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Crystallographic constants and isomorphous relations of the double chromates of the alkalis and magnesium.

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[Read January 23, 1912.]

THE interesting results which have followed the investigation by one of us [1] of the isomorphous series of double sulphates and selenates of the general formula $R'_2M''[(S, Se)O_4]_2.6H_2O$ have led us to extend the investigation to the corresponding double chromates in which M is represented by magnesium.

The ammonium salt, $(NH_4)_2Mg(CrO_4)_2.6H_2O$, was investigated by Murmann [2] and shown to belong to the monoclinic series in question. An analogous potassium salt was not obtained, the only known double chromate of potassium and magnesium crystallizing with two molecules of water, and therefore in an entirely different form, of triclinic pinakoidal

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[1] A. E. H. Tutton, Journ. Chem. Soc., 1893, vol. lxiii, p. 337; 1896, vol. lxix, p. 344; 1905, vol. lxxxvii, p. 1123; Proc. Roy. Soc., 1900, vol. lxvi, p. 248; 1900, vol. lxvii, p. 58; 1910, ser. A, vol. lxxxiii, p. 211; Phil. Trans. Roy. Soc., 1901, ser. A, vol. cxcvii, p. 255.

[2] A. Murmann, Sitzungsber. Akad. Wiss. Wien, 1858, vol. xxvii (Jahrg. 1857), p. 175.

symmetry.[1] The rubidium and caesium salts of the series have recently been prepared by Barker,[2] and proved by a few goniometrical measurements, of azimuth and polar distance with the two-circle goniometer, to belong to the monoclinic series, and by chemical analyses to contain six molecules of water of crystallization. No optical measurements were made, these, as well as fuller goniometrical details, being by friendly arrangement left for the present authors to carry out with the special equipment described in previous memoirs and books.[3]

As regards the ammonium salt, Murmann mentions that the plane of the optic axes is the symmetry-plane for green light but perpendicular thereto for red light, this salt being thus another example, from this series, of crossed-axial-plane dispersion of the optic axes. Determinations of the specific gravity of this salt were also made by Abbot.[4]

These three salts—the ammonium, rubidium, and caesium—which we have investigated in detail, form excellent crystals, well suited for goniometrical and optical measurements. Caesium magnesium chromate is the most stable, no tendency to efflorescence being observed, even ground plates and prisms maintaining their surfaces unimpaired for a considerable time. The rubidium salt is less stable, and ground surfaces rapidly deteriorate, even, after a few weeks, when covered with cemented micro-cover-glass plates. Attempts to prepare the corresponding potassium salt were unsuccessful.

AMMONIUM MAGNESIUM CHROMATE, $(NH_4)_2Mg(CrO_4)_2.6H_2O$.

An estimation of magnesium in confirmation of identity and purity, made with clear crystals of one of the crops investigated, yielded the following result: 1·1512 grams of crystals gave 0·3360 gram of magnesium pyrophosphate, which corresponds to 6·31 per cent. of magnesium, the calculated amount being 6·06 per cent.

Goniometry.

Crystal system: Monoclinic, holohedral, prismatic. (Class 5.)

Axial ratios and angle: $a : b : c = 0{\cdot}7517 : 1 : 0{\cdot}4924$; $\beta = 106^\circ 7'$.

[Murmann's values, $0{\cdot}7511 : 1 : 0{\cdot}4931$; $\beta = 106^\circ 31'$.]

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[1] G. Wyrouboff, Bull. Soc. franç. Min., 1891, vol. xiv, p. 253.

[2] T. V. Barker, Journ. Chem. Soc., 1911, vol. xcix, p. 1326.

[3] A. E. H. Tutton, 'Crystalline structure and chemical constitution,' 1910; and 'Crystallography and practical crystal measurement', 1911.

[4] F. W. Clarke, 'Table of specific gravities,' Smithsonian Miscell. Collect., 1888, No. 659, p. 104.

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

Cleavage: *r'*($\bar{2}01$), excellent. Colour: Yellow.

Habit: Short prismatic, or tabular parallel to *c*{001}.

The *b*-faces were always well developed, and sometimes very large, and invariably gave good single images of the signal. The *c*-faces were large but often striated, giving multiple images, a similar observation also applying in a lesser degree to the *p*-faces. In the dozen crystals chosen for measurement, from very numerous crops, such striation was at its minimum, and no images were taken into account involving the phenomenon. The *q*-faces were also large and gave good images. The *r'*-faces were small, but yielded satisfactory images, one of the two faces being usually more developed than the other. Faces of the forms *o* and *o'* were not always present, and the images were rarely very good. No faces of the orthopinakoid *a*{100} were observed, nor were any faces of the hemipyramid *n'*{$12\bar{1}$} observed by Murmann ever found. The crystals were sometimes tabular parallel to *b*{010}, or more often to *c*{001}, and sometimes elongated along the *b*-axis with one pair of *p*-faces more largely developed than the other. The face grown in contact with the crystallizing vessel was either *b*, *p*, or *c*; such faces were usually free from striation and afforded excellent trustworthy images, although they showed contour depressions. Two actual crystals from different crops are represented in figs. 1 and 2.

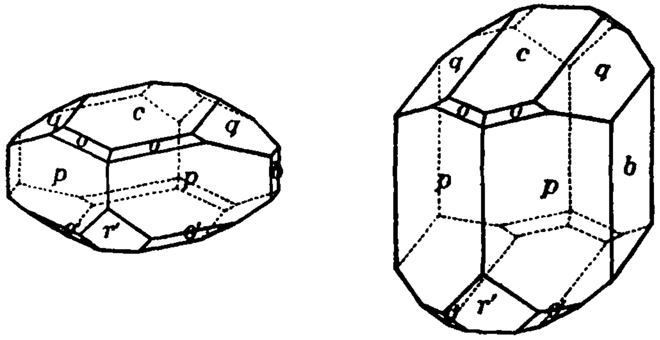

FIG. 1. FIG. 2.

Crystals of ammonium magnesium chromate.

Morphological Angles observed on Ammonium Magnesium Chromate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.*	Murmann's observed values.
$cr' = (001):(\bar{2}01)$	15	63°11′ – 63°26′	63°18′	63° 11′	63° 32′
$r'c = (\bar{2}01):(00\bar{1})$	15	116 34 – 116 48	116 42	116 49	...
$pb = (110):(010)$	32	53 59 – 54 16	54 10	*	54 14
$pp = (110):(1\bar{1}0)$	20	71 34 – 71 47	71 41	71 40	71 31
$pp = (110):(\bar{1}10)$	20	108 13 – 108 26	108 19	108 20	108 29
$cq = (001):(011)$	35	25 6 – 25 27	25 17	25 19	25 15
$qb = (011):(010)$	35	64 33 – 64 49	64 41	*	...
$co = (001):(111)$	2	33 31 – 33 48	33 39	33 40	33 47
$op = (111):(110)$	2	43 17 – 43 19	43 18	43 20	...
$cp = (001):(110)$	37	76 49 – 77 7	77 0	*	...
$po' = (110):(11\bar{1})$	8	59 0 – 59 7	59 2	59 6	59 12
$o'c = (11\bar{1}):(00\bar{1})$	6	43 46 – 43 59	43 55	43 54	44 28
$pc = (110):(00\bar{1})$	34	102 50 – 103 6	102 59	103 0	...
$bo' = (010):(\bar{1}11)$	5	65 17 – 65 24	65 20	65 22	...
$o'o' = (\bar{1}11):(\bar{1}\bar{1}1)$	3	49 17 – 49 23	49 19	49 15	...
$qp = (011):(\bar{1}10)$	29	87 11 – 87 27	87 19	87 19	...
$pq = (\bar{1}10):(0\bar{1}\bar{1})$	29	92 32 – 92 44	92 41	92 41	...
$qp = (011):(110)$	29	62 52 – 63 8	63 0	63 1	...
$pq = (110):(0\bar{1}\bar{1})$	30	116 54 – 117 8	116 59	116 59	...
$r'o' = (\bar{2}01):(\bar{1}11)$	6	34 56 – 35 5	35 1	34 57	...
$o'p = (\bar{1}11):(110)$	8	91 25 – 91 33	91 30	91 28	...
$pr' = (110):(20\bar{1})$	32	53 22 – 53 39	53 30	53 35	53 35
$r'p = (\bar{2}01):(110)$	30	126 17 – 126 37	126 28	126 25	...

