Chemistry. — *Investigations into the Constitution of Artificial Ultra-marines.* II. *On Ultramarine-blue with high Silica-content and on Silver-, Silversodium-, Selenium- and Silverselenium-Ultramarines.* By Prof. Dr. F. M. JAEGER and Mr. F. A. VAN MELLE.

§ 1. In connection with our paper, already published in these Proceedings [1]), concerning the constitution of artifical and natural *ultramarines*, it was planned by us to substitute successively a part or all of the mobile constituents of these compounds, e.g. their *sodium*-atoms by *Li, K, Rb, Cs, Zn, Ba, Sr, Ag,* etc., or their *sulphur*-atoms by *selenium*, — with the purpose to elucidate the influence of such substitutions upon the ROENTGEN-spectrograms obtained with these substances. In this way it would perhaps be possible to ascertain, which components among those were a real part of the „rigid, periodical structure" of these compounds and which were merely dispersed in a statistical way within that rigid structure.

To proceed quite systematically in this, we have restricted our studies to one species of *ultramarine* only, chosen as primary material, namely to the *ultramarine-blue*-GUIMET N⁰. 7553, which in a pure, thoroughly washed and unground condition was most kindly given us in a considerable quantity by the *Usines d'Outremer*-GUIMET in *Fleurieu sur Saône*. Its composition appeared to correspond almost exactly to the formula: $Na_6Al_4Si_6O_{23}S_3$; its colour was a vivid, brilliant blue [2]).

For the sake of completeness, in Table I the results of the analysis of a powder-spectrogram of this preparation are put together. As in all sequent cases, an improved cylindrical camera was used, having a diameter of 88,8 m.m., and allowing the photographical film to be attached to its outer side; the camera is completely inclosed in a copper box. This variation of the older instrument has satisfied us in all respects.

In total 33 interference-images were measured; the grating-constant is here: $a_0 = 9,06$ A.U.

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[1]) These Proceedings, **30**, 249, (1927).

[2]) The ultramarine used here is an ultramarine with high silica- and moderate sulphur-content; its spec. weight at (25° C.) was: 2.35. Analysis furnished: 15.4 % Na; 13.0 % Al; 19.2 % Si; 10.6 % S; 41.8 % O, in which is included 2.78 % clay-residue. For $Na_6Al_4Si_6O_{23}S_3$ is necessary: 15.6 % Na; 12.3 % Al; 19.3 % Si; 10.9 % S; 41.8 % O. In no case the substance can correspond, as HOFFMANN supposed, to the aluminium-sodium-silicate: $Na_4Al_4Si_6O_{20}$: neither does it correspond to the *Marienberger blue* used by HEUMANN, because this was a product poor in silica.

TABLE I. Powder-spectrogram of Ultramarine-blue : $Na_6\,Al_4\,Si_6\,O_{23}\,S_3$ (Guimet—III, N^0. 7553). (Fig. 1A).

N^0. of Image	$2l$ in mm.:	Estim. Intensities:	λ:	$\Sigma(h^2)$:	$\dfrac{\theta}{2}$:	$sin^2\dfrac{\theta}{2}$ (observed):	$sin^2\dfrac{\theta}{2}$ (calculated):	Indices:
1	(21.4)	4	α	2	6°54'	0.0144	0.0144	(110) only once observed
2	37.1	10	α	6	11°58'	0.0430	0.0432	(211)
3	43.6	1	β	10	14°4'	0.0591	0.0590	(310)
4	48.2	7	α	10	15°33'	0.0719	0.0720	(310)
5	53.0	8	α	12	17°6'	0.0865	0.0864	(222)
6	55.4	1⁻	β	16	17°52'	0.0941	0.0944	(400)
7	57.1	2	γ	14	18°25'	0.0999	0.1008	(321)
8	59.0	1⁻	β	18	19°2'	0.1063	0.1062	(330) ; (411)
9	61.5	4	α	16	19°50'	0.1151	0.1152	(400)
10	65.4	5	α	18	21°6'	0.1296	0.1296	(330) ; (411)
11	71.3	1	β	26	23°0'	0.1528	0.1534	(431) ; (510)
12	72.9	1	α	22	23°31'	0.1590	0.1584	(332)
13	79.6	5	α	26	25°41'	0.1877	0.1872	(431) ; (510)
14	82.4	1⁻	β	34	26°35'	0.2004	0.2006	(433) ; (530)
15	86.0	1	α	30	27°44'	0.2165	0.2160 {	(521) as β-line (600)
16	89.2	3	α	32	28°47'	0.2317	0.2304	(440)
17	92.0	2	α	34	29°41'	0.2451	0.2448	(433) ; (530)
18	95.0	2	α	36	30°39'	0.2599	0.2592	(600)
19	97.9	2	α	38	31°35'	0.2742	0.2736	(532) ; (611)
20	106.4	3	α	44	34°20'	0.3180	0.3168	(622)
21	109.1	1⁻	β	56	35°12'	0.3322	0.3304 {	(642) as α-line (631)
22	111.9	2	α	48	36°6'	0.3471	0.3456	(444)
23	114.7	1	α	50	37°0'	0.3621	0.3600	(543) ; (505) ; (710)
24	120.0	2	α	54	38°43'	0.3910	0.3888	(633) ; (721)
25	122.1	1	α	56	39°23'	0.4026	0.4032	(642)
26	124.8	1	α	58	40°16'	0.4178	0.4176	(730)
27	130.2	1	α	62	42°0'	0.4476	0.4464	(732)
28	132.8	1	α	64	42°50'	0.4620	0.4608	(800)
29	135.0	1	α	66	43°33'	0.4747	0.4752	(554) ; (741) ; (811)
30	145.5	1	α	74	46°56'	0.5337	0.5328	(750) ; (743) ; (831)
31	148.4	1	α	76	47°51'	0.5498	0.5472	(662)
32	150.9	1	α	78	48°41'	0.5640	0.5616	(752)
33	153.5	1	α	80	49°31'	0.5785	0.5760	(840)

Radius of the Camera : 44.4 mm. $V = 55000$ Volt.

Exposure : 2 hours. $\lambda_\alpha = 1,540$ A.E. ; $\lambda_\beta = 1.388$ A.U.

Quadratic Equation : $sin^2\dfrac{\theta}{2} = 0.0072\,(h^2 + k^2 + l^2)$ (α-radiation)

$$sin^2\dfrac{\theta}{2} = 0.0059\,(h^2 + k^2 + l^2)\ (\beta\text{-radiation})$$

§ **2.** To corroborate our conclusions formerly drawn about the type of the fundamental grating and about the space-groups of these compounds, we wish to give here some additional and very persuasive complementary data concerning the minerals *noseane* and *hauyne*. We happened to prepare two rotation-spectrograms of some small, really simple crystals of both minerals, which spectrograms were splendidly developed, containing a great number of interference-images, which could accurately be measured. Moreover, we succeeded in rotating the crystals in these experiments round a principal axis [100], — an experiment which formerly had been

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TABLE II. Rotation-Spectrograms of *Noseane* and *Hauyne*, if rotated round a principal axis [100].

