

Chemistry. — *Investigations about the Structure of the Artificial Ultramarines. V. On Absorption-phenomena with Ultramarine and on the Structure of Nosean, Hauyne and the Ultramarines.*
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§ 1. In a series of previous papers¹⁾ it was already mentioned that on heating *Ag-ultramarine* with solutions of *alkali-halogenides*, equilibria are reached which are determined by the concentration of the solutions and by the temperature. These equilibria are only slowly established and it is worth while studying the velocity of the substitution of the *Ag* in these compounds by the *alkali*-metals used.

For this purpose in each experiment 7 Gr. of *Ag-ultramarine* were

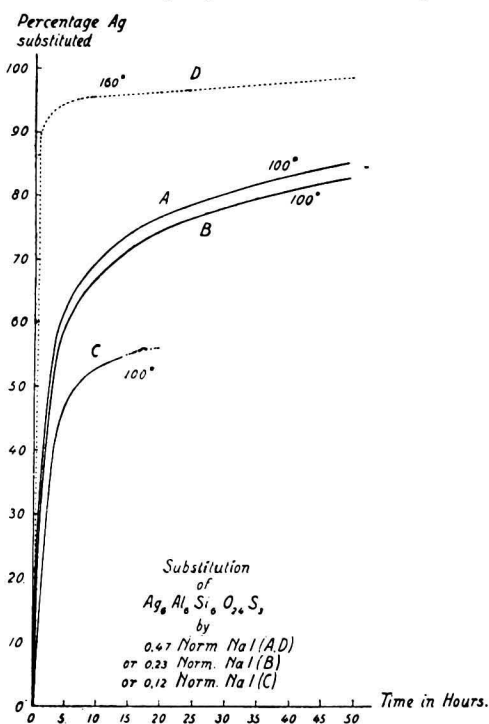


Fig. 1.

heated in sealed CARIUS-tubes with 24 Gr. *NaI* and 10 Gr. water at 100° C. in a thermostat, and the contents of the tubes studied after 1, 2, 3...50 hours' heating. After the usual purification of the products obtained, the *Ag*-content was determined, and from these numbers the amount of *Ag* replaced was afterwards calculated. The first products, for instance after 1 hour's heating, were coloured pale bluish-green, the subsequent ones pale blue; and it appeared that their colour gradually became darker, as the duration of the heating was more prolonged. (Series A).

Then the same experiments were repeated with solutions possessing only half the concentration of the first (Series B).

The results are summarized in the following table I and graphically represented in Fig 1.

¹⁾ F. M. JAEGER, H. G. K. WESTENBRINK and F. A. VAN MELLE. Proc. Acad. Sciences Amsterdam, **30**, (1927), 249; F. M. JAEGER and F. A. VAN MELLE, ibidem, 479; F. M. JAEGER, ibidem, 885.

TABLE I.
Velocity of Reaction if Ag-Ultramarine is treated with Solutions of
Sodium-iodide at 100° C.

Duration of Heating in Hours :	A. Percentage of the Silver originally present, which has been substituted by Sodium :	B. Percentage of the Silver originally present, which has been substituted by Sodium :
1	32 ⁰ / ₀	30 ⁰ / ₀
2	48	46
3	52.5	50.6
4	58	55.7
5	60.7	58.2
6	63	60
7	64.5	62
8	65.7	63.3
9	67	64.5
10	68	65.7
15	72.7	70.3
23	76.6	74.5
36	81	79
50	84.5	81.6

C. If only 2.4 Gr. *NaI* are taken, at 100° C. in 5 hours 46⁰/₀, in 10 hours 52.5⁰/₀ of the *Ag* present was replaced (concentration about $\frac{1}{3}$ of A).

D. At 160° C. in the case A in 5 hours already 94.9⁰/₀ and after 50 hours 97.7⁰/₀ of the *Ag* appeared to be substituted by *sodium*.

From these data it follows:

1. That the substitution occurs most rapidly during the first period of the reaction and the more rapidly, as the concentration of the solutions used is greater.

2. That the shape of the curves indicates the occurrence of absorption-phenomena, i.e. of processes going on at the surface of the finely powdered *ultramarine*. Evidently a state of saturation of the surface is gradually reached; the substitution takes place the more slowly, as more *Ag*-atoms have already been substituted and occurs the more rapidly, as the concentration of the solutions used is greater or the temperature higher.

The influence of such absorption-phenomena doubtlessly manifests itself

in the irregularities often met with in this kind of experiments: the greater or less degree of dispersion of the solid *Ag-ultramarine* certainly plays an important part in them. Later on we shall return more in detail to the causes of this absorption.

§ 2. An attempt was made in the following way to determine the structure of *nosean* (*haüyne*) and of the *ultramarines*.

In recent times W. L. BRAGG ¹⁾ has determined the structure of a number of *silicates*. It has become clear that this structure is for a good deal determined by a close arrangement of the *oxygen*-ions present, the diameter of their sphere of action being pretty constantly 2,6 or 2,7 A.U. It was natural to try, if the dimensions of the elementary cell as found by us: 9,1 A.U. could be brought into relation with a tetrahedral arrangement of *O*-ions, in the centre of which the *Si*-ion with its much smaller volume then could find its place. Indeed, the distance of the two middles of the opposite edges in a tetrahedron of contiguous *O*-ions, is found to be: 4,55 A.U., — i.e. exactly *half* of the height of the elementary cell of *nosean* and the *ultramarines*. The simplest formula for *nosean* requires that within the elementary cell a mass: $\text{Na}_{10}\text{Al}_6\text{Si}_6\text{O}_{32}\text{S}_2$ be included; i.e. 32 *O*-atoms (or ions) must find a place in it, which number is exactly 8×4 atoms. However, a really "closest" packing of *O*-ions cannot be present in this case: for the volume of such an *O*-ion would here be: 23,5 A.U.³, while for a tetrahedrally arranged *O*-ion, this volume cannot be greater than 14 A.U.³ Moreover, such a closest packing seems improbable with respect to the low refractive index of these *silicates* (about 1,5 for *Na*-light), which in the case of such an arrangement would have a value of about 1,7; and finally also, because of the presence of many *Na*-atoms (or ions), which by no means could find a place within the interstices left in such an arrangement.

