Monoclinic Double Selenates of the Iron Group

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VIII. *Monoclinic Double Selenates of the Iron Group.*

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The investigation of the crystals of the four salts of the series $R_2M(SeO_4)_2 . 6H_2O$, in which M is ferrous iron, and R is potassium, rubidium, cæsium, and ammonium, has at last been successfully and completely accomplished, both morphologically and optically, and the results are presented in this communication. The difficulties which have delayed it are described in a separate memoir, read at the same meeting of the Royal Society and published in the 'Proceedings,'* together with details of the manner in which these difficulties have been overcome.

The main obstacles were (1) the difficulty of preparing ferrous selenate $FeSeO_4$, a salt very much less stable than ferrous sulphate $FeSO_4$; (2) the ready oxidation of its solution in water and of the solutions of the double selenates obtained by the addition of the calculated quantity of the alkali selenate, and (3) the especial difficulty underlying the formation of potassium ferrous selenate, and the fact that even when formed the crystals of this salt decompose and become opaque like porcelain within a very few hours.

There is no record of rubidium or cæsium ferrous selenates having ever been previously either prepared or investigated, crystallographically or physically. Ammonium ferrous selenate was prepared by H. Topsøe,† and its goniometry and a density determination were described by him in his 1870 dissertation; its optics were also to a very limited extent described by him in conjunction with C. Christiansen, in their well-known memoir of 1874. Potassium ferrous selenate offered such insuperable difficulties, however, that Topsøe was only able to obtain four approximate measurements of exterior angles, and no attempt at a density determination was made; for, as he states in his 1870 dissertation, he found that the crystals which he obtained decomposed immediately after their removal from the mother liquor. The salt was consequently never able to be handed over to Prof. Christiansen‡ for optical investigation, and is entirely omitted from their joint 1874 memoir.

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* 'Roy. Soc. Proc.,' A, vol. 94, p. 352 (1918).

† 'Krystallogr.-kem. Unders. over de selensure Salte,' Copenhagen, 1870.

‡ 'Ann. Chim. Phys.,' series 5, vol. 1, p. 1 (1874). It is with great regret that the author learns of the death of Prof. Christiansen on December 28, 1917.

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It has been shown in the separate memoir on the chemistry of these double selenates that a successful and ready method of preparing ferrous selenate in solution, which automatically preserves it in the ferrous condition by retarding oxidation by atmospheric oxygen, is afforded by acting on pure ferrous sulphide in the cold with moderately dilute selenic acid. The especial difficulty of obtaining potassium ferrous selenate from the filtered solution of ferrous selenate, after admixture with the equal molecular proportion of potassium selenate in fairly concentrated solution, has been overcome by making the preparations in the coldest winter weather, the crystals successfully obtained having all been deposited during the four coldest nights of early January, 1918, which were distinguished on Dartmoor for their exceptionally low temperature. The crystallisation occurred in a partial vacuum over oil of vitriol, under the receiver of an air pump. The goniometry and optics were carried through on the succeeding day, immediately after removal from the mother liquor, in each case, during the four or five hours of the transparent life of the crystals and in a very cold room without fire or other artificial heating.

Potassium Ferrous Selenate $K_2Fe(SeO_4)_2 . 6H_2O$.

The four crops of beautifully clear, transparent, pale green crystals obtained of this remarkable salt were produced during four very cold nights in the manner just described, and given in more detail in the 'Proceedings' memoir on the chemistry of the group (p. 360). They were derived from three separate preparations, only one of which yielded a second crop on the next, also very cold, night. The temperature of the laboratory on all four nights was only just a fraction of a degree above 0° C., there being from 8° C. to 10° C. of frost outside. Further crops from these preparations, after filtering from oxidised ferric products, and all those derived from the numerous other preparations made in cold, but not such extremely cold, weather, consisted only of very minute crystals, quite unsuitable for goniometrical examination, which corresponded with those which Topsøe states are produced at ordinary temperatures on moderately mild or warm days, and which he describes as having the composition $K_2Fe(SeO_4)_2 . 2H_2O$ and as being of probably triclinic symmetry.

According to Topsøe the decomposition of the crystals of the hexahydrated salt is due to their conversion into this dihydrated salt at a temperature but a few degrees above the freezing point of water. Confirmatory evidence of this will be afforded when the density is discussed, as the author found that the density rises continuously and quite markedly during every half-hour of the life of the crystals after decomposition once starts.

There is no doubt that this potassium salt of the iron group is unstable for the reason that in the regular descent in stability, which the author has shown to be general for all the groups of salts of this hexahydrated series (including the double sulphates), from the cæsium salt through the rubidium salt to the potassium salt, the limit of existence is actually attained in the iron group when the potassium salt is reached, at a temperature which is but very slightly above 0° C.

By intensive work on the four cold days succeeding the very cold nights in question—commencing early in the morning, immediately after removing the crystals from their mother liquor and drying them with a soft handkerchief—and by keeping the room cold, it has been found possible to measure completely (1) the whole of the exterior angles of six crystals; (2) to determine the density of a considerable number; (3) to measure the extinction angles and (4) the optic axial angles, and (5) to determine all three refractive indices directly, for the usual range of the seven wave-lengths of light employed by the author. The only observations, of the author's usual scheme of work, which have not been possible with this salt are those carried out at higher temperatures, which are obviously out of the question with a salt of such extreme instability at temperatures even somewhat lower than the ordinary. At 20° C. to 30° C. decomposition is immediate, and even when working in an unpleasantly cold room the life of the crystals does not extend to a second day, even if they be covered by an inert liquid such as benzene, a device which, however, does somewhat prolong their existence, possibly by a couple of hours. On the second day the crystals were as opaque as plaster of Paris. One crystal employed, however, which was of tabular form and mounted between truly plane glass plates in a quickly drying medium of very hard Canada balsam dissolved in benzene, in a manner which entirely enveloped the crystal (all the rest of the air film between the two glass plates being filled up by the balsam) remained transparent for nearly a week. Other attempts at such preservation have not, however, succeeded. Thus 5 to 6 hours' time was the usual limit for work on any crop of crystals. To leave any particular crystal in the mother liquor until ready for work with it proved useless, for the edges became rounded as the temperature of the room inevitably rose slightly during the advance of the morning. The actual temperature of the laboratory, however, never rose above 6° C. during all the measurements and determinations, except during the density determinations, when absolutely fresh crystals were employed, surrounded by the usual mixture of methylene iodide and benzene, which preserved them completely free from decomposition during the short time which the Retgers immersion method demands. This work now described would obviously have been quite impossible in summer.

The grinding of section-plates and prisms was avoided as far as possible, because ground surfaces become opaque from decomposition with great rapidity. Special optical methods were employed for most of the work, the crystals being immersed in an inert liquid, cedar oil, which most fortunately happens to possess almost the same refractive index as the mean index of the crystals $\frac{1}{3}(\alpha + \beta + \gamma)$, and likewise a very similar dispersion. But the results, although there could thus be no doubt of their accuracy, were confirmed on the last of the four days by the successful grinding of a sufficiently transparent 60°-prism from one of the larger crystals obtained, so orientated as to afford direct values for the indices α and γ, and by the accomplishment of the determination of these indices therewith before opacity supervened (which occurred within a further hour). The values obtained from this ground prism proved to confirm fully the results previously obtained, and as the third (intermediate) index of refraction β had been afforded twice over absolutely directly by two natural prisms employed, the whole of the optical constants were thus ascertained in a manner which rendered them fully trustworthy.

Morphology.

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

Ratios of Axes.—

$a : b : c = 0\cdot7490 : 1 : 0\cdot5044$. Topsøe's approximate values $0\cdot7407 : 1 : 0\cdot5007$.

Axial Angle.—$\beta = 103° \; 50'$. Approximate value of Topsøe, 104° 15′.

Forms Observed.—$a\,\{100\}$, $b\,\{010\}$, $c\,\{001\}$, $p\,\{110\}$, $p'\,\{120\}$, $q\,\{011\}$, $r'\,\{\bar{2}01\}$, $o'\,\{\bar{1}11\}$, and $n'\,\{\bar{1}21\}$. The forms $a\,\{100\}$ and $p'\,\{120\}$ were not observed by Topsøe.

Habit.—More or less tabular parallel to $c\,\{001\}$, fig. 1, to short prismatic parallel to $p\,\{110\}$, occasionally with especial elongation of one parallel pair of the p-prism faces only (fig. 2).

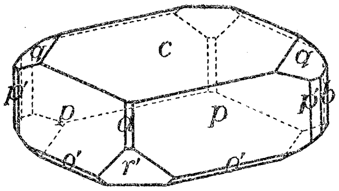

Fig. 1.

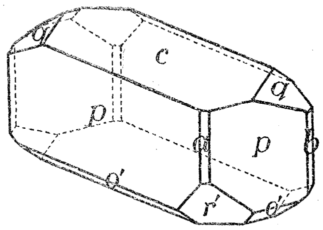

Fig. 2.

The great majority of the crystals obtained were of the tabular type illustrated in fig. 1, and this type proved very useful in the optical work, as the bisectrix of the obtuse angle between the optic axes is nearly identical with the normal to the plate, which latter is parallel to the faces of the basal plane $c\,\{001\}$. The type shown in fig. 2 was represented by one of the finest and largest crystals obtained. In all the crystals the c-faces and p-faces predominated, usually the former to the greatest extent. The q-faces were, as with all the potassium salts of the series, small. The r'-faces were generally rather large, and sometimes were very prominent indeed, a fact which has been observed to be characteristic of the iron groups of both the double sulphates and double selenates. Three good measurements were obtained from little a-faces, of a narrow type but excellently reflecting. The faces of $b\,\{010\}$, $o'\,\{\bar{1}11\}$, and $n'\,\{\bar{1}21\}$ were only very minute (usually almost imperceptible lines), and afforded no adequate reflections of the signal. Several little p'-faces were observed, however, and in two cases good measurements were obtained.

The table of angles is given on the next page, and it is a somewhat surprisingly satisfactory one, considering the circumstances under which these six crystals had to be measured.

INTERFACIAL Angles of Potassium Ferrous Selenate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.
		° ′ ° ′	° ′	° ′	′
$ac = (100) : (001)$	3	76 2– 76 16	76 8	76 10	2
$as = (100) : (101)$	—	—	—	46 46	—
$sc = (101) : (001)$	—	—	—	29 24	—
$cr' = (001) : (\bar{2}01)$	11	62 43– 63 1	62 47	62 38	9
$cs' = (001) : (\bar{1}01)$	—	—	—	37 58	—
$s'r' = (\bar{1}01) : (\bar{2}01)$	—	—	—	24 40	—
$r'a = (\bar{2}01) : (\bar{1}00)$	1	—	41 11	41 12	1
$r'c = (\bar{2}01) : (00\bar{1})$	10	117 0–117 30	117 13	117 22	9
$ap = (100) : (110)$	12	35 40– 36 11	36 1	36 1	0
$pp' = (110) : (120)$	2	19 15– 19 34	19 25	19 28	3
$p'b = (120) : (010)$	—	—	—	34 31	—
$pp''' = (110) : (130)$	—	—	—	29 21	—
$p'''b = (130) : (010)$	—	—	—	24 38	—
$pb = (110) : (010)$	—	—	—	53 59	—
$pp = (110) : (1\bar{1}0)$	9	71 31– 72 21	72 2	*	—
$pp = (110) : (\bar{1}10)$	9	107 39–108 18	107 58	107 58	0
$cq = (001) : (011)$	20	25 45– 26 26	26 6	*	—
$qb = (011) : (010)$	—	—	—	63 54	—
$qq = (011) : (01\bar{1})$	8	127 19–128 27	127 49	127 48	1
$ao = (100) : (111)$	—	—	—	49 59	—
$oq = (111) : (011)$	—	—	—	27 37	—
$aq = (100) : (011)$	—	—	—	77 36	—
$qo' = (011) : (\bar{1}11)$	—	—	—	34 12	—
$o'a = (\bar{1}11) : (\bar{1}00)$	—	—	—	68 12	—
$co = (001) : (111)$	—	—	—	35 9	—
$op = (111) : (110)$	—	—	—	43 42	—
$cp = (001) : (110)$	14	78 44– 79 8	78 51	*	—
$po' = (110) : (11\bar{1})$	—	—	—	56 54	—
$o'c = (11\bar{1}) : (00\bar{1})$	—	—	—	44 15	—
$pc = (110) : (00\bar{1})$	14	100 52–101 30	101 9	101 9	0
$bn = (010) : (121)$	—	—	—	53 41	—
$no = (121) : (111)$	—	—	—	16 8	—
$bo = (010) : (111)$	—	—	—	69 49	—
$os = (111) : (101)$	—	—	—	20 11	—
$bo' = (010) : (\bar{1}11)$	—	—	—	65 17	—
$o's' = (\bar{1}11) : (\bar{1}01)$	—	—	—	24 43	—
$o'o' = (\bar{1}11) : (\bar{1}\bar{1}1)$	—	—	—	49 26	—
$sq = (101) : (011)$	—	—	—	38 31	—
$qp = (011) : (\bar{1}10)$	13	84 57– 85 27	85 12	85 8	4
$ps = (\bar{1}10) : (\bar{1}0\bar{1})$	—	—	—	56 21	—
$pq = (\bar{1}10) : (0\bar{1}\bar{1})$	14	94 21– 95 8	94 47	94 52	5
$s'q = (\bar{1}01) : (011)$	—	—	—	44 55	—
$qn = (011) : (121)$	—	—	—	27 1	—
$np = (121) : (110)$	—	—	—	37 22	—
$qp = (011) : (110)$	9	64 2– 64 41	64 23	64 23	0
$ps' = (110) : (10\bar{1})$	—	—	—	70 42	—
$pq = (110) : (0\bar{1}\bar{1})$	9	115 19–116 7	115 37	115 37	0
$r'o' = (\bar{2}01) : (\bar{1}11)$	—	—	—	34 22	—
$o'p = (\bar{1}11) : (110)$	—	—	—	93 7	—
$pr' = (110) : (20\bar{1})$	4	52 22– 52 32	52 29	52 31	2
$r'p = (\bar{2}01) : (110)$	4	127 28–127 38	127 31	127 29	2
Total number of measurements .	166				

The forms given in the list other than a and p are the same as were observed by Topsøe. The only four angular measurements which he obtained were as follows:— $pp = (110):(1\bar{1}0) = 71^\circ\ 21'$, $cp = (001):(\bar{1}10) = 101^\circ\ 32'$, $cr' = (001):(\bar{2}01) = 63^\circ\ 1'$, and $pq = (\bar{1}10):(011) = 85^\circ\ 30'$, all of which he states were only approximate, owing to the crystals becoming dull and decomposed immediately after removal from the mother liquor. They differ considerably from the accurate values now obtained.