A. *Noseane.* The following images were observed:	**B.** *Hauyne.* The following images were observed:
Principal spectrum:	Principal spectrum:
λ_α : $(0\bar{3}\bar{1})$; $(0\bar{5}\bar{1})$; $(0\bar{4}0)$; (031) ; (033) ; (051),	λ_α : $(0\bar{1}3)$; (004) ; (015) ; $(03\bar{3})$; $(05\bar{3})$.
λ_β : $(0\bar{5}\bar{3})$; (053) ; (033).	λ_β : (004) ; (035) ; $(03\bar{3})$.
1st Accessory spectrum:	1st Accessory spectrum:
λ_α : $(1\bar{3}\bar{2})$; $(1\bar{5}0)$; (121) ; (132) ; (150) ; (152)	λ_α : $(1\bar{1}3)$; (105) ; (152) ; (121) ; $(13\bar{2})$; $(14\bar{3})$.
λ_β : (150).	λ_β : (121) ; $(14\bar{3})$.
— 1st Accessory spectrum:	— 1st Accessory spectrum:
λ_α : $(\overline{150})$; $(\overline{132})$; $(\overline{150})$; $(\overline{152})$.	λ_α : $(\overline{113})$; $(\overline{105})$; $(\overline{152})$; $(\overline{121})$; $(\overline{132})$; $(\overline{143})$.
λ_β : $(\overline{121})$; $(\overline{150})$.	λ_β : $(\overline{143})$.
2nd Accessory spectrum:	2nd Accessory spectrum:
λ_α : $(2\bar{3}\bar{1})$; (233) ; (242).	λ_α : (213) ; (215) ; $(21\bar{1})$; $(22\bar{2})$; $(23\bar{3})$; $(24\bar{2})$.
λ_β : (222).	λ_β : (253) ; (235).
— 2nd Accessory spectrum:	— 2nd Accessory spectrum:
λ_α : $(\overline{231})$; $(\overline{220})$; $(\overline{233})$; $(\overline{242})$.	λ_α : $(\overline{213})$; $(\overline{215})$; $(\overline{222})$; $(\overline{233})$; $(\overline{242})$.
λ_β : $(\overline{222})$.	λ_β : $(\overline{222})$; $(\overline{253})$.
3rd Accessory spectrum:	3rd Accessory spectrum:
λ_α : $(3\bar{3}\bar{2})$; (310) ; (321) ; (332).	λ_α : (312) ; (303) ; (314) ; (310) ; $(32\bar{1})$; $(33\bar{2})$; (350).
λ_β : (350) ; (352).	λ_β : $(35\bar{2})$; (350).
— 3rd Accessory spectrum:	— 3rd Accessory spectrum:
λ_α : $(\bar{3}\bar{4}\bar{1})$; $(\overline{310})$; $(\overline{350})$; $(\overline{352})$.	λ_α : $(\overline{312})$; $(\overline{303})$; $(\overline{314})$; $(\overline{305})$; $(\overline{310})$; $(\overline{321})$; $(\overline{332})$; $(\overline{350})$.
λ_β : $(\bar{3}\bar{3}\bar{1})$.	λ_β : $(\overline{303})$; $(\overline{350})$; $(\overline{352})$.
4th Accessory spectrum:	4th Accessory spectrum:
λ_α : $(4\bar{3}\bar{1})$; (431).	λ_α : (422) ; (413) ; $(43\bar{1})$; (420).
λ_β : $(4\bar{4}0)$.	λ_β : (404) ; $(43\bar{1})$.
— 4th Accessory spectrum:	— 4th Accessory spectrum:
λ_α : $(\bar{4}\bar{3}\bar{1})$; (431) ; (420) ; (422).	λ_α : $(\overline{422})$; $(\overline{413})$; $(\overline{420})$; $(\overline{422})$; $(\overline{431})$.
λ_β : $(\overline{440})$.	λ_β : $(\overline{431})$; $(\overline{413})$; $(\overline{404})$.

impracticable. The rotation-spectrograms obtained were graphically ana-
lysed according to BERNAL's method[1]): thus in the case of *noseane* up
to 50, in that of *hauyne* even up to 72 spots of the film, indices were
attributed in this way. The data obtained, arranged after the successive
hyperbolae, are reproduced in Table II.

No. of Image	Estim. intensities:	Radiation:	$2l$ in mm.:	$\frac{\theta}{2}$:	$sin^2\frac{\theta}{2}$ (observed):	$sin^2\frac{\theta}{2}$ (calculated):	Indices;
1	5	α	37.2	12°0'	0.0432	0.0440	(211)
2	5	β; or α	43.6	14°4'	0.0591	0.0596 {	(310) as α-line (220)
3	9	α	48.6	15°39'	0.0728	0.0733	(310)
4	5	α	53.4	17°14'	0.0878	0.0880	(222)
5	4	α	57.5	18°33'	0.1012	0.1025	(321)
6	2	β	59.2	19°6'	0.1071	0.1073	(330) or (411)
7	9	α	66.1	21°19'	0.1321	0.1319	(330) or (411)
8	1	β; or α	81.1	26°16'	0.1958	0.1907 {	(440) as α-line (431); (510)
9	2	β	87.6	28°16'	0.2243	0.2282	(611) or (532)
10	3	α	90.0	29°3'	0.2358	0.2346	(440)
11	5	α	93.0	30°0'	0.2500	0.2493	(433) or (530)
12	3	α	95.7	30°52$\frac{1}{2}$'	0.2633	0.2638	(600)
13	4	α	98.6	31°48$\frac{1}{2}$'	0.2778	0.2785	(611) or (532)
14	2	α	101.6	32°46$\frac{1}{2}$'	0.2931	0.2932	(620)
15	1	β	107.4	34°39'	0.3233	0.3218	(633) or (721)
16	1	β	112.4	36°16'	0.3499	0.3458 {	(730) as α-line (444)
17	5	α	120.9	39°0'	0.3960	0.3958	(633) or (721)
18	2	α	126.1	40°41'	0.4250	0.4251	(730)

**TABLE III. Powder-spectrograms of Silver-Ultramarine N⁰. 3
with 46.5 % *Ag*, prepared from Ultramarineblue-GUIMET III; 1st Fraction.**

Radius of the Camera: 44.4 mm. $V = 55000$ Volt. Time of exposure: 3 hours.

Quadratic Equation (α-radiation): $sin^2\frac{\theta}{2} = 0.00733\ (h^2 + k^2 + l^2)$.

(β-radiation): $sin^2\frac{\theta}{2} = 0.00596\ (h^2 + k^2 + l^2)$,

$\lambda_\alpha = 1.540$ A.U.; $\lambda_\beta = 1.388$ A.U. $\alpha_0 = 8.99$ A.U.

Body-centred, cubic grating. The colour of the compound is pale yellow.

[1]) J. D. BERNAL, Proceed. R. Soc. London, *A*, **113**, p. 117, (1927).

The conclusions formerly drawn are fully confirmed by these data, as in no case the sum $(h + k + l)$ appears to be an odd number. Undoubtedly a bodily-centred grating is, therefore, present in this structure, with $a_0 =$ about 9,1 A.U.

§ 3. Starting from this *ultramarine-blue*-GUIMET n°. 7553, now the corresponding *silver-ultramarine* was first prepared in the way described by HEUMANN [1]). 15 gramms of the *sodium-ultramarine* were constantly heated in sealed glass-tubes during 15 hours at 120° C. with 25 gramms *silvernitrate* and 20 ccm. water. The yellowish mass obtained was suspended in water, the solution of *silvernitrate* filtered-off, the residu washed [2]) thoroughly several times and during some time treated on the waterbath with a solution of a little *iodine* in *potassium-iodide*. After removing this solution by filtering, and having washed the residue, this was at 90° treated several times with a 10 %-solution of *potassium-cyanide*. This salt being removed by thoroughly washing, the powder was suspended in several litres of distilled water and repeatedly fractionated by sedimentation. In this way the *silversulphide* which has been formed, having much greater specific weight than the derived compound, can be removed almost completely, if this treatment be continued as long as black particles are observed; the fraction which remains in suspension during the longest time, is the purest and was always used in the final experiments. Analysis of this yellow compound gave (n°. 3); 46,5 % Ag; calculated for $Ag_6Al_4Si_6O_{23}S_3$: 46,6 % Ag. [3])

Of this *silver-ultramarine* a powder-spectrogram was obtained, which showed a great number of very sharp interference-images: the results of its analysis are collected in Table III.

