

Chemistry. — *Roentgenspectrographic Investigations on the Structure of the Artificial Ultramarines and the Problem concerning their Relations to the Minerals Hauyne, Nosean, Sodalite, Lazurite and Nephelite.* By Prof. Dr. F. M. JAEGER, Dr. H. G. K. WESTENBRINK and Mr. F. A. VAN MELLE.

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§ 1. Notwithstanding the extensive technical experience gradually obtained in the preparation of the *ultramarine*-dyes during almost a hundred years, and notwithstanding the very great number of investigations made with the purpose to elucidate the true structure of these remarkable compounds, — it must be acknowledged, that the problem concerning the true chemical nature of the *ultramarines* still remains unsolved.

After CLEMENT and DESORMES ¹⁾ in 1806 gave the data of a complete analysis of the blue ultramarine, GUIMET ²⁾ and GMELIN ³⁾ in 1828 discovered the methods allowing the artificial preparation in truly unlimited quantities of the precious dye formerly only obtained from *lapis lazuli*. In this case also chemical synthesis has finally surpassed nature, because experience has taught, that ultramarines of all kinds of colour can be obtained ⁴⁾ by mere variations of the applied method, by which the colouring matter was prepared by heating with *sodium-sulphide* or with a mixture of *sodium-sulphate* and coal some *sodium-aluminium-silicates* of a composition analogous to that of *nephelite*. Now, besides the original *blue* ultramarine, also *yellow, green, pink, red* and *violet* ultramarines are prepared; and within each of these colour-limits, a great number of different modifications may, moreover, be obtained, which differ from each other only by slight gradations of colour or by their particularly warm glow.

The occurrence of the blue ultramarine-dye in *lazurite* and of the blue colour in many *hauynes, noseans* and in some *sodalites*, have since long drawn the attention of mineralogists to the fact, that presumably a closer constitutional relation may exist between the natural *ultramarine* on the one side, and the remarkable minerals mentioned on the other, which minerals hitherto were considered to belong to one and the same family. More particularly BRÖGGER and BÄCKSTRÖM ⁵⁾ emphasized

¹⁾ J. K. CLÉMENT and DESORMES, Ann. de Chim. et Phys. 57, 317, (1806).

²⁾ J. B. GUIMET, Bull. de la Soc. d'Encouragement, etc., (1828).

³⁾ G. C. GMELIN, Abh. Naturw. Ges. Württemberg, (1828), 2, 191; SCHWEIGGER's Polyt. Journ. 54, 360.

⁴⁾ See also R. HOFFMANN: „Ultramarin“, Braunschweig, (1902); L. BOCK, „Die Konstitution der Ultramarine“, Braunschweig, (1924); idem, „Die Fabrikation der Ultramarinfarben“, Halle, (1918); F. SINGER, „Die künstlichen Zeolithe“, Diss. Berlin, (1911). In these works and also in C. DOELTER's „Handbuch der Mineral-Chemie“, Band 2, 2, p. 295, 286 and 229—261, (1917) a detailed review is published of the literature concerning these compounds.

⁵⁾ W. C. BRÖGGER and K. BÄCKSTRÖM, Zeitschr. f. Kryst. und Miner. 18, 209, (1890).

the mutual relations of these compounds as a result of their very detailed investigations on the *alkali-* and *calcium-garnets*. It was for this reason, that during our ROENTGENSpectrographic work on the artificial ultramarines, we simultaneously started the examination of the said minerals after the same experimental method. The results of all these investigations are published in the present paper.

According to BRÖGGER and BÄCKSTRÖM, *sodalite*, *hauyne* and *nosean* must all be placed in one and the same group of minerals, namely that of the *alkali-* and *alkali-calcium-garnets*. According to these authors, *sodalite* would surely not possess hexakisoctahedral symmetry: as well the corrosion-figures obtained by them, as also other particulars of the rhombicdodecahedrally shaped crystals, seem to indicate a hexacistetrahedral symmetry and a twin-formation parallel to $\{100\}$. They attribute the same symmetry, moreover, to *nosean* and *hauyne*, — which also crystallize in most cases in the form of rhombicdodecahedra, — by drawing attention to the great analogy which exists between these minerals and *sodalite*, and to the octahedral forms with furrowed edges, as observed by VOM RATH. This last argument, however, does not hold ¹⁾, as may be seen from the analogous phenomenon in the case of *diamond*. In the case of a colourless *nosean* we observed, moreover, that the crystal accidentally broke off exactly parallel to $\{111\}$, while *sodalite* shows a cleavage parallel to $\{110\}$; it is, however, yet hazardous to assume a cleavability parallel to $\{111\}$ in *nosean*. In the following page it will become clear, that *sodalite* has, indeed, a structure, which is quite different from that of *nosean* and *hauyne*; so that it can by no means be placed in the same group with the others, although BRÖGGER and BÄCKSTRÖM believed to have proved, that *lazurite* is a mixture of *sodalite*, *hauyne* and natural *ultramarine*.

As regards the artificial *ultramarines*, — microscopical examination has proved, that they are optically isotropous, like the natural product, and that they crystallize in the shape of microscopical, very minute rhombicdodecahedra ²⁾. Furthermore, the *sodium* of the ultramarines appears to be easily replaceable by other bases ³⁾, e.g. by the oxides of the metals *K*, *Li*, *Ca*, *Ba*, *Mg*, *Zn*, *Ag*, etc., — as is the case also in the *permutites* and some *zeolites*. As is the case in the *zeolites*, the *sodium*-atoms in these compounds are evidently highly mobile; moreover, SINGER ⁴⁾

¹⁾ Conf. F. M. JAEGER, „Inleiding tot de Studie der Kristalkunde, Groningen, (1924), p. 178, 179.

²⁾ See also F. FISCHER, DINGLER's Polyt. Journal, **221**, 562, (1876); T. MOREL, Mon. Scientifique, (1879), 785; C. GRÜNZWEIG and R. HOFFMANN, Ber. d. d. Chem. Ges., **9**, (1876), 864; W. C. BRÖGGER and H. BÄCKSTRÖM, loco cit., p. 242.

³⁾ K. HEUMANN, Ber. d. d. Chem. Ges. **10**, (1877), 991; P. G. SILBER, ibid., **14**, 941, (1881); DE FORCRAND and BALLIN, Bull. Soc. chim., **30**, 112, (1878); Compt. rend., **88**, 30, (1879); K. HEUMANN, Ann. d. Chem. u. Pharm., **201**, 262, (1880); J. SZILASI, Ann. der Chemie und Pharm., **251**, 97, (1889).

