Chemistry. — *On the Crystal-structure of Magnesium- and Nickel antimonate.* By J. BEINTEMA. (Communicated by Prof. F. M. JAEGER).

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§ 1. In a previous paper concerning the crystal-structure and the composition of the salt usually known as *sodium-dihydro-pyrostibiate*[1]), it was demonstrated that this compound must not be considered as a salt of *pyro-antimonic acid*, but as that of a hypothetical *hexa-hydroxy-acid*: $HSb(OH)_6$; thus the formula of the salt is not: $Na_2H_2Sb_2O_7 . 5H_2O$, but $NaSb(OH)_6$. This formula had already been suggested by L. PAULING[2]) in connection with the co-ordination number of *antimony* in its *oxygen* compounds. From the ionic radii, as determined by this author, it can be deduced that this co-ordination number must be *six*. The crystallized antimonates of *Mg, Co, Ni* and *Zn*, to which compounds usually the formula $Me(SbO_3)_2 . 12H_2O$[3]) or $Me(H_2SbO_4)_2 . 10H_2O$[4]) is attributed, should, according to PAULING, be derived from the same acid, so that its formula should be written: $Me(H_2O)_6\{Sb(OH)_6\}_2$.

§ 2. Crystals of these compounds can be obtained by adding a solution of potassium antimonate to a solution of the chloride or sulphate of the metal. Immediately an amorphous precipitation is formed which is eliminated by filtration. After some days small crystals prove to be deposited from the filtrate.

In the case of the *Ni* salt, these crystals had the form of hexagonal plates, limited by the basal face and by a hexagonal prism, the edges of the latter sometimes being truncated. The *Mg* salt showed, entirely conform to the description given by HAUSHOFER[5]), — besides these hexagonal plates which were usually conglomerated to rosette-shaped aggregates, — apparently monoclinic crystals. Of the *cobalt antimonate* only monoclinic crystals were deposited, which probably are isomorphous with the monoclinic crystals of the magnesium salt.

§ 3. The hexagonal crystals of the *nickel-* and *magnesium antimonate* proved to be badly developed. The angular values of the hexagonal prisms oscillated considerably and often deviated more than 1° from the theoretical value (60°). From the goniometrical investigation, therefore, no conclusion could be drawn as to the question whether the crystals were actually hexagonal. Nor could the optical behaviour of the crystals give any decisive answer in this respect. In polarized light the hexagonal plates proved to

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[1]) Proc. Royal Acad. Amsterdam, **38**, 1015 (1935).

[2]) L. PAULING, J. Am. Chem. Soc. **55**, 1895 (1933).

[3]) L. HEFFTER, Pogg. Ann. **86**, 416 (1852).

[4]) GOGUEL, *Contribution à l'étude des arséniates et antimoniates cristallisées préparées par voie humide*, Paris, 1896.

[5]) C. VON HAUSHOFER, Z. Krist. **4**, 52 (1880).

be composed of six sectors, in which the directions of extinction were normal and parallel to the faces of the prism.

The crystals are only feebly birefringent; the optical sign is *positive* in the case of the *nickel*-compound, whereas in the case of the *magnesium* salt the birefringence proved to be so weak that, because of the optical anomalies, its character could not be determined with any certainty.

As the crystals of the nickel salt were better developed than those of the magnesium salt, the determination of the structure was carried out with the former salt.

§ 4. A series of oscillation-spectrograms was made, the crystals being oscillated round their principal directions through an angle of 30°. These spectrograms had all features of being produced by one single crystal. It thus may be assumed that the optical anomaly is caused by tensions in the crystal owing to irregularities of its structure. These irregularities are probably also responsible for the deviations of the angular values observed.

The spectrograms obtained by oscillating the crystal round the *c*-axis, showed *no* plane of symmetry perpendicular to this axis. From this it may be deduced, that the crystal has *no* plane of symmetry parallel to the base. Moreover, the *c*-axis cannot be a senary axis.

The parameter could, from the distance between the layer lines, be determined to be 9.8 Å.

The more intensive reflections were only found in the principal spectrum and in the second and fourth accessory spectra.

The spectrograms obtained by oscillating the crystals round the normal to a prism face, showed a plane of symmetry perpendicular to this direction. The dimension of the elementary cell in this direction proved to be 27.7 Å $(= 16.0 \sqrt{3} \text{ Å})$.