§ 4. For the sake of comparison, we have in the same way prepared some other *silver-ultramarines* also, starting from other *ultramarines*. Thus, starting from *ultramarine-pink* GUIMET OVR (with 14,25 % Al; 19,33 % Si; 10,4 % S; spec. wgt.: 2,34 at 25° C.) a greyish looking *silver*-compound with 34,4 % Ag; from *ultramarine-blue* N°. 13 of the *Vereinigte Ultramarinfabriken*, a *silver-ultramarine* with 34,2 % Ag; and from an *ultramarine-green* N°. X of the same origin, a *silver*-derivative

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[1]) K. HEUMANN, Ann. der Chemie, **199**, 253, (1879); **201**, 262, (1880); **203**, 174, (1881).

[2]) This purification appears to be very troublesome, because the *silver-ultramarine* in contact with water, changes, like finely divided clay, into a colloidal, plastic mass, which after some time is transformed into hard, strongly conglomerating clumps. It may, therefore, be used for the fabrication of pottery, which on strongly heating, however, gets brown under loss of sulphur. Perhaps it would be possible, by heating it in the vapours of *alcali-chlorides*, to stain it superficially with a blue colour. This will be tried out afterwards.

[3]) Later-on we will publish the complete analysis of the *silver*-compound. It must be remarked, that the Ag-content appears to be somewhat variable, probably because of no complete homogeneity of the preparation.

№ of Image	$2l$ in mm.:	Intensities	λ:	$\frac{\theta}{2}$:	$sin^2\frac{\theta}{2}$ (observed):	$sin^2\frac{\theta}{2}$ (calculated):	Indices:

TABLE IV. Powderspectrogram of Silver-Ultramarine from Ultramarine-green V. U. F. N⁰. X. (Fig. 1B)

№ of Image	$2l$ in mm.:	Intensities	λ:	$\frac{\theta}{2}$:	$sin^2\frac{\theta}{2}$ (observed):	$sin^2\frac{\theta}{2}$ (calculated):	Indices:
1	34.6	2	β	11°10′	0.0374	0.0362	(211)
2	37.5	5	α	12°6′	0.0439	0.0446	(211)
3	43.7	3	β	14°6′	0.0593	0.0604 {	(310) as α-line (220)
4	49.7	8	α	16°2′	0.0763	0.0743	(310)
5	53.1	1	β	17°8′	0.0868	0.0846	(321)
6	54.5	4	α	17°35′	0.0913	0.0892	(222)
7	58.9	3	α	18°58′	0.1056	0.1040	(321)
8	60.3	2	α	19°27′	0.1108	0.1179	(400)
9	64.3	1	β	20°44′	0.1252	0.1208	(420)
10	67.0	8	α	21°37′	0.1358	0.1337	(330) and (411)
11	70.8	3	α	22°50′	0.1505	0.1486	(420)
12	74.4	2	α	24°0′	0.1655	0.1635	(332)
13	77.9	4	α	25°8′	0.1804	0.1783	(422)
14	81.2	4	α	26°12′	0.1950	0.1922	(431) and (510)
15	84.1	2	β	27°8′	0.2080	0.2054	(433) and (530)
16	86.3	1	β	27°50′	0.2180	0.2174	(600)
17	90.8	3	α	29°17′	0.2391	0.2378	(440)
18	93.8	5	α	30°16′	0.2541	0.2526	(433) and (530)
19	97.0	3	α	31°18′	0.2699	0.2675	(600)
20	99.7	4	α	32°10′	0.2835	0.2823	(532) and (611)
21	102.6	2	α	33°6′	0.2983	0.2972	(620)
22	105.6	2	α	34°4′	0.3138	0.3121	(541)
23	108.4	2	α	34°58′	0.3284	0.3269	(622)
24	110.7	1	α	35°43′	0.3408	0.3418	(631)
25	113.7	1	α	36°41′	0.3569	0.3566	(444)
26	115.6	1	α	37°17′	0.3670	0.3715	(543) ; (505) ; (701)
27	121.9	5	α	39°19′	0.4014	0.4012	(633) and (721)
28	127.3	2	α	41°4′	0.4315	0.4309	(730)
29	132.5	1	α	42°44′	0.4605	0.4607	(732)

N⁰. of Image:	$2l$ in mm.:	Intensities:	λ:	$\frac{\theta}{2}$:	$sin^2\frac{\theta}{2}$ (ob-served):	$sin^2\frac{\theta}{2}$ (cal-culated):	Indices:
30	137.8	1	α	44°28′	0.4906	0.4904	(554); (741); (811)
31	140.4	1	α	45°17′	0.5049	0.5052	(644) and (820)
32	143.2	1	α	46°12′	0.5210	0.5201	(653)
33	145.5	1	α	46°56′	0.5338	0.5350	(660); (822)
34	148.4	1	α	47°53′	0.5503	0.5499	(750); (743); (831)
35	150.9	1	α	48°41′	0.5641	0.5647	(662)
36	153.7	1	α	49°35′	0.5796	0.5795	(752)
37	155.9	1	α	50°17′	0.5917	0.5944	(840)
38	158.8	1	α	51°14′	0.6080	0.6093	(833)
39	164.4	1	α	53°2′	0.6383	0.6390	(655)
40	169.7	1	α	54°45′	0.6669	0.6687	(851)

TABLE IV (*Continued*).

Radius of the camera: 44.4 mm.

Wavelength: $\lambda_\alpha = 1.540$ A.U.; $\lambda_3 = 1.381$ A.U.; $a_0 = 8.93$ A.U.

$V = 55000$ Volt. Time of exposure: 3 hours.

Quadr. equation: $sin^2\frac{\theta}{2} = 0.00743 \ (h^2 + k^2 + l^2)$. ($\alpha$-radiation).

$$sin^2\frac{\theta}{2} = 0.00604 \ (h^2 + k^2 + l^2).$$ (³-radiation).

with 51,0 °/₀ Ag. Notwithstanding the differences in *silver*-content, the powder-spectrograms of all these preparations were *rigorously identical*. In Table IV the results of the analysis of the last mentioned spectrogram are reviewed ($a_0 = 8,93$ A.U.), because this showed the greatest number of sharp lines. The relative intensities of the most important, images are, — as far as so rough an estimation allows us to judge it, — analogous to those of Table III.

From these data the following conclusions may be drawn:

1⁰. Notwithstanding the different *Ag*-content of the compounds studied, their ROENTGEN-spectrograms appear to be practically identical.

2⁰. The original periodical structure of the *ultramarines* is preserved also after substitution.

3⁰. By the replacement of *Na* by *Ag*, the constant a_0 of the fundamental grating is *diminished*.

4⁰. Notwithstanding all the analogies mentioned, the relative intensi-

ties of corresponding interference-images in the spectrograms of the *ultramarines* and of the *silver-ultramarines* are appreciably modified. (Fig. 1; to compare *A* and *B*).
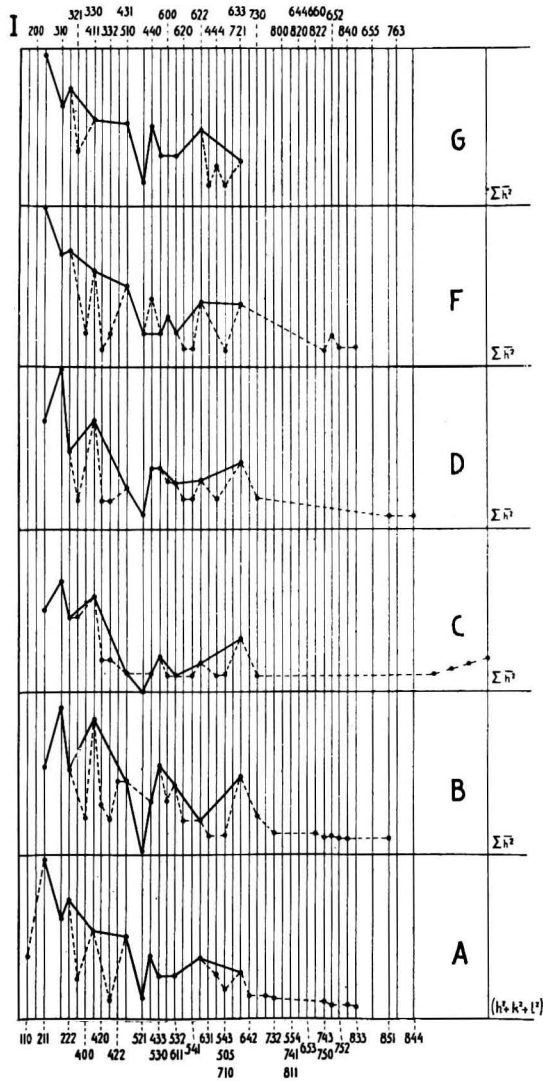

Fig. 1.