It was previously demonstrated²⁾ that the spare-groups possible here, are:

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

a definite choice between them being impossible, because the true symmetry of these *silicates*, which is probably either hexakis-octahedral or hexakis-tetrahedral, is unknown. It was, however, already pointed out, that in every case no "fixed" position could be attributed to several components of the structure; these components ought to be considered as "errant" ones. But it remains always necessary to place 6 *Al*- and 6 *Si*-atoms (or ions) within the elementary cell, which constituents probably cannot be considered as erratic ones. These atoms must, therefore, occupy

¹⁾ W. L. BRAGG and Coll., *Proceed. R. Soc. London A*, **110**, (1926), 34; *ibid.*, **A 111**, (1926), 691; *ibid.*, **A**, **113**, (1927), 642; *Zeits. f. Kryst.*, **63**, (1926), 122, 538; etc.

²⁾ *Loco cit.*, *These Proceed.* **30**, (1927), 249.

either two different *six*-fold places, or they must be distributed over a single *twelve*-fold position, — which seems not so hazardous, if one takes into account the great analogy in function of the *Al*-, and *Si*-atoms with respect to their ROENTGEN-spectrographical behaviour. But unfortunately there is in none of the space-groups mentioned, which all correspond to the *body*-centred grating, a possibility to distribute the *Al*-, and *Si*-atoms over two different *six*-fold places.

However, it must be remarked, that the presence of the *bodily*-centred grating was deduced from the fact, that reflections of planes $\{hkl\}$, in which $(h+k+l)$ is *odd*, have never been observed: all reflections actually found are such, for which the sum of the indices is an *even* number. On the other hand, this fact can also be interpreted so, that the fundamental lattice is *not* the *bodily*-centred one, but that the special arrangement and the parameters of the atoms within the cell is such, that the odd orders of the diffraction-images of planes $\{hkl\}$, for which $(h+k+l)$ is *odd*, have such weak intensities, as to make them undetectable; also in this case the impression will be left, that the grating is a *bodily*-centred one. In the case of *ions* being the building-stones, these reflections might also be completely absent, as Al^{+++} and Si^{++-} -ions have the same number of electrons.

It is for this reason, that a more promising way could perhaps be found by placing the atoms within the cell in such a way that all intensities for lines $\{hkl\}$, in which $(h+k+l)$ is *odd*, become so small that they are *practically* equal to *zero*. The choice of the space-group must, of course, be a rational one, in which the valencies of the different geometrical positions occurring in it, are in agreement with the number of atoms of the same kind to be placed into the cell.

For this attempt the space-group O_h^9 and its sub-groups: O_h^3 and O_2 on the one side and T_d^4 , T_h^1 and T^1 on the other side, appear to be well suited. The first mentioned groups O_h^9 correspond to a *bodily*-centred, the second series of groups to a simple cubic lattice. The groups O_h^3 , etc. present the advantage that the 6 *Si*-, and the 6 *Al*-atoms can be distributed over two different *six*-fold positions ($6f$ and $6g$ in WYCKOFF's notation¹⁾); in the case of *no* T_d^4 has some advantages, if also to the (SO_4) -groups of the Na_2SO_4 a "fixed" place shall be attributed. In choosing O_h^9 and its subgroups, the 6 *Al*- and 6 *Si*-atoms must be distributed over one *twelve*-fold place ($12h$ in WYCKOFF's notation); — as was already said, this is perhaps allowed for the calculation of the intensities with respect to the great analogy in diffracting power of both kinds of atoms, which in the case of their being present as *ions*, even becomes identical. As will soon become evident, however, the intensities calculated by the two methods, will appear to differ so insignificantly, when a suitable choice of the parameters is once made,

¹⁾ R. W. G. WYCKOFF, *The Analytical Expression*, etc., p. 130; p. 148.

— that it even appears questionable whether it will ever be possible to discriminate between these space-groups, solely by means of the relative intensities actually observed. It will always be difficult to decide by the spectrographical method, whether the *Al*- and *Si*-ions occupy two *six*-fold positions, or one *twelve*-fold one, in which they can substitute each other isomorphously. It is very well possible that, on account of their different chemical characters, they yet occupy two *six*-fold places in the crystalline structure. The fact, that in the *ultramaries* the atomic ratio: *Al*:*Si* is *not* constant is, as we shall see, rather an indication, however, that they really can occupy a *twelve*-fold position. It might be possible that, in some way, a gradual transition within this group of compounds from the simple-cubic into the bodycentred grating, were present.

§ 3. The calculation of the intensities has now been made in such a way that the space-group T_d^4 was assumed to be present here. To the atoms present within the elementary cell of *nosean*: $Na_{10}Al_6Si_6O_{32}S_2$ the following positions were attributed, *two* of the *Na*-atoms (or ions) being considered to be errant ones¹⁾:

To the *S*-atoms: (000) and $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$.

