CXVIII.—*The Relation of Ammonium to the Alkali Metals. A Study of Ammonium Magnesium and Ammonium Zinc Sulphates and Selenates.*

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In an earlier communication (Trans., 1903, **83**, 1049), the results were given of a study of the crystallised normal sulphate of ammonium, together with a discussion of their bearing, when considered alongside those previously published (Trans., 1894, **65**, 628) for the corresponding sulphates of potassium, rubidium, and cæsium, on the relationship of the ammonium complex, NH_4, to those three strictly comparable alkali metals belonging rigidly to the same family group of the periodic classification. The results of an investigation of the four ammonium double sulphates and selenates of the series $R_2M\left(\begin{matrix}S\\Se\end{matrix}O_4\right)_2,6H_2O$ containing magnesium and zinc are now presented, and compared with those previously given for the similar salts containing the three alkali metals (Trans., 1893, **63**, 337, and 1896, **69**, 344; *Proc. Roy. Soc.*, 1900, **66**, 248, and 1900, **67**, 58; *Phil. Trans.*, 1901, A, **197**, 255).

The two double sulphates were partially described by Murmann and Rotter in the year 1858 (*Sitzungsber. K. Akad. Wiss. Wien.*, **34**, 135), and the optical properties of the two double selenates and of ammonium magnesium sulphate were studied by Topsoe and Christiansen in the year 1874 (*Ann. Chim Phys.*, 1874, [v], **1**, 73, 76 and 87). The optical properties of ammonium zinc sulphate have also been more recently studied in greater detail by Perrot (*Arch. Sci. phys. nat.*, 1891, **25**, 26).

The two double sulphates have several times formed the subject of specific gravity determinations (see pp. 1136 and 1143), and the density of the double selenates was also determined by Topsöe. But, as was pointed out by Pettersson in regard to other salts, Topsöe's densities were frequently too low, and this will subsequently be shown to be the case pre-eminently with ammonium magnesium and ammonium zinc selenates.

The data available in respect to both morphological and physical properties of the four salts under consideration will thus be seen to be inadequate, and unsuitable for the purpose of a strict comparison with the corresponding double salts containing the alkali metals, and it was therefore desirable that these ammonium salts should be again investigated in the same detailed and more accurate manner as the salts of the alkali metals already treated of in the author's former communications.

Miers (*Phil. Trans.*, 1903, A, **202**, 459) has recently described an important phenomenon, of which numerous instances have been observed in the course of this and the author's previous investigations. It is pointed out that the primary faces of crystals are frequently replaced by two or more vicinal faces, deviating from the position of the primary plane by several minutes of arc. A study of a growing crystal of potash alum led to the observation that the images from the various faces continually altered their positions, that the angle between the adjacent faces was never the theoretical angle of the regular octahedron, and that the faces usually yielded multiple images lying very close together. The latter were subsequently found to be three in number, of which one was often very much brighter than the others, due to the octahedron face being replaced by the facets of a very flat triakis octahedron, of which one face largely predominated over the others. The three images frequently changed their positions, the lines of movement being inclined at 120° to each other, but the movement did not occur continuously but *per saltum*. It was very uncertain, however, whether the forms produced could be expressed by any rational indices, even by very high numbers. The angles of the vicinal faces varied at different times from the true octahedron face by 2′ to 30′. Similar observations were made in the cases of sodium chlorate (cubic) and the sulphates of magnesium and zinc (rhombic). In the case of zinc sulphate, the primary prism faces varied from 91°6′ to 91°15′, due to the production of various vicinal faces instead of the true primary prism {110}. In the case of magnesium sulphate, similar variations of 20′ were observed. It is pointed out that with crystals of comparatively low symmetry the mean of a number of measurements may give a result very far from the truth. In the cubic system, the mean may give the correct result, as the vicinal faces follow the symmetry; but in the case of a rhombic prism each face will, from the symmetry, be replaced by one vicinal plane only, and the prism angle afforded might be considerably too large or too small.

Miers further showed that the vicinal planes follow specific well-defined zones only, and that to replace primary faces by vicinal planes is to replace planes of the greatest possible reticular density (referring to the space-lattice structure of the crystal) by planes of the least possible reticular density. Of all possible causes of the phenomenon investigated, change of concentration during crystallisation appeared to be most actively influential.

Hence Miers suggests, as the explanation, that the escape of the water during deposition from the only slightly supersaturated solution causes the shower of solid salt particles to fall in a loosely packed condition, and if they are laid down as plane layers thus widely spaced, the plane at any moment is a vicinal face rather than the primary face itself.

These observations and speculations of Miers have a special bearing on the author's work, the most difficult part of which has been the preparation of adequately perfect crystals for the determination of the small angular differences between the crystals of different members of isomorphous series of salts. Every variety of the vicinal face phenomenon referred to by Miers has been observed, and it may at once be said that the phenomenon has not been permitted to affect in the slightest degree the results now or previously published. Even if this had not been so, the phenomenon could not have essentially altered the results for two sufficient reasons: first, because the differences (especially in the double salts, where the differences between a potassium and a cæsium salt exceed 2°) are much larger than those between the vicinal and primary planes; and, secondly, because the whole of any isomorphous series of salts is similarly affected by the phenomenon, rendering comparisons equally valid.

The phenomenon having been met with from the commencement of the work in 1892, great efforts have been made, and with invariably successful results, to eliminate it. Of each salt, a large number of crops, often exceeding a hundred, have been prepared, with every precaution against disturbance during crystallisation. A room has been entirely set apart for the crystallising work, and great labour has been expended on this all-important part of the investigation. The result has been that about half a dozen crops of each salt have been obtained, in which it has been possible to discover an adequate number of small crystals of so perfect a character as to show no sign of vicinal faces, the primary planes themselves having been well formed and inclined at the theoretical angles. These crystals have, as a rule, been much more minute than those employed by Miers, and had been deposited under conditions of extreme quietude, and from solutions screened from all rapid change of temperature.

As regards the series $R_2M\binom{S}{Se}O_4)_2,6H_2O$, the crystals generally show striation of the faces of the basal plane $c\{001\}$ and the primary prism $p\{110\}$, parallel to the symmetry plane $\{010\}$, that is, to the axes a and c, due to vicinal faces being formed instead of the simple c and p faces. The directions will be clear from the shading in Fig. 1. In the case of the c faces, when the zone $[bqc]$ is adjusted parallel to the axis of the goniometer, two images of the Websky signal, separated by about 20′, usually predominate very markedly in the bundle, symmetrically arranged to the symmetry plane, that is, about 10′ on each side of the position for a true c image. The position of the true c plane is, however, indicated by the precision of the images reflected by the faces of the clinodome $q\{011\}$, which were, in the selected crystals used for this work, generally perfect, being single and well defined; also by those from the faces of the clinopinacoid $b\{010\}$, which in the four ammonium salts now described are more largely developed than has been observed with the other salts of the series. These two forms are peculiarly free from the vicinal face phenomenon. It thus appears that the vicinal planes not only follow specific well-defined zones, but that certain forms only in such zones are particularly addicted to them. Numerous cases have been goniometrically investigated in which the q images were quite perfect, whilst the c images were of the double character (with fainter intermediate images) already mentioned. It was evident that these c faces were not true basal planes $c\{001\}$, but in each case a pair of vicinal faces of the kind described by Miers. When the zone $[cr']$ was adjusted, the c images, whether consisting of vicinal faces or of the true basal plane, were invariably trustworthy, for even in the former case the images in the bundle were arranged vertically over each other, and their narrow central parts fell

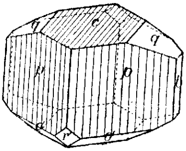

FIG. 1.

identically on the vertical cross wire when any one of them was adjusted. Hence, when good *r'* faces were present, as was the case with the crystals selected for measurement, the value of the angle *cr'* was always ascertainable with precision.

The *q* faces were absolutely perfect on the crystals measured, the angle *qq* in the zone [*bqc*] being always the same within very narrow limits, enabling the theoretical position of the *c*{001} plane (half-way between each pair) to be precisely determined, for $cq = \frac{1}{2}qq$. Moreover, in the cases of at least 6 crystals out of the 10 or more measured of each salt, the *c* faces themselves were also perfect, affording single brilliant images of the signal and no traces of vicinal faces. These perfect *c* images occupied exactly the theoretical position within 2′. Thus, for instance, in the case of ammonium magnesium selenate, six perfect *c* faces gave, with the twelve adjoining similarly perfect *q* faces, twelve angles varying from 25°27′ to 25°31′, a difference of only 4′, and their mean, 25°29′, was identical with the mean value of 38 measurements (with different faces) of the angle *cq*. Also in these cases the *b*{010} faces afforded single and brilliant images at exactly 90°0′ to the *c* faces.

In the case of the *p*{110} faces, the image corresponding exactly to {110} was always present, but generally in a bundle of which the two extremes were not symmetrical (naturally, from the nature of the symmetry) to it, that is, it was not the central image of the bundle. Also it was not usually the brightest, the latter being sometimes on one side and sometimes on the other. Perfect *p* images were, however, afforded in the cases of the specially good crystals referred to, and the values obtained with them for the angles *bp* were always the same within one or two minutes.

The true position of the *p* and *c* faces is always indicated clearly by a particularly trustworthy image being afforded whenever the crystal has grown with one of these two planes in contact with the flat bottom of the crystallising vessel. Such contact faces are always indicated by their being marked with contour lines, as shown in Fig. 2, in the case of the upper *c* face of one of the crystals of ammonium zinc sulphate, which had been during growth the lower one in contact with the bottom of the dish. These contours are due to a lifting up of the crystal during growth, with eventual production of a hollow pyramid, arranged in steps, owing to the central part of the face not being in contact with more than a film of the saturated solution, whilst the margin is in contact with ample solution and has full facility for the deposition of the shower of solid salt particles. A series of shallow steps is thus produced, the horizontal strip-like surfaces of which, bounded by contour lines resembling etched figures, are parallel to the plane undergoing growth (in this case the basal plane); and the interesting point is that the whole of these contour strips, which together make up the crystal face (in this case *c*), afford a single coincident image of the signal. This image, in the case of such *c* faces, lies accurately in the zone [*bqc*]; it is truly orientated midway between the two *q* images, and shows no trace, in the cases of well-formed crystals, of vicinal faces. A perfectly analogous remark applies to *p* faces which have been the contact planes, with respect to their accurate position in the zone [*bp*]. In all cases, the values for the angles *cq* or *bp* made by such faces are found to be coincident with the mean, that is, the true, values of these angles, and with the values derived from exceptionally perfect crystals showing no trace of ambiguity.

Enough will have been said to prove that the author's conclusions are in nowise affected by the vicinal face phenomenon, and the proof is rendered absolute by the fact that the measurements for the different salts have been rigidly comparative, as well as having been directed towards obtaining accurately the absolute values of the various angles. Hence, even if any effect had been possible—and the contrary has been conclusively shown to be the fact—it would have been equal throughout the series, leaving the comparison totally unaffected.

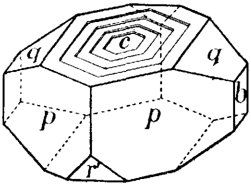

Fig. 2.

The author is glad to have this opportunity of confirming Miers' observations and general conclusions, for it is certain that this phenomenon of vicinal faces is one which promises to lead to great advances in our knowledge of the mode of deposition of crystals, and of the nature of the physical changes which accompany the act of crystallisation.

In connection with the correct setting up ("richtige Aufstellung") of crystals (*Zeit. Kryst. Min.*, 1902, **35**, 129), Fedoroff expresses the opinion that both the rhombic simple sulphates and selenates, $R_2\genfrac{}{}{0pt}{}{S}{Se}O_4$, and the monoclinic double sulphates and selenates, $R_2M\left(\genfrac{}{}{0pt}{}{S}{Se}O_4\right)_2,6H_2O$, are of pseudohexagonal type, and that they should be so considered in calculating the topic axes. The author is not responsible for the mode of setting up the crystals of the salts of these series, that is to say, for the choice, within the limits imposed by rhombic and monoclinic symmetry respectively, as to which particular faces shall be considered as the primary planes, but is merely responsible for having adopted, to save the confusion which has so often resulted from different descriptions of the same crystallised substance by different observers, the same mode of setting up in the case of the crystals of each series as that employed by Groth in his *Physikalische Krystallographie*, and which in the case of the double salt series goes back beyond the time of Murmann and Rotter (1858). The extreme closeness of approximation of the rhombic crystals of the simple salt series to true hexagonal symmetry—the difference from 60° being less than 1°—renders Fedoroff's supposition in the case of that series highly probable, and the topic axes have therefore been recalculated on that basis and are given in the following memoir. In the case of the monoclinic double salts, however, there is no approximation whatever to a pseudo-hexagonal type, the angle which should correspond to 60° being 71—73° in the various salts. They cannot, therefore, be considered as having a pseudohexagonal space lattice, and are not strictly comparable to the rhombic salts. Wulff (*Zeit. Kryst. Min.*, 1901, **34**, 472) has proposed a setting up based on the acceptance of the cleavage direction as $\{001\}$ instead of $\{\bar{2}01\}$. But if this orientation is adopted, no orthopinacoid $\{100\}$ is found developed, and the arrangement is consequently no more satisfactory than the normal one adopted by Groth and by the author. Hence, the ordinarily accepted orientation is retained for the purpose of calculating the topic axes as well as for all other purposes.

In order that no question may arise as to the accuracy of the author's values for the densities of the salts, they have been determined not only by accurate pycnometer methods, but also by the suspension method (Retgers, *Zeit. physikal. Chem.*, 1889, **3**, 289 and 497), using methylene iodide and benzene for the production of the floating liquid. This method has not been hitherto employed by the author, because it is not applicable to the cases of the simple sulphates and selenates of rubidium and cæsium, the lightest of these salts (rubidium sulphate) being slightly denser than pure methylene iodide, the only available heavy liquid without action on the salts. Hence density results of a strictly comparable character cannot thus be obtained in the case of the simple salt series. The method is, however, applicable in the case of the double salts, all of which are lighter than methylene iodide, so that the mixture of the latter with benzene can be employed.

The two pycnometers employed throughout the whole of the author's density work were each fitted with a tightly ground glass cap, which was maintained throughout the weighing pressed down over the capillary stopper by a spring forming part of a little supporting wire stand. Hence, evaporation of the liquid (carbon tetrachloride) employed was precluded. The salts were always carefully dried after pulverisation, at temperatures higher than the ordinary and which varied according to the nature of the salt, and only such dry powder was employed as passed through the meshes of a sieve of the finest platinum gauze. Consequently, any trace of mother liquor liberated from cavities by the pulverisation had been removed, and residuary cavities reduced to a minimum. Moreover, all trace of air was removed by causing the carbon tetrachloride with which the powder had been covered to boil in a Sprengel vacuum for half an hour at the ordinary temperature. The determinations have all been made at 20° by immersion of the pycnometers in a double water-bath raised to this temperature with extreme slowness. The results are, therefore, comparable in the strictest sense.

The only possible error still persisting is that due to the minimum quantity of mother liquor enclosed in minute cavities still contained by the particles of powder, and the question arises as to whether the amount of this error is appreciable. If it only affects the fourth place of decimals, it may be neglected as being less than the real differences between different crystals. But if it affects the third place, then it is of importance as regards the absolute values, although comparisons will still be valid. The suspension method having afforded results higher by one or two units in the third place of decimals in those cases investigated by Retgers, it has been assumed that the reason is that the most perfect pycnometer method is subject to such an effect on the third place of decimals. On the other hand, the possible error of the suspension method is of the opposite character, the results being possibly very slightly too high owing to the loss by evaporation of some of the more volatile lighter constituent, benzene in this case, during the interval between the floating and the determination of the density of the liquid mixture, even when working with the maximum rapidity. It has been considered by the author advisable, however, to redetermine the densities by the suspension method, and to compare the results with those obtained with the pycnometer.

The method of carrying out these determinations (Retgers, *Zeit. physikal. Chem.*, 1889, 3, 289 and 497) consists, first, in producing such a mixture of methylene iodide and benzene as is of exactly the same density as the heaviest of the small crystals employed, and, secondly, in determining the density of this liquid by weighing a pycnometer filled with it.

The specially pure methylene iodide, obtained from Merck, was only very faintly yellow, and was maintained in this condition by storing it in the dark and only making the determinations in the evening by artificial light. For the first operation, about 8 c.c. were transferred to a miniature dropping funnel, with cylindrical bulb of 20 c.c. capacity. The ten or more perfect small crystals used for the goniometrical work, which were the least likely to contain cavities, when introduced, swam on the surface of the methylene iodide. Benzene was then introduced gradually from a still smaller dropping funnel, until the crystals began to regain the surface only slowly after agitation, when all further additions of benzene were made only one drop at a time, followed by vigorous shaking, with the stopper in place. As soon as the desired equilibrium of density was attained, the stopper was replaced by a centrally bored cork carrying a thermometer reading to 0·1°, which was so arranged that its bulb lay altogether immersed in the liquid. When equilibrium of temperature is attained, the heaviest crystal should float anywhere in the liquid without rising or falling. By working with a pair of pycnometers, it is so arranged that if in the first determination the tendency of the heaviest crystal is to rise, then in the second determination with the other pycnometer it is made to show a tendency to sink. It is best to work in a room the temperature of which is approximately 20°, lower rather than higher, but preferably not lower than 15°, for all the results are presented for the constant temperature of 20°; in this case, the determinations are reduced to 20° with the aid of the knowledge of the coefficient of expansion of the crystals.

Immediately the temperature of the liquid had been read, it was run off into one of the pycnometers as rapidly as the stopcock allows, the perforated stopper was replaced, the neck of the vessel rapidly wiped dry without touching with the naked fingers, the cap fitted on, and the filled pycnometer inserted in its spring stand, which presses the cap tightly down on the neck. Rapidity is essential, and the pycnometer and stand were at once weighed.

All weighings have been corrected for the air displaced, as in former determinations. As regards the coefficient of expansion of the crystals, Retgers takes it to be 0·0001 for salts generally. This fully agrees with the results of the author's direct measurements of the coefficients of thermal expansion of the normal alkali sulphates (*Phil. Trans.*, 1899, A, **192**, 455), for the actual coefficients of cubical expansion at any temperature t were found to be:

For potassium sulphate, $0·00010475 + 0·0000001396t$.
,, rubidium sulphate, $0·00010314 + 0·0000001534t$.
,, cæsium sulphate, $0·00010170 + 0·0000001620t$.