§ 5. The fact that the gradual replacement of *Na* in *ultramarine-blue* by *Ag* is really connected with a *gradual diminution* of the edge a_0 of the fundamental cell, could, moreover, also be proved in the following way.

If *ultramarine-blue* be digested during several days on the waterbath with an ammoniacal solution of *silverchloride*, then, as HEUMANN [1] stated

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[1] K. HEUMANN, loco cit., **201**, 282, (1880).

already, the *Na* of the original compound gets partially substituted by *Ag*. HEUMANN thought that in this way *two thirds* of the *Na*-atoms were replaced by *Ag*. In our experiments the original *ultramarine-blue* was heated during 6 days on the waterbath with an ammoniacal solution of *silver-chloride*, which was three times refreshed: the product obtained (N⁰. 19ᴵ) appeared yet to contain 39,4 % *Ag*. This product was again treated in the same way during 10 subsequent days: now the carefully purified product N⁰. 19ᴵᴵ), gave on analysis: 31,6 % *Ag*. A third treatment, however, gave again a product (N⁰. 19ᴵᴵᴵ) with 34,2 % *Ag*; evidently the substitution of *Na* by *Ag* does not stop at a limiting stoechiometrical proportion of both constituents, as HEUMANN believed, but the reaction goes on until a state of *equilibrium* is reached, — in the same way as occurs in treating the *permutites* with salt-solutions of varied concentrations.

The results of the analysis of the ROENTGEN-spectrograms obtained with these preparations, are collected in the Tables V and VI.

Moreover, a product was prepared by heating, during 50 hours in a flask with reflux-cooler, the original *silver-ultramarine* with a strong solution of 20 times its weight of *sodium-chloride*. This blueish coloured product (N⁰. 9) still contained, besides sodium, 7,75 % *Ag*; its ROENTGEN-spectrum gave the results collected in Table VII (Compare Fig. 1 *F*).

From the results of the analysis, it becomes evident, that besides the original *silver*-compound, there is nowhere present here a pure compound formed by substitution in simple stoechiometrical proportions:

For: $Ag_6Al_4Si_6O_{23}S_3$, the *silver*-content is calculated at: 46.6% *Ag*; obs.: 46.5% *Ag*. (3)

For: $Ag_5NaAl_4Si_6O_{23}S_3$, „ „ : 41.3% *Ag*; } obs.: 39.4% *Ag*. (19ᴵ)

For: $Ag_4Na(NH_4)Al_4Si_6O_{23}S_3$, „ „ : 35.5% *Ag*; }

For: $Ag_3Na(NH_4)_2Al_4Si_6O_{23}S_3$, „ „ : 28.7% *Ag*; } obs.: 31.6% *Ag*. (19ᴵᴵ)

For: $Ag_2Na(NH_4)_3Al_4Si_6O_{23}S_3$, „ „ : 20.8% *Ag*; (19ᴵᴵᴵ)

For: $AgNa_5Al_4Si_6O_{23}S_3$ (in exp. N⁰. 9), „ „ : 11.2% *Ag*; obs.: 7.75% *Ag*. (9)

Moreover, if the original *silver*-compound n⁰. 3 be heated in a porcelain crucible with an excess of *sodium-iodide* just above the meltingpoint of this salt, and the molten mass be kept at this temperature for a longer time, then, after purification, an *ultramarine-blue* (n⁰. 4) is formed, which, however, appears still to contain 6 % *Ag*; its powder-spectrogram (see Table VIII) is almost identical with that of preparation n⁰. 9, also with respect to the relative intensities of the successive diffraction-lines, and with that of the original GUIMET-*blue* itself.

If the extremely weak influence on the size of the grating-constant a_0, which is exerted, as we shall see later-on, by the substitution of *Na* by the (NH_4)-radicle, be now left aside for a moment, the constant a_0 of the preparations n⁰. 3, 4, 9, 19ᴵ, 19ᴵᴵ, 19ᴵᴵᴵ, etc., appears to vary as follows:

№ of Image:	2l in m.m.:	λ:	Estim. intens.:	$\Sigma(\overline{h^2})$:	$\dfrac{\theta}{2}$:	$sin^2\dfrac{\theta}{2}$ (ob-served)	$sin^2\dfrac{\theta}{2}$ (calcu-lated):	Indices:
						TABLE V. Powderspectrogram of Silver-sodium-Ultramarine No. 19[1]. (Contains: 39.4 % Ag; Fig. 1 C).		
1	37.5	α	6	6	12°6'	0.0439	0.0439	(211)
2	43.7	β	3	10	14°6'	0.0593	0.0595	(310)
3	48.8	α	7	10	15°45'	0.0737	0.0732	(310)
4	53.5	α	5	12	17°16'	0.0881	0.0878	(222)
5	58.3	β	1	18	18°50'	0.1042	0.1071	(330) and (411)
6	58.9	α	5	14	19°0	0.1059	0.1025	(321)
7	64.2	β	1	22	20°43'	0.1251	0.1310	(332)
8	65.7	α	6	18	21°13'	0.1310	0.1318	(330) and (411)
9	68.9	α	2	20	22°14'	0.1432	0.1464	(420)
10	74.0 *)	α	3	22	23°56'	0.1646	0.1610	(332)
11	79.5	α	1	26	25°39'	0.1874	0.1903	(431) and (510)
12	89.6	α	1	32	28°54'	0.2336	0.2342	(440)
13	92.6	α	2	34	29°53'	0.2482	0.2489	(433) and (530)
14	95.5	α	1	36	30°52'	0.2622	0.2635	(600)
15	98.5	α	1	38	31°46'	0.2774	0.2782	(532) and (611)
16	100.8	α	1	40	32°31'	0.2889	0.2928	(620)
17	104.1	α	1	42	33°35'	0.3060	0.3074	(541)
18	107.0	α	2	44	34°31'	0.3211	0.3221	(622)
19	112.0	α	1	48	36°8'	0.3477	0.3514	(444)
20	115.5	α	1	50	37°16'	0.3667	0.3660	(543) ; (505) ; (710)
21	120.6	α	3	54	38°54'	0.3940	0.3953	(633) and (721)
22	126.3	α	1	58	40°44'	0.4258	0.4246	(730)
23	178.6	α	1	98	57°35'	0.7130	0.7125	(853)
24	208.0	α	2	116	67°6'	0.8486	0.8490	(864) and (10.04)

*) Only observed at one side of the central spot.

Radius of the camera: 44.4 mm. $V = 55000$ Volt; Time of exposure: 2 hours.
$\lambda_\alpha = 1.540$ A.U.; $\lambda_\beta = 1.388$ A.U.; $a_0 = 9.00$ A.U.

