{011\}$. In the potassium salt the basal plane $c\{001\}$ is largely predominating, the faces of the clinodomal prism $q\{011\}$ on each side of it being relatively small, as shown in fig. 1. In the cæsium salt, on the contrary, the two faces of $q\{011\}$ predominate, and indeed confer a prismatic character on the crystal parallel to the inclined axis a, while the basal plane $c\{001\}$ forms only a central strip, as exhibited in fig. 5. Distinctly intermediate between these two extreme types come the crystals of rubidium nickel selenate, in which the two forms are more nearly approached in relative size, the $q\{011\}$ faces being larger

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than in potassium nickel selenate but not so large as in cæsium nickel selenate. This will be clearly apparent from the typical crystal of the rubidium salt shown in fig. 3.

The ammonium salt forms crystals of all three types, but the great majority affect a more or less intermediate habit akin to that of the rubidium salt, while at the same time showing some idiosyncracies. Fig. 7 shows this well.

Crystal Elements and Angles.—The axial ratios and axial angles are compared in the following table. From an inspection of it the following facts become clear :—

Comparison of the Axial Angles and Axial Ratios.

	Axial angle.	Axial ratios.
	β.	$a : b : c$
Potassium nickel selenate . .	104° 27′	0·7467 : 1 : 0·5059
Rubidium „ „ . .	105° 20′	0·7395 : 1 : 0·5031
Ammonium „ „ . .	106° 17′	0·7395 : 1 : 0·5048
Cæsium „ „ . .	106° 11′	0·7288 : 1 : 0·4993

The morphological axial angle of rubidium nickel selenate is approximately the mean of the axial angles of potassium nickel and cæsium nickel selenates, the differences being nearly identical, 53′ and 51′. It will be remembered that the atomic weight of rubidium is almost exactly the mean of the atomic weights of potassium and cæsium. The axial angle of the ammonium salt is nearly identical with that of the cæsium salt. The morphological axial ratios of the rubidium salt are also intermediate between those for the potassium and cæsium salts. Hence, both axial angles and axial ratios for the three alkali metallic salts follow the order of the atomic weights of the alkali metals, and in the case of the axial angle with simple proportionality.

The axial ratios of the ammonium salt lie between those of the two extreme, the potassium and cæsium, salts, thus indicating true isomorphism of the ammonium salt with the alkali metallic salts.

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

Comparison of the Interfacial Angles.

Angle.	KNi selenate.	RbNi selenate.	CsNi selenate.	AmNi selenate.
	° ′	° ′	° ′	° ′
$ac = (100) : (001)$	75 33	74 40	73 49	73 43
$as = (100) : (101)$	46 15	45 36	44 51	44 56
$sc = (101) : (001)$	29 18	29 4	28 58	28 47
$cr' = (001) : (\bar{2}01)$	63 13	63 58	64 54	64 46
$cs' = (001) : (\bar{1}01)$	38 16	38 38·5	39 11	39 0
$s'r' = (\bar{1}01) : (\bar{2}01)$	24 57	25 19·5	25 43	25 46
$r'a = (\bar{2}01) : (\bar{1}00)$	41 14	41 22	41 17	41 31

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Comparison of the Interfacial Angles (continued).