The correction per degree is therefore 0·0001 multiplied by the sp. gr. of the salt.

Two pairs of determinations have been carried out for each salt, thus affording four different values of the sp. gr. by the suspension method, and the mean of these to the nearest figure in the third place of decimals is accepted for the true density. It will be shown that this is in general about two units in the third place of decimals higher than the value obtained as the mean of the pycnometer determinations with the powdered dry salt. It is thus apparent that the latter method is indeed, in spite of all precautions, affected by the presence of cavities, and this is the more clearly proved by the case of an unusually turbid (and therefore cavity-containing) salt, ammonium zinc selenate, where the difference is as much as 0·005 higher for the suspension method, as employed with the perfectly clear and cavity-free minute crystals selected for the goniometry.

In order that the comparisons of all constants involving the density may be strictly valid, redeterminations by the suspension method of the densities of the potassium, rubidium, and cæsium analogues of the salts now described are included in this memoir.

Ammonium Magnesium Sulphate, $(NH_4)_2Mg(SO_4)_2,6H_2O$.

An estimation of magnesium in a specimen of the crystals employed gave the following result: 1·0900 grams of crystals yielded 0·3461 gram of magnesium pyrophosphate, which corresponds to 6·86 per cent. of magnesium, the calculated value being 6·67 per cent.

Goniometry.

Eleven crystals of exceptional perfection and of small size were selected out of four chosen crops (upwards of a hundred crops having been prepared) for the purpose of the goniometrical measurements.

Ratio of axes: $a : b : c = 0·7400 : 1 : 0·4918$.

Axial angle: $\beta = 72°54'$.

Habit: short prismatic. Prisms formed by clinopinacoid and primary prism.

Forms observed: $b = \{010\} \infty \grave{P} \infty$, $c = \{001\} oP$, $p = \{110\} \infty P$,
$p''' = \{130\} \infty \grave{P} 3$, $q = \{011\} \grave{P} \infty$, $r' = \{\bar{2}01\} + 2 \bar{P} \infty$,
$o = \{111\} - P$, $o' = \{\bar{1}11\} + P$, $n = \{121\} - 2 \grave{P} 2$.

The results are displayed in the table of angles on pp. 1134, 1135.

The crystals of the crops employed in these measurements were generally of the types shown in Figs. 3 and 4. Both are characterised by the predominating development of the prism zone. The faces of the clinopinacoid $b\{010\}$ in this zone varied, however, considerably, from a mere strip to a good broad plane, and often on the same crystal the two faces differed in this extreme manner. The images from this form were uniformly satisfactory, and frequently quite perfect. The faces of the primary prism *p*{110} were, however, invariably largely developed. Although on the great majority of the crystals of the crops employed they were generally affected by striation due to the attempt at producing vicinal faces, as described in the introduction, the crystals chosen were free from this defect, the images being single, definite, and brilliant. In one case a *p* face was the plane of contact with the bottom of the crystallising vessel, and the image afforded was, as usual with such faces, single and perfect; the value of the corresponding angle *bp* was exactly equal to the mean value given in the table.

The two types figured show their greatest divergence as regards the development of the basal plane *c*{001}, which varied from a broad face to a strip sometimes reduced to a mere line. The faces of this form were particularly good examples, in the greater number of crystals of any crop, of the production of two vicinal faces symmetrically situated to the symmetry plane, instead of the true basal plane perpendicular to the plane of symmetry. In the 11 chosen crystals, however, this was reduced to a minimum, and several of the crystals exhibited single *c* images accurately perpendicular to the symmetry plane. In one interesting case, three images were afforded by one of the two *c* faces in the zone [*cqb*], the central image being exactly equidistant from the two *q* images, while the other two were equidistant from this central image a few minutes on each side of it.

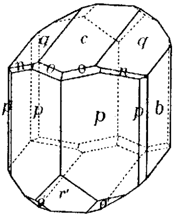

FIG. 3.

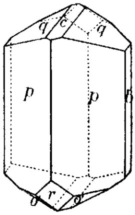

FIG. 4.

Hence, this was a case of the simultaneous presence of the true basal plane and a pair of vicinal faces. To the naked eye, the face appeared slightly curved; it consisted really of three planes very slightly inclined to each other.

The faces of the clinodome *q*{011} were invariably excellent, the reflected images of the signal being single, brilliant, and in every way suitable for the purpose of the accurate determination of the angles *bq*(010) : (011) and *qq*(011) : (0$\bar{1}$1). It will be clear from the table that the mean value of all the *cq* measurements, 25°11′, was found to be exactly the same as the complement of the mean measured *bq*, 64°49′, about which there is no shadow of possible ambiguity. Hence the measurements are absolutely unaffected by the interesting vicinal face phenomenon exhibited by the basal plane.

No faces of the orthopinacoid $a\{100\}$ were ever observed. The orthodome $r'\{\bar{2}01\}$ was generally present, and usually one of its faces greatly exceeded the other in size, the variation being from that shown in Fig. 3 to considerably less than the size of the *r′* face shown in Fig. 4. The $o'\{\bar{1}11\}$ faces were usually small, but they generally gave very trustworthy sharp reflections. Four good but small faces of the rarer pyramid $o\{111\}$ were also observed on three of the measured crystals. In addition, faces of the prism $p'''\{130\}$ and also of the pyramid $n\{121\}$ were discovered on one of these three crystals.

Morphological Angles of Ammonium Magnesium Sulphate.

Angle measured.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.
ac = (100) : (001)	—	—	—	72°54′	—
as = (100) : (101)	—	—	—	44 54	—
sc = (101) : (001)	—	—	—	28 0	—
cr′ = (001) : ($\bar{2}$01)	13	64°25′— 64°32′	64°29′	64 25	4′
cs′ = (001) : ($\bar{1}$01)	—	—	—	38 19	—
s′r′ = ($\bar{1}$01) : ($\bar{2}$01)	—	—	—	26 6	—
r′a = ($\bar{2}$01) : ($\bar{1}$00)	—	—	—	42 41	—
r′c = ($\bar{2}$01) : (00$\bar{1}$)	12	115 26 —115 34	115 31	115 35	4
ap = (100) : (110)	—	—	—	35 16	—
pp′ = (110) : (120)	—	—	—	19 28	—
p′b = (120) : (010)	—	—	—	35 16	—
pp‴ = (110) : (130)	1	—	29 26	29 29	3
p‴b = (130) : (010)	1	—	25 18	25 15	3
pb = (110) : (010)	39	54 35 — 54 50	54 44	*	—
pp = (110) : (1$\bar{1}$0)	19	70 25 — 70 46	70 34	70 32	2
cq = (001) : (011)	40	25 4 — 25 16	25 11	25 11	0
qb = (011) : (010)	40	64 43 — 64 56	64 49	*	—
ao = (100) : (111)	—	—	—	48 0	—
oq = (111) : (011)	—	—	—	26 34	—
aq = (100) : (011)	—	—	—	74 34	—
qo′ = (011) : ($\bar{1}$11)	—	—	—	34 38	—
o′a = ($\bar{1}$11) : ($\bar{1}$00)	—	—	—	70 48	—
co = (001) : (111)	4	33 25 — 33 39	33 32	33 33	1
op = (111) : (110)	4	42 23 — 42 43	42 35	42 34	1
cp = (001) : (110)	32	76 1 — 76 17	76 7	*	—
po′ = (110) : (11$\bar{1}$)	—	—	—	59 22	—
o′c = (11$\bar{1}$) : (00$\bar{1}$)	—	—	—	44 31	—
pc = (110) : (00$\bar{1}$)	31	103 44 —104 2	103 52	103 53	1

Morphological Angles of Ammonium Magnesium Sulphate (continued).

Angle measured.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.
$bn = (010) : (121)$	1	—	54 56	55 1	5
$no = (121) : (111)$	1	—	15 47	15 42	5
$bo = (010) : (111)$	2	70 37 — 70 51	70 44	70 43	1
$os = (111) : (101)$	—	—	—	19 17	—
$bo' = (010) : (\bar{1}11)$	7	65 19 — 65 28	65 22	65 22	0
$o's' = (\bar{1}11) : (\bar{1}01)$	—	—	—	24 38	—
$o'o' = (\bar{1}11) : (\bar{1}\bar{1}1)$	3	49 9 — 49 21	49 16	49 16	0
$sq = (101) : (011)$	—	—	—	36 58	—
$qp = (011) : (\bar{1}10)$	40	88 11 — 88 29	88 21	88 22	1
$ps = (\bar{1}10) : (\bar{1}0\bar{1})$	—	—	—	54 40	—
$pq = (\bar{1}10) : (0\bar{1}\bar{1})$	40	91 33 — 91 49	91 39	91 38	1
$s'q = (\bar{1}01) : (011)$	—	—	—	44 46	—
$qn = (011) : (121)$	1	—	25 58	26 2	4
$np = (121) : (110)$	1	—	36 28	36 24	4
$qp = (011) : (110)$	40	62 18 — 62 38	62 26	62 26	0
$ps' = (110) : (10\bar{1})$	—	—	—	72 48	—
$pq = (110) : (0\bar{1}\bar{1})$	40	117 23 —117 44	117 34	117 34	0
$r'o' = (\bar{2}01) : (\bar{1}11)$	—	—	—	35 17	—
$o'p = (\bar{1}11) : (110)$	—	—	—	91 36	—
$pr' = (110) : (20\bar{1})$	33	52 53 — 53 14	53 5	53 7	2
$r'p = (\bar{2}01) : (110)$	32	126 45 —127 5	126 55	126 53	2

Total number of measurements: 477.

Murmann and Rotter (*loc. cit.*) give $ac\ (\beta) = 72°54'$, $cr' = 64°47'$, $pb = 54°52'$, $pp = 70°22'$, $cq = 25°17'$, $cp = 76°6'$, $r'o' = 35°19'$, and $pr' = 53°9'$. Also for the axial ratio: $a : b : c = 0{\cdot}7376 : 1 : 0{\cdot}4891$.

Cleavage.—An excellent cleavage is developed parallel to the orthodome $r'\{\bar{2}01\}$, as in all the other salts of the series investigated.

On making a section plate parallel to the symmetry plane in the case of a large crystal with the aid of the cutting and grinding goniometer, it happened on making the final "cut-off" (second face) that the crystal broke off in continuation of the cutting (the symmetry) plane when the cutter had proceeded half-way through, and on examining the fracture, both on the plate thus suddenly completed and the crystal end cut off, it was found to be an excellent smooth face of the symmetry plane (the clinopinacoid), yielding in each case a perfect image of the signal. The angles were within 1 minute of the theoretical. Hence it would appear that the symmetry plane $b\{010\}$ is also a direction of cleavage.

Volume.

Relative Density.—The following four determinations were made by the pycnometer method with independent material:

Weight of salt employed.	Sp. gr. at 20°/4°.	
3·2298	1·7213	Mean, 1·7210.
3·4132	1·7200	
3·0623	1·7219	
2·9687	1·7206	

The following additional four were carried out by the suspension method, employing the perfect small crystals used in the goniometrical work, which, when examined microscopically, proved to be remarkably free from air or mother-liquor cavities.

		For 20°/4°.
For 19·2°/4°	1·7236	1·7235
For 17·3 /4	1·7222	1·7218
For 17·5 /4	1·7223	1·7219
For 19·0 /4	1·7228	1·7227
	Mean	1·7225

The density for 20°/4° is therefore taken as 1·723.

The results of former determinations are as follows: Playfair and Joule (*Mem. Chem. Soc.*, 1845, **2**, 401), 1·721 and (*Journ. Chem. Soc.*, 1849, **1**, 138), 1·7169; Schiff (*Ann. Chem. Pharm.*, 1858, **107**, 64), 1·680; Schröder (*Journ. pr. Chem.*, 1879, [ii], **19**, 266), 1·723 and 1·727; Perrot (*Arch. Sci. phys. nat.*, 1891, **25**, 26), 1·721.

Molecular Volume.—$\frac{M}{d} = \frac{358\cdot00}{1\cdot723} = 207\cdot78$.

Topic Axes.—$\chi : \psi : \omega = 6\cdot2320 : 8\cdot4217 : 4\cdot1418$.

Optics.

Orientation of Axes of Optical Ellipsoid.—The plane of the optic axes is the symmetry plane; the sign of the double refraction is positive.

A pair of section plates ground parallel to the symmetry plane afforded the following extinction angles:

Section 1	12°10′	behind the normal to $c(001)$.
,, 2	12°5′	,, ,, $c(001)$.
Mean	12°8′	

Hence the second median line, which corresponds to this extinction direction, is inclined 4°58′ to the vertical crystallographical axis c, the angle β of the axes ac having been shown to be 72°54′. Both median lines lie in the obtuse angle *ac*, and the first median line is inclined 12°8′ to the axis *a*.

Murmann and Rotter give 12°15′ behind the normal to (001) as the position of the second median line $[\mathfrak{a}:(001)]$, and Topsöe and Christiansen give 11°11′.

Refractive Indices.—The following are the results with six prisms, each ground so as to afford two indices directly :

Refractive Indices of Ammonium Magnesium Sulphate.

Index.	Nature of light.	Prisms 1 and 2.	Prisms 3 and 4.	Prisms 5 and 6.	Mean index.	Topsoe and Christiansen's values.
α Vibrations parallel to 2nd median line.	Li	1·4688—4		1·4686—4	1·4685	—
	C	1·4692—88	—	1·4689—7	1·4689	1·4698
	Na	1·4719—6	—	1·4716—4	1·4716	1·4717
	Tl	1·4742—0	—	1·4740—38	1·4740	—
	F	1·4773—0	—	1·4772—0	1·4771	1·4774
	G	1·4817—1	—	1·4815—3	1·4814	—
β. Vibrations parallel to symmetry axis.	Li	1·4701—698	1·4702—4	—	1·4701	—
	C	1·4705—2	1·4705—8	—	1·4705	1·4707
	Na	1·4730—27	1·4731—2	—	1·4730	1·4728
	Tl	1·4755—1	1·4756—9	—	1·4755	—
	F	1·4784—3	1·4787—9	—	1·4786	1·4787
	G	1·4829—8	1·4832—5	—	1·4831	—
γ. Vibrations parallel to 1st median line.	Li	—	1·4758—9	1·4754—2	1·4756	—
	C	—	1·4761—3	1·4758—6	1·4760	1·4751
	Na	—	1·4787—9	1·4784—3	1·4786	1·4791
	Tl	—	1·4813—4	1·4810—06	1·4811	—
	F	—	1·4842—6	1·4840—0	1·4842	1·4837
	G	—	1·4888—93	1·4886—5	1·4888	—

Mean of α, β, and γ for Na light = 1·4744.

The indices found by Topsöe and Christiansen are given in the last column, but only the β values were directly determined.

The intermediate refractive index β, corrected to a vacuum (correction = 0·0004), is expressed by the following formula for any wavelength λ, absolutely as far as the green thallium line of the spectrum, and approximately beyond that towards the violet end :

$$\beta = 1{\cdot}4581 + \frac{634\ 490}{\lambda^2} - \frac{3\ 586\ 800\ 000\ 000}{\lambda^4} + \ \cdot\ \cdot\ \cdot\ \cdot$$

The α indices are also reproduced by the formula with similar accuracy if the constant 1·4581 is diminished by 0·0015, and the γ indices if the constant is increased by 0·0056.

Alteration of Refraction by Rise of Temperature.—The following table represents the results of determinations at 70° with two of the prisms :

Refractive Indices of Ammonium Magnesium Sulphate for 70°.

Nature of light.	α.	β.	γ.
Li	1·4671	1·4684	1·4737
C	1·4675	1·4688	1·4741
Na......	1·4700	1·4712	1·4767
Tl	1·4725	1·4736	1·4792
F	1·4757	1·4766	1·4823

These values are lower than those for the ordinary temperature by an average of 0·0015 for α, 0·0018 for β, and 0·0019 for γ.

Axes of the Optical Ellipsoids.—The calculated values of these constants are as follows:

Axes of optical indicatrix: $\alpha : \beta : \gamma = 0·9991 : 1 : 1·0038$.

Axes of optical velocity ellipsoid: $\mathfrak{a} : \mathfrak{b} : \mathfrak{c} = 1·0009 : 1 : 0·9962$.

Molecular Optical Constants.—Employing the density as afforded by the suspension method, these constants work out as follows:

Axis of optical indicatrix		α.	β.	γ.
Specific refraction, $\frac{n^2-1}{(n^2+2)d} = \mathfrak{n}$	C	0·1616	0·1621	0·1637
	G	0·1653	0·1658	0·1675
Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = \mathfrak{m}$ ...	C	57·85	58·02	58·60
	G	59·17	59·35	59·95
Specific dispersion, $\mathfrak{n}_G - \mathfrak{n}_C$		0·0037	0·0037	0·0038
Molecular dispersion, $\mathfrak{m}_G - \mathfrak{m}_C$		1·32	1·33	1·35
Molecular refraction, $\frac{n-1}{d}M$.................	C	97·43	97·76	98·90

Optic Axial Angle.—The following results were obtained with three excellent pairs of section plates ground perpendicular to the first and second median lines, all affording very small rings and sharp brushes.

Determination of Apparent Angle in Air of Ammonium Magnesium Sulphate.

Light.	Section 1.	Section 2.	Section 3.	Mean 2E.
Li	79° 1′	79°15′	79°32′	79°16′
C	79 0	79 14	79 31	79 15
Na	78 56	79 10	79 27	79 11
Tl	78 42	78 59	79 12	78 58
F...........	78 18	78 44	78 46	78 36

Determination of True Optic Axial Angle of Ammonium Magnesium Sulphate.

Light.	No. of section perp. 1st median line.	Observed values of 2Ha.	No. of section perp. 2nd median line.	Observed values of 2Ho.	Calculated values of 2Va.	Mean value of 2Va.
Li….	1	45°12′	1*a*	106°45′	51°11′	51°20′
	2	45 21	2*a*	106 35	51 22	
	3	45 23	3*a*	106 28	51 26	
C ……	1	45 10	1*a*	106 41	51 10	51 18
	2	45 18	2*a*	106 30	51 20	
	3	45 20	3*a*	106 21	51 24	
Na …	1	44 54	1*a*	106 5	51 5	51 11
	2	44 56	2*a*	106 0	51 8	
	3	45 5	3*a*	105 47	51 20	
Tl……	1	44 31	1*a*	105 31	50 54	51 2
	2	44 38	2*a*	105 28	51 0	
	3	44 45	3*a*	105 15	51 12	
F ……	1	43 44	1*a*	104 35	50 26	50 36
	2	43 57	2*a*	104 35	50 38	
	3	44 4	3*a*	104 35	50 44	

Topsöe and Christiansen (*loc. cit.*) found 78°45′ for 2E and 50°40′ for 2Va. Murmann and Rotter give 77°30′ for 2E and 50°22′ for 2Va. Earlier values for the true angle are those of Brewster, 51°22′, and De Senarmont, 51°4′.