⁴⁾ F. SINGER, „Ueber künstliche Zeolithe“, Diss. Berlin, (1911).

demonstrated, by means of direct synthesis, that there exists a close relation between *permutites* and *zeolites* on the one hand, and the *ultramarines* on the other hand. Also derivatives of the ultramarines are known, in which *aluminium* is substituted by *titanium*, *silicon* by *boron*, etc., and in which *selenium* and *tellurium* hold the place of the *sulphur*-

COMPOSITION OF SOME STUDIED ULTRAMARINES.				
GUIMET I; Violet	GUIMET II; Red	GUIMET III; Blue	GUIMET IV; Green	Germ. Ultram. VIII; Blue
Specific weight : $d_{250} = 2.34$ Al = 14.25 % Si = 19.33 % S = 10.40 % Atomic ratio: Al:Si:S = 6:6.86:3.72	Specific weight : $d_{250} = 2.36$ Al = 15.53 % Si = 19.79 % S = 9.65 % Atomic ratio: Al:Si:S = 6:7.30:3.13	Specific weight : $d_{250} = 2.35$ Al = 13.10 % Si = 19.38 % S = — Atomic ratio: Al:Si:S = 6:8.52	Specific weight : $d_{250} = 2.27$ Al = 16.54 % Si = 17.21 % S = 7.98 % Atomic ratio: Al:Si:S = 6:6.06:2.44	Specific weight : $d_{250} = 2.37$ Al = 14.01 % Si = 18.33 % S = — Atomic ratio: Al:Si:S = 6:7.50
Some specific weights of German ultramarines were, in addition, also determined: D. V.; dark violet: $d_{250} = 2.41$. D. VI.; violet: $d_{250} = 2.37$. D. VII.; pink: $d_{250} = 2.48$.				

atoms¹⁾. On treating the ultramarines with acids, about one third of the *sulphur* present is made free as H_2S , while the remaining part is precipitated in the form of elementary *sulphur*.

§ 2. For this investigation we had a number of differently coloured products at our disposal from the *Usines d'Outremer-GUIMET* in *Fleurieu s/Saône*, namely: GUIMET-green N^o. 9210; blue N^o. 7553; pink N^o. 8219 and violet OVR; furthermore, a number of red, green and blue preparations from the *Vereinigte Ultramarin-Fabriken* in *Cologne*, which most kindly were supplied to us through the medium of Dr. C. O. LEVERKUS; they were partially prepared after the *sulphate*-, partially after the *soda*-, partially after the mixed *sulphate-soda*-method. With the exception of the green ultramarines, all the products investigated appeared to belong to the series of compounds with *high silica-content*; a number of analytical data obtained with the carefully dried materials, and a series of determinations

¹⁾ E. GUIMET, Bull. Soc. chim., 27, 480 (1877); Ann. d. Chim. et Phys. (5), 13, 102, (1878); D. MOREL, ibid. 28, 522, (1878); J. HOFFMANN, Koll. Zeits., 10, 275, (1911).

of the specific weights of the same preparations at 25° C., are recorded here. (See table).

From these data, which were all obtained in repeated and agreeing analyses with the aid of most carefully dried ultramarine-species, it becomes clear, that there cannot be spoken here of a really „constant” composition of these products: even the two blue preparations *G. III* and *D. VIII*, — which contain both a high percentage of silica, — appear to deviate appreciably from each other in this respect. Neither is there a simple stoichiometrical ratio of the *Al*-, *Si*-, and *S*-atoms present, it being, therefore, impossible to give here rational molecular formulae for these compounds. In literature the following data are given for the blue ultramarines of high silica-content: *Al* = 12,70 till 13,93 %; *Si* = 19,07 till 19,53 %; *S* = 13,44 till 14,09 %; while for an ultramarine of the formula: $Al_4 Na_6 Si_6 S_4 O_{20}$ these numbers should be: 12,53 %, 19,49 % and 14,85 % respectively. It is evident that the chemical composition of these dyes must be variable within rather wide limits.

For the ultramarines with a high silica-content, the empirical formulae seem to oscillate more or less round: $Na_6 Al_4 Si_6 O_{20} S_4$ for the *blue* and $Na_3 Al_4 Si_6 O_{22} S_3$ for *red* ultramarine; for *green*, which belongs to a series of „moderate” *sulphur*-content, the composition oscillates round: $Na_9 Al_6 Si_6 O_{24} S_3$ or more correctly round: $Na_8 Al_6 Si_6 O_{24} S_2$. The *sulphur*-content is highest in the ultramarines prepared after the *soda*-method, lowest in those made by means of the *sulphate*-process.

With respect to the minerals studied here, it must be remarked, that they were taken from different localities: colourless *sodalite* from the *Monte Somma, Vesuvius*; blue *hauyne* from the same spot, from the *Laacher See* in the *Eifel* and from *Niedermendig*; colourless *nosean* from the two last mentioned localities. Some of these crystals were kindly put at our disposal by Prof. RUTTEN of Utrecht and Prof. ESCHER of Leyden, to whom we also in this place wish to express once more our gratitude for their kind help. The ROENTGENspectrographic study of these minerals, and more particularly the interpretation of their rotation-spectrograms, proved to offer extraordinary difficulties, as a consequence of the fact, that all these crystals were not only very small and often inhomogeneous, but, moreover, that as well in the case of *hauyne*, as in that of *nosean* and *sodalite*, they were almost always twins. In connection with the great identity-distances of their structures in the direction of the axis of rotation, the last mentioned circumstance made a rigorous analysis of the diffraction-images obtained often very difficult and sometimes quite impossible. With the exception of the special case, that the revolution of the crystal occurred round an axis perpendicular or parallel to the twinning-plane, the analysis of the spectrograms obtained could even be considered as quite hopeless. If e.g. a twin parallel to (111) be rotated round an axis in a direction, which has the symbol, [111] for the first of the two apparent individuals of the twin, then no dist-

turbance of the spectrogram occurs, in so far as the determination of the identity-distance in that direction [111] by means of the successive hyperbolae is considered, because the said direction has the symbol $[\overline{111}]$ in the second apparent individual of the twin. But if the same twin be rotated round axes in directions as [110], $[\overline{111}]$, $[\overline{1\overline{1}1}]$, etc. in the first apparent individual, — these directions are resp. $[\overline{114}]$, $[\overline{151}]$, and $[\overline{115}]$ in the second individual. As the identity-distances in a direction $[h k l]$ in the cubic system are c. p. proportional to $\sqrt{h^2 + k^2 + l^2}$, — the succession of the hyperbolae in the spectrogram obtained will appear to be disturbed until hardly recognisable, if the crystal be rotated round axes in the directions mentioned above, and especially in the case of such minerals as are studied here, in which the mutual distances of the successive hyperbolae in the image are, after all, already very small.