To the 8 *Na*-atoms remaining:

$$(uuu), (\bar{u}\bar{u}\bar{u}), (u+\frac{1}{2}, u+\frac{1}{2}, u+\frac{1}{2}), (\frac{1}{2}-u, u+\frac{1}{2}, \frac{1}{2}-u), \\ (u\bar{u}\bar{u}), (\bar{u}u\bar{u}), (u+\frac{1}{2}, \frac{1}{2}-u, u+\frac{1}{2}), (\frac{1}{2}-u, \frac{1}{2}-u, u+\frac{1}{2}).$$

To the 6 *Al*-atoms:

$$(0\frac{1}{2}\frac{1}{2}), (\frac{1}{2}0\frac{1}{2}), (\frac{1}{2}\frac{1}{2}0), (0\frac{1}{2}\frac{3}{2}), (\frac{3}{2}0\frac{1}{2}), (\frac{3}{2}\frac{1}{2}0).$$

To the 6 *Si*-atoms:

$$(\frac{1}{2}0\frac{1}{2}), (\frac{1}{2}\frac{1}{2}0), (0\frac{1}{2}\frac{1}{2}), (\frac{1}{2}0\frac{3}{2}), (\frac{3}{2}\frac{1}{2}0), (0\frac{3}{2}\frac{1}{2}).$$

To the 8 *O*-atoms the (SO_4)-groups:

$$(vvv), (\bar{v}\bar{v}\bar{v}), (v+\frac{1}{2}, v+\frac{1}{2}, v+\frac{1}{2}), (\frac{1}{2}-v, v+\frac{1}{2}, \frac{1}{2}-v), \\ (\bar{v}\bar{v}\bar{v}), (\bar{v}\bar{v}\bar{v}), (v+\frac{1}{2}, \frac{1}{2}-v, \frac{1}{2}-v), (\frac{1}{2}-v, \frac{1}{2}-v, v+\frac{1}{2}).$$

To the 24 other *O*-atoms:

$$(xyz), (x\bar{y}\bar{z}), (\bar{x}y\bar{z}), (\bar{x}\bar{y}z), (y+\frac{1}{2}, x+\frac{1}{2}, z+\frac{1}{2}), (\frac{1}{2}-y, x+\frac{1}{2}, \frac{1}{2}-z), \\ (y+\frac{1}{2}, \frac{1}{2}-x, \frac{1}{2}-z), (\frac{1}{2}-y, \frac{1}{2}-x, z+\frac{1}{2}), \\ (zxy), (\bar{z}x\bar{y}), (\bar{z}\bar{x}y), (z\bar{x}\bar{y}), \text{ en } (x+\frac{1}{2}, z+\frac{1}{2}, y+\frac{1}{2}), (x+\frac{1}{2}, \frac{1}{2}-z, \frac{1}{2}-y), \\ (\frac{1}{2}-x, \frac{1}{2}-z, y+\frac{1}{2}), (\frac{1}{2}-x, \frac{1}{2}+z, \frac{1}{2}-y), \\ (yzx), (\bar{y}\bar{z}x), (y\bar{z}\bar{x}), (\bar{y}z\bar{x}), (z+\frac{1}{2}, y+\frac{1}{2}, x+\frac{1}{2}), (\frac{1}{2}-z, \frac{1}{2}-y, x+\frac{1}{2}), \\ (\frac{1}{2}-z, y+\frac{1}{2}, \frac{1}{2}-x), (\frac{1}{2}-z, y+\frac{1}{2}, \frac{1}{2}-x).$$

¹⁾ In a rigorously geometrical lattice, Na_2SO_4 in *nosean* and *haugne* cannot be substituted by $CaSO_4$, nor in the *ultramaries* by Na_2S_2 , Na_2S_3 , etc. From these facts alone it appears inevitable to give up the supposition of a rigorously geometrical arrangement of these components within the whole structure. Also the previous argument for the necessity of assuming the presence of such "erratic" constituents must be kept in mind in this connection.

Experience showed that the most suitable values of the parameters were: $u = 0.250$; $v = 0.103$; $x = 0$; $y = z = 0.354$.

The value: $u = 1/4$ causes the differences of the results to be annihilated as concerns the Na -ions, in the case that O_h^3 or that T_d^4 are chosen.