Dispersion of the Median Lines.—This was determined with each of the sections perpendicular to the first median line by immersion in oil of turpentine, the refractive index of which is approximately identical with the mean index of the crystals. The first median line was found to be nearer to the morphological axis *a* for red light than for blue by 18′, 17′, and 16′ respectively in the three cases, using C and F light. Hence the dispersion of the median lines is such that the first median line lies about 17′ nearer to the axis *a* for C light than for F.

Effect of Rise of Temperature on the Optic Axial Angle.

Measurements at 75° (corrected for conduction of crystal holder) gave the following results for the two ends of the spectrum:

2E at 75°. For lithium light, 71°40′, and for F light 70°10′.

Thus 2E diminishes 7°36′ for Li and 8°26′ for F, on heating from 15° (the average of the ordinary temperature determinations) to 75°. This rise of temperature is also accompanied by an increase of 50′ (between Li and F) in dispersion.

On allowing the apparatus to stand 24 hours after cooling, the value of 2E was found to be permanently reduced by somewhat over half a degree, as the effect of the heating.

Ammonium Zinc Sulphate, $(NH_4)_2Zn(SO_4)_2,6H_2O$.

An estimation of zinc in a sample of the crystals employed afforded the following result: 1·0577 grams of crystals gave 0·2122 gram of zinc oxide, corresponding to 16·10 per cent. of zinc, the calculated percentage being 16·21.

Goniometry.

Ten selected crystals were measured belonging to five different crops carefully chosen from the very numerous crops prepared.

Ratio of axes: $a:b:c = 0·7368:1:0·4997$.

Axial angle: $\beta = 73°8'$.

Habit: Thick prismatic to tabular.

Forms observed: $b=\{010\}\infty P\infty$, $c=\{001\}oP$, $p=\{110\}\infty P$,
$q=\{011\}P\infty$, $o=\{111\}-P$, $o'=\{\bar{1}11\}+P$,
$n=\{121\}-2P2$, $r'=\{\bar{2}01\}+2P\infty$.

The table on pp. 1141, 1142 exhibits the results of the measurements.

The measured crystals represented very fairly the varied types found among all the crops prepared, and three characteristic specimens are figured in the illustrations (Figs. 5, 6, and 7). In the type represented in Fig. 5, the habit is clearly prismatic along the prism zone, and not only are there large faces of the primary prism $p\{110\}$, but also tolerably large faces of the clinopinacoid $b\{010\}$. It is further distinguished by the approximately equal development of the basal plane $c\{001\}$ and clinodome $q\{011\}$.

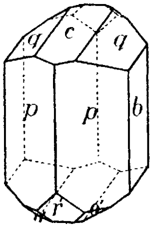

FIG. 5.

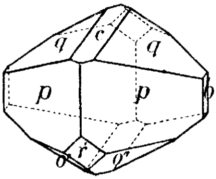

FIG. 6.

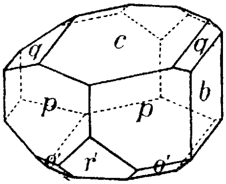

FIG. 7.

The type shown in Fig. 6 is much flatter owing to the shorter relative development of the primary prism. It shows only strips of the clinopinacoid faces, but relatively large faces of the clinodome, being, in fact, prismatic after this form. It is further characterised by an unusually large development of the faces of the hemi-pyramid $o'(\bar{1}11)$, The third type illustrated in Fig. 7 is distinguished by the relatively large development of the basal plane, and owing to the shortening of the primary prism zone is almost tabular along the basal plane.

The relative development of the orthodome $r'\{\bar{2}01\}$ faces also varies from that of Fig. 6 to that of Fig. 7. No faces of the orthopinacoid were ever observed. Small faces of the primary hemipyramid $0\{111\}$ were observed on two of the crystals measured, and an excellent face of the hemipyramid $n\{121\}$ was exhibited by one of the larger crystals employed in the optical work.

Several of the measured crystals afforded perfect images from both clinopinacoid faces, all four clinodome faces, all four primary prism faces, and both *r'* orthodome faces. Four of them also gave perfect single images from the basal plane faces, situated precisely as they should be, midway between the *q* images. Some of the others exhibited striking instances of a pair of images from two vicinal faces replacing the basal plane, as described under ammonium magnesium sulphate. Where any ambiguity of this kind was experienced, the half of the angle between the two *q* images was taken as representing the value of *cq*, for the *q* images were always excellent in the crystals measured and absolutely correctly placed. These half values of *qq* were always practically identical with the values of *cq* measured in the cases of the crystals exhibiting perfect *c* images.

Morphological Angles of Ammonium Zinc Sulphate.

Angle measured.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.
ac = (100) : (001)	—	—	—	73° 8′	—
as = (100) : (101)	—	—	—	44 40	—
sc = (101) : (001)	—	—	—	28 28	—
cr′ = (001) : $(\bar{2}01)$	16	64°51′ — 64°59′	64°54′	64 56	2′
cs′ = (001) : $(\bar{1}01)$	—	—	—	38 55	—
s′r′ = $(\bar{1}01)$: $(\bar{2}01)$	—	—	—	26 1	—
r′a = $(\bar{2}01)$: $(\bar{1}00)$	—	—	—	41 56	—
r′c = $(\bar{2}01)$: $(00\bar{1})$	16	115 0 — 115 10	115 6	115 4	2
ap = (100) : (110)	—	—	—	35 13	—
pp′ = (110) : (120)	—	—	—	19 28	—
p′b = (120) : (010)	—	—	—	35 19	—
pb = (110) : (010)	36	54 40 — 54 54	54 47	*	—
pp = (110) : $(1\bar{1}0)$	17	70 18 — 70 34	70 27	70 26	1
cq = (001) : (011)	39	25 26 — 25 37	25 33	*	—
qb = (011) : (010)	39	64 22 — 64 36	64 27	64 27	0

Morphological Angles of Ammonium Zinc Sulphate (continued).

Angle measured.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.
ao = (100) : (111)	—	—	—	47°52′	—
oq = (111) : (011)	—	—	—	26 57	—
aq = (100) : (011)	—	—	—	74 49	—
qo′ = (011) : $(\bar{1}11)$	—	—	—	35 5	—
o′a = $(\bar{1}11)$: $(\bar{1}00)$	—	—	—	70 6	—
co = (001) : (111)	5	34° 0′— 34° 4′	34° 2′	33 57	5
op = (111) : (110)	3	42 12 — 42 17	42 15	42 20	5
cp = (001) : (110)	39	76 8 — 76 23	76 17	*	—
po′ = (110) : $(11\bar{1})$	21	58 34 — 58 50	58 40	58 38	2
o′c = $(11\bar{1})$: $(00\bar{1})$	20	44 57 — 45 9	45 3	45 5	2
pc = (110) : $(00\bar{1})$	39	103 36 —103 50	103 43	103 43	0
bn = (010) : (121)	1	—	54 57	54 54	3
no = (121) : (111)	1	—	15 50	15 45	5
bo = (010) : (111)	—	—	—	70 39	—
os = (111) : (101)	—	—	—	19 21	—
bo′ = (010) : $(\bar{1}11)$	5	65 7 — 65 12	65 9	65 9	0
o′s′ = $(\bar{1}11)$: $(\bar{1}01)$	—	—	—	24 51	—
o′o′ = $(\bar{1}11)$: $(\bar{1}\bar{1}1)$	1	—	49 43	49 42	1
sq = (101) : (011)	—	—	—	37 31	—
qp = (011) : $(\bar{1}10)$	38	87 52 — 88 12	88 1	88 0	1
ps = $(\bar{1}10)$: $(\bar{1}0\bar{1})$	—	—	—	54 29	—
pq = $(\bar{1}10)$: $(0\bar{1}\bar{1})$	38	91 51 — 92 12	91 59	92 0	1
s′q = $(\bar{1}01)$: (011)	—	—	—	45 25	—
qn = (011) : (121)	1	—	26 17	26 15	2
np = (121) : (110)	1	—	36 14	36 12	2
qp = (011) : (110)	37	62 20 — 62 34	62 27	62 27	0
ps′ = (110) : $(10\bar{1})$	—	—	—	72 8	—
pq = (110) : $(0\bar{1}\bar{1})$	37	117 27 —117 36	117 33	117 33	0
r′o′ = $(\bar{2}01)$: $(\bar{1}11)$	19	35 14 — 35 34	35 24	35 22	2
o′p = $(\bar{1}11)$: (110)	21	91 52 — 92 8	92 1	92 4	3
pr′ = (110) : $(20\bar{1})$	29	52 27 — 52 45	52 36	52 34	2
r′p = (201) : (110)	28	127 15 —127 33	127 24	127 26	2

Total number of measurements: 547.

Murmann and Rotter (*loc. cit.*) found *ac* (β) = 73°19′, *cr′* = 64°41′, *pb* = 54°46′, *pp* = 70°29′, *cq* = 25°17′, *cp* = 76°26′, *po′* = 58°43′, *o′c* = 44°45′, and *pr′* = 52°30′, and for the axial ratio, $a : b : c = 0{\cdot}7375 : 1 : 0 : 5009$.

Cleavage.—The cleavage parallel to *r′* $\{\bar{2}01\}$ common to the series is well developed in this salt.

Volume.

Relative Density.

The pycnometer method :

Weight of salt employed.	Sp. gr. at 20°/4°.
5·1502	1·9294
4·5449	1·9300
5·6138	1·9290
5·4968	1·9303
Mean......	1·9297

The suspension method :

		For 20°/4°.
For 16·8°/4°	1·9345	1·9339
For 17·5°/4°	1·9308	1·9303
For 15·8°/4°	1·9324	1·9316
For 16·3°/4°	1·9325	1·9318
	Mean...........	1·9319

The value accepted for 20°/4° is therefore 1·932.

Previous results are : Playfair and Joule (*Mem. Chem. Soc.*, 1845, **2**, 401), 1·897 ; Schiff (*Ann. Chem. pharm.*, 1858, **107**, 64), 1·910 ; Schroder (*J. pr. Chem.*, 1879, [ii], **19**, 266), 1·919, 1·921, and 1·925 ; Perrot (*Arch. Sci. phys. nat.*, 1891, **25**, 26), 1·931. This last very trustworthy value is satisfactorily close to the value now given.

Molecular Volume.—$\frac{M}{d} = \frac{398{\cdot}72}{1{\cdot}932} = 206{\cdot}38$.

Topic Axes.—$\chi : \psi : \omega = 6{\cdot}1648 : 8{\cdot}3670 : 4{\cdot}1810$.

Optics.

Orientation of Axes of Optical Ellipsoid.—The optic axes lie in the symmetry plane ; the sign of double refraction is positive.

Two section-plates ground parallel to the symmetry plane gave the following angles of extinction :

Section 1.........9°50′ behind the normal to *c*(001).
„ 2.........9°57′ „ „ „
Mean...9°53′

This direction of extinction is the second median line, which, as the angle β of the axes *ac* has been shown to be 73°8′, is consequently inclined 6°59′ to the vertical morphological axis *c*. Both median lines lie in the obtuse angle *ac*, and the first median line is inclined 9°53′ to the axis *a*.

Murmann and Rotter give 8°33′ behind the normal to (001) as the direction of the second median line.

Refractive Indices.—Six excellent prisms were ground so as to yield directly two refractive indices each. The results are as under :

Refractive Indices of Ammonium Zinc Sulphate.

Index.	Nature of light.	Prisms 1 and 2.	Prisms 3 and 4.	Prisms 5 and 6.	Mean index.	Perrot's values.
α. Vibrations parallel to 2nd median line.	Li	1·4859—6	—	1·4859—9	1·4858	—
	C	1·4863—59	—	1·4862—3	1·4862	1·4862
	Na	1·4887—7	—	1·4889—8	1·4888	1·4890
	Tl	1·4915—1	—	1·4915—6	1·4914	—
	F	1·4948—4	—	1·4947—8	1·4947	1·4946
	G	1·4992—2	—	1·4991—4	1·4992	1·4987
β. Vibrations parallel to symmetry axis.	Li	1·4901—898	1·4895—905	—	1·4900	—
	C	1·4905—2	1·4899—908	—	1·4904	1·4904
	Na	1·4931—29	1·4925—35	—	1·4930	1·4934
	Tl	1·4958—7	1·4952—62	—	1·4957	—
	F	1·4992—87	1·4984—95	—	1·4990	1·4993
	G	1·5037—5	1·5032—42	—	1·5036	1·5041
γ. Vibrations parallel to 1st median line.	Li	—	1·4957—65	1·4964—4	1·4963	—
	C	—	1·4962—9	1·4968—7	1·4967	1·4971
	Na	—	1·4989—97	1·4995—4	1·4994	1·4996
	Tl	—	1·5016—24	1·5022—3	1·5021	—
	F	—	1·5049—59	1·5055—5	1·5056	1·5056
	G	—	1·5099—105	1·5102—2	1·5102	1·5103

Mean of α, β, and γ for Na light = 1·4937.

It will be observed that the author's values agree very closely with those obtained by Perrot, who employed the method of total reflection, using the Soret refractometer. It is interesting and important that this should be so, for the following reason. Hitherto the method of minimum deviation with the aid of prisms has only been partially available, that is, as far as naturally formed prisms permitted (supplemented in the work of Topsoe and Christiansen by prisms ground on a glass plate by hand); consequently Perrot chose the method of total reflection, which requires only plates of the crystals. The author, being able with the aid of the cutting and grinding goniometer (*Phil. Trans.*, 1899, A, **192**, 457) to obtain with the greatest ease 60° prisms having each the theoretical orientation to afford two indices, even with salts of such complicated (monoclinic) symmetry as those of this series, has employed the method of minimum deviation, and it is highly satisfactory to have so admirable an example of the total reflection method with which to compare the results as is afforded by Perrot's careful measurements. The limitations imposed by hand-grinding only enabled Topsoe and Christiansen to prepare prisms affording the β index directly, and it has been shown that their values of α and γ indices are generally less accurate in consequence.

The following formula expresses the value of the intermediate refractive index β for any wave-length λ, corrected to a vacuum:

$$\beta = 1{\cdot}4784 + \frac{588\ 612}{\lambda^2} - \frac{2\ 356\ 900\ 000\ 000}{\lambda^4} + \ldots$$

The α indices are also reproduced by the formula if the constant 1·4784 is diminished by 0·0042, and the γ indices if the constant is increased by 0·0064.

Alteration of Refraction by Rise of Temperature.—Two of the prisms affording respectively α and β, and α and γ, were employed for determinations at 70°, and the results are embodied in the accompanying table.

Refractive Indices of Ammonium Zinc Sulphate at 70°.

Nature of light.	α.	β.	γ.
Li	1·4845	1·4883	1·4944
C	1·4849	1·4887	1·4948
Na......	1·4874	1·4914	1·4976
Tl	1·4902	1·4942	1·5003
F	1·4935	1·4975	1·5037

These values show a diminution from those for the ordinary temperature of, on the average, 0·0013 for α, 0·0016 for β, and 0·0019 for γ.

Axes of the Optical Ellipsoids.—These work out as under:

Axes of optical indicatrix: $\alpha:\beta:\gamma = 0·9972:1:1·0043$.
Axes of optical velocity ellipsoid: $\mathfrak{a}:\mathfrak{b}:\mathfrak{c} = 1·0028:1:0·9957$.

Molecular Optical Constants.—These values calculated with the aid of the density afforded by the suspension method, are as under:

Axis of optical indicatrix		α	β	γ
Specific refraction, $\frac{n^2-1}{(n^2+2)d} = \mathfrak{n}$	C	0·1487	0·1497	0·1514
	G	0·1520	0·1532	0·1549
Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = \mathfrak{m}$ ...	C	59·27	59·71	60·36
	G	60·62	61·07	61·74
Specific dispersion, $\mathfrak{n}_G - \mathfrak{n}_C$		0·0033	0·0035	0·0035
Molecular dispersion, $\mathfrak{m}_G - \mathfrak{m}_C$		1·35	1·36	1·38
Molecular refraction, $\frac{n-1}{d}M$...............	C	100·34	101·21	102·51

Optical Axial Angle.—Three good pairs of section plates were obtained by grinding, perpendicular to the first and second median lines. The rings were very small and the brushes exceptionally sharp and clearly defined. The measurements in α-bromonaphthalene were consequently remarkably delicate. The measurements of the angle in air, however, were rendered somewhat difficult on account of the large size of the angle; sections 1 and 3 afforded very trustworthy values of it, but section 2 was too narrow in comparison with its length to permit the brushes to emerge completely, owing to the necessity at the same time for some considerable thickness of section imposed by the feeble double refraction.

Determination of Apparent Angle in Air of Ammonium Zinc Sulphate.

Light.	Section 1.	Section 3.	Mean 2E.
Li	143°30′	143°55′	143°43′
C	143 39	144 13	143 56
Na.........	144 28	144 54	144 41
Tl	145 12	145 45	145 29
F	146 0	146 31	146 16

Determination of True Optic Axial Angle of Ammonium Zinc Sulphate.

Light.	No. of section perp. 1st median line.	Observed values of 2Ha.	No. of section perp. 2nd median line.	Observed values of 2Ho.	Calculated values of 2Va.	Mean value of 2Va.
Li......	1	69°55′	1*a*	88°10′	78°57′	78°57′
	2	69 50	2*a*	88 10	78 54	
	3	70 1	3*a*	88 13	79 0	
C	1	69 53	1*a*	88 8	78 57	78 58
	2	69 49	2*a*	88 6	78 55	
	3	69 58	3*a*	88 6	79 1	
Na ...	1	69 43	1*a*	87 50	78 58	79 0
	2	69 37	2*a*	87 44	78 58	
	3	69 42	3*a*	87 40	79 3	
Tl......	1	69 22	1*a*	87 18	79 0	79 2
	2	69 17	2*a*	87 12	79 0	
	3	69 25	3*a*	87 13	79 5	
F	1	68 55	1*a*	86 38	79 2	79 3
	2	68 50	2*a*	86 33	79 1	
	3	68 56	3*a*	86 32	79 6	

Murmann and Rotter found 141°45′ for the angle in air and 78°35′ for the true angle.