Quadratic equation: $sin^2\dfrac{\theta}{2} = 0.00732\,(h^2 + k^2 + l^2)$, for the α-radiation.

$$sin^2\dfrac{\theta}{2} = 0.00595\,(h^2 + k^2 + l^2),\ \text{for the } \beta\text{-radiation.}$$

TABLE VI. Powder-spectrogram of Silver-sodium-ammonium-Ultramarine No. 19[II].
(Analysis: 31,6 % Ag; Fig. 1 D).

No. of Image:	$2l$ in mm.	Estim. intensities:	$\overline{\Sigma(h^2)}$:	λ:	$\dfrac{\theta}{2}$:	$sin^2\dfrac{\theta}{2}$ (observed):	$sin^2\dfrac{\theta}{2}$ (calculated):	Indices:
1	37.7	6	6	α	12° 9′	0.0443	0.0439	(211)
2	44.2	2	10	β	14°15′	0.0605	0.0599	(310)
3	48.9	9	10	α	15°46′	0.0738	0.0732	(310)
4	53.7	4	12	α	17°19′	0.0886	0.0878	(222)
5	58.2	1	14	α	18°46′	0.1035	0.1025	(321)
6	59.8	2	18	β	19°17′	0.1090	0.1062	(330); (411)
7	66.2	6	18	α	21°21′	0.1325	0.1318	(330); (411)
8	69.1	1	20	α	22°17′	0.1438	0.1464	(420)
9	73.8	1	22	α	23°48′	0.1628	0.1610	(332)
10	80.0	2	26	α	25°48′	0.1894	0.1903	(431); (510)
11	83.1	1	34	β	26°48′	0.2033	0.2006	(433); (530)
12	90.0	3	32	α	29° 2′	0.2356	0.2342	(440)
13	93.1	3	34	α	30° 1′	0 2502	0.2490	(433); (530)
14	95.9	2	36	α	30°56′	0.2642	0.2635	(600)
15	99.1	2	38	α	31°58′	0.2803	0.2782	(611); (532)
16	100.5	1	40	$\varkappa$	32°25′	0.2874	0.2928	(620)
17	104.5	1	42	α	33°42′	0.3078	0.3074	(541)
18	107.2	2	44	α	34°35′	0.3222	0.3221	(622)
19	112.5	1	48	α	36°17′	0.3502	0.3514	(444)
20	120.6	3	54	α	38°54′	0.3943	0.3953	(633); (721)
21	126.6	1	58	α	40°50′	0.4275	0.4246	(730)
22	172.5	1	94	α	55°39′	0.6816	0.6881	(763)
23	179.0	1	98	α	57°45′	0.7152	0.7174	(853)

Radius of the camera: 44.4 mm. $V = 55000$ Volt. Time of exposure: 3 hours.
$\lambda_\alpha = 1.540$ A.U.; $\lambda_\beta = 1.388$ A.U.; $a_0 = 9.00$ A.U.

Quadratic equation: $sin^2\dfrac{\theta}{2} = 0.00732\ (h^2 + k^2 + l^2)$, for the α-radiation.

$$sin^2\frac{\theta}{2} = 0.00599\ (h^2 + k^2 + l^2), \text{ for the } \beta\text{-radiation.}$$

TABLE VII. Powderspectrogram of a Silver-sodium-Ultramarine N⁰. 9.
(From Silver-Ultramarine by heating with a solution of NaCl during 50 hours.)
Contains: 7.75 % Ag; Fig. 1 F.

N⁰. of Image:	$2l$ in mm.:	λ:	Estim. intensities:	$\Sigma(h^2)$:	$\frac{\theta}{2}$:	$sin^2\frac{\theta}{2}$ (observed):	$sin^2\frac{\theta}{2}$ (calculated)	Indices:
1	37.5	α	10	6	12°6′	0.0439	0.0436	(211)
2	43.7	β	1	10	14°6′	0.0593	0.0591	(310)
3	48.6	α	7	10	15°41′	0.0731	0.0727	(310)
4	53.2	α	7	12	17°10′	0.0871	0.0872	(222)
5	58.9	α	4	14	19°0′	0.1059	0.1018	(321)
6	61.6	α	2	16	19°52′	0.1155	0.1163	(400)
7	64.9 *)	β	1	22	20°56′	0.1278	0.1300	(332)
8	65.9	α	6	18	21°16′	0.1315	0.1309	(330) and (411)
9	68.7	α	1	20	22°14′	0.1426	0.1454	(420)
10	73.5	α	2	22	23°43′	0.1618	0.1599	(332)
11	80.2	α	5	26	25°52′	0.1903	0.1890	(431) and (510)
12	82.6	β	1	34	26°39′	0.2012	0.2009	(433) and (530)
13	86.4	α	2	30	27°52′	0.2185	0.2181	(521)
14	89.4	α	4	32	28°50′	0.2326	0.2326	(440)
15	92.4	α	2	34	29°49′	0.2473	0.2472	(433) and (530)
16	95.6	α	3	36	30°50′	0.2627	0.2617	(600)
17	98.3	α	2	38	31°43′	0.2764	0.2763	(532) and (611)
18	100.8	α	1	40	32°31′	0.2889	0.2908	(620)
19	104.5 *)	α	1	42	33°43′	0.2081	0.3053	(541)
20	107.0	α	4	44	34°31′	0.3211	0.3199	(622)
21	112.0	α	2	48	36°8′	0.3477	0.3490	(444)
22	115.0	α	1	50	37°6′	0.3639	0.3635	(543) ; (505) ; (710)
23	120.5	α	4	54	38°52′	0.3938	0.3926	(633) and (721)
24	145.9 *)	α	1	74	47°5′	0.5361	0.5380	(743) ; (750) ; (831)
25	149.4 *)	α	2	76	48°12′	0.5557	0.5525	(662)
26	151.8 *)	α	1	78	48°58′	0.5690	0.5671	(752)
27	154.0 *)	α	1	80	49°41′	0.5814	0.5816	(840)

*) Only observed at one side of the central spot.

Radius of the camera: 44.4 mm. $V = 55000$ Volt; Time of exposition: 2 hours.

$\lambda_\alpha = 1.540$ A.U.; $\lambda_\beta = 1.388$ A.U.; $a_0 = 9.03$ A.U.

Quadratic equation: $sin^2\frac{\theta}{2} = 0.00727\ (h^2 + k^2 + l^2)$, for the α-radiation.

$$sin^2\frac{\theta}{2} = 0.00591\ (h^2 + k^2 + l^2),\ \text{for the }\beta\text{-radiation.}$$

If the *silver*-content is:

$$0 \quad {}^0/_0 \; Ag : a_0 = 9.06 \; \text{A.U.}$$
$$7.75^0/_0 \; Ag : a_0 = 9.03 \; \text{A.U.}$$
$$31.6^0/_0 \; Ag : a_0 = 9.00 \; \text{A.U.}$$
$$39.4^0/_0 \; Ag : a_0 = 9.00 \; \text{A.U.}$$
$$46.5^0/_0 \; Ag : a_0 = 8.96-8.99 \; \text{A.U.}$$
$$51 \quad {}^0/_0 \; Ag : a_0 = 8.93 \; \text{A.U.}$$

TABLE VIII. Powderspectrogram of *NaAg*-Ultramarine No. 4.
Contains about $6^0/_0$ *Ag*. (Fig. 1 G)