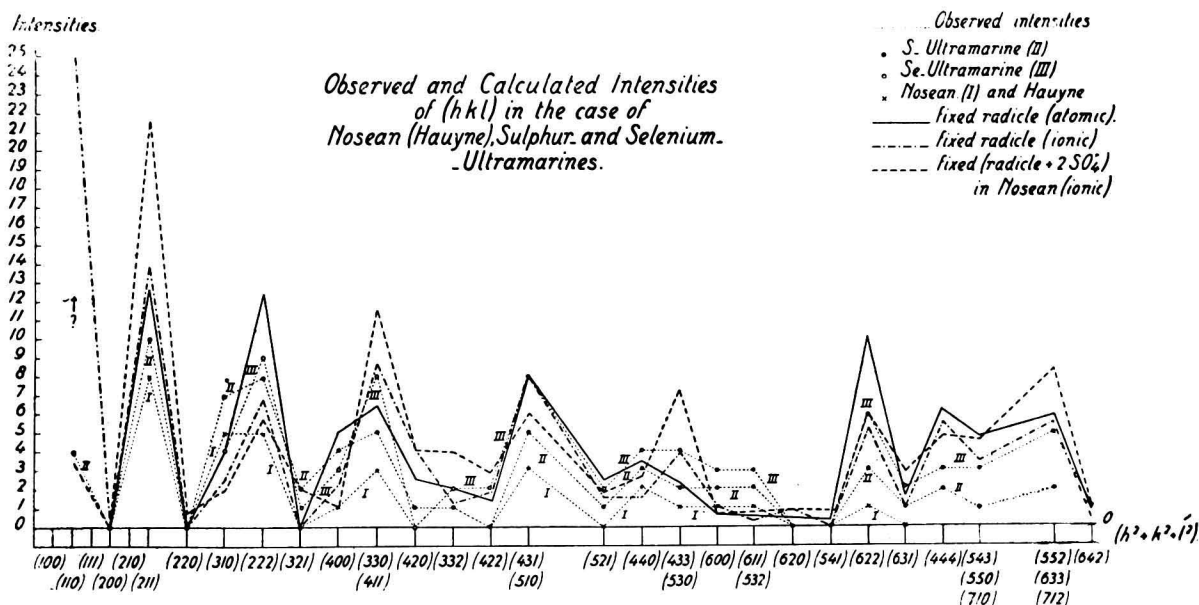


Fig. 2.

In figure 2 the calculated intensities are graphically represented, as well in the case that the "fixed" constituent: $(Na_8Al_6Si_6O_{24})$ is considered alone, be it as built-up of "atoms" (full-drawn line), or of "ions" (broken line), — as in the case that also fixed positions are attributed to the (SO_4) -groups (dotted-point-line); the observed intensities of nosean and of the S-, and Se-ultramarines are represented by the dotted lines I, II and III. The agreement between observed and calculated values appears to be a very satisfactory one, the more so, when it be remembered how subjective and rough the visual estimation of the intensities of the diffraction-images always is. Moreover, the DEBEIJE-factor causes the images of diffraction with a great value of the angle of deviation to get relatively lower intensities then the others. For this reason the apparently better agreement between observed and calculated intensities of the "fixed" radicle, if it be supposed to be built-up by atoms, instead of by ions — cannot be considered as a final argument against the presence of an ionic lattice: the fact mentioned only indicates that the diffractive power of an O^- -ion is somewhat smaller than that of an Al^{+++} -, or a Si^{++++} -ion. In every case it appears that the curve of the intensities for the radicle + two (SO_4) -groups also considered as "fixed" constituents, does not agree so well with the observations as in the case, that these

(SO₄)-groups are errant ones. But even in this case, the differences are only insignificant, if the uncertainty of visual estimation of the intensities is taken into account. *It is evident, however, that the characteristic ROENTGEN-spectrogram of nosean (hauyne) and of the ultramarines is completely determined by the diffraction-image caused by the radicle: (Na₈Al₆Si₆O₂₄)^{••} with the structure indicated in the above.* Characteristic is the absence of the images (200) and (220), and also, that (211) yields the most intensive diffraction-image. The estimation of the intensity of (110) is very uncertain, because this image is always situated within the field of heaviest blackening of the film and within the central halo, — it being, therefore, hardly discernible; in the few cases that it could be observed, its intensity appeared to be rather appreciable. The line (420) has been observed on some spectrograms, in the immediate neighbourhood of (330).

It may here be remarked once more that the arrangement of the "fixed" radicle as described above, can as well occur by means of the space-group O_h^3 and its (geometrical) sub-groups O_2 , T_d^4 , T_h^1 and T^1 . If, however, in *nosean* also to the (SO₄)-groups *fixed* places are attributed, the holohedral symmetry can by no means be maintained, and the group T_d^4 is then the most probable one.

§ 4. The structure of *nosean* as deduced before, has in Fig. 3 schematically been represented as a projection upon (001).

The Al-, Si-, and S-ions are all situated within the lateral faces of the elementary cell. The four O-ions in the centre of the cell are on zero-level, those to the left on $\frac{1}{2}$ of the cube-edge. The (SO₄)-group in the middle of the cell (in $\frac{1}{2}$ of the height of the cube) has, for the sake of clearness been omitted. To the right the (SO₄)-groups are represented, which are also visible through the hole in the centre of the basal plane and to the left in the corners. The *sodium*-ion has much free space with respect to the surrounding 6 O-ions, and may occasionally be substituted by elements having a greater atomic radius.

In the corners of the cell and in the centre of the basal face binary axes of rotation are present perpendicularly to (001); so are quaternary mirror-axes in the middle of the edges. The diagonals of the basal face are the directions of intersection with it of translatory mirror-planes, the number of them being twelve pro elementary cell. The body diagonals are ternary axes of rotation; moreover, a set of eight trigonal helicoidal axes is present, which axes are parallel to the first mentioned ones, for instance: $[111]_{0,0}$; $[111]_{\frac{1}{3}, \frac{2}{3}}$; $[111]_{\frac{2}{3}, \frac{1}{3}}$; etc.

Two cases are to be distinguished:

a. If only (Na₈Al₆Si₆O₂₄)^{••} is present as the "fixid" part (full-drawn line in Fig. 2), it appears:

1. That in each lateral face 2 Al-, and 2 Si-ions are situated, each

of them being surrounded by 4 O-ions; each of them has in T_d^4 the proper symmetry S^4 . (In O_h^3 , however, the symmetry V_D).