The reflections with high intensity are exclusively situated in the layer lines N^0. 0, 3, 6, etc.

If the oscillation axis was chosen parallel to the edge between the base and a prism face, the spectrogram obtained showed *no* plane of symmetry. Here too, the intensive reflections were situated in the principal spectrum and in the 3rd, 6th, etc. accessory spectra. In this direction the parameter of the lattice was 16.0 Å.

Evidently the elementary cell is oriented in such a way, that its edges and sides are parallel to those of the crystal.

From the symmetry of these spectrograms it may be concluded, that the symmetry of the crystals must be either D_{3d}, D_3 or C_{3v}. As the crystals showed no piezo-electricity, the symmetry: D_{3d} may be considered to be the most probable one.

§ 5. The dimensions of the elementary cell of *Mg*-antimonate, as well as of *Ni*-antimonate, were accurately determined from a powder-spectrogram in which *silver* was used as a standard of comparison: (Tabel I and II):

TABEL I.
Powder-spectrogram of Nickel-antimonate (+ Silver).

No. of line	Distance 2 l in cm	Intensity (visual)	Angle θ	$sin^2\theta$ (observed)	$sin^2\theta$ of silver	$sin^2\theta$ (corrected)	$sin^2\theta$ (calculated)	Indices (h k i l)
1	3.456	2	8°37′	0.0224		0.0224	0.0226	$(30\bar{3}0)\beta$
2	3.623	4	9° 2′	0.0247		0.0247	0.0248	(0002)
3	3.832	8	9°33′	0.0275		0.0275	0.0277	$(30\bar{3}0)$
4	4.248	2	10°36′	0.0338		0.0338	0.0338	$(30\bar{3}1)$
5	4.779	2	11°55′	0.0426		0.0426	0.0426	$(30\bar{3}2)\beta$
6	5.301	7	13°13′	0.0523		0.0523	0.0524	$(30\bar{3}2)$
7	6.716	4	16°45′	0.0831		0.0831	0.0830	$(33\bar{6}0)$
8	6.877	4	17° 9′	0.0870	0.0870			
9	6.962	4	17°22′	0.0891		0.0891	0.0892	$(33\bar{6}1)$
10	7.648	10	19° 4′	0.1068	0.1067		0.1077	$(33\bar{6}2)$
11	7.804	4	19°28′	0.1111		0.1111	0.1106	$(60\bar{6}0)$
12	7.984	3	19°55′	0.1160	0.1160			
13	8.355	4	20°50′	0.1266		0.1266	0.1267	$(30\bar{3}4)$
14	8.657	5	21°36′	0.1355		0.1355	0.1354	$(60\bar{6}2)$
15	8.883	7	22° 9′	0.1422	0.1423			
16	10.121	4	25°15′	0.1822		0.1822	0.1821	$(33\bar{6}4)$
17	10.465	4	26° 6′	0.1935		0.1935	0.1936	$(63\bar{9}0)$
18	10.645	2	26°33′	0.1998		0.1998	$\begin{cases}0.1996\\0.1999\end{cases}$	$(63\bar{9}1)$ $(71\bar{8}2)$
19	10.926	4	27°15′	0.2097		0.2097	0.2097	$(60\bar{6}4)$
20	11.168	5	27°51′	0.2183		0.2183	0.2184	$(63\bar{9}2)$
21	11.536	3	28°46′	0.2317	0.2320			
22	12.011	4	29°58′	0.2494		0.2494	$\begin{cases}0.2489\\0.2506\end{cases}$	$(90\bar{9}0)$ $(30\bar{3}6)$
23	12.646	3	31°33′	0.2737		0.2737	0.2737	$(90\bar{9}2)$
24	12.927	7	32°15′	0.2847	0.2846			
25	13.135	3	32°46′	0.2929		0.2929	0.2927	$(63\bar{9}4)$
26	13.793	2	34°24′	0.3193	0.3190			
27	14.097	3	35°10′	0.3317		0.3317	0.3319	$(6.6.\overline{12}.0)$
28	14.703	3	36°40′	0.3567		0.3567	0.3566	$(6.6.\overline{12}.2)$
29	14.760	3	36°49′	0.3591		0.3591	0.3595	$(9.3.\overline{12}.0)$
30	15.360	3	38°19′	0.3843		0.3843	0.3843	$(9.3.\overline{12}.2)$
31	15.527	7	38°44′	0.3915	0.3913			

Effective Radius of Camera: $R = 5.742_5$ cm.