No. of Image:	$2l$ in mm.:	Estim. intensities:	λ :	$\lvert\Sigma\overline{(h^2)}\rvert$:	$\dfrac{\theta}{2}$:	$sin^2 \dfrac{\theta}{2}$ (observed):	$sin^2 \dfrac{\theta}{2}$ (calculated):	Indices :
1	37.1	9	α	6	11°58′	0.0430	0.0431	(211)
2	47.9	6	α	10	15°27′	0.0710	0.0718	(310)
3	52.9	7	α	12	17° 4′	0.0861	0.0862	(222)
4	54.6	3	α	14	17°37′	0.0916	0.1004	(321)
5	57.4	1	β	18	18°31′	0.1010	0.1049	(330) and (411)
6	65.4	5	α	18	21° 6′	0.1296	0.1292	(330) and (411)
7	79.3	5	α	26	25°35′	0.1864	0.1867	(431) and (510)
8	81.0	1	β	34	26° 8′	0.1940	0.1982	(433) and (530)
9	85.7	1	α	30	27°39′	0.2153	0.2154	(521)
10	88.7	4	α	32	28°37′	0.2294	0.2298	(440)
11	91.5	3	α	34	29°31′	0.2427	0.2441	(433) and (530)
12	94.6	3	α	36	30°31′	0.2578	0.2585	(600)
13	97.4	3	α	38	31°25′	0.2717	0.2729	(532) and (611)
14	106.3	4	α	44	34°18′	0.3176	0.3159	(622)
15	108.1	1	α	46	34°53′	0.3272	0.3303	(631)
16	111.6	2	α	48	36° 0′	0.3455	0.3446	(444)
17	114.4	1	α	50	36°54′	0.3605	0.3590	(543);(505);(710)
18	119.2	3	α	54	38°27′	0.3867	0.3877	(633) and (721)

Radius of the camera: 44.4 mm. $V = 55000$ Volt; Time of exposure: 3 hours.
Wavelength: $\lambda_\alpha = 1.540$ A.U.; $\lambda_\beta = 1.388$ A.U.; $a_0 = 9.09$ A.U.

Quadratic equation: $sin^2 \dfrac{\theta}{2} = 0.00718 \; (h^2 + k^2 + l^2)$, for the α-radiation.

$$sin^2 \frac{\theta}{2} = 0.00583 \; (h^2 + k^2 + l^2), \text{ for the } \beta\text{-radiation.}$$

From these data it becomes very evident that the constant a_0 has really a tendency to *decrease*, if the *silver*-content of the preparation *increases*.

Indeed, the atomic radius for *silver*, which differs, after all, only slightly from that of *sodium*, seems, in most cases, to be somewhat *smaller* than the last one. The influence of the substitution is strongest on the side of the pure *Na*-compound: a content of 6 %, or 8 % *Ag* is in this respect not yet very appreciable, but becomes discernible only, if perhaps more than a 15 % *Ag* is introduced. This may be seen e.g. from a graph, the abscissae of which are the *silver*-contents. The same phenomenon is observed with respect to the relative intensities. For a dozen interference-images common to both kinds of *ultramarines*, namely: (211); (310); (222); (321); (330), resp. (411); (431), resp. (510); (521); (440); (433), resp. (530); (532), resp. (611); (622); and (633), resp. (721), — the most important differences in this respect for the *silver*-compound in comparison with the *sodium*-compound are the following.

For the *Na*-compound $I_{(211)}$ is always *greater* than $I_{(310)}$; also $I_{(222)}$ always is *greater* than $I_{(310)}$; $I_{(330),(411)}$ is *smaller* than $I_{(322)}$; $I_{(521)}$ has yet a discernible size; $I_{(440)}$ is *greater* than $I_{(433),(530)}$; and the last-one is, although almost equal, also *greater* than $I_{(532),(611)}$; and $I_{(622)}$ is *greater* than $I_{(532),(611)}$ and also *greater* than $I_{(633),(721)}$. For the *Ag*-compound it is just the reverse in these respects.

From Fig. 1, in which on the horizontal axis the subsequent values of $(h^2 + k^2 + l^2)$ are graphically drawn, all this may easily be seen in comparing the figures 1[A], 1[B], 1[G]; furthermore, in comparing the figures 1[C] and 1[D] for the *silver-sodium*-compounds, which have, — with the exception of a few images like (532) in 1[C] and (433) in 1[D], — yet completely the character of Fig. 1[B]. On the contrary, Fig. 1[F] shows already the type of the *Na*-ultramarines, although the compound yet contains 8 % *Ag*. The characteristic intensities of the *silver*-compound seem to become discernible, as soon as more than 12 or 15 % *Ag* has taken the place of the equivalent quantity of *Na*.

§ 6. GUIMET [1]) first demonstrated, that the *sulphur* in the *ultramarines* may be substituted by *selenium* or *tellurium*. Through kind intervention of M. A. GUILLOCHIN, director-general of the *Usines d'Outremer*-GUIMET in *Fleurieu s/Saône*, who put a small quantity of GUIMET's original, scarlet-red *selenium-ultramarine* at our disposal, — we were able to study this substance and to compare its properties with those of the corresponding *sulpher*-derivatives. The brilliantly red powder was purified and freed from the last traces of adhering *selenates* or *selenites* by repeatedly washing with distilled water; the final product (N⁰. 80) was used in these experiments and partially converted into the corresponding *silver-selenium-*

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[1]) E. GUIMET, Bull. de la Soc. chim. Paris, **27**, 480, (1877); Ann. de Chim. et Phys., (5), **13**. 102, (1878). Here also we wish once more to express our sincere thanks to M. GUILLOCHIN.

TABLE IX. Powder-Spectrogram of Selenium-Ultramarine-red-GUIMET (N⁰. 80).

N⁰. of Image:	$2l$ in mm.:	λ:	Estim. intensities:	$\Sigma\overline{(h^2)}$:	$\dfrac{\theta}{2}$	$sin^2\dfrac{\theta}{2}$ (ob-served):	$sin^2\dfrac{\theta}{2}$ (cal-culated):	Indices:
1	37.4	α	10	6	12°4′	0.0437	0.0430	(211)
2	42.0	β	1	10	13°33′	0.0550	0.0582	(310)
3	48.0	α	4	10	15°29′	0.0712	0.0716	(310)
4	53.1	α	9	12	17°8′	0.0868	0.0859	(222)
5	58.0	β	1	18	18°43′	0.1030	0.1048	(330) ; (411)
6	61.4	α	3	16	19°48′	0.1148	0.1146	(400)
7	65.1	α	8	18	21°0′	0.1284	0.1289	(330) ; (411)
8	71.0	β	1	26	22°55'	0.1516	0.1513	(431) ; (510)
9	72.9	α	2	22	23°31′	0.1592	0.1576	(332)
10	76.3	α	2	24	23°36′	0.1733	0.1718	(422)
11	79.3	α	8	26	25°34′	0.1862	0.1862	(431) ; (510)
12	82.0	β	1	34	26°27′	0.1984	0.1979	(433) ; (530)
13	85.8	α	2	30	27°40′	0.2156	0.2148	(521)
14	88.6	α	4	32	28°34′	0.2286	0.2291	(440)
15	91.7	α	4	34	29°35′	0.2437	0.2434	(433) ; (530)
16	94.6	α	3	36	30°31′	0.2578	0.2578	(600)
17	97.6	α	3	38	31°29′	0.2727	0.2721	(532) ; (611)
18	105.7	α	6	44	34°6′	0.3143	0.3150	(622)
19	108.3	α	2	46	34°56′	0.3279	0.3294	(631)
20	111.1	α	3	48	35°50′	0.3427	0.3437	(444)
21	114.0	α	3	50	36°46′	0.3583	0.3580	(543) ; (505) ; (710)
22	119.1	α	5	54	38°25′	0.3861	0.3866	(633) ; (721)
23	121.3	α	1	56	39°7′	0.3981	0.3999	(642)
24	124.6	α	1	58	40°12′	0.4166	0.4153	(730)
25	129.2	α	1	62	41°40′	0.4419	0.4439	(732)
26	131.4	α	1	64	42°23′	0.4544	0.4582	(800)
27	135.1	α	1	66	43°35′	0.4753	0.4726	(554) ; (741) ; (811)
28	145.0	α	1	74	46°48′	0.5314	0.5298	(750) ; (743) ; (831)
29	147.4	α	2	76	47°33′	0.5444	0.5442	(662)
30	149.5	α	1	78	48°13′	0.5560	0.5585	(752)
31	152.5	α	2	80	49°12′	0.5730	0.5728	(840)
32	165.5	α	1	90	53°23′	0.6442	0.6444	(851)
33	171.0	α	1	94	55°10′	0.6737	0.6730	(763)
34	173.6	α	1	96	56°1′	0.6876	0.6873	(844)

Radius of the camera: 44.4 mm. $V = 55000$ Volt. Time of exposure: 3 hours. Wavelength: $\lambda_\alpha = 1.540$ A.U.; $\lambda_\beta = 1.388$ A.U. $a_0 = 9.10$ A.U.