Angle.	KNi selenate.	RbNi selenate.	CsNi selenate.	AmNi selenate.
	° ′	° ′	° ′	° ′
$ap = (100):(110)$	35 54	35 30·5	34 58	35 22
$pp' = (110):(120)$	19 28	19 28	19 28	19 28
$p'b = (120):(010)$	34 38	35 1·5	35 34	35 10
$pb = (110):(010)$	54 6	54 29·5	55 2	54 38
$cq = (001):(011)$	26 6	25 53	25 37	25 51
$qb = (011):(010)$	63 54	64 7	64 23	64 9
$ao = (100):(111)$	49 30	48 49	48 2	48 10
$oq = (111):(011)$	27 33	27 25	27 25	27 13
$aq = (100):(011)$	77 3	76 14	75 27	75 23
$qo' = (011):(\bar{1}11)$	34 26	34 50	35 19	35 7
$o'a = (\bar{1}11):(\bar{1}00)$	68 31	68 56	69 14	69 30
$co = (001):(111)$	35 0	34 40	34 23	34 22
$op = (111):(110)$	43 20	42 54	42 25	42 25
$cp = (001):(110)$	78 20	77 34	76 48	76 47
$po' = (110):(11\bar{1})$	57 7	57 34	58 0	58 0
$o'c = (11\bar{1}):(00\bar{1})$	44 33	44 52	45 12	45 13
$bo = (010):(111)$	69 56	70 14	70 36	70 23
$os = (111):(101)$	20 4	19 46	19 24	19 37
$bo' = (010):(\bar{1}11)$	65 10	65 12	65 19	65 2
$o's' = (\bar{1}11):(\bar{1}01)$	24 50	24 48	24 41	24 58
$sq = (101):(011)$	38 27	38 9	37 55	37 56
$qp = (011):(\bar{1}10)$	85 37	86 34	87 36	87 20
$ps = (\bar{1}10):(\bar{1}0\bar{1})$	55 56	55 17	54 29	54 44
$s'q = (\bar{1}01):(011)$	45 10	45 21	45 39	45 37
$qp = (011):(110)$	63 55	63 26	63 1	62 44
$ps' = (110):(10\bar{1})$	70 55	71 13	71 20	71 39
$r'o' = (\bar{2}01):(\bar{1}11)$	34 38	34 52	35 4	35 16
$o'p = (\bar{1}11):(110)$	92 54	92 47·5	92 57	92 22
$pr' = (110):(20\bar{1})$	52 28	52 20·5	51 59	52 22

These angles have all been carefully compared for the four salts and the differences tabulated, an analysis of the tables affording the following results. For thirty-five of the thirty-six angles compared the value for the rubidium salt is intermediate between the values for the potassium and cæsium salts.

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, which forms an expressive summary of the tables of differences above referred to.

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ANGULAR Changes for Double Selenates containing Nickel.

Replacement.	Average change.	Maximum change.
	′	′ ° ′
K by Rb	23	57 = 0 57
K by Cs	47	119 = 1 59
K by NH_4	45	110 = 1 50

The average and maximum changes of angle are twice as great when potassium is replaced by cæsium as when potassium is replaced by rubidium, corresponding to the changes of atomic weight (K∼Rb = 46 and K∼Cs = 93). When potassium is replaced by ammonium the changes (average and maximum) are very nearly the same as occur when potassium is replaced by cæsium. That is to say, the average change in the crystal angles, and also the maximum amount of that change, in the cases of the metallic interchanges, are directly proportional to the change in the atomic weight of the alkali metal; while the introduction of the radicle ammonium instead of potassium produces about as much average or maximum change of angle as when potassium is replaced by cæsium, the actual amounts being very slightly less, to the extent of 2′ in the average change (out of a total of 47′) and 9′ in the maximum change (out of a total of 1° 59′).

From the above it will be clear that the differences in the crystal angles are of the same sign when potassium is replaced by rubidium on the one hand and by cæsium on the other, that is, there is a progressive change, there being only a single exception (in the case of an angle showing only a very small change) out of all the 36 cases compared; the amounts have been shown to be exactly proportional on the average to the two increments of atomic weight. In the case of the ammonium salt, 33 out of the 36 angles compared show differences on replacing potassium by ammonium in the same direction as when rubidium or cæsium are introduced instead of potassium, the only three exceptions being in cases where the differences are very minute. In 32 of the 33 cases the changes are greater than when rubidium is introduced, and in 13 cases they exceed the effect produced by introducing cæsium for potassium. The maximum change of angle for the ammonium replacement, however, has been shown to fall somewhat short of that for the cæsium replacement, and thus the crystal angles for the ammonium salt all fall within the limits of the changes for the three metallic salts, emphasising the true character of the isomorphism of all the four salts.

Volume Constants.—The densities, molecular volumes and topic axial ratios of the four salts are compared in the next table.

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VOLUME Constants of the Nickel Group of Double Selenates.