Perrot found 142°30′ for the apparent angle in red light, and 79°12′ for the true angle in the same colour.

Dispersion of the Median Lines.—Sections 1 and 3 were examined in toluene, the refractive index of which is very close to the mean index of the crystals. In both cases the first median line was found to be 10′ nearer to the morphological axis *a* for red lithium light than for greenish-blue F hydrogen light.

Effect of Rise of Temperature on the Optic Axial Angle.—On heating a section plate perpendicular to the first median line, the apparent angle in air is observed to diminish slightly. The following values were obtained with section 1 for the temperature of 75° (corrected for conduction of the crystal holder).

	2E at 75°.
For C light	138° 7′
,, Na ,, ...	138 42
,, Tl ,, ...	139 11

The diminution between 15° and 75° is thus seen to be about 6°.

After cooling 24 hours the angle for sodium light was found to be nearly a degree larger (145°20′) than it was before the heating.

Ammonium Magnesium Selenate, $(NH_4)_2Mg(SeO_4)_2,6H_2O$.

The result of an estimation of the magnesium in a sample of the crystals employed was as follows: 1·2081 grams of crystals afforded 0·3062 gram of magnesium pyrophosphate; this corresponds to 5·48 per cent. of magnesium, the theoretical percentage being 5·29.

Goniometry.

Ten crystals were chosen out of six specially good crops.

Ratio of axes: $a : b : c = 0{\cdot}7420 : 1 : 0{\cdot}4966$.

Axial angle: $\beta = 73°33'$.

Habit: prismatic along the prism zone, to tabular along the basal plane.

Forms observed: $b = \{010\}\infty \not{P} \infty$, $c = \{001\}oP$, $p = \{110\}\infty P$, $q = \{011\}\not{P}\infty$, $o' = \{\bar{1}11\} + \mathrm{P}$, $r' = \{\bar{2}01\} + 2P\!\!\!\!-\infty$.

The table on page 1149 shows the results of the measurements.

This salt readily yields perfectly transparent and very well formed crystals, which under certain circumstances may attain an inch in diameter, without exhibiting any appreciable distortion of the planeness of the faces.

Several of these large crystals, which were obtained by placing the crystallising vessels (small flat-bottomed beakers) inside a high rectangular glass case nearly a yard long, afforded excellent material for the preparation of section plates and prisms of such ample proportions as enabled them not only to be employed equally with the smaller ones for the optic axial angle measurements, but also rendered them admirable for the projection of the specially beautiful interference figures with the lantern polariscope.

Usually only four crystallising vessels were placed in the case at one time, each equidistant from the centre and a corner of the base. At the centre was placed a dish of oil of vitriol which, as the case was fairly tightly fitting on its plinth, absorbed the evaporated water vapour as fast as it was liberated. The base was covered with velvet to prevent conduction through the wood from the bottom of the crystallising vessels, and the case itself was further screened from draughts in the centre of the crystallising room, and thus sudden alterations of temperature avoided. The solutions so protected attained a considerable amount of supersaturation before depositing crystals, and the latter then grew uninterruptedly in a few days to the size already indicated, entirely under normal atmospheric pressure.

The crystals of this salt are, however, generally of a very simple character, no faces having been observed, with one imperfect exception, other than the six above-mentioned simple forms. The clinopinacoid *b*{010} is usually present, and its faces are frequently relatively large; they invariably afforded in the cases of the measured crystals excellent reflections of the signal. The orthopinacoid was never observed. The basal plane *c*{001} was frequently so largely developed as to impart to the crystal the tabular character exemplified in Fig. 8. Equally often, however, the faces of the basal plane were relatively less, and a prismatic character impressed on the crystal by the elongation of the faces of the primary prism *p*{110}, as shown in Fig. 9. The latter were particularly free in the case of this salt from the striation and distortion due to vicinal faces. In most instances the images obtained during the measurements were perfect.

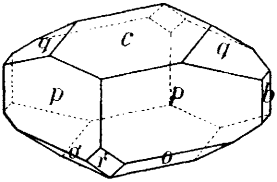

FIG. 8.

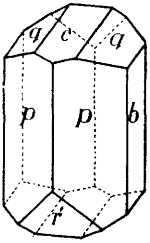

FIG. 9.

The faces of the basal plane often exhibited the vicinal face phenomenon, but the values of the angle *cq* were rendered quite trustworthy owing to the singular perfection of the faces of the clinodome *q*{011} and the brilliant definition of the images derived from them, symmetrically on either side of the basal plane. The relative development of the faces of the forms $r'\{\bar{2}01\}$ and *o*{111} varied as illustrated in the two figures. On one crystal a rough face of the form *s*{101} was observed, but the reflection from it was too imperfect for accurate allocation to the cross-wires.

Morphological Angles of Ammonium Magnesium Selenate.

Angle measured.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.
$ac = (100) : (001)$	—	—	—	73°33′	—
$as = (100) : (101)$	—	—	—	45 12	—
$sc = (101) : (001)$	—	—	—	28 21	—
$cr' = (001) : (\bar{2}01)$	18	64° 7′— 64°26′	64°15′	64 11	4′
$cs' = (001) : (\bar{1}01)$	—	—	—	38 22	—
$s'r' = (\bar{1}01) : (\bar{2}01)$	—	—	—	25 49	—
$r'a = (\bar{2}01) : (\bar{1}00)$	—	—	—	42 16	—
$r'c = (\bar{2}01) : (00\bar{1})$	18	115 37 —115 50	115 45	115 49	4
$ap = (100) : (110)$	—	—	—	35 26	—
$pp' = (110) : (120)$	—	—	—	19 28	—
$p'b = (120) : (010)$	—	—	—	35 6	—
$pb = (110) : (010)$	43	54 25 — 54 42	54 34	*	—
$pp = (110) : (1\bar{1}0)$	21	70 44 — 71 1	70 52	70 52	0
$cq = (001) : (011)$	38	25 22 — 25 37	25 29	*	—
$qb = (011) : (010)$	38	64 22 — 64 39	64 31	64 31	0
$ao = (100) : (111)$	—	—	—	48 21	—
$oq = (111) : (011)$	—	—	—	26 51	—
$aq = (100) : (011)$	—	—	—	75 12	—
$qo' = (011) : (\bar{1}11)$	—	—	—	34 38	—
$o'a = (\bar{1}11) : (\bar{1}00)$	—	—	—	70 10	—
$co = (001) : (111)$	—	—	—	33 54	—
$op = (111) : (110)$	—	—	—	42 46	—
$cp = (001) : (110)$	38	76 31 — 76 48	76 40	*	—
$po' = (110) : (11\bar{1})$	19	58 37 — 58 53	58 45	58 44	1
$o'c = (11\bar{1}) : (00\bar{1})$	19	44 28 — 44 43	44 36	44 36	0
$pc = (110) : (00\bar{1})$	38	103 11 —103 28	103 20	103 20	0
$bo = (010) : (111)$	—	—	—	70 35	—
$os = (111) : (101)$	—	—	—	19 25	—
$bo' = (010) : (\bar{1}11)$	6	65 13 — 65 19	65 16	65 16	0
$o's' = (\bar{1}11) : (\bar{1}01)$	—	—	—	24 44	—
$o'o' = (\bar{1}11) : (\bar{1}\bar{1}1)$	3	49 27 — 49 29	49 28	49 28	0
$sq = (101) : (011)$	—	—	—	37 24	—
$qp = (011) : (\bar{1}10)$	37	87 31 — 87 51	87 39	87 38	1
$ps = (\bar{1}10) : (\bar{1}0\bar{1})$	—	—	—	54 58	—
$pq = (\bar{1}10) : (0\bar{1}\bar{1})$	37	92 9 — 92 30	92 20	92 22	2
$s'q = (\bar{1}01) : (011)$	—	—	—	44 57	—
$qp = (011) : (110)$	38	62 40 — 62 54	62 46	62 46	0
$ps' = (110) : (10\bar{1})$	—	—	—	72 17	—
$pq = (110) : (0\bar{1}\bar{1})$	38	117 5 —117 24	117 14	117 14	0
$r'o' = (\bar{2}01) : (\bar{1}11)$	17	35 4 — 35 16	35 10	35 9	1
$o'p = (\bar{1}11) : (110)$	18	91 48 — 92 0	91 53	91 56	3
$pr' = (110) : (20\bar{1})$	36	52 49 — 53 1	52 55	52 55	0
$r'p = (\bar{2}01) : (110)$	35	126 58 —127 13	127 5	127 5	0

Total number of measurements : 555.

Topsöe and Christiansen (*loc. cit.*, p. 73) give $ac(\beta) = 73°23'$, $pp = (110):(1\bar{1}0) = 70°47'$, and $qq = (011:0\bar{1}1) = 50°55'$. Also for the axial ratio $a:b:c = 0·7414:1:0·4968$.

Cleavage.—The cleavage common to the series parallel to $r'\{\bar{2}01\}$ is excellently developed.

Volume.

Relative Density.

The pycnometer method:

Weight of salt employed.	Sp. gr. at 20°/4°.
4·1228	2·0562
3·7058	2·0593
6·7304	2·0556
5·7926	2·0566
Mean	2·0569

The suspension method:

		For 20°/4°.
For 16·3°/4°	2·0584	2·0577
For 17·5°/4°	2·0572	2·0567
For 18·4°/4°	2·0589	2·0586
For 16·1°/4°	2·0585	2·0577
	Mean......... ..	2·0577

The true value for 20°/4° is therefore taken as 2·058.

Topsöe (*Bull. Soc. Chim.*, 1873, **19**, 246) found the sp. gr. of a specimen 2·035.

Molecular Volume.—$\frac{M}{d} = \frac{451·56}{2·058} = 219·42.$

Topic Axes.—$\chi : \psi : \omega = 6·3299 : 8·5310 : 4·2365.$

Optics.

Orientation of Axes of Optical Ellipsoid.—The symmetry plane is the plane of the optic axes; the sign of the double refraction is positive.

Two section plates ground parallel to the symmetry plane gave the following extinction angles:

Section 1	....	16°15′	behind the normal to $c(001)$.
„ 2	....	16°13′	„ „ $c(001)$.
	Mean	16°14′	

Topsöe and Christiansen give for the same angle $[\mathfrak{a}:(001)]$, 17°7′.

This extinction direction is the second median line; it is nearly coincident with the vertical morphological axis *c*, being only 13′ in front of it. The first median line is similarly nearly normal to the orthopinacoid $a\{100\}$, and is inclined 16°14′ to the axis *a*. Both median lines thus lie in the obtuse angle of the morphological axes *ac*.

Refractive Indices.—Six particularly good prisms, each ground so as to afford two indices directly, gave the following results:

Refractive Indices of Ammonium Magnesium Selenate.

Index.	Nature of light.	Prisms 1 and 2.	Prisms 3 and 4.	Prisms 5 and 6.	Mean index.	Values of Topsöe and Christiansen.
α Vibrations parallel to second median line.	Li	1·5035—3	1·5033—3	—	1·5034	—
	C	1·5040—37	1·5037—7	—	1·5038	—
	Na	1·5072—0	1·5069—70	—	1·5070	1·5056
	Tl	1·5106—4	1·5103—2	—	1·5104	—
	F	1·5147—3	1·5144—3	—	1·5144	—
	G	1·5206—6	1·5205—3	—	1·5205	—
β Vibrations parallel to symmetry axis.	Li	1·5057—2	—	1·5058—6	1·5056	—
	C	1·5061—57	—	1·5062—1	1·5060	1·5046
	Na	1·5094—89	—	1·5097—3	1·5093	1·5075
	Tl	1·5127—3	—	1·5128—6	1·5126	—
	F	1·5167—3	—	1·5169—5	1·5166	1·5146
	G	1·5227—6	—	1·5229—6	1·5227	—
γ Vibrations parallel to first median line.	Li	—	1·5129—8	1·5136—3	1·5132	—
	C	—	1·5134—4	1·5140—36	1·5136	—
	Na	—	1·5166—7	1·5173—69	1·5169	1·5150
	Tl	—	1·5200—0	1·5205—3	1·5202	—
	F	—	1·5240—0	1·5248—1	1·5242	—
	G	—	1·5305—1	1·5309—5	1·5305	—

Mean of α, β, and γ for Na light $= 1{\cdot}5111$.

Topsöe and Christiansen's values, given in the last column, do not agree as well as usual with the author's values; only their β-values were directly determined. The disagreement would appear to be due to their salt containing admixed sulphate, for their value for the density of the salt has also been shown to be much too low.

The following formula represents the value of the β-index for any wave-length and corrected to a vacuum, absolutely as far as the green thallium line, and approximately beyond that :

$$\beta = 1{\cdot}4896 + \frac{830\ 626}{\lambda^2} - \frac{4\ 613\ 500\ 000\ 000}{\lambda^4} + \dots .$$

The α-indices are equally well reproduced by the formula if the constant 1·4896 is diminished by 0·0022, and the γ-indices if the constant is increased by 0·0076.

Alteration of Refraction by Rise of Temperature.—The refractive indices were determined at 70° with the aid of two of the prisms, furnishing respectively α and γ, and β and γ.

Refractive Indices of Ammonium Magnesium Selenate for 70°.

Nature of light.	α.	β.	γ.
Li	1·5025	1·5040	1·5116
C	1·5029	1·5044	1·5120
Na...	1·5062	1·5076	1·5153
Tl	1·5095	1·5108	1·5187
F	1·5135	1·5148	1·5227

These indices are lower than the ordinary temperature values by an average of 0·0009 for α, 0·0017 for β, and 0·0016 for γ.

Whilst the relative difference between β and γ remains substantially the same (0·0077), the separation of α and β becomes reduced to 0·0014. This relative approach of α and β indicates a considerable diminution of the optic axial angle with rise of temperature, and such will subsequently be shown to be the fact.

Axes of the Optical Ellipsoids.—

Axes of optical indicatrix :—$\alpha : \beta : \gamma$ = 0·9985 : 1 : 1·0050.

Axes of optical velocity ellipsoid :—$\mathfrak{a} : \mathfrak{b} : \mathfrak{c}$ = 1·0015 : 1 : 0·9950.

Molecular Optical Constants.—The calculated values of these constants, using the density as given by the suspension method, are as follows :

Axis of optical indicatrix		α.	β.	γ.
Specific refraction, $\frac{n^2-1}{(n^2+2)d} = \mathfrak{n}$	C	0·1438	0·1444	0·1462
	G	0·1478	0·1484	0·1502
Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = \mathfrak{m}$	C	64·95	65·19	66·01
	G	66·75	66·99	67·83
Specific dispersion, $\mathfrak{n}_G - \mathfrak{n}_C$		0·0040	0·0040	0·0040
Molecular dispersion, $\mathfrak{m}_G - \mathfrak{m}_C$		1·80	1·80	1·82
Molecular refraction, $\frac{n-1}{d}M$	C	110·54	111·02	112·69

Optic Axial Angle.—The results of measurements with the three pairs of section plates perpendicular to the two median lines are as follows :

Determination of Apparent Angle in Air of Ammonium Magnesium Selenate.

Light.	Section 1.	Section 2.	Section 3.	Mean 2E.
Li	87°52′	88°14′	88°31′	88°12′
C	87 50	88 13	88 30	88 11
Na	87 42	88 7	88 24	88 4
Tl	87 25	87 57	88 16	87 53
F	87 1	87 30	87 45	87 25

Determination of True Optic Axial Angle of Ammonium Magnesium Selenate.

Light.	No. of section perp. 1st median line.	Observed values of 2Ha.	No. of section perp. 2nd median line.	Observed values of 2Ho.	Calculated values of 2Va.	Mean value of 2Va.
Li......	1	49°46′	1*a*	108°54′	54°43′	54°57′
	2	49 46	2*a*	107 53	55 0	
	3	49 51	3*a*	107 38	55 8	
C	1	49 44	1*a*	108 46	54 42	54 55
	2	49 43	2*a*	107 48	54 58	
	3	49 47	3*a*	107 32	55 6	
Na ...	1	49 24	1*a*	108 20	54 32	54 47
	2	49 25	2*a*	107 22	54 50	
	3	49 29	3*a*	107 0	55 0	
Tl......	1	48 57	1*a*	107 51	54 16	54 33
	2	48 58	2*a*	106 57	54 34	
	3	49 5	3*a*	106 33	54 48	
F	1	48 16	1*a*	107 18	53 50	54 4
	2	48 17	2*a*	106 33	54 4	
	3	48 26	3*a*	106 14	54 18	

Topsöe and Christiansen give 85°56′ for the apparent and 53°44′ for the real optic axial angle for Na light.

Dispersion of the Median Lines.—Measurements in benzene, the refraction of which is nearly identical with the mean refraction of the crystals, indicated that the dispersion of the median lines is such that the first median line is situated 17′ nearer to the morphological axis *a* for Li light than for F light. As the angle between the morphological axis *a* and the normal to *a*(100) has been shown to be 16°27′ (the complement of β 73°33′), and the mean position of the first median line as afforded by the extinction determination to be 16°14′ from the axis *a* and in the obtuse angle of the axes *ac*, it follows that the first median line for F light is inclined 16°5′ to the axis *a* and for Li light 16°22′, and that for red light it is thus practically identical (within 5′) with the normal to the orthopinacoid *a*(100).

Effect of Rise of Temperature on the Optic Axial Angle.—Section 3 was investigated at 75° (corrected for conduction of crystal holder), with the following result :

2E at 75°.

Li	76°45′	Tl	75°50′
C..............	76 40	F..............	75 15
Na	76 15		

The optic axial angle is thus seen to diminish with rise of temperature, on the average about 12° for the interval 15—75°, and at the same time the dispersion is somewhat increased.

Ammonium Zinc Selenate, $(NH_4)_2Zn(SeO_4)_2,6H_2O$.

An estimation of zinc in a sample of the crystals employed gave the following result:—0·8028 gram of crystals yielded 0·1327 gram of zinc oxide; this corresponds to 13·26 per cent. of zinc, the calculated percentage being 13·14.

Goniometry.