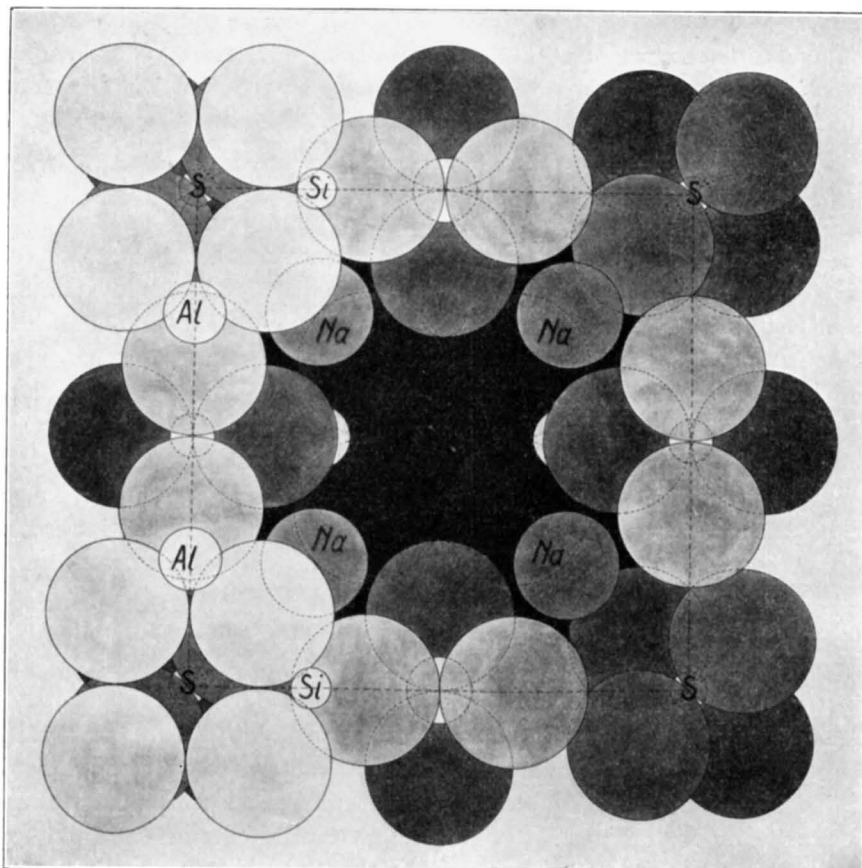


Fig. 3.

The Structure of Nosean and of the fixed radicle in Ultramarine. The lower part of the elementary cell has been projected upon (001): to the right only the basal layer, to $\frac{1}{4}$ of the height, — to the left to $\frac{1}{2}$ of the height of the cube. Hence, in the figure only that part of the contents of the cell is indicated which is situated beneath and in the plane (012). The fig. spheres represented the O-ions; etc.

2. That the 8 Na-ions are situated upon the four *body* diagonals, at $\frac{1}{4}$ and $\frac{3}{4}$ of their length; each of them is, at a distance of 2.64 A.U., surrounded by 6 O-ions. Their proper symmetry is D_3 in the space-group O_h^3 , in T_d^4 , T_h^1 and T^1 , however, C_3 (in T^1 distributed over 2 groups of 4 Na-ions). Without giving up the supposition of tetrahedrally arranged O-ions, it is impossible to place 6 of the 8 Na-ions into the middle of the lateral faces and into the middle of the edges, as ought to be the case in the only *six-fold* place present within the cell of the bodily-centred grating previously indicated. The space left free within

the interstices mentioned is namely no more than 0.54 A.U., the radius of the *Na*-ion being already 0.99 A.U.

Instead of the *Na*-ions, into the space between the 6 *O*-ions ($r=1.33$ A.U.), *Li*·, *K*· and (*NH*₄)·-ions, and also *Ag*·-ions can easily introduced, the radii of which have the same or analogous size¹⁾; but less easily *Rb*·-, and still less *Cs*·-ions can be substituted, — a fact which is also in agreement with the result previously published concerning the replaceability and the velocity of substitution of the *Na*-ions in the *ultramarines* by the interaction of the salt-solutions of these metals.

The 8 *Na*-ions, which are situated near two great cavities of the structure, at a distance from the vicinal *O*-ions that is greater than the sum of the radii of these ions, are, indeed, highly mobile ones. It is very probable that the character of the *permutites* which the *ultramarines* possess and which is exactly determined by the easy replaceability of those *Na*-ions by other mono- or bivalent metallic ions, is intimately connected with this freedom of motion within the structure proposed.

3. That the large cavity in the middle of the elementary cell (cubical space with $a_0 = 3.7$ A.U. and three cross-wise arranged, perpendicular prolongations) offers plentiful space to the negatively charged groups: *NaSO*'₄, *NaS*'₃ or (*Na, Ca*) *SO*'₄, which there and in the corners must be present as errant substitutes; they are kept electrostatically linked by the positively charged fixed part of the structure. The cavity in the middle and those in the corners of the cell can serve as a receptacle for these constituents, which in the case of *nosean* can be considered either as fixed or as errant ones, but in the case of *ultramarines* only as of the last kind, the place of which is not determined by the special symmetry of the total geometrical arrangement.²⁾ A true

¹⁾ The radii of these and other ions, which, in the course of these investigations were introduced into the *ultramarines*, have the following values:

<i>Li</i> · 0.79 A.U.	<i>Rb</i> · 1.49 A.U.	Moreover: <i>Zn</i> ·· 0.83 A.U.
<i>Na</i> · 0.99 A.U.	<i>Cs</i> · 1.65 A.U.	<i>Ca</i> ·· 1.06 A.U.
<i>K</i> · 1.33 A.U.	<i>Tl</i> · 1.49 A.U.	<i>Sr</i> ·· 1.27 A.U.
	<i>Ag</i> · 1.13 A.U.	<i>Ba</i> ·· 1.42 A.U.
<i>Mg</i> ·· 0.78 A.U.	<i>Al</i> ··· 0.57 A.U.	<i>O</i> '' 1.33 A.U.
<i>Hg</i> ·· 1.12 A.U.	<i>Si</i> ···· 0.39 A.U.	<i>Se</i> '' 1.91 A.U.
<i>Pb</i> ·· 1.32 A.U.	<i>S</i> ^{VI} 0.34 A.U.	For the <i>S</i> -atom is: $r = 1.04$ A.U.
<i>Mn</i> ·· 0.91 A.U.	<i>S</i> '' 1.74 A.U.	For the <i>Se</i> -atom in the same way: 1.13 A.U.

For the purpose of giving a place to the *Si*·, *Al*· and *S*^{VI}-ions within the tetrahedral groups of 4 *O*-ions, to them diameters must be attributed, which are not greater than 0.58 A.U.

²⁾ It may be remarked, that in *nosean* only 2 *Na*-atoms, or perhaps also the two (*SO*₄)-groups are erratic constituents; but in the *ultramarines* only the 2 *S*-atoms of those poor in *silica* and of a low degree of sulphuration (with *S*₂) can be placed into the structure. If *S*₃ or *S*₄ is present in them, these *sulphur*-atoms as well as the *Na*-atoms in excess, must all be errant ones.

“mother-silicate” is therefore, *not* present in the *ultramarines*; the underlying “fixed” component is, in a certain way, comparable to an electrically charged *radicle*: $(Na_8Al_6Si_6O_{24})^{--}$. Hence, the question as to the isolation of the underlying component, common to all these minerals, appears to be idle, in the same way as that of isolating the $(NH_4)^+$ -ion from the *ammonium*-salts. The 2 *Na*-atoms of the ten atoms present in *nosean*, which are freely movable within the large cavities mentioned above, will, in the beginning, more easily be substituted than the others by *Ag* or other metals, and this substitution will only have a feeble influence upon the relative intensities of the diffraction-lines; but such an influence may be beforehand expected as soon as also *Na*-atoms have gradually been replaced by *Ag*, so that this now occupies also places within the fixed part of the structure. Also this fact was previously stated by us; only after a certain percentage (more than 12–18 %) of the *Ag* has been introduced instead of the *Na* present, the powder-spectrograms begin to lose the character of the *sodium-ultramarines* so as to change into that of the *silver-ultramarines*.

b. If the supposition is made, — as was done in the calculation, — that besides $(Na_8Al_6Si_6O_{24})^{--}$ also both (SO_4) -groups have a “fixed” place in the structure, only 2 *Na*-ions still being erratic constituents, — then it becomes necessary to place those (SO_4) -groups into the centre and the corners of the elementary cell in such a way, that the 4 *O*-ions are again arranged tetrahedrally and in the right position with respect to their surroundings; i.e. on the *body* diagonals and contiguous to the *Na*-ions. The symmetry in this case can no longer be O_h^3 , but surely T_d^4 , O_2 , T_h^1 and T^1 . In the space-groups T_d^4 and T^1 the ternary axes are heteropolar; cube-diagonals are occupied in such a way that each *Na*-ion is situated between two *S*-atoms in the positions (000) and $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ at a certain distance from them or occasionally also exactly midway between them; each *S*-atom is surrounded by four tetrahedrally arranged *O*-ions and the distance of each *Na*-ion to the top of the subsequent tetrahedron of *O*-ions is either greater or smaller than that to the basal face of the preceding tetrahedron, etc. In the space-group T_d^4 each *Na*-ion has one variable parameter *u*, so that it can be shifted along a ternary axis, for instance into the direction of a corner or away from it. If this parameter *u* has exactly the value necessary to make it situated just in the middle of two subsequent *S*-atoms, then its distance to the top of the *O*-tetrahedron immediately following will be about 2.30 A.U.; this value is very close to that of the sum of the radii of a contiguous *Na*- and *O*-ion, namely: $(0.99 + 1.33) = 2.32$ A.U. In the space-group T_h^1 the ternary axes are no longer heteropolar; the subsequent tetrahedra of *O*-ions have, in this case, alternately reversed positions, so that each *Na*-ion is alternately situated either between two basal faces or between two tops of such tetrahedra. However, in this case the diffraction-images of faces (*hkl*), for which (*h* + *k* + *l*) is odd,

would yet appear to have detectable intensities, so that it must be concluded that the presence of this space-group T_h^1 is rather improbable.

§ 5. As is well-known, chiefly two series of *ultramarines*, those poor and those rich in *silica*, are distinguished in industry, the ratio: $Al:Si$ in the first being: $6:6=1:1$, in the last: $4:6=1:1.5$. Experience, however, teaches us, that:

1. All these *ultramarines* yield very *inconstant* results on analysis, so that it becomes certain, that their composition is *not* constant and can only approximately be expressed by definite stoichiometrical formulae;

2. All these *ultramarines* give *identical* powder-spectrograms with only slight and hardly detectable differences of their relative intensities; moreover, their fundamental gratings have practically identical dimensions;

3. They can all be separated by means of repeated decantions into fractions of different, be it only very little different, specific gravities. As these substances have towards water, however, highly troublesome (hydraulic) properties, it is practically impossible to separate from them fractions of definite specific weight to any satisfactory degree.