Cleavage.—It was not possible to determine the cleavage with accuracy, on account of the rapid decomposition of cleaved surfaces, but it would appear that the usual cleavage parallel $r'\ \{\bar{2}01\}$, developed throughout the series, is also shared by potassium ferrous selenate.

Volume.

Relative Density.—The following results were obtained in six determinations by the Retgers immersion method. The first four were with crystals belonging to one crop, and were carried out immediately after removal from the mother liquor and careful drying with a soft handkerchief; the last two were carried out on another day, with another of the crops, the crystals used being also transferred directly from the mother liquor to the immersion liquid, after a few moments occupied in the drying with a handkerchief. The results are seen to be eminently concordant. A different room was employed for the work of making the liquid of exactly the same density as the crystal, the temperature of which was higher than that of the laboratory; for it is inadvisable to work at a temperature much more than 5° below 20° C. (the standard temperature of all the author's density comparisons), on account of the large magnitude of the correction for the coefficient of expansion of the crystals which is then involved. The crystals were not at all adversely affected during the rapid work at the temperature of 13° – 15°, as they were immersed in the heavy protective liquid, being quite as transparent at the finish as when immersed, and several of them were employed immediately afterwards in the goniometrical work.

						Mean
I.	Density for	13°·0/4°	2·4931	For	20°/4° . . 2·4914	2·4921
II.	,,	15°·0/4°	2·4944	,,	20°/4° . . 2·4932	
III.	,,	13°·3/4°	2·4930	,,	20°/4° . . 2·4913	
IV.	,,	14°·4/4°	2·4939	,,	20°/4° . . 2·4925	
V.	,,	13°·6/4°	2·4955	,,	20°/4° . . 2·4939	2·4941
VI.	,,	15°·4/4°	2·4953	,,	20°/4° . . 2·4942	
				Mean	. . . 2·4928	

As it is probable that the higher mean value for the second of the two different preparations is nearer the truth for cavity-free crystals, the value accepted for 20°/4° is **2·494**.

Molecular Volume.— $\frac{M}{d} = \frac{524{\cdot}72}{2{\cdot}494} = 210{\cdot}39.$

Molecular Distance Ratios (topic axial ratios).—

$$\chi : \psi : \omega = 6{\cdot}2230 : 8{\cdot}3085 : 4{\cdot}1908.$$

In addition to the above determinations of density with clear, transparent, absolutely fresh crystals, a number of further determinations were made with crystals in the act of decomposing, employing some that were only just showing the first signs when placed in the immersion liquid, and continuing with the same crystals, a fresh determination of their density being made each half-hour. The temperatures of the liquid only varied from 13°·7 to 14°·5, and the results for 20°/4° of seven successive determinations at the half-hour intervals were 2·5211, 2·5238, 2·5296, 2·5442, 2·5551, 2·5622, and 2·5726. It is thus obvious that the crystals became denser as decomposition proceeded. This would appear to agree with the conclusion of Topsøe that the monoclinic crystals of the hexahydrated salt $K_2Fe\ (SeO_4)_2 \,.\, 6H_2O$, which are only stable up to a temperature but slightly above 0° C., break down at ordinary temperatures into microscopic triclinic crystals of the dihydrated salt $K_2Fe\ (SeO_4)_2 \,.\, 2H_2O$.

Optics.

The author's usual procedure—including the grinding of two section-plates parallel to the symmetry plane for extinction determinations of six section-plates (three perpendicular to each of the two median lines) for optic axial angle measurements, and of six 60°-prisms for refractive index determinations—was not possible with this unstable salt. As already mentioned, only four crops of the crystals were obtained, and the life of any one crystal was not more than six hours, after which it had usually become hopelessly opaque from decomposition. Hence, very rapid methods of work and avoidance of the grinding of many surfaces (which become much more rapidly opaque than natural ones) were essential, for the time lost in grinding a plate or prism, which when finished was useless, could much more profitably be spent in making confirmatory measurements with other natural crystals.

All the optical work, therefore, was carried out with three natural plates, tabular crystals parallel to the basal plane *c* {001}, two natural prisms formed by a pair of *p*-faces (inclined at 72° 2′) and a pair of *q*-faces (inclined at 52° 12′), and one ground prism (of 60°) only, the latter from the largest of the crystals obtained and ground accurately to afford the α and γ indices, the grinding of which was fortunately accomplished and the measurements obtained with it just before opacity supervened.

Each of the three crystal plates was mounted with hard balsam in benzene on a truly plane glass plate (one of the circular ones a centimetre diameter provided with the cutting and grinding goniometer) and covered with a small piece of thin cover glass, the crystal being completely protected by the balsam and its life thereby lengthened by an hour or two (in one exceptional case longer). Each crystal plate was rhombus-shaped (see fig. 1), the four *p*-faces being the main rhombus-determining edge faces. It was suspended by its circular glass mount-plate truly vertically from the adjusting apparatus of the polariscopical goniometer, so that the shorter diagonal of the rhombus (from front to back in fig. 1), the trace of the symmetry plane *b* {010}, was horizontal; it was also adjusted so that the centre of the rhombus-like *c*-face was in the optical axis of the polariscope. On raising into position the cell containing the immersion liquid, cedar oil, of similar refractive index ($\mu = 1{\cdot}5102$ for Na-light) to the mean index of the crystals,* so that the crystal occupied the centre of the cell, and then rotating the goniometer circle (with the crystal-carrying axis rigidly fixed to it) first on one side and then on the other, the optic axial interference figure was seen, with the optic axes separated at their true obtuse angle, the more accurately true the more nearly identical the refractive indices of the liquid and the crystal. For *the plane of the optic axes is the symmetry plane b* {010}, which had been horizontally adjusted; and the second median line, the obtuse bisectrix and axis α of the optical indicatrix as *the sign of the double refraction is positive*, is very nearly perpendicular to the basal plane c {001}, the plane of the crystal plate.

Three different constants were then determinable:—(1) the exact position of the second median line with reference to the normal to the basal plane c {001}, which is the same as the normal to the glass mount-plate, for the circle reading for this normal could be directly observed; (2) the true acute optic axial angle $2V_a$, for this is the supplement of the true obtuse angle $2V_o$ directly measurable, and is indeed itself directly measurable by further rotation of the circle; (3) the dispersion of the median lines. The course of these operations was as follows.

The crystal plate was first adjusted so that the plane of the plate and of its mount-plate was approximately truly vertical, parallel to the goniometer axis, and the circle reading of the polariscopical goniometer was determined for the position when the plane of the plate was exactly normal to the axis of the polariscope, the crystal-holder and the steel axis carrying it and its adjustments being locked immovably to the circle axis. This adjustment of the plate to normality was rendered readily possible by use of the Becker transparent mirror-and-lens fitting, described on p. 34 and illustrated in fig. 13 of the author's "Crystallography and Practical Crystal Measurement" (Macmillan), the fitting being placed close up in front of the analysing Nicol of the polariscope. This combination, of a glass plate transparent mirror arranged at 45° and a lens fitted in an elbow side-tube, permitted the light from a goniometer electric lamp (provided with a copper cylindrical shade perforated by a suitable circular aperture and arranged to one side of the goniometer) to be reflected along the axis of the analysing tube of the polariscope to the glass mount-plate (the crystal being behind the plate during these operations), from which it was reflected back again to the Becker fitting, and passed through the transparent mirror and the small observing aperture in the front of the fitting to the observer's eye. The images of the cross spider-lines of the analysing tube, a parallel pair of vertical lines and a single horizontal line, could be plainly seen with the aid of this fitting,

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* It was possible to forecast with considerable accuracy the optical constants of this salt from the general principles already established for the relations of the three alkali-metallic salts of each group. To be adequately certain as regards the refractive index, one of the two natural prisms was used for a determination of the intermediate index β before proceeding with the plates, as will be described later.

reflected from the mount-plate, and they were readily brought by slight rotation of the circle and plate to coincidence with the spider-lines seen directly, any slight vertical displacement being readily corrected with the aid of the appropriate (back to front) movable segment of the crystal-adjusting apparatus. When the adjustment to coincidence was perfect the reading of the circle was taken, this reading then corresponding to the identity of the normal to the plate and to the crystal face $c\,\{001\}$ with the axis of the polariscope. The cell containing the immersion liquid, cedar oil, was then raised into position so that the crystal occupied its centre. The crystal plate was next adjusted, by slight rotation in its own plane, using white light, so that the optic axial plane $b\,\{010\}$, the symmetry plane, was strictly horizontal if not already so adjusted. This was effected by viewing and adjusting the interference figure in convergent polarised light (the Nicols being crossed at 45° and 135°); the correct position was attained when the optic axial "eyes" (the very small innermost rings and sharp vertices of the hyperbolic brushes) to the right and left of the normal position, as the circle was rotated, first one way and then the other, moved exactly along the horizontal cross-spider-line, by which they were bisected. The conditions were then attained for the measurement of the optic axial angle for the usual series of six wave-lengths of light, the crystal plate remaining locked to the circle throughout the measurements. These measurements were then carried out with the aid of the spectroscopic monochromatic illuminator, the vertices of the optic "eyes" being brought to the centre of the pair of vertical spider-lines for each wave-length in turn. Not only were readings for each of the two "eyes" to right and left of the normal taken, but also the readings for the other two optic "eyes" observed on rotating through the whole circle. By this means duplicate readings 180° apart were obtained for both the obtuse and acute true optic axial angles $2V_o$ and $2V_a$, the plate being immersed in a liquid of similar index of refraction and consequently affording not merely an apparent angle in oil but the real optic axial angle within the crystal. For as the plate was rotated through a complete circle four optic eyes were met with in succession, each at its correct position as within the crystal. The mean (half-way) positions 90° apart for any one colour of light were those of the two median lines, perpendicular to each other, the axes α and γ of the optical indicatrix. The procedure will be rendered clear from the following record of the observations with Plate 1; fig. 3 will also assist in elucidating the arrangements, A representing the crystal and B the glass mount-plate,

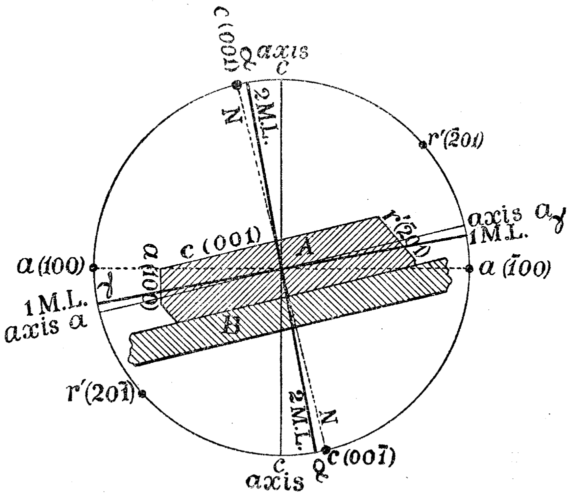

Fig. 3.

Crystal Plate 1, *Parallel c* {001}.

Circle reading for normal (N in fig. 3) to *c* (001), determined by coincidence of spider-lines with their own reflections . . . 214° 18′.

PLATE Arranged with Crystal Behind (as in fig. 3).

Light.	Observed left vertex.	Calculated 2 M.L.*	Observed right vertex.	$2V_o$.
	° ′	° ′	° ′	° ′
Li	276 1	217 36	159 11	116 50
C	276 0	217 35·5	159 11	116 49
Na	275 59	217 37	159 15	116 44
Tl	275 58	217 37·5	159 17	116 41
Cd.	275 57	217 38·5	159 20	116 37
F	275 55	217 39·5	159 24	116 31
Dispersion (Li ∼ F) .	0 6	0 3·5	0 13	

* The midway position between the observed left and right vertex readings.

PLATE Arranged with Crystal in Front.

Light.	Observed left vertex.	Calculated 2 M.L.	Observed right vertex.	$2V_o$.
	° ′	° ′	° ′	° ′
Li	96 3	37 38	339 13	116 50
C	96 3	37 38·5	339 14	116 49
Na	96 2	37 41·5	339 21	116 41
Tl	96 0	37 43·5	339 27	116 33
Cd.	95 57	37 43	339 29	116 28
F	95 55	37 42·5	339 30	116 25
Dispersion (Li ∼ F) .	0 8	0 4·5	0 17	

Light.	Mean $2V_o$.	Mean $2V_a$.	Mean 2 M.L.
	° ′	° ′	° ′
Li	116 50	63 10	217 37
C	116 49	63 11	217 37
Na	116 43	63 17	217 39
Tl	116 37	63 23	217 40
Cd	116 33	63 27	217 41
F	116 28	63 32	217 41
		Dispersion (Li ∼ F) . . .	0 4

The extreme readings, for red Li and greenish blue F light, were repeated and confirmed several times, and the fact definitely established that the optic axis emerging to the left of the normal to the plate was dispersed 7′ (within the error of experiment, which even with the beautifully small innermost rings and very sharp hyperbolic vertices obtained amounts to possibly 2′), while the right-hand optic axis was dispersed double this amount, 15′. That the extreme outside reading in each case (the highest on the left and the lowest on the right) was for red was clearly apparent, and was confirmed by the colours bordering the vertices when seen in white light, the inner margins of both being tinted red, and the left one more faintly than the right. Hence, it can be accepted with confidence that the second median line was dispersed to the extent of $\frac{15'-7'}{2}$, that is 4′. This is also clearly shown by the mean readings for the position of the second median line, given in the last column at the foot of the table, the difference between these mean readings for Li and F light being 4′. The 2′ possible error in the readings of the positions for the right and left vertices for any one wave-length is eliminated in taking this mean value, and also the mean of the two separate sets of observations (crystal behind and crystal in front of the mount plate), 3′·5 and 4′·5, is also obviously 4′. Hence, the amount of the dispersion of the median lines is undoubtedly 4′, with a possible error of only one minute on each side.

In mounting the crystal on the glass plate great care was taken to observe the orientation of the crystal, as regards particularly the direction of the little strip-face of *a* (100) replacing the *pp* edge, and that of the two faces of *r*′ {$\bar{2}$01}. The former lay to the left and the larger of the two latter to the right, as shown in fig. 3, when the crystal was behind the glass plate. The edge-face *a* (100) is parallel to the vertical crystal axis *c*, and this axis emerged 13° 50′ to the left of the normal N to *c* (001), for the plane of the latter face is parallel to the inclined crystal axis *a*, and the crystal axial angle $\beta = ac = 76°10'$. Now the reading for the normal N was 214° 18′ (see top of table), from the observation taken before the plate was wetted with the immersion liquid (cedar oil), and the readings for the second median line (the half-way positions between those of the observed left and right optic eye vertices) were shown to be 217° 37′–41′ according to the wave-length (from Li to F). These latter readings were also to the left of the normal. Hence, the second median line is inclined from the normal to *c* (001) towards the left, that is, towards the vertical crystal axis *c*, to an extent which increases regularly from 3° 19′ for red Li light to 3° 23′ for greenish blue F hydrogen light. Thus the second median line is nearer to the vertical axis *c* by 4′ for F light than for C light. The mean, 3° 21′, is the inclination for yellow sodium light of the second median line to the normal to *c* (001), and is the extinction angle which the author generally determines on the stauroscope, with a couple of section-plates parallel to the symmetry plane *b* {010}.