* For the complete series of calculated angles for comparison, see the table on p. 189.

Volume.

Two series of determinations of specific gravity were made, with a dozen of the most perfect small crystals in each case, by the Retgers immersion method, using a mixture of methylene iodide and benzene. The heaviest crystals in the two cases afforded the following results:

For 19·0°/4°...... 1·8318...... For 20°/4°...... 1·8316.
„ 18·8°/4°...... 1·8321...... „ „ ...... 1·8319.

The value accepted for the density[1] of ammonium magnesium chromate at 20°/4° is accordingly 1·832; from which are calculated the molecular volume, $\frac{M}{d} = \frac{397\cdot46}{1\cdot832} = 216\cdot92$; and the molecular distance ratios (topic axial ratios),

$$\chi : \psi : \omega = 6\cdot3751 : 8\cdot4811 : 4\cdot1761.$$

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[1] The values given by Abbot (loc. cit.) are 1·8278 (16°), 1·8293 (17°), and 1·8595 (16°). The last of these is perhaps a misprint.

Optics.

Orientation of the Optical Ellipsoid.—Three section-plates ground parallel to the symmetry-plane afforded closely concordant determinations in sodium-light, indicating that one of the directions of extinction lies 12° 40′ behind the normal to $c\{001\}$. This direction is the first median line for all wave-lengths, and as the acute axial angle *ac* is 73° 53′ this first median line lies 3° 27′ in front of the vertical axis *c*, as shown in fig. 3. The other extinction-direction in the symmetry-plane lies 12° 40′ above the axis *a*, and is the second median line for the greater part of the spectrum, from wave-length 0·000664 mm. in the bright red to the violet end. For deeper red radiations, from wave-length 0·000664 to the extreme red of the spectrum, the symmetry-axis *b* is the second median line. It was

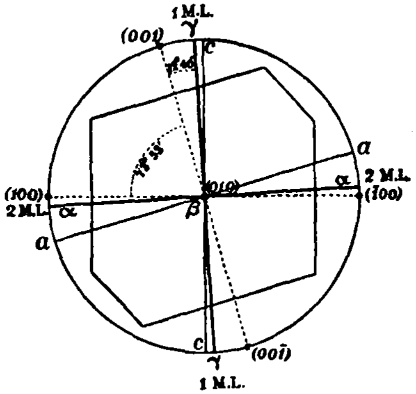

FIG. 3.—Optical orientation of ammonium magnesium chromate.

pointed out by Murmann that the plane of the optic axes is the symmetry-plane $b\{010\}$ for green light, and perpendicular thereto for red light. It will be shown that the exact wave-length for the crossing of the optic axial planes at the ordinary temperature is 0·000664 mm. in the bright red, between lithium- and C-hydrogen-light. The sign of the double refraction is positive.

Refractive Indices.—Six excellent 60°-prisms were ground, each affording two indices. The vibration-direction for the γ-index is the first median line 3° 27′ in front of the vertical axis *c*, for all wave-lengths; the direction of the symmetry-axis *b* is that of the α vibrations for red radiations beyond (of deeper red than) wave-length 0·000664 mm., but of β vibrations for all wave-lengths on the yellow side of 0·000664 right through to the blue end; while the direction 12° 40′ above the axis *a* is the β-direction for the red side and the α-direction for the yellow-green-blue side. In other words, the two refracted and perpendicularly polarized images of the signal afforded by a 60°-prism cut to transmit light vibrating parallel to the symmetry-axis and to the direction in the symmetry-plane 12° 40′ above the axis a cross one another, and become identical for red light of the wave-length 0·000664 mm. This was directly confirmed with two of the prisms employed, which were so cut (prisms 1 and 2 in the table).

Refractive Indices of Ammonium Magnesium Chromate.

Index.	Vibration direction.	Light.	Prisms 1 & 2.	Prisms 3 & 4.	Prisms 5 & 6.	Mean Index.
α	Symm. axis b.	Li	1·6247–8	...	1·6248–8	1·6248
	12° 40′ from axis a in symmetry-plane.	C	1·6263–4	1·6265–70	...	1.6265
		Na	1·6361–2	1·6364–7	...	1.6363
		Tl	1·6487–8	1·6487–93	...	1·6489
		Cd	1·6568–9	1·6574–5	...	1·6571
β	12° 40′ from a.	Li	1.6249–50	1·6250–2	...	1·6250
	symmetry-axis b.	C	1·6266–7	...	1·6268–6	1·6267
		Na	1·6371–69	...	1·6370–5	1·6371
		Tl	1·6511–3	...	1·6506–4	1·6509
		Cd	1·6602–4	...	1·6601–599	1.6602
γ	8° 27′ in front of vertical axis c.	Li	...	1·6392–4	1·6386–9	1·6390
		C	...	1·6413–8	1.6406–8	1·6411
		Na	...	1.6532–7	1.6527–8	1·6531
		Tl	...	1·6692–5	1·6682–79	1·6687
		Cd	...	1·6802–5	1·6794–5	1·6799

Mean of α, β, and γ for Na-light, 1·6422.

[For other data derived from these constants, see pp. 192–194.]

The intermediate refractive index β corrected to a vacuum (by addition of 0·0004) is expressed by the following formula for any wave-length λ within the range of visibility:

$$\beta = 1{\cdot}6057 + \frac{164\ 219}{\lambda^2} + \frac{32\ 602\ 000\ 000\ 000}{\lambda^4} + \ldots$$

The range of visibility of the spectra produced by prisms of this salt, and of the two other double chromates described in this communication, ceases before the wave-length of F-hydrogen-light is reached, owing to the excessive absorption, by these yellow crystals, of the blue and violet rays. Hence observations for F- and G-light are impossible. In order to record values as near as accuracy permits to the limit of absorption, additional observations were made for light of the green cadmium-line of wave-length 0·0005086 mm.

Refractive Indices at Higher Temperatures.—Determinations were made of the refractive indices at 80° C. The results showed that the refractive indices at 80° C. were 0·0023 lower than those for the ordinary temperature.

Optic Axial Angle.—Four excellent section-plates were obtained by grinding, perpendicular to the first median line. They all showed the optic interference-figure very clearly in monochromatic light. The figure changes remarkably as the wave-length of the light is varied, owing to the crossed-axial-plane dispersion at the ordinary temperature, the crossing occurring for bright red light between Li and C. For the deep red the optic axes are separated in a plane perpendicular to the symmetry-plane, while for red C-light they are separated in the symmetry-plane, and more and more so for orange, yellow, green, and greenish-blue. The figure becomes invisible before F-hydrogen-light is reached, owing to absorption. Hence, the last measurements were made, as in the case of the refractive indices, for light of the wave-length of the green cadmium line. The measurements of the optic axial angle for light on the red side of the crossing wave-length were made with the section-plate rotated 90°, in its own plane, from the position in which the majority of the measurements (for wave-lengths on the orange side) were made. The exact wave-length for the production of the uniaxial cross and circular rings was determined for both positions, the determinations agreeing most satisfactorily. The values for 2E are given in the first of the following tables. In the second table are given the true optic axial angles, as determined in a similar manner while the section-plate was immersed in a cell of acetylene tetrabromide, the refractive index of which liquid (1·638 for sodium-light) is almost identical with the mean index of the crystals. The usual method of employing a second section-plate perpendicular to the second median line fails in such cases, the optic axes separated at their very large obtuse angle being invisible even in monobromonaphthalene.

Apparent Optic Axial Angle 2E of Am Mg Chromate.

Plane of optic axes.	Light.	Section 1.	Section 2.	Section 3.	Section 4.	Mean.
Perp. symmetry-plane {010}.	Deep red.*	...	...	17° 10′	15° 48′	16° 29′
	Li	9° 47′	11° 57′	8 18	9 20	9 50
Parallel to symmetry-plane {010}.	C	14 56	13 27	15 25	14 6	14 29
	Na	45 47	43 53	45 55	44 57	45 8
	Tl	66 33	64 22	66 37	66 31	66 1
	Cd	...	...	...	77 43	77 43

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* For this deep red the prism-circle reading 0° 50′ of the spectro-monochromatic illuminator corresponded to the wave-length 0·000684 mm. The figure was still very clear for this wave-length in the case of two of the sections.