§ 3. In the first place a series of powder-spectrograms of the *ultra-*

No. of line:	Intensity (estimated):	2 l in mm.:	λ :	$\frac{\theta}{2}$:	$\sin^2 \frac{\theta}{2}$ (observed):	$\sin^2 \frac{\theta}{2}$ (calculated):	Indices {h k l}
1	1	16.8	α	9°37'	0.0279	0.0284	(200)
2	1	19.0	β	10°53'	0.0356	0.0352	(211)
3	8	21.0	α	12° 2'	0.0433	0.0426	(211)
4	5	27.0	α	15°28'	0.0711	0.0710	(310)
5	5	29.7	α	17° 4'	0.0861	0.0852	(222)
6	1	34.5	α	19°49'	0.1149	0.1136	(400)
7	3	36.5	α	20°58'	0.1280	0.1278	(330)
8	3	44.5	α	25°33'	0.1860	0.1846	(431)
9	2	49.5	α	28°25'	0.2265	0.2272	(440)
10	1	51.3	α	29°27'	0.2417	0.2414	(530)
11	1	53.0	α	30°22'	0.2556	0.2556	(600)
12	1	54.8	α	31°24'	0.2715	0.2698	(532)
13	1	59.5	α	34° 9'	0.3151	0.3124	(622)

Radius of camera: 25 mm.; $V = \text{ca. } 55000$ Volt; time of exposure: 3 hours.
Wave-length: $\lambda_{Cu} = 1.540$ A.U. $\lambda_{\beta} = 1,388$ A.U.

Quadratic equation: $\sin^2 \frac{\theta}{2} = 0.0071 (h^2 + k^2 + l^2)$; from which: follows:
 $a_0 = 9.13$ A.U.

marines GUIMET I—V and of a number of the ultramarines of German origin was prepared after HULL-DEBIJE's method, and, moreover, such of *nosean*, *hauyne* and *sodalite*. The remarkable result was obtained, that quite independent of the colour and the chemical composition of these ultramarines, all these spectrograms appeared to be completely identical, and, moreover, to be also quite the same as those for *nosean* and *hauyne*. On the other hand, *sodalite* gave a spectrogram, which, as well with respect to the situation of the diffraction-lines, as to their intensities, was quite different from them. Evidently no appreciable influence on the localisation and intensities of the diffraction-images is exerted here by the special circumstance, that, — as in *hauyne*, — the sodium-atoms of *nosean* are partially substituted (for about half their number) by calcium-atoms; or that the ultramarines investigated contain 3, 6, 8 or 9 atoms of sodium; or that the (SO₄)-group in *nosean*, in the transition to the ultramarines, is substituted by two, three or four sulphur-atoms. None of these changes appears to have any detectable influence whatsoever on the intensity or on the special situation of the diffraction-images.

A review of the complete analysis of these powder-spectrograms is given in the preceding table; the values of $\sin^2 \frac{\theta}{2}$ are calculated by means of the exact constant of the quadratic equation, as it was later-on accurately determined by means of BRAGG-spectrograms¹⁾.

From these data it becomes evident, that in no case ($h+k+l$) is an odd number; the fundamental BRAVAIS' grating of the structure must, therefore, be the *body-centred* one. As will be shown, this conclusion is confirmed by all later experiments. As the specific weights of the ultramarines used are known (= about: 2,36), as well as those of *nosean* and *hauyne* (about: 2,40), — the number of "molecules" of these compounds per elementary cell can be calculated in the usual way.

For *nosean* of the simplest formula: $Na_5 Al_3 Si_3 O_{16} S$, this number appears to be: 2, and for the *ultramarines* of the formulae mentioned above, it is: 1; so that in every case the mass contained in the fundamental cell corresponds to six silicon-atoms in the different formulae.

§ 4. After the identity of the structures of *nosean*, *hauyne* and all *ultramarines* had been demonstrated in this way, we endeavoured to confirm the conclusions hitherto drawn with respect to the structure of these compounds, by means of rotation-spectrograms of *nosean* and *hauyne*, and to calculate accurately the dimensions of the grating by the aid of spectrograms prepared after BRAGG's method.

Originally *hauyne* gave in no case any useful rotation-spectrograms;

¹⁾ Still better spectrograms of ultramarine were afterwards obtained with a new and improved camera. No less than 32 different diffraction-images could be measured on these films. The results obtained, however, have fully confirmed the conclusions drawn in the above. In a following paper the new data will be discussed in detail.

but later-on very good spectrograms of this kind were obtained, which will be discussed in the next paper. The crystal used, which seemingly had the shape of a perfect rhombicdodecahedron, appeared to be a twin, which, if rotated round [111] or [110], gave no analysable rotation-spectrograms. However, a BRAGG-spectrogram on (110) could be obtained, *rocksalt* parallel to (100) being simultaneously used for the purpose of comparison. Observed value: $\frac{\theta}{2} = 6^{\circ}52'$; from which follows: $d_{(110)} = 6,44$ A.U., and, therefore, $d_{(100)} = 9,11$ A.U. That the "reflection" on (110) is really of the *first* order, was confirmed later-on experimentally.

The *nosean*-crystals were rhombicdodecahedra, which were strongly elongated parallel to one of their trigonal axes; they appeared to be twins parallel to (111). If such a crystal be rotated round its longest axis, a normal spectrogram may be expected beforehand, as was already emphasized in the above. The distance between the first hyperbola in the spectrogram to the centre of the photographic image was 8 mm.; as in this case the distance of the photographic plate to the crystal was: 40 mm. here, so $tg \mu = 0,20$ and, therefore, $\mu = 11^{\circ}20'$. From this value the identity-distance in the direction of a trigonal axis is found to be:

$$I_{[111]} = \frac{\lambda}{\sin \mu} = 7,84 \text{ A.U.}$$

A BRAGG-spectrogram on a face of {110} gave $\frac{\theta}{2} = 6^{\circ}51'$; from which $d_{(100)}$ is again calculated to be: 9,13 A.U.; the formerly observed diffraction-line must, indeed, be of the 1st order.

The diagonal of the cubic cell is calculated from $d_{(100)} = 9,13$ A.U. to be: 15,80 A.U., which is nearly $= 2 \times 7,84$ A.U. From this follows, that the spacings in the direction [111] are *halved*, — which proves that the cubic cell is really the *body-centred* one. If the image on (110) had been of the *second* order, then, in accordance with the data of the rotation-spectrogram obtained by turning the crystal round [111], the bodily diagonal of the cubic cell would have to be *quartered*. This case, however, is excluded in each of the three types of cubic gratings.

A complete analysis of the rotation-spectrogram of *nosean* on turning round [111] is given in the following table. The values of $\sin^2 \frac{\theta}{2}$ are calculated here by means of the quadratic equation: $\sin^2 \frac{\theta}{2} = 0,0071(h^2 + k^2 + l^2)$, — the coefficient: 0,0071 being determined from the BRAGG-spectrogram $\left(\frac{\theta}{2} = 6^{\circ}51'\right)$ already mentioned.