Salt.	Molecular weight.	Specific gravity.	Molecular volume.	Topic axial ratios.
				χ : ψ : ω
KNi selenate . .	527·52	2·559	206·14	6·1677 : 8·2598 : 4·1786
RbNi ,, . .	619·62	2·856	216·96	6·2533 : 8·4561 : 4·2542
CsNi ,, . .	713·62	3·114	229·17	6·3317 : 8·6878 : 4·3378
NH_4Ni ,, . .	485·68	2·243	216·53	6·2520 : 8·4543 : 4·2678

The density increases with the atomic weight of the alkali metal, and is greater for the replacement of potassium by rubidium than for the replacement of rubidium by cæsium in the proportion of 6 to 5. The density of the ammonium salt is the lowest of the group, corresponding to the low molecular weight of the ammonium radicle NH_4.

The molecular volumes of the three alkali-metallic salts show progression with the atomic weight of the alkali metal; the replacement of rubidium by cæsium is accompanied by the greater change, 12·21 units as against 10·82 units for the replacement of potassium by rubidium, so that the increment of volume is an increasing one. The molecular volume of the ammonium salt is almost identical with that of the rubidium salt, a result similar to what has been observed in all the other groups of salts of the series yet investigated.

The topic axial ratios of the rubidium salt are also intermediate between those for the potassium and cæsium salts, there being a regular progressive increase in the directional (axial-edge) dimensions of the structural unit cell of the space-lattice, when potassium is replaced by rubidium and the latter in turn by cæsium. The topic axial ratios of ammonium nickel selenate are almost identical with those of rubidium nickel selenate, the structural (space-lattice) unit cells of the rubidium and ammonium salts being thus almost identically congruent, that is similar in shape and symmetry and almost exactly equal in total volume and in the dimensions of their sides and edges. This result, similar to the results with all the other groups of double selenates yet investigated and of all the double sulphates and the simple alkali sulphates, thus forms yet another confirmation of one of the most remarkable facts brought to light by the author's investigations, namely, the extraordinary congruency of the ammonium and rubidium salts of any group; the replacement of two atoms of monad rubidium by eight atoms of monad hydrogen and two atoms of triad (at least, more probably pentad) nitrogen, actually occurs without any appreciable opening up of the structure. The bearing of this important fact on the theory of valency volumes of BARLOW and POPE, with which it is in entire antagonism, is discussed in a separate communication (see Roy. Soc. Proc.).*

* 'Roy. Soc. Proc.,' A, vol. 93, p. 72 (1917).

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Cleavage.—A cleavage parallel to the orthoprism $r'\{\bar{2}01\}$ is well developed in the crystals of all four salts of the nickel double selenate group. In addition, the ammonium salt exhibits a feeble facility for cleavage parallel to the symmetry plane $b\{010\}$. This second direction of cleavage has also been observed more perfectly developed on the four double sulphates containing ammonium as the R-base and as M-metals, magnesium, nickel, manganese, and copper. It would appear to be connected with some obviously probable slight difference of structure, due to the different and more complicated chemical nature of the ammonium radicle NH_4 as compared with a simple alkali metallic atom. It is a fact which may prove later of value in elucidating the exact details of this slight difference of structure, and one which will require to be remembered in considering the meaning of the congruency with the rubidium salts referred to in the preceding paragraph.

Orientation of the Optical Ellipsoid.—This comparison is best effected by taking the position, in the crystals of the four salts, of that one of the two median lines

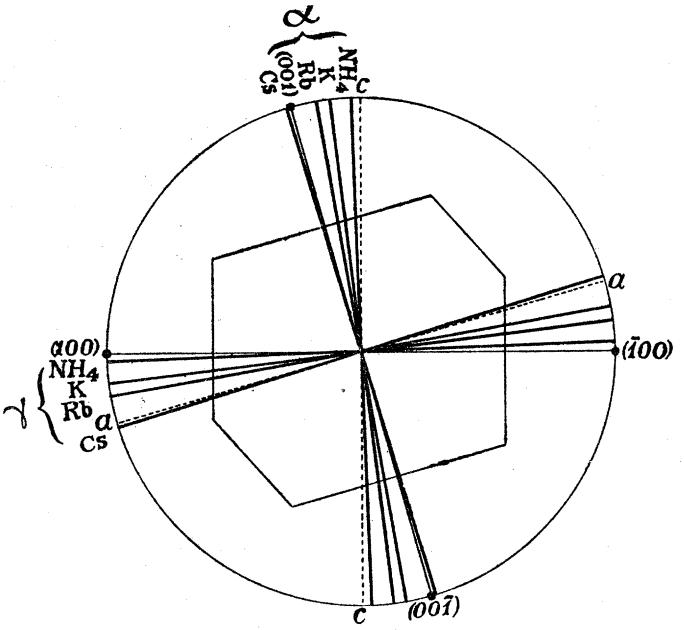

Fig. 9.