The uniaxial cross was produced for the following four readings of the prism-circle in the cases of the four respective sections: 0° 59′, 1° 1′, 1° 0′, and 1° 0′. The mean (1° 0′) of these readings is found, from the wave-length curve, to correspond to wave-length 0·000664 mm. It will be seen from the next table that this result is confirmed by the second series of observations, in which the interference-figure was seen with the axial separation at its true value.

True Optic Axial Angle $2V_a$ *of Am Mg Chromate.*

Plane of optic axes.	Light.	Section 1.	Section 2.	Section 3.	Section 4.	Mean.
Perp. symmetry-plane {010}.	Deep red.*	...	...	11°10′	10°23′	10°47′
	Li	5° 3′	7°20′	5 35	7 1	6 15
Parallel to symmetry-plane {010}.	C	8 7	8 48	9 52	8 49	8 54
	Na	26 49	26 38	26 53	27 13	26 53
	Tl	39 8	38 20	39 10	39 8	38 57
	Cd	...	43 58	44 50	45 4	44 37

* Circle reading 0° 50′ = wave-length 0·000684 mm.

The cross was produced for prism-circle readings 0° 59′, 1° 1′, 1° 0′, and 1° 0′, the mean being 1° 0′, which corresponds to wave-length 0·000664 mm.

Dispersion of the Median Lines.—For all wave-lengths between 0·000664 mm. in the bright red (between Li- and C-light) and the blue end of the spectrum the median lines both lie in the symmetry-plane, and consequently show inclined dispersion. Actual measurements of the latter were made while the section-plates 2 and 3 were immersed in acetylene tetrabromide; for the nature and amount of the dispersion were accurately shown by the readings of the optic-axial-angle goniometer, during the measurement of the true optic axial angle, the exact orientation of the section plate as regards the original crystal being known. Both series indicated that the first median line lies 1° 10′ nearer to the vertical axis *c* for green cadmium-light than for red C-light.

Effect of Rise of Temperature on the Optic Axial Angle.—When the section-plate perpendicular to the first median line is heated, the uniaxial cross becomes produced for shorter and shorter wave-lengths in turn. Thus at 25° C. the cross is produced for red C-light, and at 50° for a wave-length in the orange corresponding to the prism-circle reading of the spectro-illuminator 1° 20′ (wave-length 0·000636 mm.). That is, for successive temperatures the cross moves along the spectrum towards the yellow. If one illuminates with red C-light, the hyperbolic optic axial brushes being separated in the symmetry-plane at their angle 2E of 14½°, the effect of warming is to cause the brushes to approach each other, until they coalesce to form the cross (which is surrounded by several concentric circular rings) at 25° C. On moving the prism-circle to 1° 20′, the figure opens out again, but as soon as the temperature has reached 50° it has closed up again to form the cross. At 75° C. the optic axes are still separated 30° for sodium-light and 52° for thallium-light in the symmetry-plane, while for C-light and lithium-light they are respectively separated 32½° and 37° in the perpendicular plane. All these temperatures are corrected for the conduction of the crystal-holder, which was a special one of wood to reduce conduction to a minimum.

RUBIDIUM MAGNESIUM CHROMATE, $Rb_2Mg(CrO_4)_2.6H_2O$.

Analysis of 1·1076 grams of clear crystals gave 4·69 per cent. of magnesium (calculated 4·54).

Goniometry.

Crystal system: Monoclinic, holohedral, prismatic. (Class 5.)
Axial ratios and angle: $a : b : c = 0{\cdot}7526 : 1 : 0{\cdot}4953$; $\beta = 104° 49'$.
[Barker's values, $0{\cdot}7558 : 1 : 0{\cdot}4950$; $\beta = 104° 55'$.]
Forms observed: $a\{100\}$, $b\{010\}$, $c\{001\}$, $p\{110\}$, $r'\{\bar{2}01\}$, $o\{111\}$, $o'\{\bar{1}11\}$.
Habit: Short prismatic, or tabular parallel $c\{001\}$.
Cleavage: $r'(\bar{2}01)$, good.
Colour: Yellow, somewhat brighter than the ammonium salt.

The crystals of rubidium magnesium chromate, although apparently beautifully perfect to the eye, are not so easy to obtain with the perfection of planeness of faces which usually characterizes carefully prepared crops of the other two salts. But eventually excellent crystals were obtained, with a dozen of which the measurements were made.

In most crops the *b*-faces were either wanting, or only developed to the extent of narrow strips. The *c*-faces were always large and generally striated parallel to the edge *cq*, affording multiple images. The *p*-faces were also frequently affected by striation parallel to the edge *bp*. One crop of crystals exhibited none other than these two forms {001} and {110}. The *q*-faces were usually very small, and sometimes absent or only present to the extent of two instead of four faces. The *r′*-faces were good when present, but were often missing. The faces of the hemipyramids *o* and *o′* were frequently present, but as a rule gave poor reflections of the signal. The faces of the orthopinakoid $a\{100\}$ are characteristic of this salt, being well developed in many of the crops. The face in contact with the crystallizing dish was either *c*, *p*, or *q*, never *b*, and rarely *r′*.

The crystals were most commonly tabular parallel *c*{001} (fig. 4), and more rarely (in other crops) elongated along the *b*-axis, with two faces of *p*{110} best developed (fig. 5).

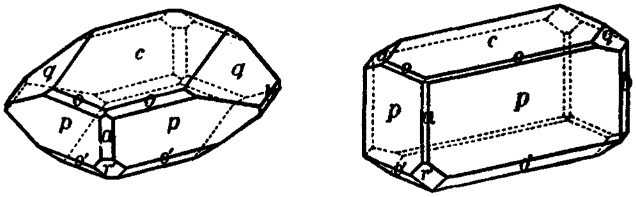

Fig. 4. Fig. 5.

Crystals of rubidium magnesium chromate.

Morphological Angles observed on Rubidium Magnesium Chromate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.
$ac = (100):(001)$	1	...	75° 10′	75° 11′
$cr' = (001):(\bar{2}01)$	21	62° 32′ – 62° 41′	62 36	62 24
$r'a = (\bar{2}01):(\bar{1}00)$	1	...	42 21	42 25
$r'c = (\bar{2}01):(00\bar{1})$	23	117 9 – 117 28	117 22	117 36
$ap = (100):(110)$	4	35 59 – 36 5	36 2	36 4
$pb = (110):(010)$	35	53 43 – 54 8	53 56	*
$pp = (110):(1\bar{1}0)$	22	72 3 – 72 14	72 9	72 8
$cq = (001):(011)$	40	25 12 – 25 48	25 36	25 35
$qb = (011):(010)$	38	64 11 – 64 40	64 25	*
$aq = (100):(011)$	1	...	76 47	76 40
$co = (001):(111)$	3	34 5 – 34 21	34 12	34 15
$op = (111):(110)$	1	...	43 49	43 49
$cp = (001):(110)$	40	77 52 – 78 12	78 4	*
$po' = (110):(11\bar{1})$	3	58 12 – 58 13	58 12	58 12
$o'c = (11\bar{1}):(00\bar{1})$	2	43 40 – 43 48	43 44	43 44
$pc = (110):(00\bar{1})$	49	101 47 – 102 7	101 56	101 56
$bo = (010):(111)$	2	70 10 – 70 15	70 12	70 11
$bo' = (010):(\bar{1}11)$	5	65 20 – 65 28	65 25	65 25
$o'o' = (\bar{1}11):(\bar{1}\bar{1}1)$	1	...	49 6	49 10
$qp = (011):(\bar{1}10)$	21	86 3 – 86 24	86 10	86 7
$pq = (\bar{1}10):(0\bar{1}\bar{1})$	24	93 35 – 93 59	93 48	93 53
$qp = (011):(110)$	21	63 43 – 63 55	63 49	63 51
$pq = (110):(0\bar{1}\bar{1})$	20	116 4 – 116 19	116 11	116 9
$r'o' = (\bar{2}01):(\bar{1}11)$	3	34 24 – 34 48	34 34	34 32
$o'p = (\bar{1}11):(110)$	3	91 52 – 92 18	92 3	92 6
$pr' = (110):(20\bar{1})$	31	53 8 – 53 24	53 16	53 22
$r'p = (\bar{2}01):(110)$	29	126 16 – 126 52	126 41	126 38

Volume.

Two series of determinations of the relative density, one made with the dozen crystals which had been used in the goniometrical measurements, yielded the following results for the heaviest crystal in each case :

For 16·5°/4°...... 2·4635...... For 20°/4°...... 2·4628.
,, 17·0°/4°...... 2·4667...... ,, ,, ... 2·4660.