As the fundamental grating is the body-centred one and as rotation took place round [111], the sum of the indices of the principal spectrum must be equal to *zero*; that of the indices of the 1st hyperbola equal to 2; that of those of the 2nd hyperbola equal to 4; that of the indices of

the 3^d hyperbola equal to 6; etc. This now appears really to be the case; so once more the conclusions drawn previously are confirmed by this.

TABLE II.					
Analysis of the Rotation-spectrogram of Nosean, when rotated round [111].					
Distance between photographic plate and crystal = 40 mm.					
Distance between spot and centre of image in mm.:	$\frac{\theta}{2}$:	$\sin^2 \frac{\theta}{2}$ (observed):	$\sin^2 \frac{\theta}{2}$ (calculated):	Indices $\{h k l\}$:	Number of hyperbolae:
18.0	12°7'	0.0441	0.0426	(2 $\bar{1}$ $\bar{1}$)	Principal spectrum
30.0	18°26'	0.1000	0.0994	(3 $\bar{2}$ $\bar{1}$)	
36.0	21°0'	0.1284	0.1278	(3 $\bar{3}$ 0)	
49.5	25°32'	0.1860	0.1846	(4 $\bar{2}$ $\bar{2}$)	
62.5	28°0'	0.2304	0.2272	(4 $\bar{4}$ 0)	
18.0	12°7'	0.0441	0.0426	(2 1 $\bar{1}$)	I
24.0	15°29'	0.0731	0.0710	(3 0 $\bar{1}$)	
41.5	23°2'	0.1531	0.1562	(3 $\bar{2}$ $\bar{3}$)	
49.5	25°32'	0.1860	0.1846	(4 1 $\bar{3}$)	
66.0	29°23'	0.2407	0.2414	(3 $\bar{3}$ $\bar{4}$) or (50 $\bar{3}$)	
17.5	11°49'	0.0419	0.0426	(2 1 1)	II
24.0	15°29'	0.0713	0.0710	(3 1 0)	
33.0	19°46'	0.1144	0.1136	(4 0 0)	
30.0	18°26'	0.1000	0.0994	(3 2 1)	III
36.0	21°0'	0.1284	0.1278	(3 3 0)	
49.5	25°32'	0.1860	0.1846	(4 3 $\bar{1}$)	
41.5	23°2'	0.1531	0.1562	(3 3 2)	IV
49.5	25°32'	0.1860	0.1846	(4 3 1)	

Wave-length. $\lambda_{Cu} = 1.540$ A.U.; $V = 55000$ Volt; time of exposure: 5 hours.

Evidently all images $\{h k l\}$ have the intensity = 0 in *odd* orders, when $(h + k + l)$ is an *odd* number. This fact could be corroborated once more by means of a BRAGG-spectrogram on a cleavage-plane of

nosean parallel to (111): after a few minutes exposure the 2nd order of the diffraction-image was present already with a very considerable intensity, while even after exposure during a full hour, not the slightest trace of a 1st order-image could be detected.

§ 5. The next problem to be discussed, is that of the symmetry of *nosean* and *hauyne*, which, — as has already been said, — are commonly considered to possess hexacistetrahedral symmetry, an opinion also advocated by BRÖGGER and BÄCKSTRÖM. But there is no valid proof adduced for this, since the analogy of these minerals with *sodalite*, as brought to the fore by these authors as an argument, can no longer be maintained now. This will be seen from what follows, because we were able to prove, that the structure of *sodalite* is quite different from that of the two other minerals. As all arguments for the determination of the space-group of *nosean* and *hauyne* must be taken into account, it is, therefore, not allowed to make beforehand any restriction with respect to the special symmetry of these minerals, and it thus appears necessary to consider all crystal-classes of the cubic system as of the same importance.

It was proved, that the fundamental grating is the body-centred one, and that all spacings $\{h\ k\ l\}$ are halved, if $(h + k + l)$ is an odd number. If these facts be taken into account, then there are *ten* space-groups, whose special symmetry may eventually be attributed¹⁾ to both minerals considered here; namely

$$T^3; T^5; T_h^7; T_h^3; T_d^6; O^5; O^8; O_h^9; \text{ and } O_h^{10}.$$

in WYCKOFF's notation.

However, we can already immediately exclude from those the groups: T_h^7 , T_d^6 and O_h^{10} , because on the BRAGG-spectrograms of $\{110\}$ the *first* order image of $\{110\}$ was observed with full certainty. Moreover, since also (200) was observed (see Table I) the group O^8 too must be excluded.

Nosean and *hauyne* can, therefore, only have the symmetry of one of the following six groups:

$$T^3; T^5; T_h^5; T_d^3; O^5, \text{ or } O_h^9.$$

It must, furthermore, be remarked, that, — as the most probable formula for pure *nosean* is: $Na_5Al_3Si_3O_{16}S$, and as twice the number of atoms of this formula is present in the elementary cell, — the last one must contain a mass, the composition of which is in the simplest case expressed by: $Na_{10}Al_6Si_6O_{32}S_2$. In the analogously built *ultramarines* there is present in each case once the number of atoms which is expressed by the formulae for these compounds as given before; so that the elementary cell of all *ultramarines* also in each case contains *six* atoms of *silicon*.

Now, — what perhaps would appear to be the final choice between

¹⁾ W. T. ASTBURY and K. YARDLEY, Phil. Trans. Royal Soc. London, A, 224, (1924) p, 254, 255, 256.

the six space-groups mentioned above, — in every case it can be proved on closer examination¹⁾, that the possible arrangement of the equivalent *twofold* and *sixfold* places in the cell manifests itself in all six groups in *quite the same way*, — in T^5 excepted, — in which group such places do not occur at all. For it can be shown, that the coordinates of these places in all those groups are: $[000]$ and $[\frac{1}{2}\frac{1}{2}\frac{1}{2}]$ for the *two-fold* places, while for the *sixfold* ones they are: $[0\frac{1}{2}0]$, $[00\frac{1}{2}]$, $[\frac{1}{2}00]$, $[\frac{1}{2}0\frac{1}{2}]$, $[\frac{1}{2}\frac{1}{2}0]$ and $[0\frac{1}{2}\frac{1}{2}]$ (See Fig. 1). All these coordinates are simply fixed

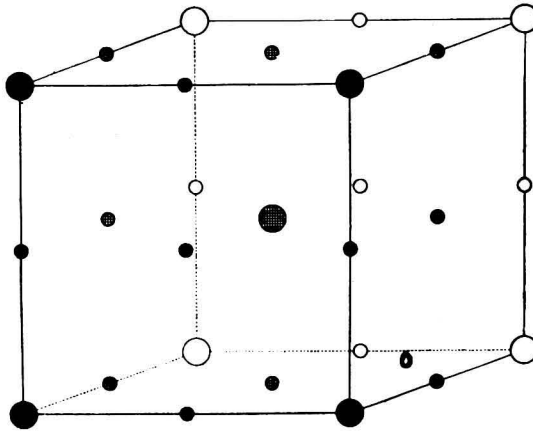


Fig. 1.