The first median line, the direction of the γ axis of the indicatrix, is, of course, always perpendicular to the second median line, which in this substance corresponds to the α axis of the indicatrix.

The order of dispersion for the first median line is, therefore, that the latter is nearer to the inclined axis a by four minutes for red C light than it is for greenish blue F light. The third axis of the indicatrix, the intermediate axis β, is identical with the crystal axis b, the symmetry axis of the monoclinic crystals, normal to the paper in fig. 3.

These measurements with Plate 1, which have afforded all the data concerning the orientation of the axes of the optical indicatrix and of the optic axes, were supplemented by similar ones derived by the use of two other tabular crystals parallel c {001}, Plates 2 and 3. The results as regards the dispersion of the median lines were identical in both cases with that derived from Plate 1, namely, that the first median line is nearer by 4′ to the inclined axis a for red C light than it is for greenish blue F light.

The Extinction Angles with the Normal to c (001), behind that normal towards the direction of the vertical axis c, derived from Plates 2 and 3, were 2° 11′ from Plate 2 and 4° 39′ from Plate 3. The two plates were not quite so perfectly developed as Plate 1, as regards the planeness and perfection of surface of the two c-faces, Plate 1 having been a remarkably perfect crystal. But the mean value of the extinction angle for sodium light for the Plates 2 and 3 is 3° 25′, only 4′ removed from the excellent value derived from Plate 1, which was 3° 21′ for sodium light. Hence the mean value of the results from all three plates, 3° 23′, may be taken with confidence as very near the truth, quite as near as is possible in the cases of the ordinary extinction angle determinations in sodium light with the stauroscope.

The final result for *the orientation of the optical ellipsoid* is therefore as follows. The crystallographic axial angle ac being 76° 10′, the angle between the normal to the c-face (001) and the vertical axis c is 13° 50′. The second median line (axis α of ellipsoid) is inclined 10° 27′ for sodium light from and in front of the vertical axis c, and 3° 23′ behind the normal to c (001). The first median line (axis γ) lies 3° 23′ above the inclined axis a of the crystal and 10° 37′ below the normal to a (100). Both median lines thus lie in the obtuse crystal-axial angle ac. These positions will be clear from fig. 3.

The values for the optic axial angle derived from Plates 2 and 3 were as under :—

Light.	Plate 2.	Plate 3.	Mean $2V_o$.	Mean $2V_a$.
	° ′	° ′	° ′	° ′
Li	116 28	117 8	116 48	63 12
C	116 27	117 7	116 47	63 13
Na	116 18	117 1	116 40	63 20
Tl	116 12	116 52	116 32	63 28
Cd	116 8	116 45	116 27	63 33
F	116 2	116 38	116 20	63 40

The mean result for these two plates, the adjustments for which were not quite so perfect as for Plate 1, on account of less true-planeness of the *c*-faces, is so close to that for Plate 1 that the mean of the two results, given in the next table, may confidently be accepted as very near the truth.

Optic Axial Angle of KFe Selenate.

Light.	$2V_o$.	$2V_a$ in cedar oil.	True $2V_a$ (corrected for difference of refraction).
	° ′	° ′	° ′
Li	116 49	63 11	64 11
C	116 48	63 12	64 12
Na	116 42	63 18	64 18
Tl	116 35	63 25	64 25
Cd	116 30	63 30	64 30
F	116 24	63 36	64·36

If the refractive index of the immersion liquid, cedar oil, were absolutely identical with the mean index of the crystals ($1/3\ (\alpha+\beta+\gamma) = 1{\cdot}5207$ for sodium light), and the two dispersions were also identical, we could be content with the final value of $2V_a$ given in the third column. After the completion of the work on these unstable crystals, however, when time was no longer so important, the refractive index of the cedar oil employed was carefully determined, with the following result:—

Refractive Indices of Cedar Oil.

Li . . .	1·5064	Na . . .	1·5102	F . . .	1·5175
C . . .	1·5068	Tl . . .	1·5135	G . . .	1·5238
		Cd . . .	1·5153		

The index for Na-light is thus 0·0105 lower than the mean crystal index, but the dispersion between Li and G-light is practically identical (0·0174) with that of the crystals 0·0171. Another liquid, monochlorbenzene, has the index 1·5248 for Na-light, 0·0041 higher than the mean crystal index. But it has the disadvantage of dissolving the cementing balsam, which cedar oil does not. The angle $2V_o$ as observed in cedar oil would thus be slightly too large, while if observed in monochlorbenzene it would appear still more slightly too small. It has been possible to calculate the exact amount of the desirable correction, from observations made in both liquids at leisure, with the permanent crystals of rubidium ferrous selenate, the mean refractive index of which is almost identical (1·5220) with that of potassium ferrous selenate. The measurement of $2V_a$ for Na-light was 74° 28′ in cedar oil and 73° 4′ in monochlorbenzene; the true value, as calculated from $2H_a$ and $2H_o$ in bromonaphthalene, was

73° 28′. The angle in cedar oil was thus 1° 24′ greater than that in monochlorbenzene, and we can consider this result as also applicable to potassium ferrous selenate, the conditions being so nearly alike. The difference between the indices of the two liquids is 0·0146, and between those of cedar oil and the crystals of KFe selenate 0·0105. Hence, the correction, to be subtracted from the angle $2V_o$ as observed in cedar oil in order to give the true angle $2V_o$ within the crystal, is

$$\frac{84' \times 0{\cdot}0105}{0{\cdot}0146} = 60'.$$

The values in the last column of the table have, therefore, been obtained by adding exactly one degree to those for $2V_a$ in the third column, which corresponds to the subtraction of a degree from the observed values of $2V_o$ in column 2, as $2V_a$ is the supplement of $2V_o$. This final corrected value for $2V_a$ is certainly very close to the truth, quite as close indeed as if the ordinary procedure of observing $2H_a$ and $2H_o$ in bromonaphthalene, with section-plates perpendicular to the first and second median lines respectively, had been employed.

For the true optic axial angles in different crystals of the same substance frequently differ more than the few minutes of any possible error in these determinations.

In confirmation, however, the true angle $2V_a$ may also be calculated, now that the exact refractive index n of the immersion liquid is known, with the aid of the intermediate refractive index β of the crystals, from the observed value of the obtuse angle $2V_o$, considered as $2H_o$, by means of the well-known formula :—

$$\cos V_a = \frac{n}{\beta} \sin H_o.$$

Inserting the values for sodium light and making the calculation we have :—

$$\cos V_a = \frac{1{\cdot}5102}{1{\cdot}5182} \sin 58^\circ\ 21',$$

from which

$$V_a = 32^\circ\ 8' \text{ and } 2V_a = 64^\circ\ 16'.$$

This result differs by only 2′ from the corrected value given in the last column of the table, thus affording a most satisfactory confirmation of the final column of values in the table.

Refractive Indices.—A series of measurements of refractive index with a natural prism affording directly the index β had been carried out previous to the work just described with the plates, in order to obtain the necessary exact knowledge of the refractive power of the crystals to enable a proper choice to be made of an immersion liquid of like refractive index, for use with those plates. The index β is but slightly higher than the mean index of the crystals, $\frac{\alpha+\beta+\gamma}{3}$, and so enabled the choice of cedar oil to be made. The prism in question was one formed by two excellent faces of *p* {110}, the pair which form the acute angle 72° 2′, and the edge between which is often replaced by a strip-face of *b* {010}. To preserve it fully transparent during the rather prolonged measurements with seven wave-lengths of light from the spectroscopic monochromatic illuminator, the two *p*-faces in question were covered with miniature glass plates cemented by quickly drying hard balsam in benzene. The edge of such a prism is parallel to the vertical crystal axis *c*, and is not very far (10° 27′) from parallel to the second median line, the α axis of the optical ellipsoid, light vibrating parallel to which affords the α index of refraction. The index corresponding to rays vibrating parallel to the prism edge would, therefore, have a value not far removed from α. The other direction of vibration of rays passing through the prism at minimum deviation was that of the symmetry axis *b* of the crystal, and as this is absolutely identical for all wave-lengths with the intermediate axis β of the optical ellipsoid it furnishes the refractive index β directly with absolute accuracy. The object of this set of measurements was thus to determine β, the image of the slit corresponding to this index being that transmitted when the Nicol prism in front of the eyepiece of the goniometer-spectrometer was arranged at 0°; the image obtained when the Nicol was at 90° corresponded to vibrations parallel to the prism edge and thus afforded a value slightly higher than that of the minimum index α.

A second natural prism was subsequently employed in a similar manner; it was formed by two excellent faces of *q* {011}, those between which also comes the narrow line-face *b* (010) when developed. The prism angle in this case is 52° 12′. The edge of such a prism is parallel to the inclined crystal axis *a*, and only 3° 23′ removed from the γ axis of the ellipsoid, so that vibrations parallel to it (those transmitted with the Nicol at 90°) afford almost exactly the γ indices. The other rectangular vibration direction of the prism, like that of the first prism, was that of the symmetry crystal axis *b*, so that this prism also afforded directly and accurately the intermediate refractive index β, the image corresponding to it being that observed when the Nicol was at the 0° position.

The two values of β obtained from these two natural prisms, and their mean value, are as follows:—

Light.	*p*-faced prism.	*q*-faced prism.	Mean β.
Li	1·5136	1·5152	1·5144
C	1·5141	1·5158	1·5149
Na	1·5173	1·5191	1·5182
Tl	1·5207	1·5223	1·5215
Cd	1·5225	1·5242	1·5234
F	1·5244	1·5262	1·5253
G	1·5307	1·5321	1·5314

The approximate values obtained for α from the p-faced prism and for γ from the q-faced prism, were as under :—

Light.	Approximate α.	Approximate γ.
Li	1·5078	1·5307
C	1·5083	1·5312
Na	1·5113	1·5345
Tl	1·5145	1·5381
Cd	1·5163	1·5400
F	1·5182	1·5422
G	1·5242	1·5484

As the direction for which this approximate value for γ was determined was only $3\frac{1}{2}$° from the exact direction for the γ axis of the ellipsoid, it is probable that the above value for γ is practically correct. The approximate value for α was determined for a direction $10\frac{1}{2}$° removed from the true direction for the α (minimum) axis of the ellipsoid, and its value is therefore somewhat too high, probably by about 0·001 to 0·002.

Finally, in the fourth and last crop of crystals obtained there was a crystal large and transparent enough to suggest an attempt at grinding a prism to afford α and γ directly. One was therefore ground in the correct orientation to afford these indices directly and absolutely. The refracting edge was parallel to the second median line, (the α axis of the ellipsoid), so that vibrations affording the signal image when the Nicol was at 90° corresponded to the α index. The two faces of the prism were symmetrical to (inclined 30° on each side of) the symmetry plane b {010}, so that the other rectangular direction of vibration within that plane, corresponding to the image transmitted when the Nicol was at 0°, was parallel to the γ axis of the ellipsoid and afforded the index γ. By working very rapidly and keeping the crystal covered with the lubricating oil after its goniometrical adjustment to the correct desired orientation, and as soon as the grinding and polishing were completed covering the prepared surfaces with balsam-cemented glass plates, the prism was completed before any serious loss of transparency had occurred; an hour was permitted for the drying of the hard balsam in benzene, and the transparency was then still such as enabled the refractive indices α and γ to be determined for all wave-lengths from Li red as far as greenish blue F of the spectrum, only the G-images being too weak for accurate allocation to the cross wires. The results are given below.

Light.	α.	γ.
Li	1·5059	1·5306
C	1·5064	1·5311
Na	1·5095	1·5345
Tl	1·5127	1·5379
Cd	1·5145	1·5399
F	1·5164	1·5421

It is obvious that, as expected, the approximate values for γ afforded by the q-faced prism were the true values within the limits of experiment (0·0002); and that the approximate α values derived from the p-faced prism were slightly higher than the true α.

It is thus now possible to give with all confidence the true values of α, β and γ, all obtained directly. They are as under, the G-values for α and β being included from the evidence of their difference from the F-values afforded by the approximate determinations with the natural prisms.

REFRACTIVE Indices of Potassium Ferrous Selenate.

Light.	α.	β.	γ.
Li	1·5059	1·5144	1·5306
C	1·5064	1·5149	1·5311
Na	1·5095	1·5182	1·5345
Tl	1·5127	1·5215	1·5379
Cd	1·5145	1·5234	1·5399
F	1·5164	1·5253	1·5421
G	1·5224	1·5314	1·5483

Mean of α, β, and γ for Na light = 1·5207.

α = Vibration direction parallel to second median line, 10° 27′ in front of axis c.
β = ” ” ” ” symmetry axis b.
γ = ” ” ” ” first median line, 3° 23′ above axis a.

Double refraction, $\text{Na}_{\gamma-\alpha} = 0·0250$.

General formula for β, for any wave-length λ, corrected to a vacuum (correction + 0·0004):—

$$\beta = 1·4984 + \frac{838\,265}{\lambda^2} - \frac{4\,754\,500\,000\,000}{\lambda^4} + \ldots .$$

The α indices are also reproduced if the constant 1·4984 be diminished by 0·0087, and the γ indices if the constant is increased by 0·0163.

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

Indicatrix . . . . $\alpha : \beta : \gamma = 0·9943 : 1 : 1·0107$.
Velocity ellipsoid . . $\mathfrak{a} : \mathfrak{b} : \mathfrak{c} = 1·0058 : 1 : 0·9894$.

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, $\frac{n^2-1}{(n^2+2)d} = \mathfrak{n}$ . .	C	0·1192	0·1209	0·1241
		G	0·1224	0·1241	0·1274
”	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = \mathfrak{m}$.	C	62·55	63·43	65·10
		G	64·21	65·13	66·85
”	Specific dispersion, $\mathfrak{n}_G - \mathfrak{n}_C$		0·0032	0·0032	0·0033
”	Molecular dispersion, $\mathfrak{m}_G - \mathfrak{m}_C$		1·66	1·70	1·75
GLADSTONE	Molecular refraction, $\frac{n-1}{d} M$	C	106·54	108·33	111·74

Mean molecular refraction (GLADSTONE), $\frac{1}{3}(\alpha+\beta+\gamma) = 108·87$.