The value accepted at 20°/4° is therefore 2·466 ; from which are calculated the molecular volume, $\frac{M}{d} = \frac{531 \cdot 36}{2 \cdot 466} = 215 \cdot 48$; and the molecular distance ratios (topic axial ratios) :

$$\chi : \psi : \omega = 6 \cdot 3403 : 8 \cdot 4246 : 4 \cdot 1727.$$

Optics.

Orientation of the Optical Ellipsoid.—Extinction determinations with three section-plates ground parallel to the symmetry-plane agreed in indicating that one of the extinction-directions lies 27° 1′ for sodium-light forward from the normal to $c\{001\}$. This direction is the third axis of the optical ellipsoid, affording the intermediate refractive index β; and the other extinction-direction in the symmetry-plane is the second median line and affords the maximum refractive index γ, the sign of the double refraction being negative. The first median line is the symmetry-axis b, and affords the minimum index α. As the acute angle between the axes a and c is 75° 11′, the third axis of the ellipsoid, the β axis of the indicatrix, lies 41° 50′ in front of the vertical axis c; the second

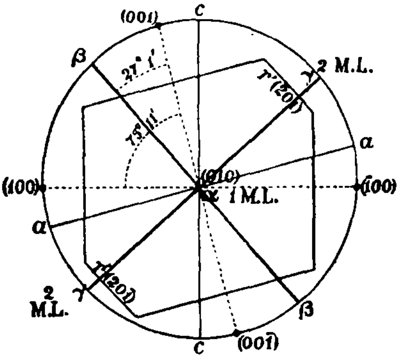

Fig. 6.—Optical orientation of rubidium magnesium chromate.

median line (γ axis) lies 48° 10′ behind the same axis c, and nearly parallel to the normal to $r'\{\bar{2}01\}$, being only 35′ behind the latter (fig. 6).

Refractive Indices.—Of the six 60°-prisms prepared by grinding, four proved satisfactory, whilst the two others being affected by turbidity were discarded.

Refractive Indices of Rubidium Magnesium Chromate.

Index.	Vibration direction.	Light.	Prism 1.	Prism 2.	Prism 3.	Prism 4.	Mean.
α	Parallel symmetry-axis b, 1st M. L.	Li	1·6105	...	1·6106	1·6103	1·6105
		C	1·6119	...	1·6121	1·6114	1·6118
		Na	1·6220	...	1·6217	1·6214	1·6217
		Tl	1·6340	...	1·6347	1·6339	1·6342
		Cd	1·6427	...	1·6429	1·6423	1·6426
β	Nearly par. $r'\{\bar{2}01\}$ in symmetry-plane.	Li	1·6209	1·6208	...	1·6207	1·6208
		C	1·6223	1·6219	...	1·6221	1·6221
		Na	1·6336	1·6326	...	1·6328	1·6330
		Tl	1·6471	1·6466	...	1·6462	1·6466
		Cd	1·6563	1·6560	...	1·6559	1·6561
γ	Nearly perp. $r'\{\bar{2}01\}$ in symmetry-plane, and par. 2nd M.L.	Li	...	1·6307	1·6313	...	1·6310
		C	...	1·6323	1·6329	...	1·6326
		Na	...	1·6430	1·6439	...	1·6435
		Tl	...	1·6575	1·6578	...	1·6577
		Cd	...	1·6671	1·6672	...	1·6672

Mean of α, β, and γ for Na-light, 1·6327.

The intermediate refractive index β corrected to a vacuum (correction $+0{\cdot}0004$) is expressed by the following general formula for any wave-length λ within the range of visibility (the blue end of the spectrum being absorbed):

$$\beta = 1{\cdot}5917 + \frac{821\ 732}{\lambda^2} + \frac{21\ 730\ 000\ 000\ 000}{\lambda^4} + \ldots$$

Refractive Indices at Higher Temperatures.—Determinations at 80° C. showed that the refractive indices α, β, and γ diminish respectively by 0·0019, 0·0024, and 0·0025 on raising the prisms from the ordinary to that temperature.

Optic Axial Angle.—Three pairs of section-plates perpendicular to the first and second median lines were obtained by grinding, and the values of $2H_a$ and $2H_0$ measured with them while the plate was immersed in each case in monobromonaphthalene. The apparent angle in air, 2E, is so large as to be unmeasurable, the true angle itself being nearly 90°, in accordance with the fact that the β refractive index is almost the mean of α and γ. The interference-figures were beautifully clear and sharp, as seen in monobromonaphthalene.

Optic Axial Angle of Rubidium Magnesium Chromate.

Light.	Section.	Observed $2H_a$.	Section.	Observed $2H_o$.	Calculated $2V_a$.	Mean $2V_a$.
Li	1	86° 15′	1 a	89° 17′	88° 26′	88° 27′
	2	86 23	2 a	89 18	88 29	
	3	86 12	3 a	89 15	88 25	
C	1	85 58	1 a	89 37	88 6	88 4
	2	86 2	2 a	89 44	88 5	
	3	85 40	3 a	89 30	88 0	
Na	1	84 35	1 a	91 11	86 34	86 32
	2	84 35	2 a	91 16	86 32	
	3	84 28	3 a	91 11	86 31	
Tl	1	82 48	1 a	93 37	84 26	84 31
	2	82 53	2 a	93 21	84 36	
	3	82 47	3 a	93 23	84 31	
Cd	1	81 47	1 a	95 1	83 12	83 15
	2	81 50	2 a	94 50	83 18	
	3	81 46	3 a	94 51	83 16	

Dispersion of the Median Lines.—Crossed dispersion of the second median line (lying in the symmetry-plane) is exhibited by the crystals of this salt, the first median line being the immovable symmetry-axis *b*. Measurements were made of the positions of the optic axes as seen in acetylene tetrabromide (refractive index for sodium-light 1·638, nearly the same as the mean index 1·633 of the crystals), and from the results the movement of the second median line was calculated. The dispersion of the axes between C- and thallium-light was found to be 3° 16′; and, as 43° 16′ is the mean semi-optic-axial-angle for sodium-light, the dispersion θ of the second median line in the symmetry-plane is afforded by the equation $\cot\theta = \sin 43^\circ\, 16' \cot 3^\circ\, 16'$, from which $\theta = 4^\circ\, 46'$. The direction of movement is such that the second median line is nearer to the axis *a* by 4° 46′ for C-light than for green thallium-light, and by the same amount nearer to the vertical axis *c* for green thallium-light than for red C-light.

This relatively large dispersion of the two principal axes of the optical ellipsoid which lie in the symmetry-plane accounts for the colour shown by a section-plate parallel to the symmetry-plane, when set for extinction in the stauroscope or polarizing microscope.

CAESIUM MAGNESIUM CHROMATE, $Cs_2Mg(CrO_4)_2.6H_2O$.

Analysis of 1·0697 grams of crystals gave 4·11 per cent. of magnesium (calculated, 3·86).

Goniometry.

Crystal system : Monoclinic, holohedral, prismatic. (Class 5).

Axial ratios and angle : $a : b : c = 0{\cdot}7431 : 1 : 0{\cdot}4888$; $\beta = 106° 4'$.

[Barker's values, $0{\cdot}7420 : 1 : 0{\cdot}4886$; $\beta = 106° 7'$.]

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

Habit : Short prismatic, or tabular parallel to $c\{001\}$.

Cleavage : $r'(\bar{2}01)$, good. Colour : Bright yellow.

The dozen individuals, selected from several different crops, used in the goniometry were exceptionally perfect, almost every crystal exhibiting all the forms given in the above list.

The b-faces were small but good. The c-faces were fairly large, but not as a rule so extensive as on the crystals of the rubidium salt. Both these and the important p-faces were frequently striated parallel to the edges cq and bp respectively, but several of the crystals selected for measurement were free from this defect. The q-faces were uniformly excellent, but sometimes two of four faces were absent. The r'-faces were good and often more largely developed than in the other two salts. The hemi-pyramids o and o' were nearly always represented by faces affording good

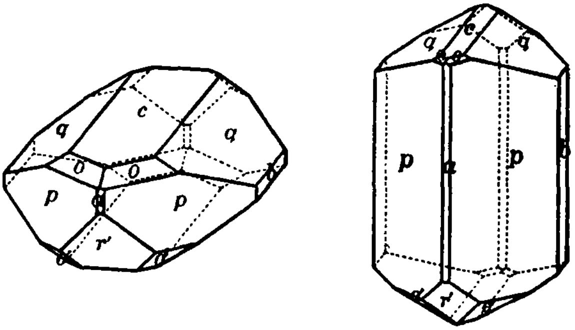

Fig. 7. Fig. 8.