lying in the symmetry plane which is not far removed from the vertical morphological axis c, and which is the α axis of the ellipsoid in all four salts. This principal axial direction of the optical ellipsoid is the second median line in all the salts but cæsium nickel selenate; in this latter salt it is by exception the first median line. Such a comparison is made in the following table, which is also illustrated by fig. 9.

Inclinations of α-Extinctions of the Ni *Double Selenates in front of Axis c.*
(1M.L. *in* CsNi *salt and* 2M.L. *in other three salts.*)

AmNi selenate	2° 0′	RbNi selenate	9° 59′
KNi ,,	6° 59′	CsNi ,,	16° 51′.

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The other principal axial direction of the ellipsoid lying in the symmetry plane shows, of course, a similar progression for the four salts, as it is always 90° from the direction compared in the table. The third rectangular axis of the ellipsoid is identical in position with the morphological symmetry axis b, and is, therefore, identical and immovable for all four salts, in accordance with monoclinic symmetry.

Thus the optical ellipsoid rotates about the symmetry axis when one alkali base is replaced by another. It is so situated in the ammonium salt that one axis is nearly identical with the vertical crystal axis c; it rotates from this position further away from c when ammonium is replaced by potassium, still further when the latter is replaced by rubidium, and yet further when rubidium is replaced by cæsium. Its position for the rubidium salt is thus intermediate between the positions for the potassium and cæsium salts, the rotations for the two replacements of K by Rb and Rb by Cs being respectively 3° 0′ and 6° 52′. The rotation is thus in the order of the atomic weights of the three alkali metals, the amount of the rotation increasing at a higher rate than in mere simple proportion to the change in atomic weight.

The Optic Axial Angles.—In making a comparison of these it has to be remembered that the first median line is differently situated in the cæsium salt; whereas for the potassium, rubidium and ammonium salts it is that principal axis of the optical ellipsoid lying near the inclined axis a, for the cæsium salt it is that axis of the ellipsoid which lies near the vertical axis c, the one 90° away near axis a being by exception in cæsium nickel selenate the second median line. We must, therefore, use the obtuse optic axial angle, the bisectrix of which lies near axis a and which is therefore comparable to the acute optic axial angles of the other three salts, the bisectrices of which lie also near axis a. With this understood, the following table affords the comparison.

Optic Axial Angles $2V_a$ of the Nickel Group of Double Selenates.

	KNi selenate.	RbNi selenate.	AmNi selenate.	CsNi selenate.
Li	72° 45′	82° 23′	86° 19′	97° 19′
C	72 45	82 22	86 19	97 17
Na	72 48	82 13	86 21	96 52
Tl	72 51	82 7	86 24	96 32
Cd	72 53	82 3	86 26	96 23
F	72 56	81 58	86 29	96 17

The optic axial angle is thus observed to increase with the rise in atomic weight of the alkali metal, the angle for the rubidium salt being intermediate between that for the potassium and cæsium salts, and the rate being again an accelerating one.

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The optic axial angle of ammonium nickel selenate is slightly greater than that of the rubidium salt.

COMPARISON of the Refractive Indices.