Wave-length: $\lambda = 1.538$ Å. $(Cu_{K\alpha})$

Quadratic Equation:
$$sin^2\theta = 0.003073\,(h^2 + hk + k^2) + 0.006193 \cdot l^2.$$
Parameters of the Lattice: $a_0 = 16.01_9$ Å; $c_0 = 9.76_8$ Å.

TABEL II.
Powder-spectrogram of Magnesium-antimonate (+ Silver).

No. of line	Distance $2l$ in cm	Intensity (visual)	Angle θ	$sin^2\theta$ (observed)	$sin^2\theta$ of silver	$sin^2\theta$ (corrected)	$sin^2\theta$ (calculated)	Indices $(hkil)$
1	3.594	4	8°59′	0.0244		0.0244	0.0244	$(000\bar2)$
2	3.815	8	9°32′	0.0274		0.0274	0.0274	$(30\bar30)$
3	4.216	3	10°32′	0.0334		0.0334	0.0336	$(30\bar31)$
4	5.269	7	13°10′	0.0519		0.0519	0.0519	$(30\bar32)$
5	6.685	4	16°42′	0.0826		0.0826	0.0824	$(33\bar60)$
6	6.870	5	17° 9′	0.0870	0.0870			
7	6.924	5	17°18′	0.0884		0.0884	0.0885	$(33\bar61)$
8	7.638	10	19° 5′	0.1069	0.1067	0.1068	0.1068	$(33\bar62)$
9	7.976	4	19°55′	0.1160	0.1160			
10	8.084	3	20°11′	0.1191		0.1190	0.1190 0.1190	$(41\bar53)$ $(51\bar62)$
11	8.293	4	20°43′	0.1251		0.1250	0.1251	$(30\bar34)$
12	8.610	4	21°30′	0.1343		0.1342	0.1342	$(60\bar62)$
13	8.872	9	22° 9′	0.1423	0.1423			
14	10.054	4	25° 7′	0.1801		0.1799	0.1800	$(33\bar64)$
15	10.421	4	26° 2′	0.1926		0.1924	0.1922	$(63\bar90)$
16	10.588	2	26°27′	0.1985		0.1983	0.1983 0.1983	$(63\bar91)$ $(71\bar82)$
17	10.853	3	27° 7′	0.2078		0.2076	0.2075	$(60\bar64)$
18	11.111	4	27°45′	0.2168		0.2166	0.2166	$(63\bar92)$
19	11.541	2	28°50′	0.2325	0.2320			
20	11.937	3	29°49′	0.2472		0.2469	0.2471 0.2472	$(90\bar90)$ $(30\bar36)$
21	12.580	3	31°25′	0.2718		0.2715	0.2715	$(90\bar92)$
22	12.914	9	32°15′	0.2848	0.2846			
23	13.781	2	34°25′	0.3196	0.3190			
24	14.020	2	35° 1′	0.3293		0.3289	0.3294	$(6,6.\overline{12}.0)$
25	14.689	2	36°41′	0.3570		0.3566	0.3569	$(9.3.\overline{12}.0)$
26	15.292	2	38°12′	0.3824		0.3820	0.3813	$(9.3.\overline{12}.2)$
27	15.513	9	38°45′	0.3918	0.3913			
28	16.344	8	40°49′	0.4273	0.4268			

Effective Radius of Camera: $R = 5.734_9$ cm.

Wave-length: $\lambda = 1.538$ Å $(Cu_{K\alpha})$.

Quadratic Equation:

$$sin^2\theta = 0.003050 \, (h^2 + k^2 + hk) + 0.006106 \cdot l^2.$$

Parameters of the Lattice: $a_0 = 16.07_9$ Å; $c_0 = 9.84_1$ Å.

Nickel antimonate: $a_0 = 16.01_9$ Å; $c_0 = 9.76_8$ Å.

Volume of the cell: $2171 \cdot 10^{-24}$ cm³.

If the cell contains 6 molecules, the specific weight, derived from these dimensions is 2.80_2.

A direct determination by the immersion method gave: 2.77.

Magnesium antimonate: $a_0 = 16.07_9$ Å; $c_0 = 9.84_1$ Å.