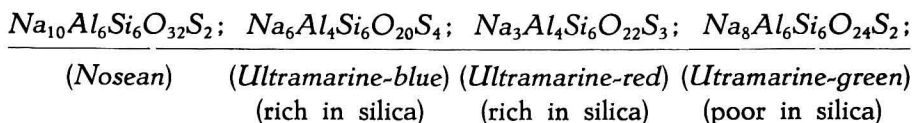
beforehand, because *they do not contain any variable parameter*. Moreover, in none of these groups can occur *univalent* or *fourfold* places; in all, however, there might be found *eight-, twelve- and twenty-four-fold* places, and in some of them also *sixteen-, forty-eight and ninety-six-fold* places. Now, because in the cells of *all* these compounds, *six silicon-atoms* appear to be present, there must certainly be present *sixfold* places in each case; so that we can also exclude beforehand the group T^5 from the six mentioned above.

But the fact that the coordinates of the necessary *six-fold* places in the cell are completely fixed and that they do not contain any variable parameter, involves the impossibility of the simultaneous occurrence of other *sixfold* places in the structure, besides just that single complex of six points, the coordinates of which are mentioned above. If these six places are once occupied by six identical atoms of a certain kind, it is, therefore, excluded *à priori*, that six atoms of a second or third kind could simultaneously be present on six equivalent places within the same elementary cell.

Now, as *all* elementary cells evidently contain 6 *Si-atoms*, it is obvious to make the supposition, that it is these six *silicon-atoms*, which really

¹⁾ R. W. G. WYCKOFF, Publ. CARNEGIE-Institut. Washington, N^o. 318, (1922), p. 122, 126, 129, 135, 148, 103.

occupy the only sixfold places available here, with the coordinates mentioned above¹). If now, however, the composition of the masses present in the elementary cell of all these compounds be taken into consideration:



it will immediately be seen, that perhaps only the O-atoms possibly could be placed in the cell in some such way as: (12 + 8); (12 + 8 + 2); 24, (or 16 + 8); (24 + 8) atoms; etc. It must be remarked, however, that the numbers of O-atoms indicated, are not very accurate, as all errors of the chemical analysis are accumulated in these numbers.

If 24 O-atoms must be placed as (16 + 8) atoms, the space-groups T_d^3 and T_3 would be excluded here also; and if the compounds studied here, were really holohedral, then the space-group O_h^9 could most probably be attributed to them. But all this is mere speculation; any thing certain cannot be said about it.

However, — in what way the question may be considered or perhaps finally decided, — there is, after all, *one* fact, which is undeniably certain: namely, *it is quite impossible to attribute to an appreciable number of components of the total mass included within each elementary cell any definite place in the structure.* For these components: Na, Al, S, — and in the case of *hauyne* also for Ca, — no place whatsoever is any more available within the fundamental cell. While it is even quite *uncertain*, which atoms on the parameterless *two-* and *sixfold* places be really present, or which atoms are perhaps situated at the 8-, 12-, 16-, and 24-fold places, — it is, after all, fairly well possible to substitute the *sixfold* places by atoms of one and the same kind, e.g. by Si-atoms; but then every further possibility will simultaneously have disappeared for localising other complexes of six identical atoms, e.g. of Al_6 or Na_6 , because there are in reality *no other sixfold* places any more available within the cell, besides the six with the fixed coordinates, as mentioned in the above. Therefore, beyond all doubt there must be an appreciable number of atoms present within each fundamental cell, which can by no means be arranged in definite places of the periodical structure; they must in space be distributed at random, in a merely statistical way, and be scattered throughout the fixed, rigorously periodical structure of these crystals, which forms, as it were, their rigid skeleton.

In the same way GOLDSCHMIDT and THOMASSEN²) in the case of

¹) It would e.g. be obvious to suppose that the two S-atoms, which in *nosean* and in the *ultramarines* are always present, be situated in the twofold places. However, our later experiments seem to indicate, that not these S-atoms, but rather two of the *sodium*-atoms must occupy these places.

²) V. M. GOLDSCHMIDT en L. THOMASSEN, Vidensk. Skrift., Christiania, (1923).

cleveite and *bröggerite* always found, by means of the ROENTGEN-ographic method, the periodical structure of UO_2 , although the chemical composition of these minerals indicates, that they chiefly consist of U_3O_8 , with as accessory components: *Pb-*, *Tho-*, *Yt-*, *Erb-*, *Ce-*, and *Fe-*derivatives, besides some H_2O . A certain amount of oxygen must, with the other accessory compounds, therefore, be statistical distributed within the UO_2 -lattice, — exactly as occurs in our case of the ultramarines; so that the ROENTGEN-spectrograms do not reveal anything of the presence of these compounds, except the diffraction-lines, which correspond more particularly to the rigorously periodical structure of the UO_2 -framework. An analogous explanation must doubtlessly be given for the facts observed by WYCKOFF, GREIG and BOWEN, that *sillimanite* and *mullite*, and also for these observed by WYCKOFF and MOREY, that a series of *sodium-calcium-metasilicates* of different chemical compositions, gave identical or hardly discernable ROENTGEN-spectrograms¹⁾.

It is because of the special circumstances present in this case, — and more particularly because of the very favourable circumstance, that the coordinates of the *two-* and *sixfold* places of the structures considered here, are completely free from *indefinite* parameters u , v , etc., — that we are inevitably compelled to the conclusion, that in the minerals studied here, — which formerly were considered as being “molecular compounds” between *silicates* and Na_2SO_4 , — as well as in the *ultramarines*, — which were considered as analogous compounds between *silicates* and *Na-polysulphides*, — there can only be question of a true periodically built frame-work of the whole, presumably consisting here of *Si-*, *Na-* and *O-*atoms, — in which a great number of other components are distributed in a merely statistical way.

This supposition gives an explication, on the one hand, of the particular “mobility” of a part of the *Na-*atoms and of their being replaceable by other atoms, — even by *Ca* (as in *hauyne*), which as a consequence of its bivalency, must substitute 2 *Na-*atoms at the same time. Otherwise it would be quite inexplicable in the last case, that the *Ca-*atom could substitute 2 *Na-*atoms of a rigorously periodical structure, without that structure being influenced in the least respect by that substitution, as we have experimentally demonstrated it to be the case in *hauyne* and *nosean*. The conception of these “errant” components within the fundamental lattice explains, why F. SINGER and others were able to show an intimate relation between such *zeolites* (and *permutites*) on the one hand and the *ultramarines* on the other²⁾; just as is the case with the H_2O -molecules in some *zeolites*, which can reversibly be deshydrated, and for

¹⁾ R. W. G. WYCKOFF, J. W. GREIG and N. L. BOWEN, Amer. Journ. Science, 11, 459, (1926); R. W. G. WYCKOFF and G. W. MOREY, Amer. Journ. Science, 12, 419, (1926).