Rubidium Ferrous Selenate, $Rb_2Fe(SeO_4)_2 . 6H_2O$.

Morphology.

This substance has not been previously investigated, either goniometrically or optically. It forms beautifully transparent and, considering its composition (as containing ferrous iron), remarkably permanent crystals of a very pale bluish green colour.

Ten crystals were measured, selected from the three best crops of the several prepared. The ferrous selenate employed in one case had been prepared by the action of selenic acid on iron wire. An equivalent of pure rubidium selenate, prepared by the action of selenic acid on rubidium carbonate, was dissolved in only slightly more than the minimum amount of water required for solution at the ordinary temperature, and added to the cold solution of ferrous selenate immediately after the filtration from the precipitated selenium, in order to avoid the somewhat rapid decomposition (oxidation) which solutions of ferrous selenate suffer. Crystallisation occurred under the receiver of an air pump, under reduced pressure. Several crops of remarkably transparent and permanent crystals of rubidium ferrous selenate were also obtained by the method described in the introduction.

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

Ratios of Axes.—

$a : b : c = 0·7424 : 1 : 0·5000$.

Axial Angle.—$\beta = 104° 57'$.

Forms Observed.—a {100}, b {010}, c {001}, p {110}, p' {120}, q {011}, r' {$\bar{2}$01}, o' {$\bar{1}$11}, and n' {$\bar{1}$21}.

Habit.—Thick blocks, more or less tabular, parallel to c {001}. A typical crystal is shown in fig. 4.

The crystals exhibited the usual characteristic relative development of the faces of the basal plane c {001} and q {011} common to all the rubidium salts of the series, namely, the c-faces predominated, but the q-faces were also well developed as fairly broad bevellings. The faces of the clinopinakoid b {010} were also frequently quite large on this salt, forming the two sides of the blocks. The ends of the blocks were formed by the faces of the primary prism p {110} and the orthopinakoid r' {$\bar{2}$01}, which latter were often relatively very large, forming the two predominating end planes. Good little faces of the primary orthopinakoid a {100} were usually present, and indeed large crystals often showed the a-faces quite considerably developed. There were also usually several faces of the hemipyramid o' {$\bar{1}$11} present, but their reflections were poor. Excellent, although narrow faces of the prism p' {120} were also observed on two of the crystals measured. Minute faces of the hemipyramid

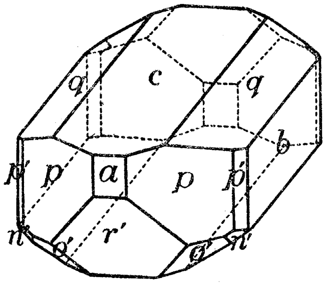

Fig. 4.

INTERFACIAL Angles of Rubidium Ferrous Selenate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.
$ac = (100):(001)$	3	75° 2′– 75° 9′	75° 6′	75° 3′	3′
$as = (100):(101)$	—	—	—	46 2	—
$sc = (101):(001)$	—	—	—	29 1	—
$cr' = (001):(\bar{2}01)$	19	63 29– 63 49	63 37	63 24	13
$cs' = (001):(\bar{1}01)$	—	—	—	38 15	—
$s'r' = (\bar{1}01):(\bar{2}01)$	—	—	—	25 9	—
$r'a = (\bar{2}01):(\bar{1}00)$	2	41 22– 41 26	41 24	41 33	9
$r'c = (\bar{2}01):(00\bar{1})$	17	116 17–116 28	116 23	116 36	13
$ap = (100):(110)$	8	35 31– 35 48	35 41	35 39	2
$pp' = (110):(120)$	3	19 24– 19 29	19 27	19 28	1
$p'b = (120):(010)$	3	34 42– 34 54	34 49	34 53	4
$pp''' = (110):(130)$	—	—	—	29 25	—
$p'''b = (130):(010)$	—	—	—	24 56	—
$pb = (110):(010)$	36	54 11– 54 30	54 21	*	—
$pp = (110):(1\bar{1}0)$	16	71 12– 71 33	71 23	71 18	5
$pp = (110):(\bar{1}10)$	17	108 25–108 44	108 35	108 42	7
$cq = (001):(011)$	38	25 21– 25 59	25 47	*	—
$qb = (011):(010)$	38	64 0– 64 28	64 13	64 13	0
$qq = (011):(01\bar{1})$	15	128 12–128 38	128 25	128 26	1
$ao = (100):(111)$	—	—	—	49 13	—
$oq = (111):(011)$	—	—	—	27 21	—
$aq = (100):(011)$	—	—	—	76 34	—
$qo' = (011):(\bar{1}11)$	—	—	—	34 28	—
$o'a = (\bar{1}11):(\bar{1}00)$	—	—	—	68 58	—
$co = (001):(111)$	—	—	—	34 38	—
$op = (111):(110)$	—	—	—	43 16	—
$cp = (001):(110)$	40	77 47– 78 8	77 54	*	—
$po' = (110):(11\bar{1})$	13	57 20– 57 46	57 30	57 39	9
$o'c = (11\bar{1}):(00\bar{1})$	14	44 25– 44 47	44 38	44 27	11
$pc = (110):(00\bar{1})$	39	101 46–102 20	102 6	102 6	0
$bn = (010):(121)$	—	—	—	54 15	—
$no = (121):(111)$	—	—	—	15 57	—
$bo = (010):(111)$	—	—	—	70 12	—
$os = (111):(101)$	—	—	—	19 48	—
$bo' = (010):(\bar{1}11)$	18	65 5– 65 21	65 13	65 20	7
$o's' = (\bar{1}11):(\bar{1}01)$	—	—	—	24 40	—
$o'o' = (\bar{1}11):(\bar{1}\bar{1}1)$	6	49 24– 49 35	49 31	49 21	10
$sq = (101):(011)$	—	—	—	38 3	—
$qp = (011):(\bar{1}10)$	35	86 1– 86 27	86 11	86 17	6
$ps = (\bar{1}10):(\bar{1}0\bar{1})$	—	—	—	55 40	—
$pq = (\bar{1}10):(0\bar{1}\bar{1})$	36	93 29– 94 3	93 49	93 43	6
$s'q = (\bar{1}01):(011)$	—	—	—	45 0	—
$qn = (011):(121)$	—	—	—	26 43	—
$np = (121):(110)$	—	—	—	37 2	—
$qp = (011):(110)$	35	63 32– 63 59	63 47	63 45	2
$ps' = (110):(10\bar{1})$	—	—	—	71 15	—
$pq = (110):(0\bar{1}\bar{1})$	34	116 2–116 28	116 13	116 15	2
$r'o' = (\bar{2}01):(\bar{1}11)$	21	34 28– 34 56	34 43	34 39	4
$o'p = (\bar{1}11):(110)$	20	92 45– 93 6	92 56	92 48	8
$pr' = (110):(20\bar{1})$	37	52 14– 52 31	52 23	52 33	10
$r'p = (\bar{2}01):(\bar{1}10)$	36	127 33–127 55	127 37	127 27	10
Total number of measurements .	599				

$n'\{\bar{1}21\}$ were also shown, but the reflections of the signal were too faint for accurate allocation to the spider-lines.

The faces of the forms $p\ \{110\}$ and $c\ \{001\}$ on the crystals of this salt were more than usually affected by striation, and only two crops were obtained sufficiently free from the defect for the purpose of the measurements. Even the 10 apparently excellent crystals selected from these crops have afforded results which show in the cases of certain angles greater differences between the calculated and observed angles than usual, compared with the salts of the series previously measured. The differences, however, are not sufficiently great to affect any of the conclusions drawn from the comparison of the results with those for the other members of the iron group of double selenates.

A table of angles is given on the previous page.

Cleavage.—There is a good cleavage developed parallel to $r'\{\bar{2}01\}$.

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

I.	Density for	16°·6/4° . . .	2·8034	For 20°/4° . . .	2·8025
II.	,,	16°·2/4° . . .	2·7986	,, 20°/4° . . .	2·7975
III.	,,	16°·4/4° . . .	2·8018	,, 20°/4° . . .	2·8008
IV.	,,	16°·1/4° . . .	2·7985	,, 20°/4° . . .	2·7974
V.	,,	16°·1/4° . . .	2·8031	,, 20°/4° . . .	2·8020
VI.	,,	16°·2/4° . . .	2·8002	,, 20°/4° . . .	2·7991
				Mean . . .	2·7999

The value accepted for 20°/4° is 2·800.

Molecular Volume.—$\frac{M}{d} = \frac{616{\cdot}82}{2{\cdot}800} = 220{\cdot}29.$

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

$$\chi : \psi : \omega = 6{\cdot}3109 : 8{\cdot}5006 : 4{\cdot}2503.$$

Optics.

Nature and Orientation of the Optical Ellipsoid.—The plane of the optic axes is the symmetry plane $b\ \{010\}$. The double refraction is positive, the first median line corresponding to the refractive index γ and the second median line to α. Extinction determinations with two plates parallel to the symmetry plane gave the following positions for one of the extinction directions with respect to the normal to $c\ \{001\}$.

Extinction Direction in the Symmetry Plane.

Plate 1 . . . . 1° 44′, Plate 2 . . . . 0° 56′,

Mean . . 1° 20′ with normal to $c\ \{001\}$.

The direction is behind the normal, towards the vertical axis *c*. It is the second median line and corresponds to the α index. As the angle between the normal to *c* {001} and the axis *c* is 14° 57′ (the angle *ac* = (100) : (001) = 75° 3′), this second median line is inclined 13° 37′ to (in front of) the axis *c*. The first median line is consequently inclined 1° 20′ to (above) the axis *a*, and lies 13° 37′ below the normal to *a* (100). Both median lines are in the obtuse angle of the crystal axes *ac*. The conditions are clearly shown in the diagram given in fig. 5.

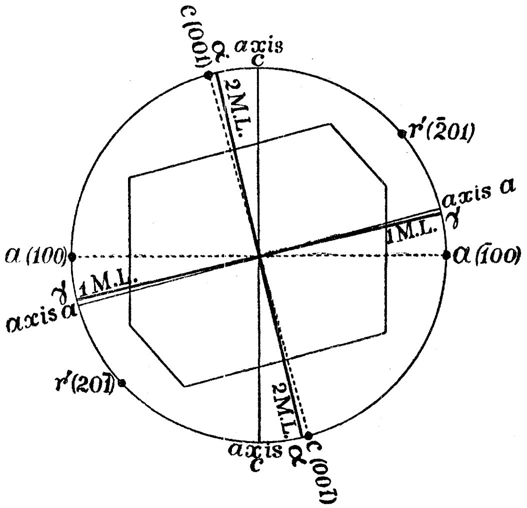

Fig. 5.

Optic Axial Angle.—Three pairs of section-plates were ground, perpendicular to the first and second median lines, and afforded the values for 2E, $2H_a$ and $2H_o$ recorded in the two following tables. The angle in air 2E is very large, and only Plates 1 and 3 of the three perpendicular to the first median line afforded it satisfactorily clearly. Monobromonaphthalene was the immersion liquid employed for the measurements of $2H_a$ and $2H_o$, for which very clear and suitable interference figures were obtained.

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

Light.	Plate 1.	Plate 3.	Mean 2E.
	° ′	° ′	° ′
Li	130 18	130 35	130 27
C	130 23	130 40	130 32
Na	131 3	131 7	131 5
Tl	131 34	131 41	131 38
Cd	131 59	132 1	132 0
F	132 36	132 30	132 33

DETERMINATION of True Optic Axial Angle in Bromonaphthalene of RbFe Selenate.

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 33	1*a*	94 31	73 32	73 35
	2	66 38	2*a*	94 30	73 36	
	3	66 38	3*a*	94 29	73 36	
C	1	66 31	1*a*	94 29	73 31	73 34
	2	66 34	2*a*	94 25	73 35	
	3	66 36	3*a*	94 25	73 36	
Na	1	66 15	1*a*	94 9	73 28	73 32
	2	66 17	2*a*	94 1	73 33	
	3	66 20	3*a*	94 5	73 34	
Tl	1	65 58	1*a*	93 47	73 26	73 30
	2	65 57	2*a*	93 32	73 32	
	3	66 2	3*a*	93 38	73 32	
Cd	1	65 45	1*a*	93 30	73 24	73 28
	2	65 47	2*a*	93 16	73 31	
	3	65 49	3*a*	93 21	73 30	
F	1	65 30	1*a*	93 15	73 20	73 26
	2	65 35	2*a*	92 58	73 30	
	3	65 36	3*a*	93 5	73 28	

Dispersion of the Median Lines.—This was determined by observations of the approximate true optic axial angle in cedar oil ($\mu = 1{\cdot}5200$) and monochlorbenzene ($\mu = 1{\cdot}5248$), the refractive indices of which liquids are respectively just lower and just higher than the mean index of the crystals. The dispersion proved to be very small, only 10′ between red C-light and green Tl-light, and is such that the first median line is nearer to the axis α by 10′ for red C-light than for green Tl-light.

Effect of Temperature on the Optical Axial Angle.—Measurements of the apparent optic axial angle in air 2E at 85° C. showed that this angle increases almost exactly two degrees for 70° C. rise of temperature (from 15° to 85°).

Refractive Indices.—Six excellent 60°-prisms were ground, each symmetrical to a principal plane of the optical ellipsoid and with the refracting edge parallel to one of the axes, so as to afford directly two of the three indices α, β, γ. The separate results for each index were satisfactorily concordant, and the mean values are given in the next table.

REFRACTIVE Indices of Rubidium Ferrous Selenate.

Light.	α.	β.	γ.
Li	1·5099	1·5165	1·5290
C	1·5104	1·5170	1·5295
Na	1·5133	1·5200	1·5328
Tl	1·5165	1·5233	1·5363
Cd	1·5184	1·5252	1·5382
F	1·5202	1·5272	1·5404
G	1·5264	1·5334	1·5467

Mean of α, β, and γ for Na light = 1·5220.
α = Vibration direction parallel to second median line, 13° 37′ in front of axis c.
β = " " " " symmetry axis b.
γ = " " " " first median line, 1° 20′ above axis a.
Double refraction, $\mathrm{Na}_{\gamma-\alpha} = 0{\cdot}0195$.

General formula for β, corrected to a vacuum :—

$$\beta = 1{\cdot}5048 + \frac{546\,205}{\lambda^2} - \frac{160\,200\,000\,000}{\lambda^4} + \dots.$$

The α indices are also very closely reproduced by the formula if the constant 1·5048 be diminished by 0·0067, and the γ indices also if the constant be increased by 0·0128.

Observations at 65° indicated that the refractive indices are diminished by about 0·0016 for α, 0·0018 for β, and 0·0021 for γ, by a rise of temperature of 50° C. (from 15° to 65°).