Volume of the cell: $2203 \cdot 10^{-24}$ cm³.

If the cell contains 6 molecules, the specific weight is calculated to be 2.63_3. By the immersion method it was found to be 2.59_8. Thus there can be no doubt that the elementary cell contains the mass of 6 molecules.

§ 6. The complete analysis of the principal spectrum and the first and second accessory spectra of the spectrograms, obtained by oscillating the crystal round its principal axis, revealed the presence of the following diffracting-images:

Principal spectrum: $(30\bar{3}0)$ **9** $(41\bar{5}0)$ **3** $(33\bar{6}0)$ **9** $(60\bar{6}0)$ **9** $(71\bar{8}0)$ **2**
$(63\bar{9}0)$ **10** $(90\bar{9}0)$ **10** $(8.2.\bar{10}.0)$ **2** $(7.4.\bar{11}.0)$ **3**
$(6.6.\bar{12}.0)$ **10** $(10.1.\bar{11}.0)$ **3** $(9.3.\bar{12}.0)$ **10**
$(12.0.\bar{12}.0)$ **10**

1st Acc. spectrum: $(30\bar{3}1)$ **6** $(41\bar{5}1)$ **3** $(33\bar{6}1)$ **8** $(60\bar{6}1)$ **3** $(52\bar{7}1)$ **1**
$(\bar{5}2\bar{7}1)$ **2** $(71\bar{8}1)$ **1** $(\bar{7}1\bar{8}1)$ **3** $(63\bar{9}1)$ **5** $(\bar{6}3\bar{9}1)$ **3**
$(8.2.\bar{10}.1)$ **2** $(\bar{8}.\bar{2}.10.1)$ **3** $(7.4.\bar{11}.1)$ **2**
$(\bar{7}.\bar{4}.11.1)$ **2** $(6.6.\bar{12}.1)$ **4** $(\bar{6}.\bar{6}.12.1)$ **5**
$(10.1.\bar{11}.1)$ **2** $(\bar{10}.\bar{1}.11.1)$ **2** $(9.\bar{3}.12.1)$ **4**

2nd Acc. spectrum: $(10\bar{1}2)$ **4** $(11\bar{2}2)$ **3** $(20\bar{2}2)$ **3** $(21\bar{3}2)$ **3** $(\bar{2}1\bar{3}2)$ **3**
$(30\bar{3}2)$ **10** $(22\bar{4}2)$ **1** $(\bar{2}2\bar{4}2)$ **2** $(31\bar{4}2)$ **3** $(\bar{3}1\bar{4}2)$ **3**
$(40\bar{4}2)$ **3** $(32\bar{5}2)$ **2** $(\bar{3}2\bar{5}2)$ **3** $(41\bar{5}2)$ **7** $(\bar{4}1\bar{5}2)$ **4**
$(50\bar{5}2)$ **3** $(33\bar{6}2)$ **9** $(\bar{3}3\bar{6}2)$ **10** $(42\bar{6}2)$ **1** $(51\bar{6}2)$ **2**
$(\bar{5}1\bar{6}2)$ **2** $(60\bar{6}2)$ **9** $(43\bar{7}2)$ **2** $(\bar{4}3\bar{7}2)$ **2** $(52\bar{7}2)$ **3**
$(\bar{5}2\bar{7}2)$ **4** $(61\bar{7}2)$ **3** $(\bar{6}1\bar{7}2)$ **3** $(70\bar{7}2)$ **1** $(44\bar{8}2)$ **2**
$(53\bar{8}2)$ **2** $(\bar{5}3\bar{8}2)$ **2** $(62\bar{8}2)$ **3** $(\bar{6}2\bar{8}2)$ **1** $(71\bar{8}2)$ **3**
$(\bar{7}1\bar{8}2)$ **1** $(63\bar{9}2)$ **9** $(\bar{6}3\bar{9}2)$ **9** $(72\bar{9}2)$ **1** $(\bar{7}2\bar{9}2)$ **1**
$(81\bar{9}2)$ **1** $(\bar{8}1\bar{9}2)$ **1** $(90\bar{9}2)$ **8** $(\bar{7}.\bar{3}.10.2)$ **1**
$(8.\bar{2}.10.2)$ **2** $(9.1.\bar{10}.2)$ **2** $(\bar{9}.\bar{1}.10.2)$ **2**
$(6.5.\bar{11}.2)$ **1** $(7.4.\bar{11}.2)$ **2** $(\bar{7}.\bar{4}.11.2)$ **1**
$(6.6.\bar{12}.2)$ **8** $(\bar{6}.\bar{6}.12.2)$ **8** $\left.\begin{array}{l}(10.1.\bar{11}.2)\\(\bar{10}.\bar{1}.11.2)\end{array}\right\}$ **3**
$(8.4.\bar{12}.2)$ **2** $(\bar{8}.\bar{4}.12.2)$ **2** $(9.3.\bar{12}.2)$ **8**
$(\bar{9}.\bar{3}.12.2)$ **8**.