²⁾ That the ultramarines possess e.g. “hydraulic” properties, and that they are even able to increase the binding-power of cements, has first been shown by ROHLAND; vid.: Zeits. f. angew. Chemie, 17, 609, (1904).

which an analogous supposition about their constitution now must generally be adopted. It also permits of giving in some degree an explication of the factors, on which the coloration of the ultramarines depend, and of the fact, that all these differently coloured preparations, — yellow, red, green, blue or violet, — always give almost completely *identical* diffraction-images. That colour is probably determined by the greater or smaller complexes of *S*-atoms, or of *AlS*- and *NaS*-groups, etc., and of their special degree and mode of dispersion within the total bulk of the solid mass. It is now fairly certain, that the *ultramarines* can *not* any longer be considered as compounds of a constant stoichiometrical composition; — a fact, to which also is pointed by the deviating results of the chemical analysis in different cases. The attribution to them of empirical formulae, — and much less that of “structural” formulae, — has no longer any significance: these substances consist of a regular, periodical structure as bearer of an irregularly distributed company of other atomic individuals, amongst which *Na*, *Al*, and *S* are the most predominant, and the number and nature of which greatly depend on the special conditions of the preparative processes. The colour of the solid mass seems to be undeniably bound to the presence of the element *sulphur*, — perhaps in a way analogous to that recently described by VON WEIMARN¹⁾, or otherwise by the special degree of dispersion of *S*-containing components. The stability of the ultramarines at red heat, on the other hand, makes it rather improbable, that *free sulphur*²⁾ should be the cause of their colours, as some authors have suggested.

§ 6. In the beginning of this paper it has been said, that *sodalite* (*Monte Somma*) yielded quite another type of powder-spectrogram than *nosean*, *hauyne*, etc., — although formerly *sodalite* has always been considered to be a compound of a structure perfectly analogous to that of the others, *sodiumsulphate* in the latter being simply substituted by *sodiumchloride*, but in combination with the same fundamental silicate. This conception of the constitution of all the substances of this series seemed to be strongly corroborated by the results of the artificial syntheses³⁾ of these minerals.

From the investigations of BRÖGGER and BACKSTRÖM, who place all these minerals also in one and the same group, it follows with certainty, that the symmetry of *sodalite* is surely *not hexaxisoctahedral*: the corrosion-figures obtained by them were, on the contrary, in better agreement

1) P. VON WEIMARN, Koll. Chem. Beihefte, **22**, 38, (1926); J. HOFFMANN, Koll. Zeits., **10**, 275, (1912); F. KNAPP, DINGLER's Polyt. Journ., **233**, 479, (1879); Idem **229**, 74, (1878).

2) Vid. i.a.: PATERNÒ and MAZZUCHELLI, Atti R. Acad. Lincei, (V), **16**, I, 465, (1907).

3) J. LEMBERG, Zeits. d. Geol. Ges., **28**, 603, (1876); **35**, 583, (1883); J. MOROZEWICZ, Tscherm. Min. Mitt., **18**, 143, (1899); O. MÜGGE, in ROSENBUSCH' „Mikrosk. Physiogr., I, 323, (1892); Z. WEYBERG, Z. Min. (1905), 653; CH. and G. FRIEDEL, Bull. Soc. min., **13**, 183, (1890); S. J. THUGUTT, N. Jahrb. Min., etc., Beil. Bnd. **9**, 568, (1894).

with *hexacistetrahedral* symmetry. In that case, the apparently simple rhombicdodecahedra of *sodalite* must be considered to be twins parallel to $\{100\}$. This, indeed, is in perfect agreement with our experience in preparing rotation-spectrograms of a transparent crystal of rhombicdodecahedral shape: on rotating the crystals round $[100]$, the spectrograms obtained appeared to be quite normal; but on rotating them round $[111]$, they were completely irregular and not suited for analysis, just as it was before observed in the case of *hauyne*, — in reversed sequence, however.

In the first place in Table III are reviewed the data, relating to the powder-spectrogram of *sodalite*; the values of $\sin^2 \frac{\theta}{2}$ are calculated

N ^o . of the Lines:	Intensities estimated:	$2l$ in mm.:	Wave-length:	$\frac{\theta}{2}$:	$\sin^2 \frac{\theta}{2}$: (observed):	$\sin^2 \frac{\theta}{2}$: (calculated):	Indices $\{h k l\}$:
1	1	23.1	λ_{β}	13°14'	0.0524	0.0503	(220)
2	8	25.5	λ_{α}	14°37'	0.0637	0.0608	(220)
3	2	31.2	λ_{α}	17°53'	0.0943	0.0912	(222)
4	3	34.3	λ_{α}	19°39'	0.1131	0.1064 or 0.1216	(321) or (400)
5	3	37.5	λ_{α}	21°29'	0.1341	0.1368	(330)
6	3	41.3	λ_{α}	23°40'	0.1611	0.1596	(421)
7	3	42.3	λ_{α}	24°14'	0.1685	0.1672	(332)
8	1	50.1	λ_{α}	28°43'	0.2309	0.2280	(521)
9	1	53.0	λ_{α}	30°25'	0.2563	0.2584	(530)
10	1	56.3	λ_{α}	32°16'	0.2850	0.2812 or 0.2888	(601) or (611)

Radius of camera: 25 mm. $V = 55000$ Volts; time of exposure: 3 hours.
 Quadratic equation: $\sin^2 \frac{\theta}{2} = 0.0076 (h^2 + k^2 + l^2)$ for α -radiation of 1.540 A.U.
 From this a_0 calculated to be 8.81 A.U.

from the coefficient of the quadratic equation, as this was deduced from the numerical results of the BRAGG-spectrogram to be described later-on. Among the indices of Table III such symbols as: $\{321\}$, $\{421\}$, $\{332\}$, $\{521\}$, etc. are present, for which, therefore, $(k+l)$, or $(h+k)$, or $(h+l)$ are *odd*. Moreover, there are also symbols present, for which $(h+k+l)$ is *odd*. From all these facts it must be concluded, that the fundamental

BRAVAIS' lattice of the structure of *sodalite* is the *simple cubic* lattice, — as contrasted with what was found in the case of *nosean* and *hauyne*.