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

$$\alpha : \beta : \gamma = 0{\cdot}9956 : 1 : 1{\cdot}0084.$$
$$\mathfrak{a} : \mathfrak{b} : \mathfrak{c} = 1{\cdot}0044 : 1 : 0{\cdot}9916.$$

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, $\frac{n^2-1}{(n^2+2)d} = \mathfrak{n}$ . .	C	0·1069	0·1080	0·1102
		G	0·1097	0·1109	0·1132
"	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = \mathfrak{m}$.	C	65·93	66·65	68·00
		G	67·66	68·41	69·83
"	Specific dispersion, $\mathfrak{n}_G - \mathfrak{n}_C$		0·0028	0·0029	0·0030
"	Molecular dispersion, $\mathfrak{m}_G - \mathfrak{m}_C$		1·73	1·76	1·83
GLADSTONE	Molecular refraction, $\frac{n-1}{d} M$	C	112·44	113·89	116·65

Mean molecular refraction (GLADSTONE), $\frac{1}{3}(\alpha + \beta + \gamma) = 114{\cdot}33$.

Cæsium Ferrous Selenate, $Cs_2Fe(SeO_4)_2 . 6H_2O$.

Morphology.

The salt was prepared in the manner described in the introduction, the ferrous selenate being prepared by the action of selenic acid on ferrous sulphide, and the cæsium selenate by the action of selenic acid on pure cæsium carbonate.

Ten crystals were measured, selected from four different crops, all of which were composed of excellent transparent single crystals, sometimes grown to a considerable size, and of a pale (almost colourless) bluish green colour containing more yellow than the crystals of rubidium ferrous selenate.

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

Ratios of Axes.—$a : b : c = 0·7308 : 1 : 0·4979$.

Axial Angle.—$\beta = 106° 2'$.

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

Habit.—Prismatic parallel to the inclined axis a.

A typical crystal is represented in fig. 6.

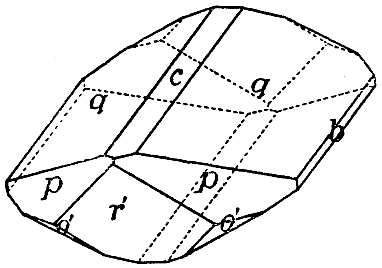

Fig. 6.

The crystals were usually very definitely of this habit, which is distinguished by narrow faces of c {001} and broad faces of q {011}, and which is very characteristic of the cæsium salts of the series. In a few crops the c-faces were somewhat broader, and almost conferred a tabular habit on the crystals. As in several of the double sulphates containing iron, notably ammonium ferrous sulphate, the faces of the orthopinakoid r' {$\bar{2}01$} were usually more prominent than those of the primary prism p {110}, and in many cases practically formed the ends of the prisms, the p-faces being very small. The faces of the clinopinakoid b {010} and of the hemipyramid o' {$\bar{1}11$} were only occasionally present, and then were very subsidiary, although some good reflections were obtained from them.

Cleavage.—There is an excellent cleavage parallel to r' {$\bar{2}01$}.

Volume.

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

I.	Density for	15°·9/4° . . .	3·0497	For 20°/4° . . .	3·0484
II.	,,	15°·7/4° . . .	3·0485	,, 20°/4° . . .	3·0472
III.	,,	16°·2/4° . . .	3·0495	,, 20°/4° . . .	3·0483
IV.	,,	16°·1/4° . . .	3·0504	,, 20°/4° . . .	3·0492
				Mean	3·0483

Accepted value for 20°/4°, **3·048.**

INTERFACIAL Angles of Cæsium Ferrous Selenate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.
		° ′ ° ′	° ′	° ′	′
$ac = (100):(001)$	—	—	—	73 58	—
$as = (100):(101)$	—	—	—	45 9	—
$sc = (101):(001)$	—	—	—	28 49	—
$cr' = (001):(\bar{2}01)$	22	64 16– 64 43	64 32	64 29	3
$cs' = (001):(\bar{1}01)$	—	—	—	38 51	—
$s'r' = (\bar{1}01):(\bar{2}01)$	—	—	—	25 38	—
$r'a = (\bar{2}01):(\bar{1}00)$	—	—	—	41 33	—
$r'c = (\bar{2}01):(00\bar{1})$	22	115 17–115 45	115 28	115 31	3
$ap = (100):(110)$	—	—	—	35 7	—
$pp' = (110):(120)$	—	—	—	19 28	—
$p'b = (120):(010)$	—	—	—	35 25	—
$pp''' = (110):(130)$	—	—	—	29 31	—
$p'''b = (130):(010)$	—	—	—	25 22	—
$pb = (110):(010)$	8	54 43– 55 1	54 52	54 53	1
$pp = (110):(1\bar{1}0)$	19	70 6– 70 23	70 14	*	—
$pp = (110):(\bar{1}10)$	19	109 35–109 57	109 46	109 46	0
$cq = (001):(011)$	37	25 20– 25 42	25 34	*	—
$qb = (011):(010)$	8	64 23– 64 39	64 28	64 26	2
$qq = (011):(01\bar{1})$	18	128 44–129 2	128 52	128 52	0
$ao = (100):(111)$	—	—	—	48 19	—
$oq = (111):(011)$	—	—	—	27 16	—
$aq = (100):(011)$	—	—	—	75 35	—
$qo' = (011):(\bar{1}11)$	—	—	—	35 3	—
$o'a = (\bar{1}11):(\bar{1}00)$	—	—	—	69 22	—
$co = (001):(111)$	—	—	—	34 18	—
$op = (111):(110)$	—	—	—	42 39	—
$cp = (001):(110)$	40	76 48– 77 4	76 57	*	—
$po' = (110):(11\bar{1})$	4	58 3– 58 15	58 11	58 7	4
$o'c = (11\bar{1}):(00\bar{1})$	4	44 46– 44 57	44 52	44 56	4
$pc = (110):(00\bar{1})$	40	102 50–103 13	103 3	103 3	0
$bn = (010):(121)$	—	—	—	54 47	—
$no = (121):(111)$	—	—	—	15 47	—
$bo = (010):(111)$	—	—	—	70 34	—
$os = (111):(101)$	—	—	—	19 26	—
$bo' = (010):(\bar{1}11)$	2	65 21– 65 27	65 24	65 21	3
$o's' = (\bar{1}11):(\bar{1}01)$	—	—	—	24 39	—
$o'o' = (\bar{1}11):(\bar{1}\bar{1}1)$	1	—	49 14	49 18	4
$sq = (101):(011)$	—	—	—	37 47	—
$qp = (011):(\bar{1}10)$	40	87 21– 87 43	87 30	87 27	3
$ps = (\bar{1}10):(\bar{1}0\bar{1})$	—	—	—	54 46	—
$pq = (\bar{1}10):(0\bar{1}\bar{1})$	40	92 19– 92 37	92 30	92 33	3
$s'q = (\bar{1}01):(011)$	—	—	—	45 22	—
$qn = (011):(121)$	—	—	—	26 33	—
$np = (121):(110)$	—	—	—	36 35	—
$qp = (011):(110)$	40	62 49– 63 13	63 6	63 8	2
$ps' = (110):(10\bar{1})$	—	—	—	71 30	—
$pq = (110):(0\bar{1}\bar{1})$	40	116 44–117 4	116 54	116 52	2
$r'o' = (\bar{2}01):(\bar{1}11)$	6	34 51– 35 14	34 58	34 59	1
$o'p = (\bar{1}11):(110)$	6	92 40– 92 51	92 45	92 46	1
$pr' = (110):(20\bar{1})$	40	52 1– 52 28	52 16	52 15	1
$r'p = (\bar{2}01):(110)$	39	127 32–127 56	127 44	127 45	1
Total number of measurements . .	495				

Molecular Volume.—$\frac{M}{d} = \frac{710{\cdot}82}{3{\cdot}048} = 233{\cdot}21.$

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

$$\chi : \psi : \omega = 6{\cdot}3847 : 8{\cdot}7366 : 4{\cdot}3499.$$

Optics.

Nature and Orientation of Optical Ellipsoid.—The symmetry plane b {010} is the plane of the optic axes. The double refraction is positive, so that the first median line corresponds to γ and the second median line to α. Extinction determinations with two section-plates ground parallel to the symmetry plane afforded the following positions for one of the extinction directions which lies nearly normal to the basal plane c {001} :—

Extinction Direction in the Symmetry Plane.

Plate 1 . . . . 4° 47′, Plate 2 . . . . 5° 16′,
Mean . . 5° 2′ with normal to c {001}.

The direction is in front of the normal, further away than the latter from the vertical axis c; it is the second median line and corresponds to the refractive index α. As the angle between the normal to c {001} and the vertical axis is 16° 2′ (ac = 73° 58′), the angle between the vertical axis c and the second median line is 21° 4′ in front of the axis. The first median line lies 5° 2′ below the inclined axis a, and thus lies in the acute crystallographic axial angle ac, while the second median line lies in the obtuse angle β between the crystal axes a and c lying in the symmetry plane. The conditions are graphically shown in fig. 7.

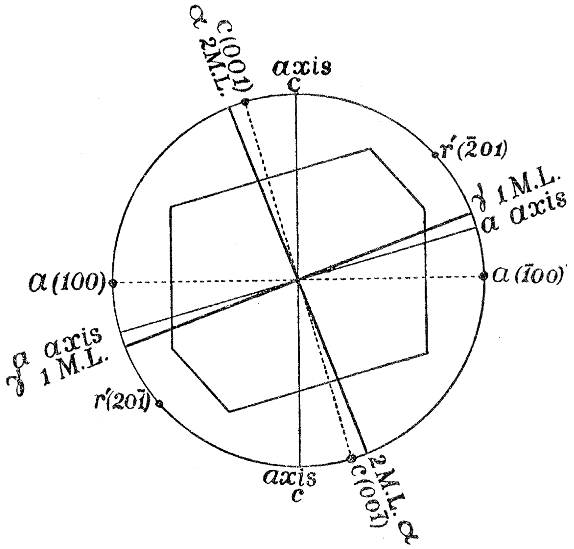

Fig. 7.

Optic Axial Angle.—Three pairs of section-plates were ground, 1, 2, and 3 perpendicular to the first median line and 1*a*, 2*a*, and 3*a* perpendicular to the second median line. The optic axial angle in air 2E is so large that it could not be measured, it being impossible to get the hyperbolic brush-vertices quite to the cross-wires before disappearance. In monobromonaphthalene excellent measurements of $2H_a$ with sections 1, 2, and 3, and of $2H_o$ with sections 1*a*, 2*a*, and 3*a* were obtained, the central rings being small and the brush-vertices very sharp. The values obtained, and those of the true optic axial angle $2V_a$ calculated therefrom, together with the mean $2V_a$, are given in the next table.

DETERMINATION of True Optic Axial Angle, in Bromonaphthalene, of CsFe Selenate.

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	75 38	1*a*	87 18	83 14	82 58
	2	75 25	2*a*	87 48	82 50	
	3	75 21	3*a*	87 44	82 50	
C	1	75 33	1*a*	87 15	83 12	82 56
	2	75 20	2*a*	87 46	82 48	
	3	75 17	3*a*	87 42	82 48	
Na	1	75 2	1*a*	87 8	82 56	82 47
	2	75 0	2*a*	87 32	82 42	
	3	74 59	3*a*	87 25	82 44	
Tl	1	74 27	1*a*	86 51	82 42	82 33
	2	74 25	2*a*	87 16	82 28	
	3	74 25	3*a*	87 12	82 30	
Cd	1	74 8	1*a*	86 43	82 34	82 25
	2	74 8	2*a*	87 8	82 20	
	3	74 6	3*a*	87 4	82 22	
F	1	73 53	1*a*	86 34	82 28	82 20
	2	73 50	2*a*	87 0	82 13	
	3	73 56	3*a*	86 52	82 20	

Dispersion of the Median Lines.—The mean refractive index of the crystals for sodium light will be shown to be 1·5357. Methylsalicylate has almost exactly the same refractive index for sodium light, 1·5363, so that this substance was employed as the immersion liquid for the determination of the dispersion of the median lines, with the two best sections 1 and 3 perpendicular to the first median line. The first median line proves to lie very slightly nearer to the inclined axis *a* for greenish blue F-light than for red Li-light, the amount indicated by section 1 being 11′, and that indicated by the measurements with section 3 being 13′, the results thus in the mean affording the amount 12′. The mean values of the true optic axial angle $2V_a$, afforded by these observations in a liquid of so very nearly the same refraction as the crystals, were 82° 41′ for Li-light and 81° 33′ for F-light, direct observations which amply confirm both the actual values given in the table for the true angle, by calculation from $2H_a$ and $2H_o$, and the order of the dispersion.

Refractive Indices.—The refractive indices were determined with six prisms of about 60° angle, ground so that the faces were symmetrical to the principal planes and the refracting edges parallel to the axes of the optical ellipsoid, so that each prism yielded two of the three refractive indices α, β, γ directly. The results for the same index from the different prisms were all remarkably concordant, and the mean values are given in the next table.

REFRACTIVE Indices of Cæsium Ferrous Selenate.

Light.	α.	β.	γ.
Li	1·5269	1·5317	1·5379
C	1·5274	1·5322	1·5384
Na	1·5306	1·5352	1·5414
Tl	1·5339	1·5385	1·5450
Cd	1·5359	1·5405	1·5470
F	1·5379	1·5425	1·5491
G	1·5442	1·5488	1·5555

Mean of α, β, and γ for Na light = 1·5357.

α = Vibration direction parallel to second median line, 21° 4′ in front of axis c.
β = ,, ,, ,, ,, symmetry axis b.
γ = ,, ,, ,, ,, first median line, 5° 2′ below axis a.

Double refraction, $Na_{\gamma-\alpha}$ = 0·0108.

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

$$\beta = 1{\cdot}5200 + \frac{546\,452}{\lambda^2} - \frac{170\,930\,000\,000}{\lambda^4} + \ldots .$$

The α indices are also reproduced by the formula if the constant 1·5200 be diminished by 0·0047, and the γ indices if the constant be increased by 0·0063.

Observations of refractive index at 65° with one of the prisms indicated the usual slight diminution of refraction with rise of temperature, the amount indicated for 50° C. of rise of temperature (from 15° to 65°) being about 0·0012.