Index.	Light.	KNi selenate.	RbNi selenate.	NH_4Ni selenate.	CsNi selenate.
α	Li	1·5142	1·5161	1·5246	1·5358
	C	1·5147	1·5166	1·5251	1·5363
	Na	1·5181	1·5198	1·5285	1·5395
	Tl	1·5212	1·5231	1·5320	1·5428
	Cd	1·5232	1·5248	1·5339	1·5447
	F	1·5251	1·5268	1·5360	1·5467
	G	1·5314	1·5335	1·5423	1·5533
β	Li	1·5232	1·5253	1·5332	1·5412
	C	1·5237	1·5258	1·5337	1·5417
	Na	1·5272	1·5291	1·5370	1·5450
	Tl	1·5305	1·5325	1·5405	1·5483
	Cd	1·5325	1·5342	1·5425	1·5504
	F	1·5344	1·5362	1·5447	1·5525
	G	1·5407	1·5429	1·5510	1·5589
γ	Li	1·5387	1·5351	1·5419	1·5451
	C	1·5392	1·5356	1·5424	1·5456
	Na	1·5427	1·5390	1·5460	1·5489
	Tl	1·5464	1·5424	1·5496	1·5526
	Cd	1·5486	1·5443	1·5517	1·5547
	F	1·5507	1·5466	1·5539	1·5568
	G	1·5571	1·5534	1·5602	1·5631
Mean refractive index $\frac{1}{3}(\alpha+\beta+\gamma)$ for Na light		1·5293	1·5293	1·5372	1·5445
Double refraction, $Na_{\gamma-\alpha}$		0·0246	0·0192	0·0175	0·0094

Refractive Indices.—The refractive indices are compared in the above table. It will be seen that the α and β indices for the rubidium salt are intermediate between those of the potassium and cæsium salts. Owing, however, to the great diminution in double refraction ($\gamma-\alpha$), which progressively diminishes as the atomic weight of the alkali metal present increases, the γ indices for the rubidium salt do not quite reach the value of these indices for the potassium salt. As another consequence of this the mean refractive index (mean of all three indices α, β, γ for Na light) for the potassium and rubidium salts works out to be only just the same. As, however, the optical change is an accelerating one with the atomic weight of the alkali metal, in spite of the further diminution in double refraction when the cæsium salt is reached, all the indices (including the mean) for the cæsium salt show an advance.

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The indices of the ammonium salt are intermediate between those of the rubidium and cæsium salts.

The Double Refraction.—This is a property which shows the optical accelerating progression with the atomic weight of the alkali metal particularly well, as will be obvious from the values given at the foot of the table. Its effect is greater in this nickel group than in the magnesium and zinc groups already studied, in which groups the mean refractive index of the rubidium salt showed a considerable advance on that of the potassium salt.

Axial Ratios of the Optical Indicatrix.

		α : β : γ	α : β : γ
KNi	selenate . . .	0·9940 : 1 : 1·0101	0·9940 : 1 : 1·0101
RbNi	„ . . .	0·9939 : 1 : 1·0065	0·9952 : 1·0012 : 1·0077
NH_4Ni	„ . . .	0·9945 : 1 : 1·0059	1·0009 : 1·0064 : 1·0123
CsNi	„ . . .	0·9964 : 1 : 1·0025	1·0080 : 1·0116 : 1·0142

Axial Ratios of the Optical Velocity Ellipsoid.

		a : b : c	a : b : c
KNi	selenate . . .	1·0060 : 1 : 0·9900	1·0060 : 1 : 0·9900
RbNi	„ . . .	1·0061 : 1 : 0·9936	1·0049 : 0·9988 : 0·9923
NH_4Ni	„ . . .	1·0055 : 1 : 0·9942	0·9991 : 0·9936 : 0·9878
CsNi	„ . . .	1·0036 : 1 : 0·9975	0·9920 : 0·9885 : 0·9860

Axial Ratios of the Optical Ellipsoid.—The values of these ratios are given in the accompanying tables for both ellipsoids. The left hand series in each case are calculated with the β value for each salt taken as unity. The right hand series exhibit the total change in the dimensions of the optical ellipsoid on passing from one salt of the group to another, the β value for the initial potassium salt being taken as unity for all four salts. The main fact that these latter ratios indicate is the accelerating nature of the change in dimensions of the ellipsoid as the atomic weight of the alkali metal rises. The slight set-back of the γ values for the rubidium salt is due to the effect of the diminution in double refraction, as already explained. The dimensions of the ellipsoid of the ammonium salt are intermediate, another proof of the true character of the isomorphism, for they lie within the values for the extreme metallic salts of the eutropic series.