§ 7. These conclusions, now, were more particularly corroborated by the analysis of a number of rotation-spectrograms and of such obtained after BRAGG's method.

A BRAGG's spectrogram on a face of $\{110\}$, in combination with one on $\{100\}$ of *rocksalt* at the same distance, for the purpose of comparison, gave the value: 8,81 A.U. for $a_0 = d_{(110)} \cdot \sqrt{2}$; from this the coefficient of the quadratic equation for $\sin^2 \theta/2$ is calculated to be: 0,0076, which value was already formerly used in calculating the data of the powder-spectrogram.

A rotation-spectrogram obtained by turning the crystal round a principal axis $[001]$, gave the results, which are recorded in Table IV (see next page).

The distance between the principal spectrum and the first hyperbola being 7.3 mm., $tg \mu$ was equal to 0,1791; from which follows: $\mu = 10^\circ 11'$, and for $I_{[100]}$, — being the identity-distance in the direction of the principal axis: $I_{[100]} = \frac{\lambda_x}{\sin \mu} = 8,72$ A.U., — which is in perfect accordance with the exact value: 8,81 A.U., calculated from the BRAGG-spectrogram at (110).

For the number n of atomic complexes of the formula: $Na_4 Al_3 Si_3 O_{12} Cl$, which are present per fundamental cell, we find, as the specific weight d is 2,30 here:

$$n = \frac{2,30 \times (8,81)^3}{485 \times 166} = 1.96 \text{ (i.e. } = 2).$$

Thus in each elementary cell a total mass is present, whose composition in the simplest case is expressed by: $Na_8 Al_6 Si_6 O_{24} Cl_2$. If the strongly deviating data of the analysis of different *sodalites* be taken into account, as they are given in literature, the question may be raised, whether also in this case there can be properly spoken of a rational stoichiometrical composition or not? Nor is, in this case, the possibility by no means excluded, that there is only question of a chemical composition, oscillating within rather wide limits.

§ 8. If the *hexacistetrahedral* symmetry of *sodalite*, as suggested by BRÖGGER and BÄCKSTRÖM, be adopted, only two space-groups: T_d^1 and T_d^4 need be considered here, because the fundamental lattice was proved to be the simple cubic one. But in ROENTGEN-analysis the spacings of net-planes with the symbol $\{hhl\}$, in which l is an *odd* number, will in T_d^4 always appear to be halved ¹⁾. With absolute certainty, however, a spot (221) has been found on the rotation-spectrogram, although its

¹⁾ W. T. ASTBURY and K. YARDLEY, loco cit., p. 255.

TABLE IV.

Rotation-spectrogram of Sodalite from Monte Somma.

(Distance between plate and cristal : 40.5 mm.)

The axis of revolution here was the principal axis [001].

Distances of spots from the centre in mm. :	$\theta/2$:	$\sin^2 \theta/2$ (observed) :	$\sin^2 \theta/2$ (calculated) :	Indices $\{h k l\}$:	Sequence of hyperbolae :
25.3	16° 0'	0.0760	0.0760	(310)	Principal spectrum.
32.0	19° 9'	0.1076	0.1131	(330) λ_β	
38.9	21°56'	0.1395	0.1368	(330) λ_α	
42.0	23° 1'	0.1529	0.1520	(420)	
52.0	26° 3'	0.1927	0.1900	(500) of (430)	
64.1	28°51'	0.2328	0.2204	(520)	
70.0	29°59'	0.2496	0.2432	(440)	
18.7	12°24'	0.0461	0.0456	(211)	I.
31.5	18°56'	0.1053	0.1064	(321)	
39.1	22° 0'	0.1402	0.1368	(411)	
52.0	26° 3'	0.1928	0.1976	(501) or (431)	
18.7	12°24'	0.0461	0.0456	(112)	II.
24.0	15° 9 1/2'	0.0684	0.0699	(212)	
28.0	17°20'	0.0888	0.0912	(222)	
32.1	19°12'	0.1081	0.1064	(312)	
39.0	23°41'	0.1613	0.1596	(412)	
48.0	24°55'	0.1775	0.1824	(422)	
62.5	28°32'	0.2282	0.2204	(432)	
75.0	30°49'	0.2625	0.2508	(522)	
82.0	31°51'	0.2785	0.2736	(442)	
25.8	16°15'	0.0783	0.0760	(103)	III.
31.8	19°41'	0.1067	0.1064	(123)	
37.9	21°33'	0.1348	0.1368	(303)	
45.6	24°12'	0.1682	0.1672	(233)	
72.0	30°20'	0.2553	0.2584	(433) or (503)	
48.6	25° 6'	0.1799	0.1824	(224)	IV.
55.8	27° 1'	0.2063	0.2010	(314)	
77.9	31°16'	0.2694	0.2628	(334)	

Wave-length : $\lambda_{cu} = 1.540$ A.U. : $V = 55000$ Volts ; time of exposure : 5 hours.Quadratic Equation : $\sin^2 \theta/2 = 0.0076 (h^2 + k^2 + l^2)$. Accordingly : $a_0 = 8.81$ A.U.

intensity was relatively weak. For that reason *sodalite* must necessarily ¹⁾ belong to the space-group T_d^1 .

In this space-group T_d^1 there occur *no twofold* places; but there are *two* different kinds of *sixfold* places, the coordinates of which all contain, however, a variable parameter u . Now evidently Si_6 , as well as Al_6 , can both be placed in those localities; so that, in contrast with the case of *nosean*, it is *not* absolutely certain here, whether also in *sodalite* such "errant" constituents must be supposed to be present in its structure, distributed in it at random in all directions. But even then, the empirical, coordinative or structural formulae, as occasionally proposed for *sodalite*, cannot be considered as being in real agreement with the different kinds of available places in its elementary cell.

§ 9. Some intensely coloured, dull blue and opaque individuals of *lazurite* from *Afghanistan*, which superficially had the appearance of rhombic-dodecahedra, were used for comparison with the substances hitherto investigated. However, on the apparent {110}-faces no BRAGG-spectrograms whatsoever could be obtained, notwithstanding several endeavours were made. Evidently the so-called "crystals" were no true individuals, but probably conglomerates having only an approximate resemblance with a rounded rhombicdodecahedron. Moreover, the blue masses were very inhomogeneous and they contained a number of alien and incrustated substances, i.a. *pyrite*.