Quadratic equation: $sin^2\dfrac{\theta}{2} = 0.00716\,(h^2 + h^2 + l^2)$, for the α-radiation.

$$sin^2\dfrac{\theta}{2} = 0.00582\,(h^2 + k^2 + l^2),\ \text{for the } \beta\text{-radiation.}$$

TABLE X. Powderspectrogram of Silverselenium-Ultramarine.
(Analysis: 25.8 % Ag).

No. of Image:	$2l$ in mm.:	Estim. intensities:	$\Sigma\overline{(h^2)}$:	λ:	$\dfrac{\theta}{2}$:	$sin^2\dfrac{\theta}{2}$ (observed):	$sin^2\dfrac{\theta}{2}$ (calculated):	Indices:
1	37.9	8	6	α	12°14′	0.0449	0.0445	(211)
2	43.9	1	10	β	14°10′	0.0600	0.0603	(310)
3	49.3	7	10	α	15°54′	0.0750	0.0742	(310)
4	54.1	5	12	α	17°25′	0.0896	0.0890	(222)
5	57.3	3	14	α	18°29′	0.1005	0.1039	(321)
6	66.7	7	18	α	21°31′	0.1345	0.1336	(330) and (411)
7	70.0	1	20	α	22°35′	0.1475	0.1484	(420)
8	74.2	1	22	α	23°56′	0.1646	0.1632	(332)
9	78.0	1	24	α	25° 7′	0.1801	0.1781	(422)
10	81.1	2	26	α	26°10′	0.1945	0.1930	(431) and (510)
11	83.7	1	34	β	27° 0′	0.2061	0.2050	(433) and (530)
12	90.7	3	32	α	29°15′	0.2387	0.2374	(440)
13	93.7	4	34	α	30°13′	0.2533	0.2523	(433) and (530)
14	96.6	2	36	α	31°10′	0.2678	0.2671	(600)
15	99.7	3	38	α	32° 9′	0.2832	0.2820	(532) and (611)
16	102.0	1	40	α	32°55′	0.2953	0.2968	(620)
17	105.5	1	42	α	34° 2′	0.3132	0.3116	(541)
18	108.3	2	44	α	34°56′	0.3279	0.3265	(622)
19	110.6	1	46	α	35°41′	0.3403	0.3413	(631)
20	113.6	1	48	α	36°39′	0.3563	0.3562	(444)
21	116.5	1	50	α	37°35′	0.3720	0.3710	(543);(505);(710)
22	122.1	4	54	α	39°23′	0.4026	0.4007	(633) and (721)
23	127.3	2	58	α	41° 4′	0.4316	0.4304	(730)
24	132.7	3	62	α	42°48′	0.4616	0.4600	(732)
25	137.9	1	66	α	44°29′	0.4910	0.4897	(554);(741);(811)
26	140.6	1	68	α	45°21′	0.5061	0.5046	(644) and (820)
27	150.9	2	76	α	48°41′	0.5641	0.5639	(662)
28	156.7	2	80	α	50°33′	0.5963	0.5936	(840)
29	159.2	1	82	α	51°21′	0.6099	0.6084	(833)
30	164.5	1	86	α	53° 4′	0.6389	0.6381	(655)
31	169.8	1	90	α	54°47′	0.6675	0.6678	(851)
32	193.1	1	106	α	62°18′	0.7839	0.7865	(950)
33	197.2	2	108	α	63°37′	0.8025	0.8014	(666)
34	200.1	1	110	α	64°33′	0.8153	0.8162	(10. 3. 1)
35	206.9	1	114	α	66°45′	0.8442	0.8459	(774) and (855)
36	211.1	1	116	α	68° 6′	0.8609	0.8607	(864) and (10.0.4)

Radius of the camera: 44.4 mm. $V = 55000$ Volt. Time of exposure: 2 hours.
$\lambda_\alpha = 1.540$ A.U.; $\lambda_\beta = 1.388$ A.U.; $a_0 = 8.94$ A.U.

Quadratic equation: $sin^2 \dfrac{\theta}{2} = 0.00742 \ (h^2 + k^2 + l^2)$, for the α-radiation.

and $sin^2 \dfrac{\theta}{2} = 0.00603 \ (h^2 + k^2 + l^2)$, tor the β-radiation.

ultramarine (N⁰. 81) (with 25,8 % *Ag*, according to its analysis), whose colour is orange-yellow or brownish-yellow in this case, and which preparation was purified by frequent decantation and sedimentation. Of both these substances, which are poor in *Ag*-content, powder-spectrograms were made; the results of their analysis are collected in the Tables IX and X.
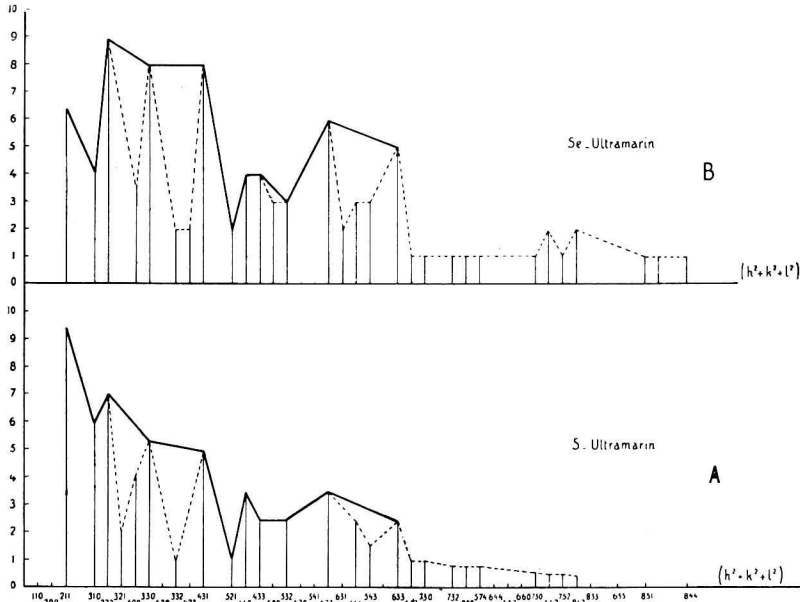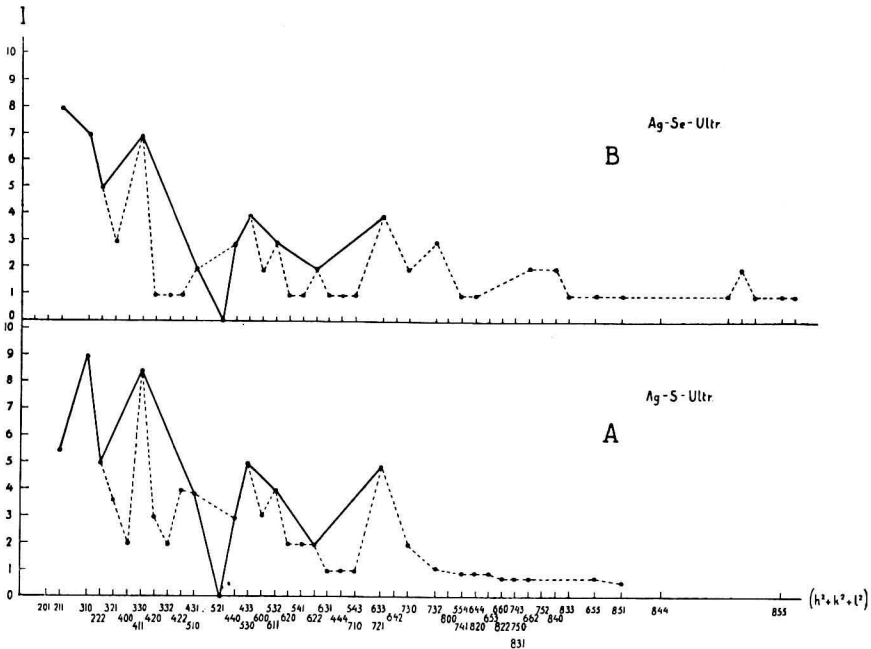

Fig. 2.