Molecular Optical Constants.—These are by far the most valuable of the optical constants, and they are set forth in order in the three next tables.

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TABLE of Specific Refraction and Dispersion (LORENZ).

Salt.	Specific refraction, $\frac{n^2-1}{(n^2+2)\,d} = \mathfrak{n}$.						Specific dispersion. $\mathfrak{n}_G - \mathfrak{n}_C$.		
	For ray C (Hα).			For ray Hγ near G.					
	α.	β.	γ.	α.	β.	γ.	α.	β.	γ.
AmNi selenate	0·1366	0·1385	0·1404	0·1404	0·1422	0·1442	0·0038	0·0037	0·0038
KNi ,,	0·1178	0·1195	0·1225	0·1210	0·1227	0·1258	0·0032	0·0032	0·0033
RbNi ,,	0·1059	0·1074	0·1091	0·1088	0·1104	0·1121	0·0029	0·0030	0·0030
CsNi ,,	0·1002	0·1010	0·1016	0·1028	0·1037	0·1043	0·0026	0·0027	0·0027

TABLE of Molecular Refraction and Dispersion (LORENZ).

Salt.	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = \mathfrak{m}$.						Molecular dispersion. $\mathfrak{m}_G - \mathfrak{m}_C$.		
	For ray C (Hα).			For ray Hγ near G.					
	α.	β.	γ.	α.	β.	γ.	α.	β.	γ.
KNi selenate	62·14	63·04	64·60	63·82	64·75	66·37	1·68	1·71	1·77
RbNi ,,	65·59	66·57	67·61	67·39	68·38	69·47	1·80	1·81	1·86
AmNi ,,	66·37	67·27	68·19	68·18	69·08	70·03	1·81	1·81	1·84
CsNi ,,	71·49	72·09	72·52	73·37	73·98	74·44	1·88	1·89	1·92

MOLECULAR Refraction (GLADSTONE and DALE).

Salt.	$\frac{n-1}{d}$ M for ray C.			Mean molecular refraction for ray C. $\frac{1}{3}(\alpha+\beta+\gamma)$.
	α.	β.	γ.	
KNi selenate	106·10	107·96	111·10	108·39
RbNi ,, ...	112·08	114·07	116·20	114·12
AmNi ,, ...	113·70	115·56	117·45	115·57
CsNi ,, ...	122·90	124·14	125·03	124·02

The whole of the specific and molecular optical constants of rubidium nickel selenate are intermediate between those of potassium nickel selenate and cæsium nickel selenate.

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The molecular refraction increases considerably more when cæsium replaces rubidium than when the latter displaces potassium, the proportion being roughly as 5 to 3. The changes are nearly alike along the α and β axis, but are less along the γ axis. These results are independent of the temperature, as both refractive power and density diminish (alter in the same direction) when the temperature is raised. The changes are obviously independent of the formulæ employed, for the results are similar whether the values compared are calculated by the formula of LORENZ or by that of GLADSTONE and DALE.

The position of ammonium nickel selenate with respect to molecular refraction is very close to that of the rubidium salt, in all cases less than one Lorenz or two Gladstone units higher. This result is very similar to that for the structural properties (dimensions), and again offers proof of the true isomorphism of the ammonium salt with the salts of the three alkali metals.

It is interesting to compare these results for the nickel double selenate group with those for the corresponding nickel double sulphate group. A comparison of the Lorenz and Gladstone values for the molecular refraction shows that the selenate values are higher by 6·9 to 8·1 Lorenz units, or 12·7 to 14·4 Gladstone units. As there are two atoms of sulphur or selenium present, this gives as the increase per atom, when sulphur is replaced by selenium, 3·5 to 4 Lorenz units or 6·3 to 7·2 Gladstone units. The following little table shows how these results for the replacement of sulphur by selenium in the nickel group compare with those obtained for the other groups already studied.

INCREASE of Molecular Volume on Replacing S by Se.