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

$$\alpha : \beta : \gamma = 0{\cdot}9970 : 1 : 1{\cdot}0040.$$

$$\mathfrak{a} : \mathfrak{b} : \mathfrak{c} = 1{\cdot}0030 : 1 : 0{\cdot}9960.$$

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

	Axis of optical indicatrix . . .		α.	β.	γ.
LORENZ	Specific refraction, $\frac{n^2-1}{(n^2+2)\,d} = \mathfrak{n}$ . .	C	0·1009	0·1017	0·1027
		G	0·1036	0·1043	0·1054
”	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = \mathfrak{m}$.	C	71·74	72·29	72·99
		G	73·64	74·16	74·91
”	Specific dispersion, $\mathfrak{n}_G - \mathfrak{n}_C$		0·0027	0·0026	0·0027
”	Molecular dispersion, $\mathfrak{m}_G - \mathfrak{m}_C$		1·90	1·87	1·92
GLADSTONE	Molecular refraction, $\frac{n-1}{d} M$	C	122·99	124·11	125·56

Mean molecular refraction (GLADSTONE), $\frac{1}{3}(\alpha+\beta+\gamma) = 124·22$.

Ammonium Ferrous Selenate $(NH_4)_2\,Fe\,(SeO_4)_2 . 6H_2O$.

Morphology.

An investigation of ammonium ferrous selenate, as regards goniometry and specific gravity only, was carried out by HALDOR TOPSØE* in the year 1870, and as regards the optics of the crystals by TOPSØE and CHRISTIANSEN† in 1874.

The crystals employed in the present investigation were prepared by the method described in the introduction, the ferrous selenate being prepared by the action of selenic acid on ferrous sulphide. They were clear and transparent, and of a very pale yellowish green colour. Ten excellent little crystals were measured, belonging to eight different crops.

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

Ratios of Axes.—$a : b : c = 0·7433 : 1 : 0·5019$. Values of TOPSØE, 0·7405 : 1 : 0·5012.

Axial Angle.—$\beta = 106° 9'$. Value of TOPSØE, 106° 13′.

Forms Observed.—$b\,\{010\}$, $c\,\{001\}$, $p\,\{110\}$, $q\,\{011\}$, $r'\{\bar{2}01\}$, and $o'\{\bar{1}11\}$. The same forms, and these only, were observed by TOPSØE.

Habit.—From somewhat (thick) tabular parallel to $c\,\{001\}$, to short prismatic parallel to $p\,\{110\}$ and the vertical axis c, and with $r'\{\bar{2}01\}$ more prominent than usual in the series.

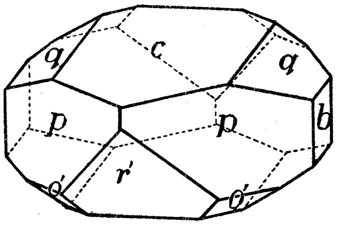

Fig. 8.

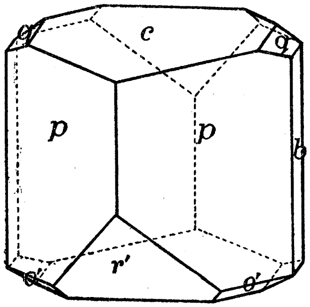

Fig. 9.

A typical crystal of the first type is represented in fig. 8, and one of the second type in fig. 9.

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[*] ‘Kryst.-kem. Unders. o. d. selens. Salte, Dissertation,’ Copenhagen, 1870.

[†] ‘Ann. Chim. Phys.’ (1874), series 5, vol. 1, p. 83.

INTERFACIAL Angles of Ammonium Ferrous Selenate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.	Values of TOPSØE.
		° ′ ° ′	° ′	° ′	′	° ′
$ac = (100):(001)$	—	—	—	73 51	—	—
$as = (100):(101)$	—	—	—	45 13	—	—
$sc = (101):(001)$	—	—	—	28 38	—	—
$cr' = (001):(\bar{2}01)$	19	64 16– 64 26	64 22	64 17	5	64 24
$cs' = (001):(\bar{1}01)$	—	—	—	38 36	—	—
$s'r' = (\bar{1}01):(\bar{2}01)$	—	—	—	25 41	—	—
$r'a = (\bar{2}01):(\bar{1}00)$	—	—	—	41 52	—	—
$r'c = (\bar{2}01):(00\bar{1})$	19	115 33–115 50	115 38	115 43	5	—
$ap = (100):(110)$	—	—	—	35 30	—	—
$pp' = (110):(120)$	—	—	—	19 28	—	—
$p'b = (120):(010)$	—	—	—	35 2	—	—
$pp''' = (110):(130)$	—	—	—	29 27	—	—
$p'''b = (130):(010)$	—	—	—	25 3	—	—
$pb = (110):(010)$	12	54 27– 54 44	54 33	54 30	3	54 28
$pp = (110):(1\bar{1}0)$	20	70 46– 71 13	71 0	*	—	70 50
$pp = (110):(\bar{1}10)$	20	108 41–109 17	109 0	109 0	0	—
$cq = (001):(011)$	35	25 37– 25 56	25 44	*	—	25 42
$qb = (011):(010)$	11	64 11– 64 24	64 17	64 16	1	64 19
$qq = (011):(01\bar{1})$	17	128 19–128 36	128 31	128 32	1	—
$ao = (100):(111)$	—	—	—	48 25	—	—
$oq = (111):(011)$	—	—	—	27 5	—	—
$aq = (100):(011)$	—	—	—	75 30	—	—
$qo' = (011):(\bar{1}11)$	—	—	—	34 48	—	34 34
$o'a = (\bar{1}11):(\bar{1}00)$	—	—	—	69 42	—	—
$co = (001):(111)$	—	—	—	34 14	—	—
$op = (111):(110)$	—	—	—	42 41	—	—
$cp = (001):(110)$	40	76 47– 77 2	76 55	*	—	76 54
$po' = (110):(11\bar{1})$	6	58 0– 58 20	58 10	58 13	3	57 59
$o'c = (11\bar{1}):(00\bar{1})$	7	44 41– 45 6	44 55	44 52	3	—
$pc = (110):(00\bar{1})$	40	102 55–103 15	103 5	103 5	0	103 9
$bn = (010):(121)$	—	—	—	54 33	—	—
$no = (121):(111)$	—	—	—	15 51	—	—
$bo = (010):(111)$	—	—	—	70 24	—	—
$os = (111):(101)$	—	—	—	19 36	—	—
$bo' = (010):(\bar{1}11)$	4	65 2– 65 20	65 11	65 7	4	—
$o's' = (\bar{1}11):(\bar{1}01)$	—	—	—	24 53	—	—
$o'o' = (\bar{1}11):(\bar{1}\bar{1}1)$	1	—	49 47	49 46	1	49 42
$sq = (101):(011)$	—	—	—	37 45	—	—
$qp = (011):(\bar{1}10)$	31	87 10– 87 22	87 16	87 15	1	87 27
$ps = (\bar{1}10):(\bar{1}0\bar{1})$	—	—	—	55 0	—	—
$pq = (\bar{1}10):(0\bar{1}\bar{1})$	31	92 39– 92 52	92 44	92 45	1	—
$s'q = (\bar{1}01):(011)$	—	—	—	45 15	—	—
$qn = (011):(121)$	—	—	—	26 23	—	—
$np = (121):(110)$	—	—	—	36 29	—	—
$qp = (011):(110)$	33	62 45– 63 1	62 53	62 52	1	62 51
$ps' = (110):(10\bar{1})$	—	—	—	71 53	—	—
$pq = (110):(0\bar{1}\bar{1})$	33	116 59–117 22	117 8	117 8	0	—
$r'o' = (\bar{2}01):(\bar{1}11)$	7	35 5– 35 13	35 9	35 9	0	34 56
$o'p = (\bar{1}11):(110)$	5	91 52– 92 21	92 12	92 10	2	—
$pr' = (110):(20\bar{1})$	34	52 28– 52 46	52 36	52 41	5	52 35
$r'p = (\bar{2}01):(110)$	34	127 15–127 33	127 24	127 19	5	—
Total number of measurements . .	459					

Although the crystals were largely of the two principal types just mentioned, and shown in the figures, practically all the types of crystals met with in this large series of double sulphates and double selenates were observed. That is, crystals were found of the three main types (and also of all intermediate varieties) which have been shown in previous communications to be characteristic respectively of the potassium, rubidium, and cæsium salts of the series; namely, for the potassium salts prismatic parallel $p\,\{110\}$ with large broad $c\,\{001\}$, and very small $q\,\{011\}$, for the cæsium salts prismatic parallel $q\,\{011\}$ with narrow $c\,\{001\}$, and for the rubidium salts the midway type with only moderately prominent $c\,\{001\}$ faces and with $q\,\{011\}$ faces relatively smaller than the immense ones of the cæsium salts yet larger than the very small ones of the potassium salts. One prominent characteristic was noticeable, however, on these crystals of ammonium ferrous selenate, namely, the very pronounced development of the orthopinakoid $r'\{\bar{2}01\}$. This form is characteristically well and often obtrusively developed in all the iron salts of this grand series, both those of the double sulphates and those of the double selenates, and is remarkably so in the common well-known salt ferrous ammonium sulphate, which ferrous ammonium selenate closely resembles.

The reflections from the crystals measured were of general excellence, and relatively but little trouble was experienced from striation of the c and p-faces. Certain crops rarely showed any traces of the faces of $b\,\{010\}$ and $o'\{\bar{1}11\}$, while on the crystals of other crops these faces were quite well developed.

Cleavage.—A good cleavage was observed parallel to $r'\{\bar{2}01\}$, the cleavage direction common to the whole series. No trace could be discovered of cleavage parallel to $b\,\{010\}$, which has been observed to be developed in some of the ammonium salts of the series.

Volume.

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

I.	Density for	17°·9/4° . . .	2·1915	For 20°/4° . . .	2·1910
II.	,,	19°·0/4° . . .	2·1904	,, 20°/4° . . .	2·1902
III.	,,	19°·1/4° . . .	2·1914	,, 20°/4° . . .	2·1912
IV.	,,	18°·8/4° . . .	2·1914	,, 20°/4° . . .	2·1911
				Mean . . .	2·1909

Accepted value for 20°/4°, **2·191**.

The value 2·160 was obtained by Topsøe.

Molecular Volume.—$\frac{M}{d}=\frac{482 \cdot 88}{2 \cdot 191}=220 \cdot 39$.

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

$$\chi : \psi : \omega = 6 \cdot 3212 : 8 \cdot 5043 : 4 \cdot 2684.$$

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, the first median line corresponding to the refractive index γ, and the second median line to α.

Extinction determinations with two section-plates ground parallel to the symmetry plane afforded the following results with respect to the normal to $c\{001\}$.

Extinction Direction in the Symmetry Plane.

Plate 1 . . . 11° 2′, Plate 2 . . . 10° 28′.
Mean . . 10° 45′, behind the normal to $c\{001\}$.

This direction, between the normal to $c\{001\}$ and the vertical axis c, is the second median line. As the angle between the normal to $c\{001\}$ and the vertical axis is 16° 9′ (the acute axial angle ac being 73° 51′), the inclination of the second median line to and in front of the vertical axis c is 5° 24′. The rectangular direction (the other axis of the optical ellipsoid also lying in the symmetry plane) is the first median line, and is inclined 10° 45′ to and above the inclined axis a. Both median lines thus lie in the obtuse axial angle ac, and the positions will be rendered clear by a reference to fig. 10.

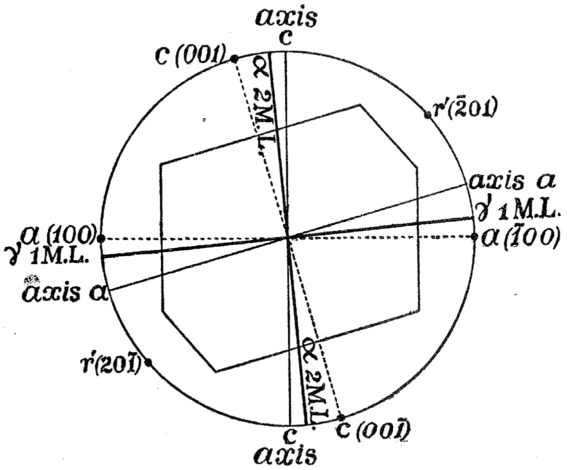

Fig. 10.

Topsøe and Christiansen (*loc. cit.*) give 6° 50′ and 9° 23′ for the two extinction positions, axis c : second median line, and axis a : first median line, respectively.

Optic Axial Angle.—Three pairs of section plates, ground perpendicular to the first and second median lines respectively, afforded the values given in the two following tables for the apparent optic axial angle in air 2E, and the apparent acute and obtuse optic axial angles in monobromonaphthalene $2H_a$ and $2H_o$. The values of the true optic axial angle $2V_a$ from these two latter determinations are given in the penultimate column of the second table, and the mean $2V_a$ in the last column.

APPARENT Optic Axial Angle in Air, 2E, of AmFe Selenate.

Light.	Plate 1.	Plate 2.	Plate 3.	Mean 2E.
	° ′	° ′	° ′	° ′
Li	145 35	145 50	145 37	145 41
C	145 53	146 18	145 51	146 1
Na	148 56	149 4	147 46	148 35
Tl	149 21	149 40	149 10	149 24
Cd	151 8	150 7	150 18	150 31
F	152 10	151 0	151 20	151 30

DETERMINATION of True Optic Axial Angle, in Bromonaphthalene, of AmFe Selenate.

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	70 28	1*a*	91 45	77 34	77 36
	2	70 32	2*a*	91 47	77 36	
	3	70 32	3*a*	91 42	77 38	
C	1	70 27	1*a*	91 43	77 35	77 37
	2	70 31	2*a*	91 44	77 37	
	3	70 30	3*a*	91 39	77 39	
Na	1	70 14	1*a*	91 10	77 42	77 44
	2	70 24	2*a*	91 15	77 46	
	3	70 17	3*a*	91 7	77 45	
Tl	1	70 2	1*a*	90 37	77 49	77 50
	2	70 8	2*a*	90 42	77 50	
	3	70 5	3*a*	90 36	77 52	
Cd	1	69 53	1*a*	90 21	77 50	77 52
	2	69 59	2*a*	90 26	77 52	
	3	69 55	3*a*	90 18	77 54	
F	1	69 48	1*a*	90 13	77 52	77 54
	2	69 51	2*a*	90 12	77 54	
	3	69 45	3*a*	90 0	77 56	

The values obtained by TOPSØE and CHRISTIANSEN were for 2E 142° 50′ and for $2V_a$ 76° 48′.

Dispersion of the Median Lines.—This is very small, and was determined with section-plate No. 3 immersed in monochlorbenzene, the refractive index of which

(1·5248 for Na-light) is very close to the mean refractive index of the crystals. The median lines are so dispersed in the symmetry plane that the first median line lies nearer to the inclined crystal-axis a by 9′ for red Li-light than for green Cd-light.

Effect of Temperature on the Optic Axial Angle.—Determinations with section-plate No. 2 at 75° C. showed that the apparent optic axial angle in air 2E diminished by 11° 24′ on heating the plate to 75°, the angle being 137° 40′ for Na-light at this temperature, whereas for 15° it was 149° 4′.