Crystals of caesium magnesium chromate.

images of the signal. The faces of the orthopinakoid *a*{100} were observed, but were very narrow and the images unsatisfactory, although adequate as evidence of identity. The contact-faces (grown in contact with the crystallizing vessel) were *b*, *a*, *c*, *p*, and *r′*, and all such *c* and *p*-faces were free from striation and afforded perfect images of the signal.

Morphological Angles observed on Caesium Magnesium Chromate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.
{ *cr′* = (001) : ($\bar{2}$01)	17	63° 13′ — 63° 37′	63° 25′	63° 20′
{ *r′c* = ($\bar{2}$01) : (00$\bar{1}$)	17	116 23 — 116 50	116 29	116 40
{ *pb* = (110) : (010)	48	54 24 — 54 37	54 30	*
{ *pp* = (110) : (1$\bar{1}$0)	28	70 48 — 71 6	71 0	71 0
{ *cq* = (001) : (011)	39	24 50 — 25 20	25 9	25 10
{ *qb* = (011) : (010)	38	64 40 — 65 10	64 50	*
oq = (111) : (011)	3	26 27 — 26 43	26 37	26 39
{ *co* = (001) : (111)	1	...	33 47	33 41
{ *cp* = (001) : (110)	47	76 50 — 77 7	76 59	*
{ *po′* = (110) : (11$\bar{1}$)	21	58 50 — 59 11	58 58	59 4
{ *o′c* = (11$\bar{1}$) : (00$\bar{1}$)	22	43 50 — 44 9	44 2	43 57
{ *pc* = (110) : (00$\bar{1}$)	47	102 50 — 103 11	103 0	103 1
bo = (010) : (111)	1	...	70 43	70 41
{ *bo′* = (010) : ($\bar{1}$11)	17	65 27 — 65 56	65 38	65 34
{ *o′o′* = ($\bar{1}$11) : ($\bar{1}\bar{1}$1)	9	48 49 — 49 4	48 58	48 52
{ *qp* = (011) : ($\bar{1}$10)	35	87 23 — 87 45	87 33	87 32
{ *pq* = ($\bar{1}$10) : (0$\bar{1}\bar{1}$)	35	92 15 — 92 37	92 27	92 28
{ *qp* = (011) : (110)	30	63 6 — 63 20	63 14	63 12
{ *pq* = (110) : (0$\bar{1}\bar{1}$)	33	116 41 — 116 55	116 47	116 48
{ *r′o′* = ($\bar{2}$01) : ($\bar{1}$11)	15	34 33 — 34 59	34 50	34 49
{ *o′p* = ($\bar{1}$11) : (110)	25	91 37 — 92 5	91 55	91 54
{ *pr′* = (110) : (20$\bar{1}$)	28	53 2 — 53 20	53 9	53 17
{ *r′p* = ($\bar{2}$01) : (110)	28	126 40 — 126 58	126 51	126 43

Volume.

Three series of determinations of specific gravity, made by the Retgers immersion method, gave :—

For 19·6°/4°...... 2·7466...... For 20°/4°...... 2·7465.
" 18·8°/4°...... 2·7454...... " " ...... 2·7451.
" 19·6°/4°...... 2·7466...... " " ...... 2·7465.

The accepted value at 20°/4° is consequently 2·747 ; from which are calculated the molecular volume, $\frac{M}{d} = \frac{625{\cdot}28}{2{\cdot}747} = 227{\cdot}62$; and the molecular distance ratios (topic axial ratios):

$$\chi : \psi : \omega = 6{\cdot}4441 : 8{\cdot}6718 : 4{\cdot}2388.$$

Optics.

Orientation of the Optical Ellipsoid.—Extinction determinations with two section-plates ground parallel to the symmetry-plane *b*{010} indicated that one of the extinction-directions in this plane is situated for sodium-light 25° 26′ behind the normal to *c*{001}, and therefore 9° 22′ behind the vertical axis *c*. This direction is the first median line, and the direction of vibration for the maximum refractive index γ. The other extinction-direction normal to this in the symmetry-plane lies 25° 26′ above the axis *a*, and is inclined 9° 22′ above the normal to *a*{100} and 80° 38′ in front of the vertical axis *c*. This principal axis of the optical ellipsoid is the third such axis, and the normal to the optic axial plane, and direction of vibration for the intermediate refractive index β. The symmetry-axis *b* is the second median line and the direction of vibration for the minimum refractive index α. The plane of the optic axes is thus perpendicular to the symmetry-plane. The sign of the double refraction is positive. The above facts will be clear from fig. 9.

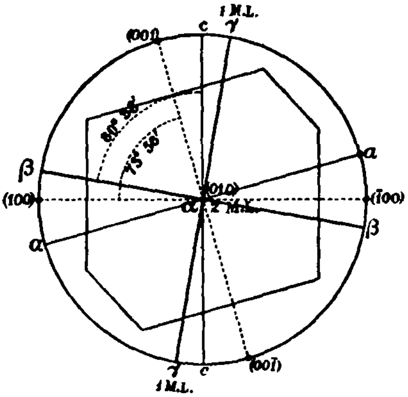

FIG. 9.—Optical orientation of caesium magnesium chromate.

Refractive Indices.—Six excellent 60°-prisms were obtained by grinding on the cutting-and-grinding goniometer. Each prism was orientated so as to afford two indices directly, and the results obtained are collected in the following table :

Refractive Indices of Caesium Magnesium Chromate.

Index.	Vibration direction.	Light.	Prisms 1 & 2.	Prisms 3 & 4.	Prisms 5 & 6.	Mean.
α	Parallel symmetry-axis b, 2nd M. L.	Li	...	1·6258-7	1·6261-52	1·6257
		C	...	1·6270-3	1·6275-64	1·6271
		Na	...	1·6367-71	1·6373-65	1·6369
		Tl	...	1·6493-4	1·6495-88	1·6493
		Cd	...	1·6578-9	1·6581-73	1·6578
β	9° 22′ from normal to orthopinakoid $a\{100\}$	Li	1·6312-3	...	1·6311-04	1·6310
		C	1·6324-7	...	1·6325-18	1·6324
		Na	1·6429-6	...	1·6426-19	1·6425
		Tl	1·6554-5	...	1·6552-46	1·6552
		Cd	1·6641-2	...	1·6642-33	1·6640
γ	Parallel 1st M.L. 9° 22′ behind vertical axis c.	Li	1·6425-6	1·6420-6	...	1·6424
		C	1·6437-41	1·6435-8	...	1·6438
		Na	1·6549-50	1·6544-5	...	1·6547
		Tl	1·6684-8	1·6682-77	...	1·6683
		Cd	1·6780-3	1·6780-70	...	1·6778

Mean of α, β, and γ for Na-light, 1·6447.

The intermediate refractive index β corrected to a vacuum (correction $+0{\cdot}0004$) is expressed for any wave-length λ by the following general formula, with great accuracy for the region from C to Tl, and approximately outside these limits:

$$\beta = 1{\cdot}6051 + \frac{694\ 806}{\lambda^2} + \frac{21\ 436\ 060\ 000\ 000}{\lambda^4} + \ldots$$

Refractive Indices at Higher Temperatures.—Determinations at 80° C. indicated that the refractive indices were reduced by about 0·0026 by raising the prisms from the ordinary to that temperature.

Optic Axial Angle.—Three pairs of section-plates were ground perpendicular to the first and second median lines, and very good values for 2E, $2H_a$, and $2H_o$ were obtained from them, the two latter by immersion in monobromonaphthalene. A fourth very large plate perpendicular to the first median line was also prepared, with natural faces left still visible as evidence of orientation. The following tables express the results:

Apparent Optic Axial Angle 2E of Caesium Magnesium Chromate.