Salt group.	Lorenz units.	Gladstone units.
Nickel	3·5–4·0	6·3–7·2
Magnesium	3·4–3·6	6·3–6·7
Zinc	3·5–3·7	6·5–6·9
Simple salts	3·4–3·8	6·2–7·2

The values for the three groups of double salts are identical in the mean with those derived from the comparison of the simple rhombic alkali sulphates and selenates, which are therefore included in the table. This mean increase in molecular volume, when a sulphur atom is replaced by a selenium atom, in either series, is 3·6 Lorenz units, or 6·7 Gladstone units.

Summary of Main Conclusions.

The results now presented for the nickel group of double selenates, of the monoclinic series $R_2M\left(\begin{matrix}S\\Se\end{matrix}O_4\right)_2.6H_2O$, are in line with those previously communicated for the

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magnesium and zinc groups of double selenates, and for the eight groups of double sulphates, the investigation of which was completed by the publication of the author's last memoir (of June, 1915).* The two main results are that the progression of all the morphological and optical properties of the crystals, with the atomic weight of the alkali metal (K = 38·85, Rb = 84·9, Cs = 131·9, and Rb−K = 46, Cs−Rb = 47), is beautifully shown once more in this nickel group of double selenates; and that the true isomorphism, but not eutropism, of the ammonium salt with the potassium, rubidium and cæsium salts is clearly indicated by the principal determinative constants (such as interfacial angles, size of the unit cell of the space-lattice, refractive indices and molecular refraction) of the ammonium salt never falling outside the limits of these constants for the two extreme, potassium and cæsium, salts of the group.

The former of these two main results is admirably illustrated by the fact that both the average and the maximum amounts of interfacial angular change, brought about by replacing one alkali metal by another, are directly proportional to the change in atomic weight. The differences of atomic weight between potassium and rubidium and between the latter and cæsium are practically the same (46 and 47), and the changes in angle, whether the mean of all the changes of the 36 angles measured or the greatest change of angle observed, are also equal; or to express it differently, the replacement of K by Cs is accompanied by twice as much angular change as that of K by Rb (average changes K by Rb, 23′, and K by Cs, 47′, maxima 57′ and 119′), just as the change of atomic weight Cs−K (= 93) is double that for Rb−K (= 46). The amounts are so large as to be entirely removed from any possibility of error, which, on a generous estimate, cannot exceed 3′.

The second main fact is illustrated by the closeness of the structural dimensions (those of the unit cell of the space-lattice) of the ammonium and rubidium salts, the rubidium salt being the intermediate metallic salt. So very close are the total volumes of the cells (the molecular volumes, for the Rb salt 216·96 and for the NH_4 salt 216·53) and their edge-lengths (the topic axial ratios), that the crystals of the two salts are practically iso-structural, that is, their space-lattices are congruent, practically identical, capable of being represented by the same model on any scale within reason.

The author has the more confidence in putting forward this important result inasmuch as the similar result found with regard to the simple rhombic alkali sulphates has just been verified in the laboratory of Prof. Bragg, by Prof. Ogg and Mr. F. Lloyd Hopwood,† who have succeeded in measuring the actual dimensions of the space-lattice cells (the distances separating analogous atoms of contiguous structural units in space) by means of the X-rays, these absolute lengths being in remarkable concordance with the author's published topic axial ratios. For this result, as to congruency of the ammonium and rubidium salts, has been general for

* 'Phil. Trans.,' **A**, vol. 216, p. 1 (1916).

† 'Phil. Mag.,' November, 1916, vol. 32, p. 518.

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all the rubidium and ammonium salts dealt with by the author, and it is most satisfactory to have it confirmed in such an incontrovertible and authoritative manner. Incidentally also, the value of molecular volume and of topic axial ratios, when used, as the author has always solely done, for the strictly comparable members of isomorphous series such as those now under discussion, is confirmed and enhanced.

The bearing of the very interesting work of Prof. Ogg and Mr. Hopwood on the theory of valency volumes is dealt with in a separate memoir.*

[*Added, February 7, 1917.*]

With equal validity "atomic number" can be substituted for "atomic weight" in the statement of the author's law of progression of the crystallographic properties. For the differences between potassium, rubidium, and cæsium are similarly related as regards both functions, rubidium standing half-way between potassium and cæsium in both respects, as will be clear from the following comparison :—

	K.	Rb – K.	Rb.	Cs – Rb.	Cs.	Cs – K.
Atomic weights . .	38·85	46	84·9	47	131·9	93 = 2 × 46·5
Atomic numbers . .	19	18	37	18	55	36 = 2 × 18

The differences between K and Rb, and Rb and Cs, are thus equal for both constants, namely, 46 or 47 in atomic weight and 18 in atomic number, and the difference between the two extreme members of the family group, potassium and cæsium, is double as much, namely, 93 for atomic weight and 36 for atomic number.