The thought arises from all these facts, that one has to deal here with *mixtures* of analogous, *isomorphous* substances, and that this is the true cause as well of their *inconstant* composition, as of the identity of their ROENTGEN-spectrogram.

According to what has been said in the above about their probable structure, the sum of the number of their *Al*- and *Si*-ions will be *twelve*. As only inappreciable differences of the diffractive power exist in the case of an *Al*- or a *Si*-atom and these differences are even zero in the cases of Al^{\cdots} and Si^{\cdots} -ions, — also *ultramarines*, in which the place of an *Al*-atom is occasionally occupied by a *Si*-atom¹⁾ and vice-versa, will show a distribution of their intensities, which practically cannot be distinguished from that of a *silicate* having a fixed part with the ratio: $Al:Si=6:6$. Thus, for instance, *ultramarines*, in which the „fixed” radicles are:



will all show powder-spectrograms, which are practically *identical* with that of the *ultramarine* poor in *silica*. It must then be evident, however, that the *mixtures* of such isomorphous *ultramarines* can very well show empirical chemical compositions, which very closely approach to that of an apparent “compound”, in which the ratio $Al:Si$ is about $1:1.5$. Thus, for instance, a mixture of 2 “mol” of an *ultramarine* with $(Na_8Al_4Si_8O_{24})^{\cdots}$ as fixed radicle, and 1 “mol” of one containing as

¹⁾ It must be remarked in this connection, that in 1910 J. HOFFMANN already drew attention to the fact, that the quantity of *boron* found by him in the completely *silica-free boron-ultramarines*, exactly corresponds to the sum of all *Si*-, and *Al*- of the ordinary *ultramarines*; so that it seems able to substitute as well the congenial *Al*-ion, as the *Si*-ion.

such the radicle: $(Na_8Al_6Si_6O_{24})''$, corresponds to an empirical composition of an apparent "mol" with the radicle: $(Na_8Al_{4.6}Si_{7.3}O_{24})$, in which the ratio: $Al:Si$ will be: 1:1.57, etc. It is also very well possible that the symmetry of the corresponding space-group is somewhat lowered by such substitutions, for instance to that of one of the other space-groups. But, as was already mentioned before, even this circumstance will hardly, if at all, be detectable by the relative intensities calculated. From all this it becomes clear, that it is no use attributing a definite chemical formula to any species of *ultramarine*, only on the ground of the results of analysis accidentally found. For quite independently of the way in which the substitution of Al by Si , or reversily, has taken place, — the powder-spectrograms, remain practically identical, — even if the erratic constituents of the structure: NaS'_2 , NaS'_3 , NaS'_4 , $NaS_2O'_3$, etc., be replaced by others¹⁾.

Another fact may still be brought to the fore here: in the *ultramaries* with S_2 as well as with S_3 or S_4 , the *sulphur*-atom surely is *not* hexavalent, as was supposed to be the case in the (SO_4) -groups of *nosean*; but it is, at the highest, *bivalent*. But the radius of the S'' -ion is: 1.74 A.U., hence its diameter: 3.48 A.U. Therefore, 2 S'' -ions can surely replace the total (SO_4) -groups of *nosean*; but as the last have a greater volume, the 2 S'' -ions will have considerable space to move freely. In the *ultramaries* of higher degrees of sulphuration, — which, like the *polysulphides*, are the more intensely coloured, the higher their *sulphur*-content is, — the whole remaining part of the *sulphur* must, under all circumstances, therefore, certainly be "erratic". But will this be in the form of ions or atoms? We do not know; perhaps that *S-atoms*, if dispersed in a medium built-up by electrically-charged *ions*, may cause the occurrence of the blue coloration, as this has been observed also in the case of other systems containing dispersed sulphur²⁾.

§ 6. Also the absorption-phenomena described previously in this paper become more comprehensible now, when considered in the light of these conceptions about the structure of the *ultramaries*. For the fixed component, consisting of the doubly electrically-charged radicle: $(Na_8Al_6Si_6O_{24})''$ or of others, differing from it only by the partial substitution of Al by Si and reversily, — represents the proper absorbent crystalline skeleton of all these compounds; hence, it is conceivable that the surface of the *ultramarine*-granules is highly "activated" and that

¹⁾ The presence of a radicle: $NaS_2O'_3$ remains as yet hypothetical, as long as no *thio-sulphate* has directly been separated from *ultramaries*: it is equally well possible, that a mixture of S' and $(SO_4)''$ forms the errant components.

²⁾ J. HOFFMANN, loco cit.: F. KNAPP, Dingler's Polyt. Journ., 233, (1879), 479; P. VON, WEIMARN, Koll. Beihefte, 22, (1926), 38; WO. OSTWALD, ibid., 2, (1911), 409, J. HOFFMANN, Koll. Zeits., 10, (1912), 275; PATERNO and MAZZUCHELLI, Atti R. Acad. d. Lincei, (5) 16, I, (1907), 465.