Light.	Section 1.	Section 2.	Section 3.	Section 4.	Mean 2*E*.
Li	131° 3′	131° 7′	131° 0′	131° 0′	131° 3′
C	132 1	131 34	131 35	131 36	131 27
Na	133 19	133 1	132 41	132 39	132 55
Tl	133 39	133 27	133 3	133 17	133 22

The values for the angle in cadmium-light were not sufficiently trustworthy, as the angle was growing so large as to be on the verge of invisibility, and the light feeble owing to absorption.

True Optic Axial Angle of Caesium Magnesium Chromate.

Light.	Section.	Observed $2H_a$.	Section.	Observed $2H_o$.	Calculated $2V_a$.	Mean $2V_a$.
Li	1	67° 10′	1 a	113° 29′	66° 58′	67° 9′
	2	66 59	2 a	113 32	66 50	
	3	66 41	3 a	110 11	67 40	
C	1	67 6	1 a	113 30	66 55	67 7
	2	66 54	2 a	113 34	66 46	
	3	66 40	3 a	110 12	67 39	
Na	1	66 59	1 a	113 35	66 49	67 3
	2	66 48	2 a	113 34	66 42	
	3	66 39	3 a	110 13	67 38	
Tl	1	66 33	1 a	114 1	66 23	66 33
	2	66 17	2 a	113 58	66 12	
	3	66 12	3 a	111 3	67 3	
Cd	1	65 51	1 a	114 28	65 46	65 57
	2	65 52	2 a	114 35	65 44	
	3	65 40	3 a	112 1	66 22	

Dispersion of the Median Lines.—That there was considerable horizontal dispersion of the first median line was clear during the measurements of $2H_a$, the apparent angle in monobromonaphthalene; for the section-plate required to be rotated slightly parallel to the vertically arranged symmetry-plane, in order to adjust the optic axial plane (arranged horizontally) exactly to the horizontal cross-wire for the various colours of the spectrum in succession. One mode of determining the amount of the horizontal dispersion would be to have the adjusting segments of the polariscopical goniometer (the large optic-axial-angle apparatus) graduated, and it is proposed to have silver divided arcs provided on a new instrument for the purpose. The section-plate No. 4—the orientation of which was clearly known from the crystal-faces left on the edges—was arranged so that the plane of the optic axes was vertical, and the planes of the nicols were made vertical and horizontal. The section was then tilted by one of the adjusting segments until one of the optic axes, as seen first in monobromonaphthalene and subsequently in acetylene tetrabromide, was adjusted to the horizontal cross-wire. It was then brought exactly to the vertical wire for red lithium-light, and then for green cadmium-light, by rotation of the goniometer circle, and the readings of the latter for each position taken. The difference of the readings was the apparent dispersion of that optic axis in the liquid employed. Monobromonaphthalene has a somewhat higher refractive index (1·6657 for sodium-light), and acetylene tetrabromide a somewhat lower one (1·6380), than the mean crystal index (1·6447), and the mean of the indications may be taken as the true value. It proved to be 3° 14′ in the latter liquid and 3° 10′ in the former one, so that the mean 3° 12′ may be safely taken as the true dispersion of that axis. Similar operations carried out with the other optic axis gave an identical result. The direction is such that the median line will be nearer to the vertical axis c for green cadmium-light than for red lithium-light. The semi-optic-axial-angle for sodium-light being 33° 32′, the dispersion θ of the median line is given by the formula: $\cot\theta = \sin(90° - 33° 32') \cot 3° 12'$, from which θ is found to be 3° 50′. Hence, the first median line is dispersed in the symmetry-plane so that it is nearer to the vertical axis c by 3° 50′ for green cadmium-light than it is for red lithium-light. An identical result was obtained by determining also the position of the axes for sodium-light, and then calculating the difference of position for lithium-light on one side and for cadmium-light on the other. The sum of the two was 3° 50′.

Effect of Rise of Temperature on the Optic Axial Angle.—One of the section-plates perpendicular to the first median line was heated to 70° C. in the heating apparatus of the larger Fuess optic-axial-angle goniometer. The optic axial angle gradually diminished as the temperature rose, until when the latter was constant at 70° (corrected for conduction of the crystal-holder, which was a special one of wood, the correction being even then 10°, the actual reading of the two thermometers in the air-bath being 80°) the apparent angle in air 2E was 130° 3′, whereas at 14° C., under the same conditions before starting the heating, the angle was 132° 27′. There is thus a diminution of 2° 24′ between 14° C. and 70° C., or 2½° for 56° C. of rise of temperature.

COMPARISON AND DISCUSSION OF RESULTS.

Morphology.

Habit.—The rubidium and caesium double chromates containing magnesium exhibit the same general relations of habits as the analogous double sulphates and selenates, namely, on passing from the rubidium to the caesium salt a diminution in the relative development of the basal pinakoid $c\{001\}$ and an increase in the importance of the clinodomal prism $q\{011\}$. The ammonium salt has been found to exhibit almost every variety of habit observed in the series, a property also characteristic of the ammonium salts of the series in general.

Axial Ratios and Axial Angles.—These are compared below:

	a		b		c	β
Ammonium magnesium chromate	0·7517	:	1	:	0·4924	106° 7′
Rubidium „ „	0·7526	:	1	:	0·4953	104° 49′
Caesium „ „	0·7431	:	1	:	0·4888	106° 4′

The axial ratios of the ammonium salt are very close to those for the rubidium salt, and between the latter values and those for the caesium salt. The relations of the axial ratios of the rubidium and caesium salts are similar to those for all the groups (a group containing the same dyad M-metal) of the series, namely, the ratios diminish on passing from the rubidium to the caesium salt.

The axial angles of the ammonium and caesium salts are very nearly identical, a fact which has been shown to be true in all the groups of double sulphates and selenates yet fully investigated. The axial angle increases by 75′ on replacing rubidium by caesium, and this fact also is in complete agreement with the results for the double sulphates and selenates, an increase of slightly more than a degree being general on replacement of rubidium by caesium.

The Crystal Angles.—These are compared in the accompanying table, from an inspection of which the following conclusions may be drawn:

The differences between the angles of the rubidium and caesium salts are of the same sign and order as those between the rubidium and caesium salts of all the groups of double sulphates and double selenates known to belong to the series $R'_2M''[(S, Se)O_4]_2.6H_2O$. Thus, for instance, if one compares the last column of the table, which shows these differences for the magnesium group of double chromates, with the column of differences given in the tables of angles of the rubidium and caesium salts of the manganese and cadmium groups of double sulphates[1]—groups which are especially similar, as no potassium salts have yet been obtained belonging to them—it will be found that the signs indicating the direction of change (an increase of angle being + and a diminution −) are the same, and that the actual amounts of change are very similar. The same is true if any of the other six tables given in that memoir for the other groups of double sulphates are compared with the table now given; and also if the tables for the magnesium and zinc groups of double selenates[2] are examined.

Hence there can be no doubt that if the potassium salt of this magnesium chromate group could be prepared, the three salts of the magnesium group

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[1] A. E. H. Tutton, loc. cit., 1893, pp. 379 and 418.

[2] A. E. H. Tutton, loc. cit., 1905, p. 1167.

Comparison of the Calculated Morphological Angles.