The atomic number, the sequence number of the element, when all the elements are arranged in order of ascending atomic weight in the periodic table, has acquired great significance from the work of Moseley, who in two memoirs on "The High Frequency Spectra of the Elements" † has shown definitely and experimentally that the atomic number represents the value of the charge N of positive electricity on the atomic nucleus. For we already knew from the work of Sir J. J. Thomson, Sir E. Rutherford, Barkla, van den Broek, and Bohr, sufficient concerning the structure of the atom to render it certain that there is an inner positively charged nucleus, surrounded by a number of negatively charged electrons approximately equal to half the atomic weight, and together equivalent electrically to the positive charge on the nucleus; and van den Broek and Bohr had suggested that the nuclear charge N would prove to be equal to the atomic number. Now N increases from the atom of one element to the atom of the next in the periodic table always by a

* 'Roy. Soc. Proc.,' A, vol. 93, p. 72 (1917).

† 'Phil. Mag.,' series 6, vol. 26, p. 1024 (1913), and vol. 27, p. 703 (1914); see also "Obituary Notice," by Sir E. Rutherford, 'Roy. Soc. Proc.,' A, vol. 93, p. xxv. (1917).

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single positive unit, the positive charge carried by the nucleus being in all cases an integral multiple of the charge on the hydrogen nucleus; thus, for instance, while hydrogen has one nuclear charge helium has two such charges, and lithium three. The decisive work of MOSELEY, in his latest (unhappily last) research,* has been to show (a) that the X-ray spectra of the line series known as K are derived from the innermost ring of electrons, while those of the L series are derived from electrons further from the centre of the atom; (b) that the frequency of the spectra is proportional to $(N-a)^2$ where a is a constant dependent on the line series used, its value being 1 for the K series and 7·4 for the L series (for the α line in each case); and (c) that N itself, the nuclear charge, is none other than the atomic number.

The atomic number, or element sequence number, is thus a very important factor in the constitution of the atom, and it is therefore very likely to be a correspondingly governing factor in determining the relative properties of an isomorphous series of salts, formed by the interchange of atoms of elements of the same family group of the periodic classification, such as the three alkali metals, which differ regularly from one another in position by two whole horizontal rows of elements at a time (18 elements). Indeed, the work of MOSELEY shows clearly that the properties of the atom are better defined by the atomic number than by the atomic weight. It has always been difficult to see why mere atomic weight should wield the influence which has been pointed out by the author, and the author has been careful to emphasise that he regarded atomic weight as only another progressively changing property, very convenient, however, for purposes of reference as regards the chemical position of the element, but equally with all the other progressing properties dependent on some hitherto unknown fundamental difference in the chemical elementary atoms. This fundamental difference is now proved by MOSELEY to be the positive electric charge on the atomic nucleus, and as this determines the atomic electronic complexity and the atomic number is its measure, there is a logical reason why increase in the atomic number, in the case of a regularly ascending series of family group elements, should be effective in similarly progressively modifying the crystallographic and physical properties of isomorphous salts containing those elements. Moreover, the fact that both atomic weight and atomic number have been shown above to be similarly related, in the case of the alkali metals, rubidium standing exactly midway between potassium and cæsium in both respects, affords full explanation for the progression according to atomic weight which has been pointed out by the author to occur in the eutropically isomorphous series, both the rhombic simple salts and the monoclinic double salts, which have been described and compared in this and the author's former communications.

* 'Phil. Mag.,' series 6, vol. 26, p. 1024 (1913), and vol. 27, p. 703 (1914); see also "Obituary Notice," by Sir E. RUTHERFORD, 'Roy. Soc. Proc.,' A, vol. 93, p. xxv. (1917).