Eleven crystals were selected in the manner already described, from six different crops.

Ratio of axes:—$a : b : c = 0·7409 : 1 : 0·5040$.

Axial angle: $\beta = 73°46'$.

Habit: prismatic along the prism zone, to thickly tabular along the basal plane.

Forms observed: $b = \{010\}\infty\not{P}\infty$, $c = \{001\}oP$, $p = \{110\}\infty P$, $p' = \{120\}\infty\grave{P}2$, $q = \{011\}\not{P}\infty$, $o' = \{\bar{1}11\}+P$, $r' = \{\bar{2}01\}+2\grave{P}\infty$.

The table on p. 1155 expresses the results of the measurements.

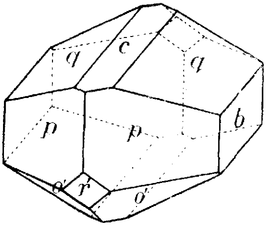

FIG. 10.

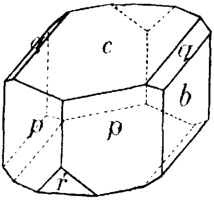

FIG. 11.

The preparation of perfect crystals of this salt proved more difficult than in the cases of the other three salts, owing to the tendency to opacity of the crystals of many of the crops. Out of the hundred or more crops prepared, however, an adequate number consisted of perfectly transparent crystals, and the best half-dozen were employed in the goniometrical measurements.

Crystals were observed of all the types illustrated in the various figures given for the other three salts, and in addition the two types represented in Figs. 10 and 11. The latter are both characterised by elongation along the axis of the zone [*bqc*], and merely differ in the relative development of the basal plane *c*{001} and the clinodome *q*{011}. The faces of the clinopinacoid *b*{010} were prominent in both, and excellent images were always obtained from the faces of this form and from those of the clinodome.

On several of the measured crystals the four faces of the relatively large primary prism *p*{110} afforded perfect reflections, single and

Morphological Angles of Ammonium Zinc Selenate.

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

Total number of measurements: 470.

quite satisfactory for the purpose of allocation to the cross-wires, and the values of the angle *bp* given in the table coincided with the mean values derived from these excellent faces alone. In other cases, the vicinal face phenomenon was observed, as was also the case in regard to 14 of the 22 faces of the basal plane present on the 11 measured crystals. The other 8 of the latter afforded single trustworthy images unaffected by the presence of any vicinal faces at exactly 90° to the perfect *b* images and equidistant from the excellent *q* images.

The faces of the orthodome $r'\{\bar{2}01\}$ were often particularly brilliant and relatively large, and the images reflected from them especially perfect. Also the hemipyramid $o'\{\bar{1}11\}$ was often represented by good plane faces almost as large as those of *r'*. Occasionally, however, crops were obtained which showed neither of these forms, or, if present, only as very minute faces.

On one crystal a good but small face of the prism $p'\{120\}$ was observed.

Topsöe and Christiansen give $ac(\beta) = 73°49'$, $pp = (110):(1\bar{1}0) = 70°55'$ and $qq = (011):(0\bar{1}1) = 51°52'$; also $a:b:c = 0{\cdot}7416 : 1 : 0{\cdot}5062$.

Cleavage.—There is an excellent cleavage parallel to $r'\{\bar{2}01\}$. Good images of the signal were obtained from the cleavage faces, within 2′ of the theoretical position for the *r'* plane.

Volume.

Relative Density.

The pycnometer method :

Weight of salt employed.	Sp. gr. at 20°/4°.
5·8146	2·2558
4·7318	2·2568
5·3778	2·2553
5·3587	2·2557
Mean......	2·2559

The suspension method :

		For 20°/4°.
For 18·9°/4°	2·2617	2·2614
For 19·3°/4°	2·2609	2·2607
For 14·0°/4°	2·2630	2·2617
For 16·7°/4°	2·2622	2·2615
	Mean............	2·2613

The value accepted for 20°/4° is therefore 2·261.

The value yielded by the suspension method in this case is more than usually higher than that afforded by the pycnometer method. This is doubtless due to the fact already referred to in the description of the crystals, namely, their frequent turbidity, which is probably owing to their greater tendency to the formation of cavities.

The value given by Topsöe (*Chem. Centr.*, 1873, 4, 78), 2·200, is obviously much too low, as was also his value for ammonium magnesium selenate.

Molecular Volume.— $\frac{M}{d} = \frac{492{\cdot}28}{2{\cdot}261} = 217{\cdot}73.$

Topic Axes :— $\chi : \psi : \omega = 6{\cdot}2742 : 8{\cdot}4684 : 4{\cdot}2681.$

Optics.

Orientation of Axes of Optical Ellipsoid.—The plane of the optic axes is that common to the whole series of salts, the symmetry plane. The sign of the double refraction is positive.

The following extinction angles were afforded by two section plates ground parallel to the symmetry plane :

Section 1 .... 12°44′ behind the normal to $c(001)$.
„ 2 .... 12°56′ „ „ $c(001)$.

Mean 12°50′

Topsöe and Christiansen give 13°4′ for the same angle.

This direction is that of the obtuse bisectrix of the optic axial angle, and it is thus situated (as $ac[\beta]=73°46'$) 3°24′ in front of the vertical morphological axis *c*. The first median line is inclined 12°50′ to the morphological axis *a*, and, like the second median line, lies also in the obtuse morphological axial angle *ac*.

Refractive Indices.—The results with six excellent ground prisms follow.

Refractive Indices of Ammonium Zinc Selenate.

Index.	Nature of light.	Prisms 1 and 2.	Prisms 3 and 4.	Prisms 5 and 6.	Mean index.	Topsöe and Christiansen's values.
α. Vibrations parallel to 2nd median line.	Li	1·5198—201	1·5202—2	—	1·5201	—
	C	1·5204—8	1·5207—5	—	1·5206	—
	Na	1·5237—40	1·5242—2	—	1·5240	1·5233
	Tl	1·5270—4	1·5275—4	—	1·5273	—
	F	1·5313—8	1·5317—7	—	1·5316	—
	G	1·5377—81	1·5382—2	—	1·5381	—
β. Vibrations parallel to symmetry axis.	Li	1·5258—61	—	1·5262—59	1·5260	—
	C	1·5263—6	—	1·5268—4	1·5265	1·5259
	Na	1·5299—302	—	1·5301—0	1·5300	1·5292
	Tl	1·5331—4	—	1·5336—4	1·5334	—
	F	1·5376—9	—	1·5380—76	1·5378	1·5366
	G	1·5440—3	—	1·5445—4	1·5443	—
γ. Vibrations parallel to 1st median line.	Li	—	1·5345—4	1·5344—2	1·5344	—
	C	—	1·5350—49	1·5350—47	1·5349	—
	Na	—	1·5385—5	1·5385—3	1·5385	1·5372
	Tl	—	1·5421—19	1·5420—18	1·5420	—
	F	—	1·5464—2	1·5464—3	1·5463	—
	G	—	1·5530—29	1·5530—27	1·5529	—

Mean of α, β, and γ for sodium light = 1·5308.

Similar remarks apply to the disagreement of the author's values and those of Topsöe and Christiansen as in the case of ammonium magnesium selenate, but the disagreement is in this instance less pronounced.

The β index, corrected to a vacuum (correction $= +0{\cdot}0004$) for any wave-length λ, is accurately represented by the following formula as far as the green thallium ray, and approximately beyond that part of the spectrum:

$$\beta = 1{\cdot}5080 + \frac{964\,040}{\lambda^2} - \frac{6\,471\,000\,000\,000}{\lambda^4} + \ldots$$

The α indices are also afforded by the formula if the constant 1·5080 is diminished by 0·0060, and the γ indices if the constant is increased by 0·0085.

Alteration of Refraction by Rise of Temperature.—The indices were redetermined at 70° with the aid of two of the prisms furnishing respectively α and β and α and γ.

Refractive Indices of Ammonium Zinc Selenate for 70°.

Nature of light.	α.	β.	γ.
Li	1·5189	1·5246	1·5325
C	1·5194	1·5251	1·5330
Na	1·5229	1·5286	1·5367
Tl	1·5265	1·5321	1·5403
F	1·5308	1·5364	1·5446

These values are lower than those for the ordinary temperature by an average of 0·0011 for α, 0·0014 for β, and 0·0018 in the case of γ.

Axes of the Optical Ellipsoids.

Axes of optical indicatrix: $\alpha : \beta : \gamma = 0{\cdot}9961 : 1 : 1{\cdot}0056$.

Axes of optical velocity ellipsoid: $\mathfrak{a} : \mathfrak{b} : \mathfrak{c} = 1{\cdot}0039 : 1 : 0{\cdot}9945$.

Molecular Optical Constants.—Employing the density as afforded by the suspension method, the following are these constants:

Axis of optical indicatrix.		α.	β.	γ.
Specific refraction, $\frac{n^2-1}{(n^2+2)d} = \mathfrak{n}$.........	C	0·1346	0·1359	0·1377
	G	0·1384	0·1397	0·1415
Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = \mathfrak{m}$...	C	66·26	66·88	67·77
	G	68·11	68·76	69·66
Specific dispersion, $\mathfrak{n}_G - \mathfrak{n}_C$....................		0·0038	0·0038	0·0038
Molecular dispersion, $\mathfrak{m}_G - \mathfrak{m}_C$		1·85	1·88	1·89
Molecular refraction, $\frac{n-1}{d}M$	C	113·35	114·63	116·46

Optic Axial Angle.—Three pairs of section-plates perpendicular to the two median lines were prepared as usual with the aid of the cutting and grinding goniometer. The angle in air is so large, however, and at the same time the double refraction relatively so feeble, that only such section-plates perpendicular to the first median line as are of very considerable width (compared with the thickness of about two millimetres essential for the production of small rings and sharp brushes) exhibit the axes emerging in air. Such large plates require large crystals, and after many attempts one was at last obtained sufficiently large and perfect to enable such a section to be cut and ground. The values of 2E given in the following table were obtained with this exceptionally fine section:

Apparent Angle in Air of Ammonium Zinc Selenate.

Light.	2E.
Li	167°30′
C	167 50
Na	170 0
Tl	172 0
F	174 30

All the six sections afforded very good rings and brushes when immersed in α-bromonaphthalene; in F light the diameter of the innermost rings was only about an apparent millimetre, so that the delicacy of the measurements of 2Ha and 2Ho was quite remarkable, and enabled the exceptionally small dispersion of the optic axes, $2Va_{F \sim Li}$, to be determined with certainty.

Determination of True Optic Axial Angle of Ammonium Zinc Selenate.

Light.	No. of section perp. 1st median line.	Observed values of 2Ha.	No. of section perp. 2nd median line.	Observed values of 2Ho.	Calculated values of 2Va.	Mean value of 2Va.
Li	1	74°31′	1*a*	88° 1′	82° 8′	82° 5′
	2	74 35	2*a*	88 9	82 7	
	3	74 34	3*a*	88 23	81 59	
C	1	74 30	1*a*	88 0	82 8	82 5
	2	74 34	2*a*	88 7	82 8	
	3	74 32	3*a*	88 19	82 0	
Na	1	74 14	1*a*	87 35	82 10	82 7
	2	74 18	2*a*	87 40	82 10	
	3	74 12	3*a*	87 51	82 1	
Tl	1	73 58	1*a*	87 12	82 12	82 9
	2	74 0	2*a*	87 13	82 12	
	3	73 54	3*a*	87 25	82 2	
F	1	73 32	1*a*	86 38	82 13	82 10
	2	73 37	2*a*	86 43	82 14	
	3	73 29	3*a*	86 52	82 3	

Topsöe and Christiansen give 81°22′ for 2Va. For 2E they give 141°20′ in the text and 171°20′ in the concluding table; the latter figure is doubtless the correct one, for it agrees fairly with the author's value.

Dispersion of the Median Lines.—Measurements of optic axial angle were made for lithium and F light with the sections perpendicular to the first median line immersed in chlorobenzene, the refractive index of which for sodium light is 1·5248, slightly lower than the mean index (1·5308) of the crystals, and subsequently in methyl salicylate, the index of which for sodium light is 1·5360, to the same extent slightly higher than the mean refraction of the crystals. Both series indicated that the first median line is so dispersed that it lies 12′ nearer to the morphological axis *a* for lithium light than for F light.

Effect of Rise of Temperature on the Optic Axial Angle.—A series of measurements were carried out at 80° with the large section (section 3 in the table), which alone enabled 2E to be accurately determined. After very slow heating and attaining constancy at 80° (corrected for conduction of holder) for half an hour, the following values were obtained:

Nature of light.	2E at 80°.
C	151°46′
Na	153 10
Tl	154 40

The apparent angle in air is thus found to diminish by about 16½° on heating the crystal from 15° to 80°. It was also observed that the first median line moved nearer to the morphological axis *a* as the temperature rose, for the optic axial movement appeared to be chiefly on the part of one of the hyperbolic brushes, that corresponding to the optic axis lying in the obtuse angle of the crystallographic axes *ac*, the other remaining almost stationary.

Redetermination of Density

of analogous salts containing potassium, rubidium, and cæsium by the suspension method.

Potassium Magnesium Sulphate, $K_2Mg(SO_4)_2,6H_2O$.

		For 20°/4°.
For 14·1°/4°................	2·0341	2·0329
,, 14·9°/4°................	2·0351	2·0341
,, 16·2°/4°................	2·0350	2·0342
,, 16·7°/4°................	2·0341	2·0334
	Mean	2·0337

The value accepted therefore for 20°/4° is 2·034.

The result formerly obtained for the powdered salt was 2·0277, and the highest of the individual values 2·0282.

Molecular Volume.—$\frac{M}{d} = \frac{399{\cdot}84}{2{\cdot}034} = 196{\cdot}58$.

Topic Axes.—$\chi : \psi : \omega = 6{\cdot}0711 : 8{\cdot}1899 : 4{\cdot}0892$.

Rubidium Magnesium Sulphate, $Rb_2Mg(SO_4)_2,6H_2O$.

		For 20°/4°
For 13°/4°	2·3880	2·3863
,, 12·4°/4°.....	2·3878	2·3860
,, 13°/4°	2·3877	2·3860
,, 12·8°/4°......	2·3870	2·3853
	Mean...........	2·3859

Accepted value for 20°/4°, 2·386.

The result previously published for the powdered salt was 2·3822, and the highest of the individual values 2·3856.

Molecular Volume.—$\frac{M}{d} = \frac{491{\cdot}94}{2{\cdot}386} = 206{\cdot}18$.

Topic Axes.—$\chi : \psi : \omega = 6{\cdot}1803 : 8{\cdot}3518 : 4{\cdot}1550$.

Cæsium Magnesium Sulphate, $Cs_2Mg(SO_4)_2,6H_2O$.

		For 20°/4°.
For 13·7°/4°.................	2·6784	2·6767
,, 13·6°/4°.................	2·6770	2·6753
,, 13·8°/4°..........	2·6782	2·6765
,, 12·4°/4°.................	2·6775	2·6755
	Mean...........	2·6760

The previous result for the powdered salt was 2·6704, and the highest of the individual values 2·6728.

Molecular Volume.—$\frac{M}{d} = \frac{585{\cdot}94}{2{\cdot}676} = 218{\cdot}96$.

Topic Axes.—$\chi : \psi : \omega = 6{\cdot}2608 : 8{\cdot}6012 : 4{\cdot}2541$.

Potassium Zinc Sulphate, $K_2Zn(SO_4)_2,6H_2O$.

		For 20°/4°.
For 14°/4°	2·2468	2·2454
,, 14·8°/4°.........	2·2472	2·2460
,, 15°/4°	2·2465	2·2454
,, 15·2°/4°.................	2·2474	2·2463
	Mean...........	2·2458

Accepted value for 20°/4° : 2·246

The former result for the powdered salt was 2·2413, and the highest of the individual values 2·2426.

Molecular Volume.—$\frac{M}{d} = \frac{440\cdot56}{2\cdot246} = 196\cdot16$.

Topic Axes.—$\chi : \psi : \omega = 6\cdot0462 : 8\cdot1562 : 4\cdot1141$.

Rubidium Zinc Sulphate, $Rb_2Zn(SO_4)_2,6H_2O$.

		For 20°/4°.
For 13·3°/4°	2·5924	2·5907
,, 13·8°/4°	2·5924	2·5908
,, 14·4°/4°	2·5920	2·5905
,, 13·7°/4°	2·5916	2·5900
	Mean	2·5905

Accepted value for 20°/4°: 2·591.

The previous result for the powder was 2·584, and the highest of the individual values 2·5888.

Molecular Volume.—$\frac{M}{d} = \frac{532\cdot66}{2\cdot591} = 205\cdot58$.

Topic Axes.—$\chi : \psi : \omega = 6\cdot1436 : 8\cdot3326 : 4\cdot1754$.

Cæsium Zinc Sulphate, $Cs_2Zn(SO_4)_2,6H_2O$.

		For 20°/4°.
For 16°/4°	2·8767	2·8755
,, 14°/4°	2·8761	2·8744
,, 14·1°/4°	2·8777	2·8760
,, 14°/4°	2·8771	2·8754
	Mean	2·8753

Accepted value for 20°/4°: 2·875.

The former result for the powder was 2·8670, and the highest individual value 2·8707.

Molecular Volume.—$\frac{M}{d} = \frac{626\cdot66}{2\cdot875} = 217\cdot97$.

Topic Axes.—$\chi : \psi : \omega = 6\cdot2415 : 8\cdot5808 : 4\cdot2561$.

Potassium Magnesium Selenate, $K_2Mg(SeO_4)_2,6H_2O$.

		For 20°/4°.
For 17·9°/4°	2·3642	2·3637
,, 18·4°/4°	2·3659	2·3655
,, 19·8°/4°	2·3634	2·3634
,, 19·1°/4°	2·3656	2·3654
	Mean	2·3645

Accepted value for 20°/4°: 2·365.

The previous result for the powder was 2·3630, and the highest of the individual values 2·3634.

Molecular Volume.—$\frac{M}{d} = \frac{493{\cdot}4}{2{\cdot}365} = 208{\cdot}63$.

Topic Axes.—$\chi : \psi : \omega = 6{\cdot}2124 : 8{\cdot}2998 : 4{\cdot}1756$.

Rubidium Magnesium Selenate, $Rb_2Mg(SeO_4)_2,6H_2O$.