Angle.	Am Mg Chromate.	Rb Mg Chromate.	Cs Mg Chromate.	Diff. between Rb and Cs salts.
$ac = (100):(001)$	73° 58′	75° 11′	73° 56′	−75′
$as = (100):(101)$	45 51	46 40	45 47	−53
$sc = (101):(001)$	28 2	28 31	28 9	−22
$cr' = (001):(\bar{2}01)$	63 11	62 24	63 20	+56
$cs' = (001):(\bar{1}01)$	37 33	37 21	37 43	+22
$s'r' = (\bar{1}01):(\bar{2}01)$	25 38	25 8	25 37	+34
$r'a = (\bar{2}01):(\bar{1}00)$	42 56	42 25	42 44	+19
$r'c = (\bar{2}01):(00\bar{1})$	116 49	117 36	116 40	−56
$ap = (100):(110)$	35 50	36 4	35 30	−34
$pp' = (110):(120)$	19 28	19 28	19 28	0
$p'b = (120):(010)$	34 42	34 28	35 2	+34
$pp''' = (110):(130)$	29 23	29 20	29 27	+ 7
$p'''b = (130):(010)$	24 47	24 36	25 3	+27
$pb = (110):(010)$	54 10	53 56	54 30	+34
$pp = (110):(1\bar{1}0)$	71 40	72 8	71 0	−68
$cq = (001):(011)$	25 19	25 35	25 10	−25
$qb = (011):(010)$	64 41	64 25	64 50	+25
$ao = (100):(111)$	48 57	49 47	48 51	−56
$oq = (111):(011)$	26 31	26 53	26 39	−14
$aq = (100):(011)$	75 28	76 40	75 30	−70
$qo' = (011):(\bar{1}11)$	33 57	33 46	34 10	+24
$o'a = (\bar{1}11):(\bar{1}00)$	70 35	69 34	70 20	+46
$co = (001):(111)$	33 40	34 15	33 41	−34
$op = (111):(110)$	43 20	43 49	43 18	−31
$cp = (001):(110)$	77 0	78 4	76 59	−65
$po' = (110):(11\bar{1})$	59 6	58 12	59 4	+52
$o'c = (11\bar{1}):(00\bar{1})$	43 54	43 44	43 57	+13
$pc = (110):(00\bar{1})$	103 0	101 56	103 1	+65
$bn = (010):(121)$	54 45	54 13	54 59	+46
$no = (121):(111)$	15 47	15 58	15 42	−16
$bo = (010):(111)$	70 32	70 11	70 41	+30
$os = (111):(101)$	19 28	19 49	19 19	−30
$bo' = (010):(\bar{1}11)$	65 22	65 25	65 34	+ 9
$o's' = (\bar{1}11):(\bar{1}01)$	24 38	24 35	24 26	− 9
$o'o' = (\bar{1}11):(\bar{1}\bar{1}1)$	49 15	49 10	48 52	−18
$sq = (101):(011)$	37 4	37 35	37 3	−32
$qp = (011):(\bar{1}10)$	87 19	86 7	87 32	+85
$ps = (\bar{1}10):(\bar{1}0\bar{1})$	55 37	56 18	55 25	−53
$pq = (\bar{1}10):(0\bar{1}\bar{1})$	92 41	93 53	92 28	−85
$s'q = (\bar{1}01):(011)$	44 13	44 11	44 17	+ 6
$qn = (011):(121)$	26 8	26 26	26 9	−17
$np = (121):(110)$	36 58	37 25	37 3	−22
$qp = (011):(110)$	63 1	63 51	63 12	−39
$ps' = (110):(10\bar{1})$	72 46	71 58	72 31	+33
$pq = (110):(0\bar{1}\bar{1})$	116 59	116 9	116 48	+39
$r'o' = (\bar{2}01):(\bar{1}11)$	34 57	34 32	34 49	+17
$o'p = (\bar{1}11):(110)$	91 28	92 6	91 54	−12
$pr' = (110):(20\bar{1})$	53 35	53 22	53 17	− 5
$r'p = (\bar{2}01):(110)$	126 25	126 38	126 43	+ 5

of double chromates containing respectively potassium, rubidium, and caesium as the R-metal would form a eutropic series, exhibiting the progression according to the atomic weight of the alkali metal, which has been shown to be a general property in all the groups of this isomorphous series.

As regards the angles of the ammonium salt, they are so similar to those of the other two salts that there can be no hesitation whatever in allocating ammonium magnesium chromate to the monoclinic isomorphous series in question; and in the great majority of cases the angles are very close indeed to those of caesium magnesium chromate. A careful analysis shows that out of 48 angles compared, 36 are nearer (usually very near) to the corresponding angle of the caesium salt, and only 12 are nearer to that of the rubidium salt. In 27 cases the value for the ammonium salt lies between the values for the rubidium and caesium salts, in 16 cases it lies beyond the caesium salt, and in 5 cases below the rubidium salt.

Thus the ammonium salt, although belonging to the isomorphous series, shows no progression entitling it to inclusion in the eutropic series to which the rubidium and caesium salts belong.

It is interesting to see what is the effect on the angular magnitudes of the replacement of sulphur by selenium and by chromium. A comparison has been made of the respective analogous angles of rubidium magnesium sulphate, selenate, and chromate, and also of those of caesium magnesium sulphate, selenate, and chromate. No progression according to the atomic weights of sulphur, chromium, and selenium (respectively 31·82, 51·6, and 78·6) is exhibited. The vast majority of the angles of the chromate lie beyond those of the selenate, a very few indeed lying between those of the sulphate and selenate. Thus the fact that chromium does not belong to the eutropic series containing sulphur and selenium is clearly brought out. For chromium belongs to the even series of Mendeléeff's sixth group, while sulphur and selenium belong to the odd series.

Volume.

The volume constants are compared in the next table:

Volume Constants of Magnesium Chromate Group.

Salt.	Density at 20°/4°.	Molecular volume.	Molecular distance ratios.		
			χ	ψ	ω
Am Mg chromate	1·832	216·92	6·3751	8·4811	4·1761
Rb Mg ,,	2·466	215·48	6·3403	8·4246	4·1727
Cs Mg ,,	2·747	227·62	6·4441	8·6718	4·2388

The molecular volume and molecular distance ratios of the ammonium salt are thus nearly identical with those of the rubidium salt, and lie between those for the rubidium and caesium salts. This is a similar result to that afforded by a comparison of the ammonium salts of the sulphate and selenate groups investigated. The increase of molecular volume brought about by the replacement of rubidium by caesium is 12·14 units, which is very close to the average increase, 12·7 units, observed in the sulphate and selenate groups; and the extension of the structure, indicated by the increase of the molecular distances, is also of the same order as that observed in these groups.

Optics.

Orientation of the Optical Ellipsoid.—It has been shown to be general throughout the whole isomorphous series, that the optical ellipsoid rotates about the symmetry-axis *b* when the alkali base is changed. This rotation has, further, been shown to follow the order of the atomic weights of the metals in the cases of potassium, rubidium, and caesium salts. The order has always been[1]: ammonium salt, potassium salt, rubidium salt, caesium salt. The *a* axis of the ellipsoid of the ammonium salt has always been close to the vertical axis *c*, and that of the potassium salt has followed closely at a slightly greater angle in front of the vertical axis; then in front of this again come the rubidium and caesium *a* axes in succession; and the result in all cases has been that the rubidium *a* axis is about midway between the

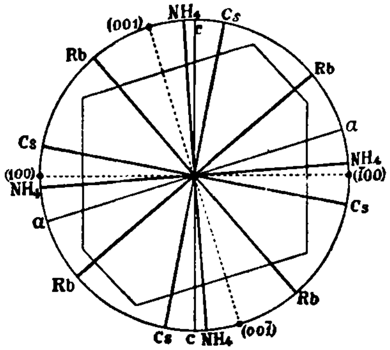

FIG. 10.—Optical orientation of the double chromates.

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[1] A. E. H. Tutton, loc. cit., 1905, p. 1172.

ammonium a axis and the caesium a axis. Throughout the whole series of the double sulphates and selenates the optic axes lie in the symmetry-plane. This is precisely so in the case of the magnesium chromate group under discussion, as regards the extinction-directions in the symmetry-plane, as will be clear both from fig. 10 and from the following table, which gives the angular distance of one of the axes of the ellipsoid from the vertical axis c.

Inclination of Axis of Indicatrix to (in front of) Vertical Axis c.

Am Mg chromate	3° 27′
Rb Mg ,, ...	41 50
Cs Mg ,, ...	80 38

The chromates show their individuality, however, by the fact that the axis in question is not the a axis, but the β axis in the case of the rubidium and caesium salts, and the γ axis in the case of the ammonium salt.

Refractive Indices.—The principal and mean indices, the double refraction, etc., for sodium-light are compared in the following table (for other wave-lengths see the detailed description of each salt):

	Am Mg chromate.	Rb Mg chromate.	Cs Mg chromate.
a (Na-light) ...	1·6363	1·6217	1·6369
β ,, ...	1·6371	1·6330	1·6425
γ ,, ...	1·6531	1·6435	1·6547
$\frac{1}{3}(a+\beta+\gamma)$,, ...	1·6422	1·6327	1·6447
$\gamma-a$,, ...	0·0168	0·0218	0·0178
Sign of double refraction ...	positive	negative	positive
2V (Na-light) ...	26° 53′	86° 32′	67° 3′
Axes of the optical indicatrix $a:\beta:\gamma$ (Na)	0·9995 : 1 : 1·0098	0·9931 : 1 : 1·0064	0·9966 : 1 : 1·0074

The refractive power of the crystals of this group is very high, much higher even than that of thallium zinc sulphate, of which the mean index is 1·6064, the maximum hitherto observed in the series. This will be clearly apparent from the following comparison of the mean refractive indices (for sodium-light) of the nine salts of the three groups containing magnesium. And it is again obvious that the double chromates, although belonging to the same isomorphous series, are not in the same eutropic series as the double sulphates and selenates.