Fig. 3.

With the same time of exposure, viz. 3 hours, the background of the photographic film in the case of *selenium-ultramarine* appeared to be appreciably more and very homogeneously clouded, than in the case of the ordinary *sulphur-ultramarines*. The intensity of the diffraction-images was great and the different lines were very sharp.

From the data thus obtained, as well on comparing Fig. 2 and Fig. 3, — which in the same way as Fig. 1, give the estimated, relative intensities of corresponding diffraction-images in both patterns, — it may be deduced, that:

1^{stly}. The substitution of S in the ordinary *ultramarines* by Se leaves the general structure unchanged. Under comparable conditions of exposure the film is, in the case of the *selenium*-derivatives, more intensily and generally clouded: which doubtlessly is caused by the greater diffracting power of the Se-atoms, in comparison with that of the S-atoms. However, the general character of the relative intensities of corresponding diffraction-images and their sequence, appears to remain the same; only a few exceptions are present, e.g. that $I_{(222)}$ in the case of the Se-compound is *greater* than $I_{(211)}$; and that the same occurs for $I_{(433), (530)}$ in comparison with $I_{(522),(611)}$ and for $I_{(422)}$, which last intensity in the case of the S-ultramarine is practically equal to zero. The grating-constant a_0 of the Se-derivative ($a_0 = 9,10$ A.U.) is only *very slightly* greater than that of S-ultramarine.

2^{ndly}. The substitution of S by Se in *silver-ultramarine* does neither change its structure to any appreciable extent, while also the relative intensities of the successive corresponding images appear to be quite analogous in both cases, with the only exception (Fig. 3) that $I_{(211)}$ of the Se-Ag-ultramarine is *greater* than $I_{(310)}$, and the reverse occurs in the S-Ag-derivative. Also in this case both grating-constants a_0 do not differ appreciably.

§ 7. From the investigations described it must become clear now, that the substitution of the atoms of the alcali-metal in GUIMET-*blue* by more than about 15 $^0/_0$ Ag, has an appreciably greater influence on the relative intensity-sequence of the diffraction-images in the corresponding ROENTGEN-spectograms, than has the substitution of the S-atoms in it by Se; this last substitution hardly, and only in some few respects, influencing the said intensities for some of the diffracting sets of planes, but chiefly causing only a general clouding of the background of the photographic films. In this an indication might be found that the Na- and Ag-atoms take a more important part in the formation of the "rigid" periodical structure of the *ultramarines*, than do the S- or Se-atoms. Notwithstanding this, it cannot yet be considered to be finally proved, that the S- (or Se)-atoms are, therefore, to be supposed to be statistically dispersed throughout the whole fixed structure, while the Na- (or Ag)-atoms would, at least partially, represent the true building-

stones in the fixed, invariable, periodical structure of these remarkable substances. The experience hitherto obtained can only give a few more arguments in favour of the probability of such a conception, but as yet no complete certainty about it. Further experiments in this direction have already been started.

§ **8.** In the course of these investigations again a second tentative was made to find amongst the cubic zeolites a type of compound showing the peculiarities of the ROENTGENspectrograms, as observed in *hauyne, noseane* and the *ultramarines*. In this case *analcite* was chosen as the object of such a study; but also this beautifully crystallized and cubic *sodium-aluminium-silicate*, chemically closely related to the said silicates, appeared to possess *quite another structure* than the *ultramarines*. Although we intend to publish the more detailed data about the structure of *analcite* in the near future, — when at the same time we shall have an opportunity to discuss the question of the presence of "errant" constituents, namely of H_2O-molecules; in it, — we wish to communicate here already shortly some of the principal results of this investigation.

At our disposal were splendidly built, translucent crystals from the Cyclopic Isles, which were bordered principally by the forms $\{100\}$ and $\{211\}$.

With the aid of powder-spectrograms, of BRAGG's spectrograms on the faces of $\{100\}$ and $\{211\}$, and of rotation-spectrograms in which the crystals were turned round the directions [100], [110] and [111], — we were able to demonstrate, that this mineral has a structure to be described by the space-group O_h^{10}. In each cubic cell, the edge of which is equal to 13.71 A.U., 16 molecules are present of the composition: $NaAl\,Si_2\,O_6, H_2O$. If to the 16 Na-, and the 16 Al-atoms the two only possible, parameterless 16-fold places be attributed:

$[0\ 0\ 0]$; $[\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4}]$; $[\frac{3}{4}\ \frac{3}{4}\ \frac{3}{4}]$; $[\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}]$;	$[\frac{1}{8}\ \frac{1}{8}\ \frac{1}{8}]$; $[\frac{1}{8}\ \frac{7}{8}\ \frac{3}{8}]$; $[\frac{3}{8}\ \frac{1}{8}\ \frac{7}{8}]$; $[\frac{7}{8}\ \frac{3}{8}\ \frac{1}{8}]$;
$[\frac{1}{2}\ \frac{1}{2}\ 0]$; $[\frac{3}{4}\ \frac{3}{4}\ \frac{1}{4}]$; $[\frac{1}{4}\ \frac{1}{4}\ \frac{3}{4}]$; $[0\ 0\ \frac{1}{2}]$;	$[\frac{7}{8}\ \frac{7}{8}\ \frac{7}{8}]$; $[\frac{7}{8}\ \frac{1}{8}\ \frac{5}{8}]$; $[\frac{5}{8}\ \frac{7}{8}\ \frac{1}{8}]$; $[\frac{1}{8}\ \frac{5}{8}\ \frac{7}{8}]$;
$[\frac{1}{2}\ 0\ \frac{1}{2}]$; $[\frac{3}{4}\ \frac{1}{4}\ \frac{3}{4}]$; etc.	$[\frac{3}{8}\ \frac{3}{8}\ \frac{3}{8}]$; $[\frac{1}{8}\ \frac{3}{8}\ \frac{5}{8}]$; etc.
to one of both kinds of atoms,	to the other of both kinds of atoms,

and if to the Si-atoms the 32-fold position $32\,f$ (after WIJCKOFF's notation; it has *one* variable parameter u) be given, — then there are yet available only two 24-fold, parameterless positions, two 48-fold positions with a single variable parameter v, and one 96-fold position with three variable parameters. Indeed, in this way it appears possible also to fix the positions of the 96 O-atoms of the complex $Na_{16}\,Al_{16}\,Si_{32}\,O_{96} + {}+ H_{32}\,O_{16}$; but *there is no place any more available for the* 16 O-atoms *of the water-molecules*, and it seems inevitable, to assume these very

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"mobile" crystalwater-molecules to be also "errant" constituents of the structure. In short we hope to resume this topic in detail. As formerly already pointed out, for the *ultramarines* the space-group O_h^{10} cannot be taken into account.

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