		For 20°/4°.
For 17·9°/4°.................	2·6863	2·6857
,, 18°/4°	2·6827	2·6822
,, 19·2°/4°......	2·6832	2·6830
,, 18·5°/4°.................	2·6842	2·6838
	Mean...........	2·6837

Accepted value for 20°/4°: 2·684.

The former result for the powdered crystals was 2·6805, and the highest individual value 2·6808.

Molecular Volume.—$\frac{M}{d} = \frac{585{\cdot}5}{2{\cdot}684} = 218{\cdot}15$.

Topic Axes.—$\chi : \psi : \omega = 6{\cdot}2885 : 8{\cdot}4705 : 4{\cdot}2445$.

Cæsium Magnesium Selenate, $Cs_2Mg(SeO_4)_2,6H_2O$.

		For 20°/4°.
For 17·2°/4°......	2·9398	2·9390
,, 17·6°/4°.................	2·9402	2·9395
,, 17·8°/4°.	2·9396	2·9390
,, 18·7°/4°.................	2·9394	2·9390
	Mean...........	2·9391

Accepted value for 20°/4°: 2·939.

The previous result for the powdered salt was 2·9388, and the highest individual value 2·9391.

Molecular Volume.—$\frac{M}{d} = \frac{679{\cdot}5}{2{\cdot}939} = 231{\cdot}20$.

Topic Axes.—$\chi : \psi : \omega = 6{\cdot}3807 : 8{\cdot}7239 : 4{\cdot}3270$.

Potassium Zinc Selenate, $K_2Zn(SeO_4)_2,6H_2O$.

		For 20°/4°.
For 17·9°/4°........	2·5575	2·5570
,, 19°/4°	2·5584	2·5581
,, 19·2°/4°......	2·5587	2·5585
,, 18°/4°	2·5587	2·5582
	Mean...........	2·5580

The previous value for 20°/4° for the powdered crystals was 2·5537, and the highest individual value 2·5546.

Molecular Volume.—$\frac{M}{d} = \frac{534{\cdot}12}{2{\cdot}558} = 208{\cdot}80$.

Topic Axes.—$\chi : \psi : \omega = 6{\cdot}1812 : 8{\cdot}2880 : 4{\cdot}2045$.

Rubidium Zinc Selenate, $Rb_2Zn(SeO_4)_2,6H_2O$.

		For 20°/4°.
For 18°/4°	2·8692	2·8686
,, 18°/4°	2·8694	2·8688
,, 18·6°/4°	2·8670	2·8666
,, 18·6°/4°	2·8666	2·8662
	Mean	2·8676

Accepted value for 20°/4°: 2·868.

The former result for the powdered crystals was 2·8604, and the highest individual value 2·8611. The crystals of this salt showed a decided tendency to opacity, a sign of internal cavities, which probably accounts for the somewhat larger difference than usual, the new determinations having been made with the particularly clear, small crystals used in the goniometrical measurements.

Molecular Volume.—$\frac{M}{d} = \frac{626{\cdot}22}{2{\cdot}868} = 218{\cdot}35$.

Topic Axes.—$\chi : \psi : \omega = 6{\cdot}2913 : 8{\cdot}4662 : 4{\cdot}2492$.

Cæsium Zinc Selenate, $Cs_2Zn(SeO_4)_2,6H_2O$.

		For 20°/4°.
For 15·9°/4°	3·1211	3·1198
,, 15·8°/4°	3·1220	3·1207
,, 17·4°/4°	3·1214	3·1206
,, 16·2°/4°	3·1219	3·1207
	Mean	3·1205

Accepted value for 20°/4°: 3·121.

The previous result for the powder was 3·1153, and the highest value obtained 3·1175.

Molecular Volume.—$\frac{M}{d} = \frac{720{\cdot}22}{3{\cdot}121} = 230{\cdot}77$.

Topic Axes.—$\chi : \psi : \omega = 6{\cdot}3710 : 8{\cdot}7106 : 4{\cdot}3300$.

Comparison of Results

with those previously obtained for analogous salts containing potassium, rubidium, and cæsium (compare Trans., 1893, **63**, 337 and 1896, **69**, 344; also *Proc. Roy. Soc.*, 1900, **67**, 58, and *Phil. Trans.*, 1901, A, **197**, 255).

Morphology.

Habit.—No characteristic habit has been observed for the crystals of the ammonium salts; every variety has been found, from that which distinguishes the potassium salts (stout primary prism with large basal plane) to that proper to the cæsium salts (clinodome-prism with narrow basal plane). A large proportion of crystals, however, showed the intermediate habit (primary prism, basal plane, and clinodome more or less equally developed) exhibited by the rubidium salts.

Axial Ratios.—These are compared in the following table:

Morphological Axial Ratios.

Salt.	Ratios of Axes. $a : b : c$
Potassium magnesium sulphate	0·7413 : 1 : 0·4993
Rubidium ,, ,,	0·7400 : 1 : 0·4975
Ammonium ,, ,,	0·7400 : 1 : 0·4918
Cæsium ,, ,,	0·7279 : 1 : 0·4946
Potassium zinc sulphate	0·7413 : 1 : 0·5044
Rubidium ,, ,,	0·7373 : 1 : 0·5011
Ammonium ,, ,,	0·7368 : 1 : 0·4997
Cæsium ,, ,,	0·7274 : 1 : 0·4960
Potassium magnesium selenate	0·7485 : 1 : 0·5031
Rubidium ,, ,,	0·7424 : 1 : 0·5011
Ammonium ,, ,,	0·7420 : 1 : 0·4966
Cæsium ,, ,,	0·7314 : 1 : 0·4960
Potassium zinc selenate	0·7458 : 1 : 0·5073
Rubidium ,, ,,	0·7431 : 1 : 0·5019
Ammonium ,, ,,	0·7409 : 1 : 0·5040
Cæsium ,, ,,	0·7314 : 1 : 0·4971

The principal fact indicated by the table is that the ratios of the ammonium salts are so similar to those of the analogous potassium, rubidium, and cæsium salts that true isomorphism undoubtedly exists. In the case of the ratio $a:b$, the value for the ammonium salt is almost identical with that for the rubidium salt. In the case of the ratio $c:b$, no rule obtains, but in three of the groups the value for the ammonium salt lies between the values for the potassium and cæsium salts, whilst in the magnesium sulphate group the value for the ammonium salt lies just outside those limits.

Monoclinic Axial Angle.—The following table exhibits the values of this fundamental angle [complement of $ac=(100):(001)$] for the various salts.

Values of Axial Angle β.

For KMg sulphate	104°48′	For KMg selenate	104°18′
,, RbMg ,,	105 59	,, RbMg ,,	105 14
,, CsMg ,,	107 6	,, CsMg ,,	106 17
,, AmMg ,,	107 6	,, AmMg ,,	106 27
,, KZn ,,	104 48	,, KZn ,,	104 12
,, RbZn ,,	105 53	,, RbZn ,,	105 16
,, CsZn ,,	107 1	,, CsZn ,,	106 11
,, AmZn ,,	106 52	,, AmZn ,,	106 14

Comparison of the Angular Magnitudes.

Angle.	KMg sulphate.	RbMg sulphate.	CsMg sulphate.	AmMg sulphate.	KZn sulphate.	RbZn sulphate.	CsZn sulphate.	AmZn sulphate.
$ac = (100) : (001)$	75°12′	74° 1′	72°54′	72°54′	75°12′	74° 7′	72°59′	73° 8′
$as = (100) : (101)$	46 8	45 25	44 28	44 54	45 56	45 16	44 28	44 40
$sc = (101) : (001)$	29 4	28 36	28 26	28 0	29 16	28 51	28 31	28 28
$cr' = (001) : (\bar{2}01)$	63 17	64 2	65 10	64 25	63 38	64 20	65 15	64 56
$cs' = (001) : (\bar{1}01)$	38 12	38 25	39 3	38 19	38 32	38 45	39 9	38 55
$s'r' = (\bar{1}01) : (\bar{2}01)$	25 5	25 37	26 7	26 6	25 6	25 35	26 6	26 1
$r'a = (\bar{2}01) : (\bar{1}00)$	41 31	41 57	41 56	42 41	41 10	41 33	41 46	41 56
$ap = (100) : (110)$	35 38	35 26	34 50	35 16	35 37	35 22	34 51	35 13
$pp' = (110) : (120)$	19 28	19 28	19 28	19 28	19 28	19 28	19 28	19 28
$p'b = (120) : (010)$	34 54	35 6	35 42	35 16	34 55	35 10	35 41	35 19
$pb = (110) : (010)$	54 22	54 34	55 10	54 44	54 23	54 38	55 9	54 47
$cq = (001) : (011)$	25 48	25 35	25 17	25 11	25 58	25 44	25 23	25 33
$qb = (011) : (010)$	64 12	64 25	64 43	64 49	64 2	64 16	64 37	64 27
$ao = (100) : (111)$	49 18	48 35	47 35	48 0	49 10	48 27	47 37	47 52
$oq = (111) : (011)$	27 24	27 2	27 0	26 34	27 34	27 17	27 3	26 57
$aq = (100) : (011)$	76 42	75 37	74 35	74 34	76 44	75 44	74 40	74 49
$qo' = (011) : (\bar{1}11)$	34 27	34 40	35 17	34 38	34 42	34 55	35 21	35 5
$o'a = (\bar{1}11) : (\bar{1}00)$	68 51	69 43	70 8	70 48	68 34	69 21	69 59	70 6
$co = (001) : (111)$	34 41	34 9	33 49	33 33	34 54	34 24	33 54	33 57
$op = (111) : (110)$	43 20	42 53	42 13	42 34	43 7	42 42	42 12	42 20
$cp = (001) : (110)$	78 1	77 2	76 2	76 7	78 1	77 6	76 6	76 17
$po' = (110) : (11\bar{1})$	57 35	58 21	58 52	59 22	57 14	57 59	58 42	58 38
$o'c = (11\bar{1}) : (00\bar{1})$	44 24	44 37	45 6	44 31	44 45	44 55	45 12	45 5
$bo = (010) : (111)$	70 12	70 30	70 53	70 43	70 5	70 24	70 51	70 39
$os = (111) : (101)$	19 48	19 30	19 7	19 17	19 55	19 36	19 9	19 21
$bo' = (010) : (\bar{1}11)$	65 23	65 18	65 21	65 22	65 13	65 13	65 19	65 9
$o's' = (\bar{1}11) : (\bar{1}01)$	24 37	24 42	24 39	24 38	24 47	24 47	24 41	24 51
$sq = (101) : (011)$	38 6	37 38	37 20	36 58	38 21	37 54	37 27	37 31
$qp = (011) : (\bar{1}10)$	86 11	87 15	88 32	88 22	86 5	87 7	88 24	88 0
$ps = (\bar{1}10) : (\bar{1}0\bar{1})$	55 43	55 7	54 8	54 40	55 34	54 59	54 9	54 29
$s'q = (\bar{1}01) : (011)$	44 58	45 2	45 24	44 46	45 19	45 22	45 31	45 25
$qp = (011) : (110)$	63 52	63 5	62 28	62 26	63 47	63 6	62 29	62 27
$ps' = (110) : (10\bar{1})$	71 10	71 53	72 8	72 48	70 54	71 32	72 0	72 8
$r'o' = (\bar{2}01) : (\bar{1}11)$	34 35	35 0	35 18	35 17	34 42	35 1	35 19	35 22
$o'p = (\bar{1}11) : (110)$	92 54	92 18	92 20	91 36	93 2	92 36	92 25	92 4
$pr' = (110) : (20\bar{1})$	52 31	52 42	52 22	53 7	52 16	52 23	52 16	52 34

Comparison of the Angular Magnitudes.

Angle.	KMg selenate.	RbMg selenate.	CsMg selenate.	AmMg selenate.	KZn selenate.	RbZn selenate.	CsZn selenate.	AmZn selenate.
ac = (100) : (001)	75°42′	74°46′	73°43′	73°33′	75°48′	74°44′	73°49′	73°46′
as = (100) : (101)	46 30	45 50	45 3	45 12	46 19	45 47	45 3	45 1
sc = (101) : (001)	29 12	28 56	28 40	28 21	29 29	28 57	28 46	28 45
cr′ = (001) : $(\bar{2}01)$	62 53	63 37	64 31	64 11	63 12	63 42	64 36	64 36
cs′ = (001) : $(\bar{1}01)$	38 1	38 20	38 46	38 22	38 22	38 24	38 52	38 52
s′r′ = $(\bar{1}01)$: $(\bar{2}01)$	24 52	25 17	25 45	25 49	24 50	25 18	25 44	25 44
r′a = $(\bar{2}01)$: $(\bar{1}00)$	41 25	41 37	41 46	42 16	41 0	41 34	41 35	41 38
ap = (100) : (110)	35 55	35 38	35 6	35 26	35 52	35 38	35 4	35 26
pp′ = (110) : (120)	19 28	19 28	19 28	19 28	19 28	19 28	19 28	19 28
p′b = (120) : (010)	34 37	34 54	35 26	35 6	34 40	34 54	35 28	35 6
pb = (110) : (010)	54 5	54 22	54 54	54 34	54 8	54 22	54 56	54 34
cq = (001) : (011)	26 0	25 47	25 29	25 29	26 8	25 50	25 31	25 50
qb = (011) : (010)	64 0	64 13	64 31	64 31	63 52	64 10	64 29	64 10
ao = (100) : (111)	49 43	49 3	48 11	48 21	49 35	48 59	48 12	48 15
oq = (111) : (011)	27 27	27 16	27 9	26 51	27 42	27 19	27 14	27 11
aq = (100) : (011)	77 10	76 19	75 20	75 12	77 17	76 18	75 26	75 26
qo′ = (011) : $(\bar{1}11)$	34 16	34 34	35 0	34 38	34 31	34 37	35 6	35 0
o′a = $(\bar{1}11)$: $(\bar{1}00)$	68 34	69 7	69 40	70 10	68 12	69 5	69 28	69 34
co = (001) : (111)	34 54	34 33	34 7	33 54	35 11	34 34	34 13	34 20
op = (111) : (110)	43 34	43 7	42 37	42 46	43 21	43 5	42 36	42 30
cp = (001) : (110)	78 28	77 40	76 44	76 40	78 32	77 39	76 49	76 50
po′ = (110) : $(11\bar{1})$	57 13	57 45	58 24	58 44	56 50	57 43	58 14	58 4
o′c = $(11\bar{1})$: $(00\bar{1})$	44 19	44 35	44 52	44 36	44 38	44 38	44 57	45 6
bo = (010) : (111)	69 57	70 14	70 39	70 35	69 51	70 13	70 37	70 23
os = (111) : (101)	20 3	19 46	19 21	19 25	20 9	19 47	19 23	19 37
bo′ = $(0\bar{1}0)$: $(\bar{1}11)$	65 16	65 15	65 22	65 16	65 10	65 14	65 22	65 3
o′s′ = $(\bar{1}11)$: $(\bar{1}01)$	24 44	34 45	24 38	24 44	24 50	24 46	24 38	24 57
sq = (101) : (011)	38 19	38 0	37 37	37 24	38 36	38 2	37 43	37 54
qp = (011) : $(\bar{1}10)$	85 34	86 29	87 42	87 38	85 26	86 30	87 37	87 16
ps = $(\bar{1}10)$: $(\bar{1}0\bar{1})$	56 7	55 31	54 41	54 58	55 58	55 28	54 40	54 50
s′q = $(\bar{1}01)$: (011)	44 55	45 4	45 16	44 57	45 15	45 8	45 21	45 31
qp = (011) : (110)	64 5	63 32	62 58	62 46	64 7	63 30	63 5	62 46
ps′ = (110) : $(10\bar{1})$	71 0	71 24	71 46	72 17	70 38	71 22	71 34	71 43
r′o′ = $(\bar{2}01)$: $(\bar{1}11)$	34 30	34 48	35 3	35 9	34 33	34 49	35 2	35 14
o′p = $(\bar{1}11)$: (110)	92 54	92 37	92 34	91 56	93 10	92 39	92 43	92 17
pr′ = (110) : $(20\bar{1})$	52 36	52 35	52 23	52 55	52 17	52 32	52 15	52 29

It will appear from the second table on p. 1165 that the monoclinic angle β for the crystals of each ammonium salt is very nearly identical with that of the crystals of the analogous cæsium salt. This angle is the obtuse angle between the crystallographic axes a and c. The axis b is the symmetry axis at right angles to the plane of symmetry containing a and c.

Morphological Angles.—The principal angles between the faces of the crystals of the sixteen salts are tabulated on the two preceding pages. An analysis of the tables reveals the following facts.

Out of 36 angles compared, the alteration of angle brought about by replacing potassium by ammonium occurs in the same direction as that produced by replacing potassium by rubidium or cæsium, in 34 cases in each of the two double sulphate groups, and in 33 and 32 cases respectively in the magnesium and zinc double selenate groups. In the exceptions, the changes are extremely small.

Hence, in general, the change of angle when ammonium replaces potassium is in the same direction (that is, greater or smaller) as when that metal is replaced by rubidium or cæsium.

The amount of the change is generally larger than that which accompanies the replacement of potassium by rubidium, and in a large proportion of angles it is either approximately the same as when cæsium replaces potassium or is in excess of that amount.

These facts will be rendered clearer by the following statistical analysis:

Analysis of Comparison of 36 *Angles.*

Group.	No. in which change is in same direction as on replacing K by Rb or Cs.	No. of those in col. 2 in which change is greater than for replacement of K by Rb.	No. of those in col. 3 in which value of angle lies		
			Between values for Rb and Cs salts, but nearer to Rb.	Between values for Rb and Cs salts, but nearer to Cs.	Outside value for Cs salt.
Mg sulphate series	34	28	6	9	13
Zn ,, ,,	34	31	5	18	8
Mg selenate ,,	33	31	6	10	15
Zn ,, ,,	32	29	6	11	12

It will next be useful to compare the average and maximum amounts of angular change, irrespective of sign, that is, of the direction of the change. This is done in the following table.

Group	Average change for replacement of K by			Maximum change for replacement of K by		
	Rb.	Cs.	NH_4.	Rb.	Cs.	NH_4.
Mg sulphate series	29′	58′	56′	71′	141′	138′
Zn ,, ,, ...	26	56	50	65	139	124
Mg selenate ,, ...	23	52	53	56	128	129
Zn ,, ,, ...	27	52	49	64	131	122

It will be observed that both the average change and the maximum change for the replacement of potassium by ammonium is approximately equal to that which accompanies the replacement of potassium by cæsium, and this again is about double that due to the replacement of potassium by rubidium. The latter is a new and important fact as regards the relations of potassium, rubidium, and cæsium. It did not occur to the author in compiling the memoir on the double salts containing those metals to compare the average change, but only the individual changes, which do not show the relationship so clearly, especially the direct proportionality between change of angle and of atomic weight.