The third accessory spectrum showed the same character as the first, the fourth the same as the second accessory spectrum.

As evidently no systematic extinctions are stated, the underlying lattice is the simple hexagonal cell. The space-groups D_{3d}^5 and D_{3d}^6, therefore, may be excluded; equally the space-groups D_{3d}^3 and D_{3d}^4 need not be taken into consideration either, as in these space-groups the dyad axes are parallel to the edges of the elementary cell, whilst on the contrary these axes in the crystal in question include angles with these edges of 30° and 90° resp. As reflections of the type: $(h, h, \overline{2h}, l)$ occurred, when l was *odd*, (for instance: (0003), (3361) etc.), D_{3d}^1 remains as the only possible space-group to be taken into account.

§ 7. From the oscillation-spectrograms it was apparent that those reflections, the indices h and k of which are a multiple of *three*, while l is even, — as for instance (30$\overline{3}$0), (63$\overline{9}$2) etc., — have high intensities. The atoms with a high diffracting power must, therefore, be arranged in such a way, that their centres form a simple hexagonal lattice. The latter is parallel to the crystal lattice, but its parameters are $\dfrac{a_0}{3}$ and $\dfrac{c_0}{2}$. The number of these strongly diffracting atoms: $6\,Ni$ and $12\,Sb$, is just sufficient to form such a lattice.

It must be investigated, in what way the $12\,Sb$-atoms and the $6\,Ni$-atoms can be arranged in such a lattice, without getting into conflict with the properties of symmetry of the space-group D_{3d}^1. The answer is that *three* possibilities must be taken into account:

1^0. Ni is placed in the two onefold positions (a) and (b) of WYCKOFF's *Tables*[1]) and in the two twofold positions (c) and (d); Sb must than be placed in two sixfold positions (k), with $u = \frac{1}{3}$, $v = 0$ and $u = \frac{1}{3}$, $v = \frac{1}{2}$ respectively.

Ni: $0,0,0$; $\;0,0,\frac{1}{2}$; $\;\frac{1}{3},\frac{2}{3},0$; $\;\frac{2}{3},\frac{1}{3},0$; $\;\frac{1}{3},\frac{2}{3},\frac{1}{2}$; $\;\frac{2}{3},\frac{1}{3},\frac{1}{2}$.

Sb: $\frac{1}{3},\frac{1}{3},0$; $\;0,\frac{2}{3},0$; $\;\frac{2}{3},0,0$; $\;\frac{1}{3},0,0$; $\;\frac{2}{3},\frac{2}{3},0$; $\;0,\frac{1}{3},0$;
$\quad\;\; \frac{1}{3},\frac{1}{3},\frac{1}{2}$; $\;0,\frac{2}{3},\frac{1}{2}$; $\;\frac{2}{3},0,\frac{1}{2}$; $\;\frac{1}{3},0,\frac{1}{2}$; $\;\frac{2}{3},\frac{2}{3},\frac{1}{2}$; $\;0,\frac{1}{3},\frac{1}{2}$.

2^0. Ni is present in a sixfold position (k) with $u = \frac{1}{3}$, $v = 0$; in this case the Sb-atoms must occupy the positions (a), (b), (c), (d), and, moreover, a position (k) with $u = \frac{1}{3}$, $v = \frac{1}{2}$.

Ni: $\frac{1}{3},\frac{1}{3},0$; $\;0,\frac{2}{3},0$; $\;\frac{2}{3},0,0$; $\;\frac{1}{3},0,0$; $\;\frac{2}{3},\frac{2}{3},0$; $\;0,\frac{1}{3},0$.