A small piece of this blue *lazurite*, as homogeneous as possibly, could be separated out of the inner parts of the mass; it was finely powdered now and used for the preparation of a powder-spectrogram after HULL-DEBIJE's method. The photograph obtained after five hours exposure, was rather weak, but the lines were sharp enough to be localised by means of a comparator. It was found, that by far the greater number of the diffraction-lines coincided with those of *hauyne* and the *ultramarines*; more especially the spectrogram of *lazurite* showed the following lines of those substances (numbers as in Table I): no's 2, 3, 4, 5, 6, 7, 9, 10, 11 and 13, while no's 8 and 12 were absent. Moreover, three very weak lines were observed, which must correspond to other constituents; although two of them rather exactly coincided with the lines no's 7 and 10 of *sodalite* (Table III), it is yet highly problematic, whether they can be attributed to that mineral, because the most conspicuous and intense line of *sodalite*, no. 2 of Table III, was certainly *not* present. There are undoubtedly other substances present in the blue mass as accessory products; but *it is quite certain now, that the spectrogram of lazurite is chiefly identical with that of hauyne and of the artificial ultramarines*. This result

¹⁾ TH. BARTH, Norsk Geol. Tidskr., 9, 40, (1926). The paper published by this author appeared, when the structure of *sodalite* had already been determined by us. Mr. BARTH was, moreover, not able to fix his choice between the two space-groups possible here; this problem is now settled here definitely.

is in partial agreement with BRÖGGER and BÄCKSTRÖM's supposition of *lazurite* being a mixture of *hauyne*-substance, natural *ultramarine* and other accompanying substances; but their suspicion, that *sodalite* would be the accessory mineral, is *not* confirmed beyond all doubt by the results described in this paper. As *sodalite* and *hauyne* have different structures and, most probably, also different symmetries, — it is quite improbable, that *lazurite* can be considered as a kind of mixed crystal of isomorphous components, as *hauyne* and *sodalite* by the Swedish authors are evidently and erroneously supposed to be.

§ 10. Finally we have kept in view the question, in how far there may exist any relation between the constitution of the *ultramarines* and *nephelite*, the composition of which is in the simplest case expressed by the formula: $Na Al Si O_4$. *Nephelite* itself is hexagonal-pyramidal; its axial ratio, according to VON BAUMHAUER, is: $a : c = 1 : 0,8314$. That there is really some relation between the so-called „ultramarine-base” and a *sodium-aluminium-silicate* of the composition as given above, is acknowledged by all authors, who have occupied themselves with the synthesis of the ultramarines. BRÖGGER and BÄCKSTRÖM¹⁾ indicate, how by a *moderate* heating during six hours of *kaoline* with somewhat more than the theoretical quantity of Na_2CO_3 , a silicate of the composition mentioned is obtained, which would be *optically-isotropic*. But, besides the hexagonal form of *nephelite* already mentioned, hitherto only a single modification of it is known: the *carnegiïte*, which is stable only at much higher temperatures²⁾, and which is certainly *not* cubic. A preparation of the composition: $Na Al Si O_4$, obtained by repeatedly sintering at 900° C. of a mixture of $2 Si O_2$, $Na_2 CO_3$ and $Al_2 O_3$ or of $Na Al O_2$ and $Si O_2$, and homogenizing the product, appeared to be identical with natural *nephelite*; the powder-spectrogram was in every respect the same as that of natural *nephelite* from the *Monte Somma, Vesuvius*.

The crystals of this *nephelite* were prismatic, with $\{10\bar{1}0\}$ and $\{0001\}$, and occasionally with the pyramid $\{10\bar{1}1\}$; according to VON BAUMHAUER, they are twins or double twins after $\{10\bar{1}0\}$ and $\{0001\}$, as e.g. becomes clear from the lack of symmetry and the special shape of the corrosion-figures on $\{10\bar{1}0\}$. This twin-formation will, however, not disturb the rotation-spectrograms, obtained by turning the crystal round an axis $[0001]$, as has already been discussed.

In such a spectrogram, made with a cylindrical film, the distance between the principal spectrum and the top of the first hyperbola, was found to be: 9,5 mm., the distance between photographic plate and crystal being 50 mm.; therefore, $tg \mu = 0,190$, or $\mu = 10^\circ 46'$, from which follows: $I_{[0001]} = 8,3$ A.U.²⁾.

1) W. C. BRÖGGER en H. BÄCKSTRÖM, Zeits. f. Kryst., 18, 242, (1891).

2) During the correction of this proof the said rotation-spectrogram was made with a new cylindrical camera and an intensifying screen. The new measurements made it necessary to improve the numbers of the Dutch publication.

This dimension could be determined more exactly by means of a BRAGG-spectrogram on (0001), $d_{(0001)}$ being found to be equal to: 4,19 A.U. $= \frac{1}{2} \times 8,38$ A.U. The dimension of the hexagonal cell in the direction of the c -axis is, therefore, equal to: 8,38 A.U., this spacing being halved apparently in ROENTGEN-analysis. Of all space-groups in the hexagonal system, where this can occur, only C_6^2 can be attributed to this mineral of hexagonal-pyramidal symmetry.

On rotating the crystal round a perpendicular to $(10\bar{1}0)$, a rotation-spectrogram was obtained, from which the identity-distance in that direction was deduced to be: 16,75 A.U. For the identity-distance in the direction of the a -axis, therefore, the value: 9,67 A.U. is obtained. A BRAGG-spectrogram on $(10\bar{1}0)$ showing two diffraction-lines, gave however: $d_{(10\bar{1}0)} = 2,85$ A.U. and 4,28 A.U. respectively; as: $3 \times 2,85 = 2 \times 4,28 = 8,56$ A.U., the diffraction-images observed here are evidently of the 3rd, respectively of the 2nd order. No reflexion of the 1st order was ever observed; and for the dimension of the cell in the direction of the a -axis, the exact value: 9,87 A.U. is immediately deduced. Thus the axial ratio $a : c$ is equal to: $9,87 : 8,38 = 1 : 0,849$; it appears, therefore, that to the form $\{10\bar{1}1\}$ in VON BAUMHAUER's measurements, really the symbol: $\{10\bar{1}1\}$ must be given.

As the specific gravity of the *nephelite* is: 2,62, the number n of the "molecules" of the composition: $NaAlSiO_4$, which are present within a hexagonal cell (i.e. in $\frac{1}{3}$ of the total combination of six triangular prisms), is calculated to be 8. In each triangular prism, therefore, the total mass present, must be written as: $Na_4Al_4Si_4O_{16}$. In the space-group C_6^2 only *two*- and *sixfold* places, the last ones with three variable parameters, — can be present; as the number of atoms per cell is so great and the values of the dimensions in the directions a and c are also very considerable, — it may be considered impossible to determine these parameters for all atoms present. The same is true for the powder-spectrogram obtained with the artificial silicate prepared from $2 SiO_2$, Al_2O_3 and Na_2CO_3 , mentioned above. Of course, in no case can there be question to state already now a closer relation of this silicate with the ultramarines.

Whether it will appear to be possible to ascertain completely, which constituents form the rigid crystal-skeleton of the ultramarines and which are the "errant" ones, can only be decided by further experiments, which are already in progress.

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