Volume.

Relative Densities.—The densities as afforded by the suspension method for the whole sixteen salts are set out in the next table.

	Sp. gr. at 20°/4°.		Sp. gr. at 20°/4°.
AmMg sulphate	1·723	AmMg selenate	2·058
KMg ,, ...	2·034	KMg ,, ...	2·365
RbMg ,, ...	2·386	RbMg ,, ...	2·684
CsMg ,, ...	2·676	CsMg ,, ...	2·939
AmZn ,, ...	1·932	AmZn ,, ...	2·261
KZn ,, ...	2·246	KZn ,, ...	2·558
RbZn ,, ...	2·591	RbZn ,, ...	2·868
CsZn ,, ...	2·875	CsZn ,, ...	3·121

It will be observed that the ammonium salt is the lightest in each group, the densities following the order of the molecular weights.

Molecular Volumes.—These are similarly compared below.

	Molecular volume.	Diff. from K salt.		Molecular volume.	Diff. from K salt.
KMg sulphate	196·58	—	KMg selenate	208·63	—
RbMg ,,	206·18	9·60	RbMg ,,	218·15	9·52
AmMg ,,	207·78	11·20	AmMg ,,	219·42	10·79
CsMg ,,	218·96	22·38	CsMg ,,	231·20	22·57
KZn ,,	196·16	—	KZn ,,	208·80	—
RbZn ,,	205·58	9·42	AmZn ,,	217·73	8·93
AmZn ,,	206·38	10·22	RbZn ,,	218·35	9·55
CsZn ,,	217·97	21·81	CsZn ,,	230·77	21·97

The molecular volume of the ammonium salt of each group is very nearly identical with that of the rubidium salt, being just slightly higher in the first three groups and slightly less in the zinc selenate group. This is a similar result to that found in the case of the simple sulphates of the alkalis, the molecular volume of ammonium sulphate being slightly higher than that of rubidium sulphate. The average difference for the replacement of potassium by rubidium is 9·5 units, for that of potassium by ammonium 10·3 units, and for that of potassium by cæsium 22·2 units.

Topic Axes (*Distance Ratios*).—The next table presents these in comparative form.

Salt.	Topic axes (distance ratios).		
	χ.	ψ.	ω.
Potassium magnesium sulphate	6·0711 :	8·1899 :	4·0892
Rubidium ,, ,,	6·1803 :	8·3518 :	4·1550
Ammonium ,, ,,	6·2320 :	8·4217 :	4·1418
Cæsium ,, ,,	6·2608 :	8·6012 :	4·2541
Potassium zinc sulphate	6·0462 :	8·1562 :	4·1141
Rubidium ,, ,,	6·1436 :	8·3326 :	4·1754
Ammonium ,, ,,	6·1648 :	8·3670 :	4·1810
Cæsium ,, ,,	6·2415 :	8·5808 :	4·2561
Potassium magnesium selenate	6·2124 :	8·2998 :	4·1756
Rubidium ,, ,,	6·2885 :	8·4705 :	4·2445
Ammonium ,, ,,	6·3299 :	8·5310 :	4·2365
Cæsium ,, ,,	6·3807 :	8·7239 :	4·3270
Potassium zinc selenate	6·1812 :	8·2880 :	4·2045
Rubidium ,, ,,	6·2913 :	8·4662 :	4·2492
Ammonium ,, ,,	6·2742 :	8·4684 :	4·2681
Cæsium ,, ,,	6·3710 :	8·7106 :	4·3300

These ratios show that the replacement of potassium by ammonium in this series of salts is accompanied by very nearly the same amount of extension of the distances separating the centres of the structural units (considering a structural unit as a whole molecule of the salt), along each of the three morphological axial directions, as that which accompanies the substitution of rubidium for potassium. In nine cases out of the twelve the extension is slightly greater, and in the other three cases slightly less, for the ammonium substitution than for the rubidium one. In no case does the extension for the replacement of potassium by ammonium attain the amount which is observed when potassium is replaced by cæsium. The average position of the ammonium salt is 0·0225 beyond the rubidium salt.

It is thus a fact that the molecule of the ammonium double salt of any group of this series occupies, as regards its dimensions in space, both as to total volume and its directional dimensions, a position very close to that of the corresponding rubidium salt of that group.

In other words, the replacement of the two atoms of the alkali metal by the ten atoms comprising two ammonium groups is accompanied by only very slightly more expansion of the molecular dimensions * than occurs when two atoms of the metallic family analogue, rubidium, are substituted for those of potassium, and by far less than that which accompanies the exchange of potassium for cæsium atoms.

A precisely similar fact has already been proved in the case of the simple alkali sulphates. Thus the ammonium group not only simulates the chemical behaviour of the alkali metals, but can also pack itself into a similar space or sphere of action or motion.

The suggestion made in the memoir on ammonium sulphate (*loc. cit.*, p. 1067) that this may be due to the looseness of the spacial packing, the free space unoccupied by matter being large compared with the amount of the actual matter of the molecule contained in the whole space defined by the topic axes, applies no less to these double salts than to the simple alkali sulphates.

The essentially different natures of an ammonium group and an alkali metallic atom is, however, clearly shown by the slight vagaries of the directional changes accompanying the ammonium replacement, no general rule being apparently capable of expressing these.

Optics.

Orientation of the Optical Indicatrix (Ellipsoid).—The optical indicatrix has been shown throughout the whole series of double sulphates and selenates already studied by the author to rotate about the symmetry axis when one alkali metal is replaced by another, and it is now found that the replacement of potassium by ammonium is also accompanied by a similar rotation. The best means of expressing the relative positions of the ellipsoid will be to tabulate the inclinations, to the vertical crystallographical axis c, of that axis of the ellipsoid which is not far removed from the normal to the basal plane $c\{001\}$. In all the sixteen salts now compared, it is the second median line, and minimum axis α of the indicatrix or maximum axis $\mathfrak{a}$ of the optical velocity ellipsoid. The dispersion of the median lines (the two axes of the ellipsoid lying in the symmetry plane) has been shown to be very small throughout, never exceeding 20′, so that the values given in the table are the mean positions for white light or the middle of the spectrum.

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* By "molecular dimensions" in this and the preceding paragraph must be clearly understood the dimensions defined by the topic axes; they will be shown later, in this and the following memoir, to be more correctly described as "limits of molecular range," for much intermolecular space, as well as the matter of the molecules, is included.

Inclination of Axis a of Indicatrix to Vertical Axis c, in Front of Latter.

AmMg	sulphate	4°58′	AmMg	selenate	0°13′
KMg	,,	13 38	KMg	,,	11 18
RbMg	,,	21 14	RbMg	,,	16 24
CsMg	,,	46 43	CsMg	,,	36 47
AmZn	,,	6°59′	AmZn	,,	3°24′
KZn	,,	10 18	KZn	,,	9 9
RbZn	,,	16 43	RbZn	,,	13 13
CsZn	,,	30 16	CsZn	,,	21 57

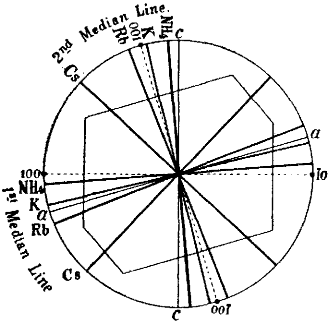

FIG. 12.

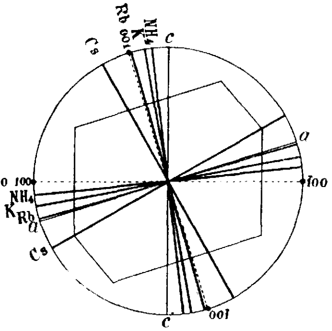

FIG. 13.

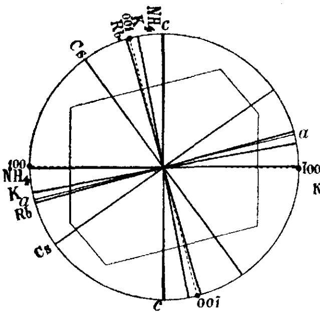

FIG. 14.

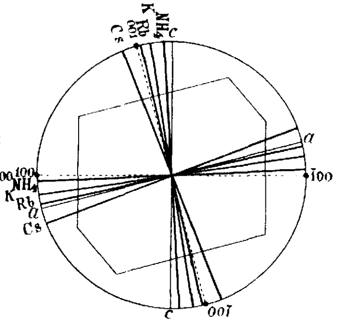

FIG. 15.

The positions will be rendered clearer by Figs. 12, 13, 14, and 15, which represent graphically the positions of the median lines in the magnesium sulphate, zinc sulphate, magnesium selenate, and zinc selenate groups of salts respectively.

It will be observed that the position in the case of each ammonium salt lies nearest to the crystallographical axis *c*, the ellipsoid having been rotated backwards towards that axis by the replacement of potassium by ammonium, and in the contrary direction to that in which rotation occurs when potassium is replaced by rubidium or cæsium. The salts stand in respect to this property in the order of their molecular weights.

Refractive Indices.—These are compared in the accompanying table:

Comparative Table of Refractive Indices.

Index.	Nature of light.	KMg sulphate.	RbMg sulphate.	AmMg sulphate.	CsMg sulphate.	KZn sulphate.	RbZn sulphate.	AmZn sulphate.	CsZn sulphate.
α	Li	1·4581	1·4646	1·4685	1·4828	1·4748	1·4807	1·4858	1·4994
	C	1·4585	1·4650	1·4689	1·4832	1·4752	1·4811	1·4862	1·4998
	Na	1·4607	1·4672	1·4716	1·4857	1·4775	1·4833	1·4888	1·5022
	Tl	1·4631	1·4695	1·4740	1·4880	1·4797	1·4857	1·4914	1·5047
	F	1·4658	1·4724	1·4771	1·4912	1·4826	1·4886	1·4947	1·5079
	G	1·4699	1·4762	1·4814	1·4956	1·4866	1·4929	1·4992	1·5125
β	Li	1·4603	1·4664	1·4701	1·4830	1·4805	1·4856	1·4900	1·5020
	C	1·4607	1·4668	1·4705	1·4834	1·4809	1·4860	1·4904	1·5024
	Na	1·4629	1·4689	1·4730	1·4858	1·4833	1·4884	1·4930	1·5048
	Tl	1·4652	1·4713	1·4755	1·4881	1·4857	1·4908	1·4957	1·5073
	F	1·4678	1·4743	1·4786	1·4912	1·4889	1·4938	1·4990	1·5104
	G	1·4720	1·4782	1·4831	1·4957	1·4929	1·4980	1·5036	1·5151
γ	Li	1·4727	1·4755	1·4756	1·4888	1·4938	1·4947	1·4963	1·5064
	C	1·4731	1·4759	1·4760	1·4892	1·4942	1·4951	1·4967	1·5068
	Na	1·4755	1·4779	1·4786	1·4916	1·4969	1·4975	1·4994	1·5093
	Tl	1·4778	1·4805	1·4811	1·4940	1·4994	1·5001	1·5021	1·5119
	F	1·4810	1·4835	1·4842	1·4970	1·5027	1·5033	1·5056	1·5152
	G	1·4853	1·4876	1·4888	1·5015	1·5067	1·5078	1·5102	1·5199

Index.	Nature of light.	KMg selenate.	RbMg selenate.	AmMg selenate.	CsMg selenate.	KZn selenate.	RbZn selenate.	AmZn selenate.	CsZn selenate.
α	Li	1·4936	1·4978	1·5034	1·5143	1·5087	1·5129	1·5201	1·5290
	C	1·4941	1·4983	1·5038	1·5148	1·5092	1·5134	1·5206	1·5295
	Na	1·4969	1·5011	1·5070	1·5178	1·5121	1·5162	1·5240	1·5326
	Tl	1·4999	1·5041	1·5104	1·5210	1·5151	1·5194	1·5273	1·5358
	F	1·5035	1·5077	1·5144	1·5248	1·5189	1·5233	1·5316	1·5399
	G	1·5091	1·5133	1·5205	1·5304	1·5244	1·5288	1·5381	1·5459
β	Li	1·4958	1·4997	1·5056	1·5145	1·5146	1·5188	1·5260	1·5326
	C	1·4963	1·5002	1·5060	1·5150	1·5151	1·5193	1·5265	1·5331
	Na	1·4991	1·5031	1·5093	1·5179	1·5181	1·5222	1·5300	1·5362
	Tl	1·5022	1·5060	1·5126	1·5211	1·5212	1·5253	1·5334	1·5394
	F	1·5058	1·5098	1·5166	1·5248	1·5252	1·5293	1·5378	1·5435
	G	1·5114	1·5152	1·5227	1·5305	1·5307	1·5351	1·5443	1·5495
γ	Li	1·5103	1·5100	1·5132	1·5201	1·5297	1·5294	1·5344	1·5375
	C	1·5108	1·5105	1·5136	1·5206	1·5302	1·5299	1·5349	1·5380
	Na	1·5139	1·5135	1·5169	1·5236	1·5335	1·5331	1·5385	1·5412
	Tl	1·5172	1·5167	1·5202	1·5269	1·5369	1·5365	1·5420	1·5446
	F	1·5210	1·5205	1·5242	1·5308	1·5410	1·5405	1·5463	1·5488
	G	1·5266	1·5264	1·5305	1·5364	1·5471	1·5466	1·5529	1·5549

The whole of the refractive indices of the four ammonium salts lie between those of the analogous rubidium and cæsium salts, and nearer to those of the rubidium salt in the first three groups, but somewhat nearer to those of the cæsium salt in the zinc selenate group.

A concise expression of the relationship is afforded by a comparison of the mean refractive indices (mean of all three indices for sodium light) given in the next table.

Mean Refractive Indices, $1/3(\alpha+\beta+\gamma)$ *for Na Light.*

KMg sulphate	1·4664	KMg selenate	1·5033
RbMg ,,	1·4713	RbMg ,,	1·5059
AmMg ,,	1·4744	AmMg ,,	1·5111
CsMg ,,	1·4877	CsMg ,,	1·5198
KZn ,,	1·4859	KZn ,,	1·5212
RbZn ,,	1·4897	RbZn ,,	1·5238
AmZn ,,	1·4937	AmZn ,,	1·5308
CsZn ,,	1·5054	CsZn ,,	1·5367

The mean refractive index of the ammonium salt of each group is seen to be somewhat greater than the mean index of the rubidium salt of the same group, but not so high as that of the cæsium salt. The value is quite close to that of the rubidium salt in the group of lowest molecular weight, but moves farther away with rise of molecular weight, until for the group of highest molecular weight the value is slightly nearer to that for the cæsium salt.

Double Refraction.—The double refraction, as measured by the difference between the two extreme indices α and γ for sodium light, will next be compared.

Comparison of the Double Refraction Na $\gamma-\alpha$.

KMg sulphate	0·0148	KMg selenate	0·0170
RbMg ,,	0·0107	RbMg ,,	0·0124
AmMg ,,	0·0070	AmMg ,,	0·0099
CsMg ,,	0·0059	CsMg ,,	0·0058
KZn ,,	0·0194	KZn ,,	0·0214
RbZn ,,	0·0142	RbZn ,,	0·0169
AmZn ,,	0·0106	AmZn ,,	0·0145
CsZn ,,	0·0071	CsZn ,,	0·0086

It will be evident from this table that in respect to double refraction also the ammonium salt of each group takes its place between the rubidium and cæsium salts of the same group. Its position is nearer to that of the cæsium salt in the group of least molecular weight, and nearer to that of the rubidium salt in the group of highest molecular weight, the movement being in the opposite sense to that of the mean refraction.

The relative refractive power of the crystals of the four salts of each group is best shown by the calculated values of the axes of the optical indicatrix, or of its polar reciprocal, the optical velocity ellipsoid, taking the β axis of the potassium salt as unity.

Those for the indicatrix are given in the next table.

Axial Ratios of Optical Indicatrix, $\beta_{K\text{salt}} = 1$.

Salt.	α.	β.	γ.
Potassium magnesium sulphate	0·9985	: 1	: 1·0086
Rubidium ,, ,, ...	1·0030	: 1·0041	: 1·0103
Ammonium ,, ,, ...	1·0060	: 1·0069	: 1·0107
Cæsium ,, ,, ...	1·0156	: 1·0157	: 1·0196
Potassium zinc sulphate..................	0·9961	: 1	: 1·0092
Rubidium ,, ,, ...	1·0000	: 1·0034	: 1·0096
Ammonium ,, ,, ...	1·0037	: 1·0065	: 1·0109
Cæsium ,, ,, ...	1·0127	: 1·0145	: 1·0175
Potassium magnesium selenate	0·9985	: 1	: 1·0099
Rubidium ,, ,, ...	1·0013	: 1·0027	: 1·0096
Ammonium ,, ,, ...	1·0053	: 1·0068	: 1·0119
Cæsium ,, ,, ...	1·0125	: 1·0126	: 1·0163
Potassium zinc selenate	0·9960	: 1	: 1·0101
Rubidium ,, ,, ...	0·9988	: 1·0027	: 1·0099
Ammonium ,, ,, ...	1·0039	: 1·0078	: 1·0134
Cæsium ,, ,, ...	1·0096	: 1·0119	: 1·0152

It will be observed that the indicatrix expands along each of the three axes when potassium is replaced by ammonium, and to an extent which is greater than that accompanying the substitution of rubidium for potassium, but not so great as that due to the introduction of cæsium instead of potassium. In the first three groups, the dimensions in the case of the ammonium salt are much nearer to those of the rubidium salt; in the zinc selenate group, two of the axes of the ammonium salt approximate somewhat nearer to those of the cæsium salt.

Molecular Optical Constants.—These are compared in the next four tables.

All the values for the metallic salts have been recalculated, employing the densities determined by the suspension method and the molecular volumes derived therefrom, so as to be rigidly comparable with the values for the ammonium salts.