the molecules of the solutions, brought into contact with them and entering the large cavities of their structure, will be easily fixed upon these grains, especially after the solvent has taken up a part of the errant constituents within those cavities. It would, for instance, not be at all absurd to suppose, that the negative O-ions which are situated in the walls of the central cavity, subsequently would help to fix upon them the cations of the molecules already absorbed in this way. It must be remarked, moreover, that the surface of these *ultramarine*-granules with their characteristic "honeycomb"-structure and their cavities, is essentially different from the architecture of an atomic plane in a crystal-species like *sodiumchloride*. This loose structure, characterized by a relatively great specific surface, probably causes those "surface-actions" to come more particularly to the fore. Subsequently a gradual substitution of the *sodium*, — in the first place of the erratic Na-atoms and afterwards also of the Na-atoms (or ions) in the fixed radicle, — will possibly take place. The great velocity of the process in the beginning, is probably related to such an absorption of the salt-solution in the cavities and the loosening and substitution of the erratic constituents in them, while the farther, more intrinsic substitution then more particularly corresponds to the flatter part of the curve in Fig. 1. It is even most probable that the "hydraulic" properties of the *ultramaries* are also connected with those facts: the molecules of H_2O also will penetrate into the said cavities and evidently they too will readily settle down upon the electrically charged surface of the structural skeleton, after the errant components have been removed.

§ 7. After all that has been said it must have become clear now, that all attempts to express the constitution of these minerals and more particularly that of the *ultramaries* are to be considered as failures and that they inevitably were predestined to be so. The same is true for those, in which it is tried to express that constitution by means of WERNER's views about co-ordinative arrangement¹⁾ and the *ultramaries* are considered as derivatives of a complex ion: $\{Al(SiO_4)_3\}^{IX}$. In general, such *silicates* in the solid state only appear to be regular aggregations of atoms or ions, in which more particularly the *oxygen*-ions have a predominant part. There is, however, no special reason to assume a stronger link between some of them, than between others, — with perhaps the exception of such groups as (SiO_3) , (SiO_4) , etc. The principle according to which Al- and Si-atoms may mutually replace each other within such *silicate*-structures as those of *alumo-silicates*, — as both kinds of atoms only differ by the possession of a single electron less or more, — without any appreciable variation of the general character of the structure itself, seems to us to be a sound one and to be of importance with respect

¹⁾ Conf. i.a. J. JACOB, Zeits. f. anorg. Chem., **106**, (1919), 229; Helv. Chim. Acta, **3**, (1920), 669; E. GRUNER, Zeits. f. angew. Chem., (1928), 447, 448.

to the future elucidation of the structures of other solid *silicates*; and this is even more probable in the case that Al^{+++} -en Si^{++++} -ions play a part, both having the configuration of *neon*. The same is true with respect to the supposition made about the possible occurrence of errant constituents in such *silicates*, which components may be intercalated within the void spaces between the fixed parts of the whole structure; and in the first place we remember, in this connection, of the *zeolites*.

§ 8. By the aforesaid investigations the more than a hundred years old problem concerning the constitution of the *ultramarines*, etc., is certainly brought appreciably nearer to its solution, but yet we are far from a final decision. In the first place it will be necessary to check the structure developed in this paper also in those cases in which *sodium* is substituted by Ag^+ , Li^+ , Rb^+ , Cs^+ , Tl^+ -ions or by those of Ca^{++} , Ba^{++} , Sr^{++} , Pb^{++} , Hg^{++} etc.

This includes still a great number of tedious and lengthy calculations of the intensities, the more so, as for instance the 8 *Na*-ions will be replaced by 4 probably tetrahedrally arranged ions of the bivalent metals mentioned, and occasionally even other space-groups ought to be taken into account then. Moreover, it will be necessary still to do much analytical work with the purpose of ascertaining whether in the substitution-products obtained in the various reactions there is still *Na* present and to what amount; and also, whether *Al*- or *Si*-atoms are removed, as was the case in the transformation of GUIMET's blue into *silver-ultramarine*. Not until all such questions shall have been answered will the structure of the *ultramarines* be finally known.

Even then the explanation of the intense and strong coloration-phenomena of the *ultramarines* remains to be given. That they depend on the errant constituents: in the first place on the presence of *S*-atoms or S'^{-} -ions, or NaS'_n -ions respectively, — is certain. The blue colour increases with the *sulphur*-content, — exactly as the colour of the *poly-sulphides* in general appears to get deeper, as they contain more *sulphur*; but at the same time, this colour is also a function of the metal present: Na^+ -, Li^+ -, Tl^+ -, Ag^+ -, Hg^+ -*ultramarines* on the one hand, Ca^{++} -, Sr^{++} -, Ba^{++} -, Zn^{++} - and Pb^{++} -*ultramarines* on the other hand, can demonstrate the truth of this. Also the example of the *boron-ultramarines* which contain neither *Si*, nor *Al*, and in which, according to HOFFMANN, the blue colour *suddenly* appears, as soon as the molten mass or the solid phase has been brought into definite physical conditions, — always contain a certain amount of an electropositive metal like *sodium*.

The blue colour of systems containing *sulphur* seems to be connected with *dissociation*-, or, at least, with *dislocation*-phenomena, occurring in the *sulphur*-compounds used. Thus, for instance, *potassiumrhodanide* becomes quite blue if melted; but this blue colour again disappears when the molten mass is cooled. This phenomenon must be connected in some

way with a reversible transformation, for instance, with a reaction of the form: $KCNS \rightleftharpoons KCN + S$ or $\rightleftharpoons K' + CN' + S_{(act)}$. Indeed, *sulphur* introduced into molten *KCN* appears to behave in a similar way. It would be interesting in this respect to study the optical properties of finely dispersed *sulphur* in fields of strong electrostriction, as here a physical phenomenon presents itself, which is still unexplained. Also in this respect many investigations will still have to be made, before the mystery of the *ultramarines* can be said to be definitively solved.

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