Mean Refractive Indices of the Salts of the three Magnesium Groups.

	Chromate.	Sulphate.	Selenate.
Am Mg	1·6422	1·4744	1·5111
Rb Mg	1·6327	1·4713	1·5059
Cs Mg	1·6447	1·4877	1·5198

The refractive indices of rubidium magnesium and caesium magnesium chromates show the usual progression with atomic weight, which has been shown to be general throughout the series. The crystals of ammonium magnesium chromate prove to refract light to almost the same extent as the caesium salt, the mean refractive index being slightly lower than that of the latter but much higher than the mean index of the rubidium salt. The α and β indices of the ammonium salt are almost identical for the red end of the spectrum, and indeed they are actually identical for bright red light of wave-length 0·000664 mm. (between lithium- and C-light), the directions of vibration for the α and β indices interchanging on the two sides of this wave-length.

The double refraction is also high as compared with that of the double sulphates and selenates. It shows a diminution on passing from the rubidium to the caesium salt, in accordance with the rule found for the whole series: namely, that in any eutropic series of which potassium, rubidium, and caesium are the interchangeable metals the double refraction diminishes with rise of atomic weight of the interchanged metal. The double refraction of the ammonium salt is slightly lower still than that of the caesium salt, whereas in the sulphates and selenates it is always intermediate between the values for the rubidium and caesium salts.

Dispersion.—The dispersion is also much higher than in the double sulphate and selenate groups. The maximum dispersion in the magnesium sulphate group between lithium- and G-light is 0·0132 (in the case of ammonium magnesium sulphate), and in the magnesium selenate group 0·0173 (for ammonium magnesium selenate). The following much higher figures are found for the magnesium chromate group, and they refer to a less extended part of the spectrum, from the red lithium to the green cadmium-line only, as absorption occurs beyond this, the crystals being deeply coloured yellow.

Dispersion of Double Chromates between Li- and Cd-light.

	α	β	γ
Am Mg chromate	0·0323	0·0352	0·0409
Rb Mg ,,	0·0321	0·0358	0·0362
Cs Mg ,,	0·0321	0·0330	0·0354

Molecular Refraction, etc.—The following values are calculated from the data recorded in previous pages:

Molecular Optical Constants.

		α	β	γ	Mean $\frac{1}{3}(\alpha+\beta+\gamma)$
Specific refraction, $\frac{n^2-1}{(n^2+2)d}$ for ray C.	Am Mg chromate	0·1933	0·1934	0·1969	
	Rb Mg ,,	0·1409	0·1428	0·1448	
	Cs Mg ,,	0·1290	0·1299	0·1372	
Molecular refraction, $\frac{n^2-1}{n^2+2}\cdot\frac{M}{d}$ (Lorenz) for ray C.	Am Mg chromate	76·84	76·86	78·26	77.32
	Rb Mg ,,	74·88	75·90	76·92	75.90
	Cs Mg ,,	80·69	81·23	85·80	82.57
Molecular refraction, $\frac{n-1}{d}M$ (Gladstone & Dale) for ray C.	Am Mg chromate	135·90	135·94	139·07	136·97
	Rb Mg ,,	131·83	134·05	136·31	134·06
	Cs Mg ,,	142·74	143·95	146·54	144·41

The molecular refraction of the ammonium salt is thus seen to be very slightly higher than that of the rubidium salt, and the increase of atomic weight when rubidium is replaced by caesium is accompanied by a considerable increase of molecular refraction. Both facts are analogous to those previously found for the double sulphate and selenate groups containing either magnesium or any other of the eight dyad-acting metals forming the series.

These conclusions are independent of the temperature; for it was definitely determined that the refractive indices of the crystals diminished on raising the temperature, so that the effect of rise of temperature acts in the same direction, that of lowering, on both the refraction and the density.

GENERAL CONCLUSIONS.

Three main conclusions are to be derived from this investigation, concerning respectively (1) the relations of the rubidium and caesium magnesium chromates, (2) the position of ammonium magnesium chromate, and (3) the relations of these double chromates to the analogous double sulphates and selenates previously studied.

(1) Rubidium magnesium chromate and caesium magnesium chromate have been found to exhibit crystallographic characters precisely similar in

their mutual relationships to those of the rubidium and caesium salts of every group of double sulphates and double selenates already studied. The parallelism extends to every property investigated. There can be no doubt that if the potassium salt of the group were capable of formation and could be prepared, the three double chromates containing potassium, rubidium, and caesium would exhibit the progression of a eutropic series, in accordance with the atomic weight of the alkali metal, the revelation of which has been one of the main results of the previous investigations by one of us. Indeed, it would be quite simple to predict the crystallographic constants of the missing potassium salt. We have here only another evidence of the eutropic progression, for the caesium salt is highly stable, the rubidium salt exhibits a tendency to efflorescence and to become opaque in course of time, while the potassium salt will not form at all. This progression as regards facility of formation of potassium, rubidium, and caesium salts was also well shown in the case of the copper group of double sulphates, in which the potassium salt was obtained with difficulty, in very small crystals which only very occasionally were clear and transparent; the rubidium salt was more readily obtained in crystals free from turbidity; while those of caesium copper sulphate were characteristically clear and limpid.

(2) The position of the ammonium salt in the magnesium group of double chromates has been shown to be similar to that found in general for the ammonium salt of any group of double sulphates or double selenates of the series. As regards morphology the crystal angles have been shown to be in a large majority of cases very nearly identical with those of caesium magnesium chromate, and in general so similar to the angles of both the rubidium and caesium salts that there can be no hesitation in allocating ammonium magnesium chromate to the isomorphous series $R'_2M''[(S,Se,Cr)O_4]_2.6H_2O$. No rule of progression with atomic or molecular weight applies, however, so that the ammonium salt stands outside the eutropic set of which the only two members yet produced are the rubidium and caesium magnesium chromates. As regards structure, the molecular volume and distance ratios of the ammonium salt have been shown to be nearly identical with those of the rubidium salt, the slight difference leaning towards the caesium values. A similar remark applies to the molecular refraction, while the actual values of the refractive indices, of the mean refractive index, and of the amount of double refraction, are very near to those of the caesium salt. The similarity of the structural constants of the ammonium and rubidium salts of this group confirm in a particularly valuable manner, owing to the independent nature of chromic

acid as distinguished from sulphuric and selenic acids, the conclusion derived from former work, that the replacement of potassium by ammonium in any group of this isomorphous series is accompanied by practically no more extension of the crystal structure than when rubidium is introduced for potassium, the ten atoms of the two ammonium groups NH_4 apparently going into the same space as the two atoms of rubidium.

(3) With respect to the effect of replacing the negative element sulphur or selenium by chromium, the evidence is clear that these three elements do not give rise to a eutropic series including all three, sulphur and selenium alone belonging to a eutropic series which might also conceivably include tellurium. Chromium, like ammonium in the case of the bases, in the form of chromic acid gives rise to double chromates which belong truly to this isomorphous series, which may thus be written legitimately as $R'_2M''[(S,Se,Cr)O_4]_2.6H_2O$; but these double chromates show no progression according to the atomic weight of chromium, that is the order S, Cr, Se (31·82, 51·6, and 78·6) is not followed in these salts. The refractive indices of the double chromates, and also their double refraction and dispersion, are much higher than those of the double sulphates and selenates, and even their molecular refractions are outstandingly high, although their structural constants, the molecular volume and distance ratios, lie mainly between the values for the corresponding sulphates and selenates, and entirely so as regards the volume. In many other details of the optical properties the double chromates have also shown their individuality. The interfacial angles lie mostly beyond those of the double selenates.

The final result of this investigation has thus been to afford a further and independent proof of the relations between the ammonium, potassium, rubidium, and caesium salts of any one and the same group (containing the same M-metal) of this isomorphous series; and to confirm in every detail the conclusions derived from those former investigations, that the potassium, rubidium, and caesium salts of any such group form a eutropic set or inner series, rigidly following a law of progression of the crystallographic properties with the atomic weight of the alkali metal, while the ammonium salt of the group belongs truly to the isomorphous series but not to the more exclusive eutropic series within it.