Table of Specific Refractions and Dispersions (*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 G(Hγ).					
	α.	β.	γ.	α.	β.	γ.	α.	β.	γ.
AmMg sulphate...	0·1616	0·1621	0·1637	0·1653	0·1658	0·1675	0·0037	0·0037	0·0038
KMg ,, ...	0·1343	0·1348	0·1379	0·1371	0·1377	0·1410	0·0028	0·0029	0·0031
RbMg ,, ...	0·1159	0·1162	0·1181	0·1183	0·1187	0·1207	0·0024	0·0025	0·0026
CsMg ,, ...	0·1068	0·1068	0·1079	0·1091	0·1091	0·1102	0·0023	0·0023	0·0023
AmZn ,, ...	0·1487	0·1497	0·1514	0·1520	0·1532	0·1549	0·0033	0·0035	0·0035
KZn ,, ...	0·1254	0·1267	0·1297	0·1280	0·1294	0·1324	0·0026	0·0027	0·0027
RbZn ,, ...	0·1098	0·1108	0·1126	0·1121	0·1131	0·1150	0·0023	0·0023	0·0024
CsZn ,, ...	0·1023	0·1027	0·1035	0·1045	0·1049	0·1057	0·0022	0·0022	0·0022
AmMg selenate ...	0·1438	0·1444	0·1462	0·1478	0·1484	0·1502	0·0040	0·0040	0·0040
KMg ,, ...	0·1231	0·1236	0·1266	0·1263	0·1268	0·1299	0·0032	0·0032	0·0033
RbMg ,, ...	0·1093	0·1096	0·1115	0·1120	0·1124	0·1144	0·0027	0·0028	0·0029
CsMg ,, ...	0·1026	0·1026	0·1035	0·1052	0·1052	0·1062	0·0026	0·0026	0·0027
AmZn ,, ...	0·1346	0·1359	0·1377	0·1384	0·1397	0·1415	0·0038	0·0038	0·0038
KZn ,, ...	0·1168	0·1179	0·1208	0·1197	0·1209	0·1240	0·0029	0·0030	0·0032
RbZn ,, ..	0·1049	0·1059	0·1077	0·1075	0·1086	0·1105	0·0026	0·0027	0·0028
CsZn ,, ...	0·0989	0·0995	0·1002	0·1014	0·1020	0·1028	0·0025	0·0025	0·0026

Table of Molecular Refractions and Dispersions (*Lorenz*).

Salt.	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = \mathfrak{m}$.						Mol. dispersion. $\mathfrak{m}_G - \mathfrak{m}_C$.		
	For ray C(Hα).			For ray G(Hγ).					
	α.	β.	γ.	α.	β.	γ.	α.	β.	γ.
KMg sulphate ...	53·69	53·91	55·16	54·84	55·05	56·37	1·15	1·14	1·21
RbMg ,, ...	57·00	57·19	58·14	58·18	58·38	59·36	1·18	1·19	1·22
AmMg ,, ...	57·85	58·02	58·60	59·17	59·35	59·95	1·32	1·33	1·35
CsMg ,, ...	62·56	62·58	63·21	63·92	63·93	64·57	1·36	1·35	1·36
KZn ,, ...	55·25	55·81	57·12	56·37	57·00	58·35	1·12	1·19	1·23
RbZn ,, ...	58·51	59·02	59·96	59·73	60·26	61·26	1·22	1·24	1·30
AmZn ,, ...	59·27	59·71	60·36	60·62	61·07	61·74	1·35	1·36	1·38
CsZn ,, ...	64·09	64·37	64·85	65·46	65·74	66·25	1·37	1·37	1·40
KMg selenate ...	60·74	60·98	62·48	62·30	62·54	64·10	1·56	1·56	1·62
RbMg ,, ...	63·97	64·18	65·30	65·58	65·80	67·00	1·61	1·62	1·70
AmMg ,, ...	64·95	65·19	66·01	66·75	66·99	67·83	1·80	1·80	1·82
CsMg ,, ...	69·70	69·72	70·36	71·47	71·47	72·14	1·77	1·75	1·78
KZn ,, ...	62·37	62·98	64·52	63·93	64·57	66·23	1·56	1·59	1·71
RbZn ,, ...	65·67	66·30	67·44	67·32	67·99	69·20	1·65	1·69	1·76
AmZn ,, ...	66·26	66·88	67·77	68·11	68·76	69·66	1·85	1·88	1·89
CsZn ,, ...	71·23	71·63	72·18	73·06	73·46	74·06	1·83	1·83	1·88

Molecular Refractions (*Gladstone and Dale*), $\frac{n-1}{d}$M, *for Ray* C.

	α.	β.	γ.
Potassium magnesium sulphate	90·13	90·56	93·00
Rubidium ,, ,, ...	95·87	96·24	98·12
Ammonium ,, ,, ...	97·43	97·76	98·90
Cæsium ,, ,, ...	105·80	105·84	107·11
Potassium zinc sulphate	93·21	94·33	96·94
Rubidium ,, ,, ...	98·91	99·91	101·78
Ammonium ,, ,, ...	100·34	101·21	102·51
Cæsium ,, ,, ...	108·94	109·51	110·47
Potassium magnesium selenate.........	103·08	103·54	106·57
Rubidium ,, ,, ...	108·70	109·12	111·37
Ammonium ,, ,, ...	110·54	111·02	112·69
Cæsium ,, ,, ...	119·02	119·07	120·36
Potassium zinc selenate	106·32	107·55	110·71
Rubidium ,, ,, ...	112·10	113·39	115·70
Ammonium ,, ,, ...	113·35	114·63	116·46
Cæsium ,, ,, ...	122·19	123·02	124·15

Mean Molecular Refractions, $1/3(\alpha+\beta+\gamma)$ *for Ray* C.

KMg sulphate	91·23	KMg selenate	104·40
RbMg ,, ...	96·74	RbMg ,, ...	109·73
AmMg ,, ...	98·03	AmMg ,, ...	111·42
CsMg ,, ...	106·25	CsMg ,, ...	119·48
KZn ,, ...	94·83	KZn ,, ...	108·19
RbZn ,, ...	100·20	RbZn ,, ...	113·73
AmZn ,, ...	101·35	AmZn ,, ...	114·81
CsZn ,, ...	109·64	CsZn ,, ...	123·12

As regards the specific refraction and dispersion constants, the ammonium salt of each group stands first, with higher constants than the potassium salt. The order is, indeed, that of the molecular weights of the salts, but the differences diminish as the molecular weight rises.

With respect to molecular refraction, whether calculated by the formula of Lorenz or by that of Gladstone and Dale, the value along each of the three axes of the optical ellipsoid of the ammonium salt of each group is just slightly higher than the value for the corresponding rubidium salt. The same fact is succinctly expressed by the mean molecular refractions of the crystals. Hence, as regards molecular refraction, the ammonium salt occupies the same position in the series, just after the rubidium salt, which it has been shown to occupy as regards the molecular dimensions in space (the topic axes).

With respect to molecular dispersion, the values for the ammonium salt of each group approximate nearer to those of the corresponding cæsium salt, and in the two selenate groups the cæsium salt values are slightly exceeded.

Optic Axial Angles.—These are dependent in the case of each salt on the relations between the lengths of the three axes of the optical ellipsoid of that salt; the latter are most conveniently expressed by considering the axis of intermediate length β or $\mathfrak{b}$ as unity. For these ratios determine the *loci* of the circular sections of the ellipsoid to which the optic axes are perpendicular. They are compared in the following table, for the indicatrix ellipsoid.

Axial Ratios of Indicatrix.

	α.		β.		γ.
Potassium magnesium sulphate	0·9985	:	1	:	1·0086
Rubidium ,, ,, ...	0·9988	:	1	:	1·0061
Ammonium ,, ,, ...	0·9991	:	1	:	1·0038
Cæsium ,, ,, ...	0·9999	:	1	:	1·0039
Potassium zinc sulphate	0·9961	:	1	:	1·0092
Rubidium ,, ,, ...	0·9966	:	1	:	1·0061
Ammonium ,, ,, ...	0·9972	:	1	:	1·0043
Cæsium ,, ,, ...	0·9983	:	1	:	1·0030
Potassium magnesium selenate	0·9985	:	1	:	1·0099
Rubidium ,, ,, ...	0·9987	:	1	:	1·0069
Ammonium ,, ,, ...	0·9985	:	1	:	1·0050
Cæsium ,, ,, ...	0·9999	:	1	:	1·0038
Potassium zinc selenate	0·9960	:	1	:	1·0101
Rubidium ,, ,, ...	0·9961	:	1	:	1·0072
Ammonium ,, ,, ...	0·9961	:	1	:	1·0056
Cæsium ,, ,, ...	0·9977	:	1	:	1·0033

It will be observed that on the whole the position of the ammonium salt of any group is again between the rubidium and cæsium salts; the two variations from this rule are only to the extent of 0·0001 and 0·0002 respectively.

As regards the optic axial angles themselves, those of the two magnesium groups do not lend themselves to complete comparison, owing to the exceptional phenomena (including crossed-axial-plane dispersion) displayed by the cæsium salts of these groups, which have been fully referred to in the memoirs concerning those salts, and which have been shown to be the direct consequence of the accelerating progression (diminution) of the double refraction with rise of atomic weight of the alkali metal.

Optic Axial Angles 2Va.

Light.	KMg sulphate.	RbMg sulphate.	AmMg sulphate.
Li	48° 0′	49° 6′	51°20′
C	47 59	49 2	51 18
Na	47 54	48 46	51 11
Tl	47 48	48 29	51 2
F	47 40	48 10	50 36

Optic Axial Angles 2Va (continued).

	KMg selenate.	RbMg selenate.	AmMg selenate
Li	39°43′	47°26′	54°57
C	39 42	47 24	54 55
Na	39 38	47 3	54 47
Tl	39 34	46 37	54 33
F	39 25	46 6	54 4

	KZn sulphate.	RbZn sulphate.	CsZn sulphate.	AmZn sulphate
Li	68°17′	73°42′	74°30′	78°57′
C	68 16	73 40	74 27	78 58
Na	68 14	73 33	74 11	79 0
Tl	68 12	73 27	73 52	79 2
F	68 9	73 18	73 31	79 3

	KZn selenate.	RbZn selenate.	AmZn selenate.	CsZn selenate.
Li	66°12′	75°16′	82° 5′	83°33′
C	66 13	75 14	82 5	83 30
Na	66 15	75 8	82 7	83 6
Tl	66 17	75 2	82 9	82 43
F	66 20	74 55	82 10	82 14

It will be seen that the optic axial angles of the two ammonium magnesium salts are somewhat beyond those of the corresponding rubidium salts in magnitude. In the two zinc groups also the ammonium salts occupy positions beyond the rubidium salts; in the case of the zinc selenate group, the angle is not quite so large as that of the cæsium salt, whilst in the zinc sulphate group it is larger than that of the cæsium salt.

It must be remembered, however, that these mutual relationships of the three axes of the optical ellipsoid on which the optic axial angles are dependent are secondary effects of the total change in (expansion of) the ellipsoid on passing from one salt to another of the group, and that, moreover, the whole ellipsoid rotates about the symmetry axis at the same time, and to different extents for different wave-lengths of light; and also that the rapid change in the amount of the double refraction produces marked effects on the optic axial angle phenomena, particularly on the dispersion of the optic axes for different wave-lengths of light. Hence the optic axial angle phenomena are highly complicated, and not likely to show clearly the effect of change of atomic weight or the position of the ammonium radicle in the alkali series. But the total change (expansion) of the axial dimensions of the optical ellipsoid, the rotation of the ellipsoid, and the magnitude of the double refraction have all been shown to be subservient to definite laws connecting the atomic weight of the alkali metal, the molecular weight of the whole salt, and the position of the ammonium complex in the alkali series.

Summary of Conclusions.

The main results of this investigation are remarkably similar to those derived from the study of ammonium sulphate (*loc. cit.*, p. 1073), and their comparison with those for the sulphates of potassium, rubidium, and cæsium previously studied. The differences are chiefly due to the difference of crystalline symmetry. The rhombic series of normal sulphates and selenates show exceedingly small differences in the angles between the external faces, the maximum difference observed between a potassium and a cæsium salt being only two-thirds of a degree (41′), whereas the monoclinic double sulphates and selenates exhibit differences of morphological angle exceeding 2 degrees, the maximum being 141′ in the case of the salts now under comparison. It might, perhaps, have been expected that the replacement of a so much greater integral part of the molecule as the alkali metal forms of the simple salt $R_2\overset{S}{\underset{Se}{}}O_4$ would be accompanied by a greater amount of angular change than when the same replacement occurs in the very much larger molecule of the double salt $R_2M\left(\overset{S}{\underset{Se}{}}O_4\right)_2,6H_2O$, of which the alkali metal forms a much smaller integral part. But it appears to be connected with the order of symmetry, and indicates that the higher the order of symmetry the smaller are the angular changes between the exterior faces, when one member of the family of metals or radicles forming the series of salts replaces another. It also emphasises the dominating influence of the alkali metal in determining the crystallographical properties of the salts. It is much easier, therefore, to locate the position of the ammonium group in the series of double salts, as regards the external morphology of the crystals, than in the case of the simple salt series.

The replacement of potassium by the ammonium group is accompanied by alterations in the *interfacial angles* in the same direction as when potassium is replaced by rubidium or cæsium, and both the average amount and the maximum amount of the change are approximately the same as when cæsium replaces potassium. The fundamental *axial angle* β follows the same rule, the value in the case of the four ammonium salts now described being identical within 10′ with the value for the analogous cæsium salt.

A new fact as regards the relations of the three alkali metals has also been discovered, namely, that the average and maximum alterations of the interfacial angles when potassium is replaced by rubidium or cæsium are approximately directly proportional to the change in atomic weight, the values in the case of the rubidium salt being almost precisely midway between those of the potassium and cæsium salts.

The *morphological axial ratios* of the ammonium salt of each group are very similar to those of the potassium, rubidium, and cæsium salts of the group, and generally lie within the limits of the latter. The true axial relations of the four salts of each group are only, however, indicated by the topic axes, which are obtained by combining the axial ratios with the molecular volume and represent the distances apart, along the directions of the three crystallographical axes, of the centres of contiguous structural units, understanding by a structural unit a complete molecule $R_2M\left(\begin{smallmatrix}S\\Se\end{smallmatrix}O_4\right)_2,6H_2O$.

The *densities* follow the order of the molecular weights of the salts, but the *molecular volume* of the ammonium salt of each group is almost identical with that of the rubidium salt of the same group.

The *topic axes* indicate that the extension of the structural unit (the increase of separation of the centres of contiguous structural units) along each of the three crystallographical axes, when potassium is replaced by ammonium, is nearly identical with that which accompanies the replacement of potassium by rubidium, and on the average just slighter greater.

The *cleavage* is identical for all the salts studied, namely, parallel to the orthodome $r'\{\bar{2}01\}$.

The *optical scheme* is also identical for all the salts, the plane of the optic axes being the symmetry plane. Besides showing larger changes in the interfacial angles, the monoclinic double salt series differs from the rhombic simple salt series in that the *optical ellipsoid* is no longer fixed, with its axes identical with the three crystallograpical axes, but is free to rotate about the single symmetry axis. This possible rotation actually occurs, as shown in the memoirs on the potassium, rubidium, and cæsium salts, in accordance with the rule connecting the atomic weight of the alkali metal with the amount of rotation. It is now found that the rotation in the case of replacing potassium by ammonium is such as to leave the four positions of the ellipsoid, for the four salts of any group, in the order of their molecular weights, the ammonium salt being at one end of the swing and the cæsium salt at the other.

The *refractive indices* of the ammonium salt of any group lie between those of the rubidium and cæsium salts, the values being generally closer to those of the rubidium salt. The *mean refractive index* shows the same relationship, but the value approaches towards that of the cæsium salt as the molecular weight of the salt rises.

The *axial ratios* (relative axial dimensions) *of the optical ellipsoid* of any ammonium salt are also intermediate between those of the analogous rubidium and cæsium salts, and in general much nearer to those of the rubidium salt.

The *specific refractions* and *dispersions* follow the order of the molecular weights of the salts.

The *molecular refraction*, both the three directional values and the mean, of each ammonium salt is very close to the value for the analogous rubidium salt, being just slightly higher than (on the cæsium side of) that value.

It has now been shown with respect to the three properties which refer to the fundamental structural unit of the crystals, namely, the molecular volume, the topic axes, and the molecular refraction (a measure of the molecular effect on the velocity of light transmission), that the ammonium salt of any group of the series yet studied behaves almost exactly like the rubidium salt. It was similarly previously shown with regard to the molecular constants of ammonium sulphate that the place of this salt in the series of alkali sulphates is immediately after rubidium.

With respect to the properties of the crystals themselves, they are found to be of two kinds. Those of the one kind follow the order of the molecular weights, in which case the ammonium salt stands first in the series; in this category come the densities, the rotation of the optical ellipsoid, and the specific refraction and dispersion. Thus, while the whole of the properties of the crystals of the potassium, rubidium, and cæsium salts have been shown to be functions of the atomic weight of the alkali metal, and therefore of the molecular weight of the whole salt, only these four properties obey a similar law in the case of the ammonium salts, at once marking an essential difference between the ammonium complex and an alkali metal. In those of the other kind, the ammonium salt occupies positions which vary for the different properties from a position quite close to the rubidium salt and just beyond it on the cæsium side, to one closely approximating to that of the cæsium salt. In this class fall the interfacial angles, the monoclinic axial angle, the three refractive indices (corresponding to the three axes of the optical ellipsoid), the mean refractive index for the whole crystal, the double refraction, and the axial ratios of the optical ellipsoid.

It will be interesting to see whether these three main results concerning matters of indubitable fact as regards the groups now investigated are true equally for other groups of the series, to which the author intends to turn his attention. In the meantime, ample scope is afforded for speculation as to their meaning, and particularly as to the spacial conditions which permit of the replacement of 2 atoms of the alkali metal potassium by 10 atoms of the two ammonium complexes, with no more effect on the crystallographical characters and on the dimensions and properties of the fundamental structural unit than if merely an exchange for two cæsium atoms had occurred, and indeed, in general, with but slightly more effect than if the two replacing metallic atoms had been those of rubidium. Leaving speculation entirely aside, however, one further important fact would appear to be proved and to stand out from this investigation, namely, that the space defined by the topic axes is not filled with matter, but that relatively large intermolecular free spaces occur, in which these extra atoms can be readily stowed away. The optical results further indicate that the spaces are not only intermolecular but also interatomic.