Refractive Indices.—Six 60°-prisms were ground, the two faces of each being symmetrical to (30° from) a principal axial plane of the optical ellipsoid, and the refracting edge of each being parallel to a principal axis of the ellipsoid. Each prism thus yielded directly two of the three refractive indices α, β, γ, and the combination of prisms was so arranged that α, β, and γ were each obtained four times in all. The four individual results for each index, for each of the seven wave-lengths employed, were remarkably close, and the final mean values of the four are given in the next table.

REFRACTIVE Indices of Ammonium Ferrous Selenate.

Light.	α.	β.	γ.
Li	1·5177	1·5241	1·5343
C	1·5182	1·5246	1·5348
Na	1·5216	1·5280	1·5381
Tl	1·5251	1·5314	1·5416
Cd	1·5271	1·5334	1·5437
F.	1·5291	1·5354	1·5457
G.	1·5356	1·5422	1·5524

Mean of α, β, and γ for Na light = 1·5292.

α = Vibration direction parallel to second median line, 5° 24′ in front of vertical axis c.
β = ,, ,, ,, ,, symmetry axis b.
γ = ,, ,, ,, ,, first median line, 10° 45′ above inclined axis a.

Double refraction, $\mathrm{Na}_{\gamma-\alpha}$ = 0·0165.

Only the β-indices were determined directly by TOPSØE and CHRISTIANSEN, for C, Na, and F-light, the values obtained being respectively 1·5226, 1·5260, and 1·5334.

General formula for β, for light of any wave-length λ, corrected to a vacuum (correction + 0·004):—

$$\beta = 1{\cdot}5076 + \frac{862\,174}{\lambda^2} - \frac{4\,865\,900\,000\,000}{\lambda^4} + \ldots .$$

The α indices are equally well reproduced by the formula if the constant 1·5076 be diminished by 0·0064, and the γ indices if it be increased by 0·0102.

Observations at 65° C. indicated that the index α diminishes by 0·0013 on heating to this temperature, β by 0·0016, and γ by 0·0018.

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

Indicatrix . . . . $\alpha : \beta : \gamma = 0{\cdot}9958 : 1 : 1{\cdot}0066.$
Optical Velocity Ellipsoid . . $\mathfrak{a} : \mathfrak{b} : \mathfrak{c} = 1{\cdot}0042 : 1 : 0{\cdot}9934.$

Molecular Optical Constants.—These are given in the next table, calculated by both the formulas of LORENZ and of GLADSTONE and DALE.

	Axis of optical indicatrix . . .		α.	β.	γ.
LORENZ	Specific refraction, $\frac{n^2-1}{(n^2+2)d} = \mathfrak{n}$ . .	C	0·1384	0·1398	0·1420
		G	0·1422	0·1437	0·1459
,,	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = \mathfrak{m}$.	C	66·81	67·50	68·59
		G	68·68	69·38	70·46
,,	Specific dispersion, $\mathfrak{n}_G - \mathfrak{n}_C$		0·0038	0·0039	0·0039
,,	Molecular dispersion, $\mathfrak{m}_G - \mathfrak{m}_C$		1·87	1·88	1·87
GLADSTONE	Molecular refraction, $\frac{n-1}{d}M$	C	114·21	115·62	117·87

Mean molecular refraction (GLADSTONE), $\frac{1}{3}(\alpha+\beta+\gamma) = 115{\cdot}90.$

Comparison of Results.

The successful completion of the investigation of the potassium salt of this ferrous iron group enables a full comparison to be made of the crystals of all the four salts of this group, on exactly the same lines as the four salts of each of the three groups (zinc, magnesium, and nickel) of double selenates already described have been compared. The fact that crystals of potassium ferrous selenate only form at temperatures very near to 0° C., and spontaneously decompose into an opaque porcelain-like substance, in less than half a day in moderately cold weather and almost immediately at the temperature of a warm day, together with the fact that the crystals of cæsium ferrous selenate are magnificently transparent and relatively permanent, capable of preservation in closed vessels for years, afford striking proof of the *progression in stability* with the rise of atomic weight and atomic number of the alkali metal.

Habit.—The progression in habit which has been observed in the other groups of both double selenates and double sulphates is very clearly exhibited by the ferrous iron group of double selenates. An inspection of figs. 1 and 2 (potassium salt), 4 (rubidium salt), and 6 (cæsium salt) will make clear the progressive diminution in the relative development of the faces of c {001}, and the relative growth of the faces of q {011} from very small and subordinate in the potassium salt to predominatingly large in the cæsium salt, through the intermediate stage of a moderate size in the rubidium salt. The importance of the faces of p {110} similarly diminishes more or less regularly from the potassium to the cæsium salt, through the rubidium salt. The ammonium salt, shown in figs. 8 and 9, forms crystals of all types of development, but a great majority are of the intermediate type exhibited in fig. 8. Fig. 9 illustrates a crystal showing faces of $c\,\{001\}$ and $q\,\{011\}$ very like those of a potassium salt of the series. In all four salts of the iron group there is a marked tendency for a larger development of the faces of $r'\{\bar{2}01\}$ than in the other groups of double selenates studied. A similar fact was observed with respect to the ferrous iron group of double sulphates.

Crystal Elements and Angles.—The axial angles and axial ratios are compared in the following table.

Comparison of the Axial Angles and Axial Ratios.

	Axial angle.	Axial ratios.
	β.	$a : b : c$
Potassium ferrous selenate . .	103° 50′	0·7490 : 1 : 0·5044
Rubidium " " . .	104° 57′	0·7424 : 1 : 0·5000
Ammonium " " . .	106° 9′	0·7433 : 1 : 0·5019
Cæsium " " . .	106° 2′	0·7308 : 1 : 0·4979

The differences between the morphological axial angles of the three alkali metallic salts are 1° 7′ between the potassium and rubidium salts, 1° 5′ between the rubidium and cæsium salts, and 2° 12′ between the potassium and cæsium salts. Obviously, therefore, the axial angle β increases in direct proportion to the increase of the atomic weight and atomic number of the alkali metal. As the values of the two latter constants will be constantly required in the course of these comparisons, they are given below for reference.

	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

As rubidium stands precisely half-way between potassium and cæsium as regards atomic weight and atomic number, so does the crystallographic (monoclinic) axial angle β stand half-way in the case of the rubidium salt.

The axial angle of ammonium ferrous selenate is very nearly identical with (7′ larger than) that of the cæsium salt.

The morphological axial ratios of the rubidium salt are intermediate between those for the potassium and cæsium salts. Those of the ammonium salt are close to those of the rubidium salt, and thus partake of an intermediate character in the group. This fact is in complete harmony with the supposition of true isomorphism of the ammonium salt with the three alkali metallic salts of the group.

The following table institutes a complete comparison of the crystal angles of the four salts. A careful analysis of these results has been made, by tabulating all the differences between analogous angles of the four salts, and the results of the analysis are concentrated in the short table which follows that of the angles.

Comparison of the Interfacial Angles.

Angle.	KFe selenate.	RbFe selenate.	CsFe selenate.	AmFe selenate.
	° ′	° ′	° ′	° ′
ac = (100) : (001)	76 10	75 3	73 58	73 51
as = (100) : (101)	46 46	46 2	45 9	45 13
sc = (101) : (001)	29 24	29 1	28 49	28 38
cr′ = (001) : $(\bar{2}01)$	62 38	63 24	64 29	64 17
cs′ = (001) : $(\bar{1}01)$	37 58	38 15	38 51	38 36
s′r′ = $(\bar{1}01)$: $(\bar{2}01)$	24 40	25 9	25 38	25 41
r′a = $(\bar{2}01)$: $(\bar{1}00)$	41 12	41 33	41 33	41 52
ap = (100) : (110)	36 1	35 39	35 7	35 30
pp′ = (110) : (120)	19 28	19 28	19 28	19 28
p′b = (120) : (010)	34 31	34 53	35 25	35 2
pb = (110) : (010)	53 59	54 21	54 53	54 30
pp‴ = (110) : (130)	29 21	29 25	29 31	29 27
p‴b = (130) : (010)	24 38	24 56	25 22	25 3
cq = (001) : (011)	26 6	25 47	25 34	25 44
qb = (011) : (010)	63 54	64 13	64 26	64 16
ao = (100) : (111)	49 59	49 13	48 19	48 25
oq = (111) : (011)	27 37	27 21	27 16	27 5
aq = (100) : (011)	77 36	76 34	75 35	75 30
qo′ = (011) : $(\bar{1}11)$	34 12	34 28	35 3	34 48
o′a = $(\bar{1}11)$: $(\bar{1}00)$	68 12	68 58	69 22	69 42
co = (001) : (111)	35 9	34 38	34 18	34 14
op = (111) : (110)	43 42	43 16	42 39	42 41
cp = (001) : (110)	78 51	77 54	76 57	76 55
po′ = (110) : $(11\bar{1})$	56 54	57 39	58 7	58 13
o′c = $(11\bar{1})$: $(00\bar{1})$	44 15	44 27	44 56	44 52
bo = (010) : (111)	69 49	70 12	70 34	70 24
os = (111) : (101)	20 11	19 48	19 26	19 36
bo′ = (010) : $(\bar{1}11)$	65 17	65 20	65 21	65 7
o′s′ = $(\bar{1}11)$: $(\bar{1}01)$	24 43	24 40	24 39	24 53
sq = (101) : (011)	38 31	38 3	37 47	37 45
qp = (011) : $(\bar{1}10)$	85 8	86 17	87 27	87 15
ps = $(\bar{1}10)$: $(\bar{1}0\bar{1})$	56 21	55 40	54 46	55 0
s′q = $(\bar{1}01)$: (011)	44 55	45 0	45 22	45 15
qp = (011) : (110)	64 23	63 45	63 8	62 52
ps′ = (110) : $(10\bar{1})$	70 42	71 15	71 30	71 53
r′o′ = $(\bar{2}01)$: $(\bar{1}11)$	34 22	34 39	34 59	35 9
o′p = $(\bar{1}11)$: (110)	93 7	92 48	92 46	92 10
pr′ = (110) : $(20\bar{1})$	52 31	52 33	52 15	52 41

ANGULAR Changes for Double Selenates containing Ferrous Iron.

Replacement.	Average change.	Maximum change.
	′	′ ° ′
K by Rb	27	69 = 1 9
K by Cs	55	139 = 2 19
K by NH_4	54	139 = 2 19

In 37 of the 38 angles compared the value for the rubidium salt is intermediate between the values for the potassium and cæsium salts. In the case of the single exception the change is very small.

The average and maximum changes of angle are exactly twice as large when potassium is replaced by cæsium as when potassium is replaced by rubidium, corresponding precisely to the change in atomic weight ($K \sim Cs = 93$ and $K \sim Rb = 46$), or atomic number ($K \sim Cs = 36$ and $K \sim Rb = 18$). Thus the average change of angle, and also the maximum amount of angular alteration observed, are directly proportional to the change in the atomic weight or number.

As regards the position of the ammonium salt, in 35 of the 38 compared angles the changes for the K by NH_4 replacement are in the same direction as for the metallic replacements K by Rb and K by Cs, and the other three are cases where the changes are very minute.

In 34 of these 35 cases the changes for the K by NH_4 replacement are greater than when potassium is replaced by rubidium, and in 15 of them the changes are somewhat greater than those which occur when potassium is replaced by cæsium. When all the K by NH_4 changes are added together (as regards amounts, irrespective of sign), and the mean taken, in the same manner as was done for the metallic replacements, this average change for the ammonium replacement of potassium is found to be practically identical with the average change which occurs when potassium is replaced by cæsium; the maximum amount of change observed (for K by NH_4) is also identical with that which occurs for the K by Cs replacement. Thus the angular effect of replacing potassium by ammonium is of the same order as that of the weightier metallic interchange, a fact in full keeping with the supposition of the isomorphism.

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

Volume Constants of the Iron Group of Double Selenates.

Salt.	Molecular weight.	Specific gravity.	Molecular volume.	Topic axial ratios.
				$\chi : \psi : \omega$
KFe selenate . .	524·72	2·494	210·39	6·2230 : 8·3085 : 4·1908
RbFe ,, . .	616·82	2·800	220·29	6·3109 : 8·5006 : 4·2503
CsFe ,, . .	710·82	3·048	233·21	6·3847 : 8·7366 : 4·3499
NH_4Fe ,, . .	482·88	2·191	220·39	6·3212 : 8·5043 : 4·2684

The *density* increases with the atomic weight of the alkali metal, and is greater by 6 to 5 for the K by Rb replacement than for the Rb by Cs interchange. The ammonium salt is the lightest member of the group, corresponding to the low molecular weight of the radicle NH_4.

The *molecular volumes* of the three alkali metallic salts progress at an accelerating rate with the rise in atomic weight or atomic number of the alkali metal. When potassium is replaced by rubidium the increase is to the extent of 9·9 units, but when rubidium is replaced by cæsium the increase amounts to 12·92 units. The interchange of cæsium for potassium is accompanied by an increase of 22·82 units. The molecular volume of ammonium ferrous selenate is almost exactly identical with that of rubidium ferrous selenate, being 0·1 unit higher, the replacement of potassium by ammonium being accompanied by an increase of exactly 10 units.

The *topic axial ratios* follow similar rules, being the directional expression of the volume along the directions of the crystallographic axes, and proportionately to the lengths of those axes. The values of corresponding ratios are always intermediate in the case of the rubidium salt, between the values for the potassium and cæsium salts; a regular extension of the edges of the unit cell of the structural space-lattice thus occurs as potassium is replaced by rubidium and the latter in turn by cæsium. The lengths of the cell edges for the ammonium salt are almost the same as, very slightly greater than, those for rubidium ferrous selenate.

This striking fact of the congruency of the ammonium and rubidium salts—which is in keeping with all the author's previous results for the other groups of double selenates yet investigated, for the whole of the groups of double sulphates of this monoclinic series, and for the two rhombic groups of simple alkali sulphates and selenates—affords yet another confirmation of those former results, and further substantiates the important conclusions which were drawn therefrom in a memoir* read to the Royal Society in November, 1916.

Cleavage.—All four salts exhibit the development of cleavage parallel to $r'\{\bar{2}01\}$, the cleavage common to the whole series. Some of the ammonium salts of the series

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

have in addition shown cleavage parallel to the symmetry plane, *b* {010}, but this has not been observed in the case of ammonium ferrous selenate.

Orientation of the Optical Ellipsoid.—The optical ellipsoid (either the indicatrix or the optical velocity ellipsoid) rotates on the symmetry axis *b* of the crystal—which is identical with the intermediate axis of the ellipsoid (β of the indicatrix or $\mathfrak{b}$ of the velocity ellipsoid) and is the only one of the three axes which is fixed, in accordance with monoclinic symmetry—when one of the alkali bases is replaced by another. The best mode of comparing its position is to state the inclination of the α axis of the indicatrix or $\mathfrak{a}$ axis of the velocity ellipsoid to the vertical crystal-axis *c*, as is done in the next table.

Inclinations of α-Extinctions of the Fe *Double Selenates in front of Axis c.*
(2M.L. *in all four salts.*)

AmFe selenate	5° 24′	RbFe selenate	13° 37′,
KFe ,,	10° 27′	CsFe ,,	21° 4′.

The table is also expressed graphically in fig. 11, which further shows the positions of the other perpendicular axis γ also lying in the symmetry plane, which is that of

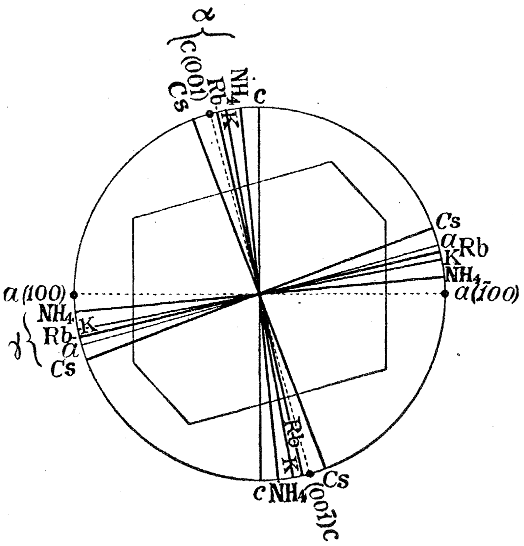

Fig. 11.

the paper. The α axis is the second median line (obtuse bisectrix of optic axial angle) in all four salts, the γ axis being the direction of the first median line (acute bisectrix of optic axial angle).

The position of the ellipsoid is seen to be such that its axis lies close in front of (only 5° 24′ from) the vertical axis *c*, in the case of the ammonium salt; it rotates so that its α axis is 10° 27′ from axis *c* for the potassium salt; further, till the axis is 13° 37′ inclined for the rubidium salt, and still further to 21° 4′ for the cæsium salt.

The position of the ellipsoid for the rubidium salt is thus intermediate between its positions for the potassium and cæsium salts, and the amount of rotation is an accelerating one as the atomic weight and number of the alkali metal rises.

Optic Axial Angles.—These can be directly compared, as the double refraction is positive and the first median line is analogously disposed, subject to the rotation just described, in all four salts. The values are set out in the next table.

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

	KFe selenate.	RbFe selenate.	AmFe selenate.	CsFe selenate.
Li	64° 11′	73° 35′	77° 36′	82° 58′
C	64 12	73 34	77 37	82 56
Na	64 18	73 32	77 44	82 47
Tl	64 25	73 30	77 50	82 33
Cd	64 30	73 28	77 52	82 25
F	64 36	73 26	77 54	82 20

It will be apparent that the optic axial angle increases as the atomic weight and number of the alkali metal rises, and the value for the rubidium salt is about midway between the values for the potassium and cæsium salts. The optic axial angle of ammonium ferrous selenate is slightly larger than that of rubidium ferrous selenate.

Refractive Indices.—The refractive indices are compared in the table on next page, together with the mean refractive index for sodium light and the magnitude of the double refraction.

It will be observed that the mean refractive index for the rubidium salt is intermediate between the values for the potassium and cæsium salts, although the advance of this specific refractive constant in the case of the rubidium salt is not much beyond that of the potassium salt. The double refraction (difference between α and γ indices) progressively diminishes (with acceleration) as the atomic weight and number of the alkali metal rises, and the result of this is curious on the γ indices, these indices for the rubidium salt being brought lower than those for the potassium salt. Although the increasingly progressive diminution of the double refraction tends also to reduce the γ indices of the cæsium salt, the rapidly accelerating progressive growth of refracting power causes even these indices of the cæsium salt, like the α and β indices, to show a clear advance in the refractive indices of this salt. The real progression in the refractive power is shown, however, by the molecular refraction, which will presently be dealt with.

The refractive indices of ammonium ferrous selenate are intermediate between those of rubidium and cæsium ferrous selenates.

COMPARISON of the Refractive Indices.

Index.	Light.	KFe selenate.	RbFe selenate.	NH_4Fe selenate.	CsFe selenate.
α	Li	1·5059	1·5099	1·5177	1·5269
	C	1·5064	1·5104	1·5182	1·5274
	Na	1·5095	1·5133	1·5216	1·5306
	Tl	1·5127	1·5165	1·5251	1·5339
	Cd	1·5145	1·5184	1·5271	1·5359
	F	1·5164	1·5202	1·5291	1·5379
	G	1·5224	1·5264	1·5356	1·5442
β	Li	1·5144	1·5165	1·5241	1·5317
	C	1·5149	1·5170	1·5246	1·5322
	Na	1·5182	1·5200	1·5280	1·5352
	Tl	1·5215	1·5233	1·5314	1·5385
	Cd	1·5234	1·5252	1·5334	1·5405
	F	1·5253	1·5272	1·5354	1·5425
	G	1·5314	1·5334	1·5422	1·5488
γ	Li	1·5306	1·5290	1·5343	1·5379
	C	1·5311	1·5295	1·5348	1·5384
	Na	1·5345	1·5328	1·5381	1·5414
	Tl	1·5379	1·5363	1·5416	1·5450
	Cd	1·5399	1·5382	1·5437	1·5470
	F	1·5421	1·5404	1·5457	1·5491
	G	1·5483	1·5467	1·5524	1·5555
Mean refractive index $\frac{1}{3}(\alpha+\beta+\gamma)$ for Na light		1·5207	1·5220	1·5292	1·5357
Double refraction, $Na_{\gamma-\alpha}$		0·0250	0·0195	0·0165	0·0108

Double Refraction.—This property has been shown to diminish at a rate accelerating with the rise of the atomic weight of the alkali metal. The total diminution between potassium and cæsium ferrous selenates is 0·0142. For the two analogous salts of the nickel group last studied* it was found to be 0·0152; while for the zinc and magnesium groups previously studied it was less and still less, 0·0128 and 0·0112. This smaller change in the double refraction in the two last-mentioned groups was only just adequate to reverse the progression of the γ indices in RbZn and RbMg selenates, these indices being lower than those of KZn and KMg selenates by 0·0004 only.

AXIAL Ratios of the Optical Indicatrix.

	$\alpha : \beta : \gamma$	$\alpha : \beta : \gamma$
KFe selenate	0·9943 : 1 : 1·0107	0·9943 : 1 : 1·0107
RbFe ,,	0·9956 : 1 : 1·0084	0·9968 : 1·0012 : 1·0096
NH_4Fe ,,	0·9958 : 1 : 1·0066	1·0022 : 1·0064 : 1·0131
CsFe ,,	0·9970 : 1 : 1·0040	1·0082 : 1·0112 : 1·0153

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* ‘Phil. Trans.,’ A, vol. 217, p. 229 (1917).

AXIAL Ratios of the Optical Velocity Ellipsoid.

		𝔞 : 𝔟 : 𝔠	𝔞 : 𝔟 : 𝔠
KFe	selenate	1·0058 : 1 : 0·9894	1·0058 : 1 : 0·9894
RbFe	,, ...	1·0044 : 1 : 0·9916	1·0032 : 0·9988 : 0·9905
NH_4Fe	,, ...	1·0042 : 1 : 0·9934	0·9978 : 0·9936 : 0·9871
CsFe	,, ...	1·0030 : 1 : 0·9960	0·9919 : 0·9889 : 0·9849

Axial Ratios of the Optical Ellipsoid.—The values of these ratios are given in the two preceding tables. Besides the ratios calculated with the β value for each salt as unity, a second set is given (as in the cases of the previous groups studied) in which the β value for the potassium salt is taken as unity for all the four salts of the group, thus enabling the progress of the axial directional change in the dimensions of the optical ellipsoid to be followed on the passage from one salt to another. The left-hand series show a regular progression with the atomic weight and number of the alkali metal. The right-hand series emphasise the accelerating nature of the change, modified by the effect of the diminution of double refraction in causing the set-back of the γ values, which is apparent in the case of rubidium ferrous selenate.

The position of the ammonium salt is seen to be intermediate between the rubidium and cæsium salts, as regards both series of ratios, which may be considered as yet another confirmation that ammonium ferrous sulphate is correctly regarded as truly isomorphous with potassium, rubidium, and cæsium ferrous selenates.

Molecular Optical Constants.—These constants are as valuable with regard to the optics of the group as were the molecular volumes and topic axial ratios in indicating the true relations of the salts in regard to their morphology. They are given in the next three tables. The conclusions derivable from them are the following.

The whole of the molecular optical constants of the rubidium salt are intermediate between those of the potassium and cæsium salts of the group. The important molecular refraction, whether calculated by the formula of LORENZ or by that of GLADSTONE and DALE, increases with increase of atomic weight and atomic number of the interchangeable alkali metals, and at an accelerating rate, the replacements respectively of potassium by rubidium and rubidium by cæsium being accompanied by increases in mean molecular refraction of 5·46 and 9·89 Gladstone units, which are in the proportion of 3 : 5. The result is unaffected by temperature change, as the effect of the latter is similar on both the density and refractive power, both diminishing on raising the temperature.

The molecular refraction of the ammonium salt is very close indeed to that of the rubidium salt, being very slightly higher to the extent of one Lorenz or two Gladstone units; the mean molecular refraction by GLADSTONE'S formula is 1·57 higher. This result is analogous to that regarding the structural dimensions, the ammonium salt being shown to be practically isostructural with the rubidium salt.

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.
AmFe selenate	0·1384	0·1398	0·1420	0·1422	0·1437	0·1459	0·0038	0·0039	0·0039
KFe ,,	0·1192	0·1209	0·1241	0·1224	0·1241	0·1274	0·0032	0·0032	0·0033
RbFe ,,	0·1069	0·1080	0·1102	0·1097	0·1109	0·1132	0·0028	0·0029	0·0030
CsFe ,,	0·1009	0·1017	0·1027	0·1036	0·1043	0·1054	0·0027	0·0026	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.
KFe selenate	62·55	63·43	65·10	64·21	65·13	66·85	1·66	1·70	1·75
RbFe ,,	65·93	66·65	68·00	67·66	68·41	69·83	1·73	1·76	1·83
AmFe ,,	66·81	67·50	68·59	68·68	69·38	70·46	1·87	1·88	1·87
CsFe ,,	71·74	72·29	72·99	73·64	74·16	74·91	1·90	1·87	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.	
KFe selenate	106·54	108·33	111·74	108·87
RbFe ,, ...	112·44	113·89	116·65	114·33
AmFe ,, ...	114·21	115·62	117·87	115·90
CsFe ,, ...	122·99	124·11	125·56	124·22

On comparing the results for the molecular refraction of the iron group of double selenates with the similar ones for the iron group of double sulphates,* in order to

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* 'Roy. Soc. Proc.,' A, vol. 88, p. 382 (1913).

arrive at the effect of replacing sulphur by selenium, it is found that the selenate values are higher by 6·94 to 8·06 Lorenz units or 12·76 to 14·23 Gladstone units. As there are two atoms present of the sulphur or selenium, this affords as the increase per atom on replacing sulphur by selenium 3·47 to 4·03 Lorenz units or 6·38 to 7·12 Gladstone units. The following, therefore, is the table for the effect of the replacement of sulphur by selenium in the monoclinic hexahydrated double salt series brought up to date as regards the groups of double selenates now completely investigated.

It will be remembered that the double sulphate series has been quite completed, as regards all the eight known groups.

INCREASE of Molecular Refraction on Replacing S by Se.

Salt group.	Lorenz units.	Gladstone units.
Iron	3·5–4·0	6·4–7·1
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 table also includes the effect of replacing sulphur in the simple alkali sulphates by selenium, and the result is seen to be almost (and in the mean exactly) identically the same. The effect of replacing sulphur by selenium as regards molecular refraction, is thus found to be on the average 3·6 or 6·7 units, according as the formula of LORENZ or that of GLADSTONE and DALE is employed.

Summary of Main Conclusions.

The outstanding result of this investigation of the iron group of double selenates of this grand series of isomorphous salts $R_2M\left(\begin{matrix}S\\Se\end{matrix}O_4\right)_2 . 6H_2O$, is to add further evidence of the truth of the general law of progression of the crystallographic, structural, and optical properties with the atomic weight and atomic number of the interchangeable alkali metals (represented by R) potassium, rubidium, and cæsium. The change in the principal interfacial and axial angle, the monoclinic angle β, the mean change of all the 38 different interfacial angles, and the maximum change of angle, when one alkali metal is replaced by another, are all directly proportional to the change in the atomic weight or number, to a degree of precision which is surprising. The change in the dimensions of the structural unit cell of the space-lattice, as indicated by the molecular volumes and the topic axial ratios, and the corresponding optical change as indicated by the molecular refraction, are instances and expressions of the accelerating progressive effect of the increase of the atomic weight or number of the alkali metal.

The mystery as to why this should be so, formerly surrounding the similar results derived from the three groups of double selenates and eight groups of double sulphates previously described by the author, has now been completely lifted, as shown in the addendum of February 7, 1917, to the author's last communication,* by the brilliant discovery of MOSELEY, that the atomic sequence number is a fundamental constant governing the structure and complexity of the chemical atom. For as the atomic number is itself a measure of the positive charge on the atomic nucleus, and therefore correspondingly governs the number of negative electrons clustered around it, it must of necessity follow that a family group of chemical elements so vigorous as that of the monovalent alkali metals, each differing from the next by two whole rows (series) of elements in the periodic classification, must bring about by their successive replacement of each other a progressive change, corresponding to the increased atomic complexity, in the properties of the crystals of the salts in which they replace one another as dominating elements. As the atomic weight varies similarly to the atomic number, the differences between potassium and rubidium on the one hand and rubidium and cæsium on the other being similarly related (equal) with respect to both constants, the law of progression may be stated with respect to either constant with like validity. To state it with respect to the atomic number is the better and more logical way, however, as the reason for the law is then at once apparent.

One other important result is the further confirmation afforded, by the results for this iron group of double selenates, of the isostructural relationship of the ammonium and rubidium salts of any group of the series. The interesting application of this conclusion as a test for the Pope-Barlow theory of valency volume to which special reference was made in a former communication,† is still further justified by the results now presented, which are clearly incompatible with that theory.

In concluding this description of the ferrous double selenates satisfaction may, perhaps, be legitimately expressed that it has, after attempts lasting over several years, been at last found possible to isolate and investigate completely crystals so difficult to prepare, and so extremely fugitive when prepared, as those of potassium ferrous selenate.

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* 'Phil. Trans.,' A, vol. 217, p. 234 (1917).

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