Sb: $0,0,0$; $\;0,0,\frac{1}{2}$; $\;\frac{1}{3},\frac{2}{3},0$; $\;\frac{2}{3},\frac{1}{3},0$; $\;\frac{1}{3},\frac{2}{3},\frac{1}{2}$; $\;\frac{2}{3},\frac{1}{3},\frac{1}{2}$;
$\quad\;\; \frac{1}{3},\frac{1}{3},\frac{1}{2}$; $\;0,\frac{2}{3},\frac{1}{2}$; $\;\frac{2}{3},0,\frac{1}{2}$; $\;\frac{1}{3},0,\frac{1}{2}$; $\;\frac{2}{3},\frac{2}{3},\frac{1}{2}$; $\;0,\frac{1}{3},\frac{1}{2}$.

3^0. Ni is situated in a position (k) with the parameters $u = \frac{1}{3}$, $v = \frac{1}{4}$. To the Sb-atoms then a sixfold position (k) with the parameters $u = \frac{1}{3}$, $v = \frac{3}{4}$, a twofold position (e) with $u = \frac{1}{4}$ and a fourfold position (h) with $u = \frac{1}{4}$ must be attributed.

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[1]) L. W. G. WYCKOFF, *The Analytical Expression*, etc. p. 155.

Ni: $\frac{1}{3},\frac{1}{3},\frac{1}{4}$; $0,\frac{2}{3},\frac{1}{4}$; $\frac{2}{3},0,\frac{1}{4}$; $\frac{1}{3},0,\frac{3}{4}$; $\frac{2}{3},\frac{2}{3},\frac{3}{4}$; $0,\frac{1}{3}.\frac{3}{4}$.

Sb: $\frac{1}{3},\frac{1}{3},\frac{3}{4}$; $0,\frac{2}{3},\frac{3}{4}$; $\frac{2}{3},0,\frac{3}{4}$; $\frac{1}{3},0,\frac{1}{4}$; $\frac{2}{3},\frac{2}{3},\frac{1}{4}$; $0,\frac{1}{3},\frac{1}{4}$;

$0,0,\frac{1}{4}$; $0,0,\frac{3}{4}$; $\frac{1}{3},\frac{2}{3},\frac{1}{4}$; $\frac{1}{3},\frac{2}{3},\frac{3}{4}$; $\frac{2}{3},\frac{1}{3},\frac{1}{4}$; $\frac{2}{3},\frac{1}{3},\frac{3}{4}$.

The latter of these three possibilities involves the most homogeneous distribution of the electric charges, so that it, beforehand, seems to be the most probable one.

As the Sb-atoms and the Ni-atoms possess unequal diffracting powers, the choice between the three possibilities mentioned above can be made by discussing and comparing the intensities of the different spots of the spectrograms.

If the atoms were distributed according to 1⁰., — the influence of the O-atoms for a moment being neglected, — then, besides the intensive reflections $(3m, 3n, 2p)$, only such of the type $(3m + 1, 3n + 1, 2p)$ and $(3m + 2, 3n + 2, 2p)$ would occur (m, n and p are integers).

In the case of a distribution according to 2⁰., — besides the intensive reflections $(3m, 3n, 2p)$, — the reflections $(3m, 3n, 2p + 1)$ would occur and, less intensive, also: $(3m + 1, 3n + 1, 2p)$, $(3m + 2, 3n + 2, 2p)$, $(3m + 1, 3n + 1, 2p + 1)$ and $(3m + 2, 3n + 2, 2p + 1)$.

If the distribution were according to 3⁰., — besides the reflections $(3m, 3n, 2p)$, — only such of the type: $(3m + 1, 3n + 1, 2p + 1)$ and $(3m + 2, 3n + 2, 2p + 1)$ would occur and, although with smaller intensities: $(3m + 1, 3n + 1, 2p)$ and $(3m + 2, 3n + 2, 2p)$.

When the intensities, as they actually were observed, are compared with the ones mentioned above, it becomes obvious that a distribution as sub 3⁰. cannot satisfactorily explain the rather high intensities of reflections as: (0003), (0005), $(30\bar{3}1)$, $(33\bar{6}1)$, $(63\bar{9}1)$, etc. On the contrary, the high intensities of the latter images prove, that the true distribution of the atoms must be that mentioned sub 2⁰. Thus these atoms are arranged in layers containing both kinds of atoms and in alternating layers, containing only Sb-atoms. The number of Ni-atoms in the former layers is twice that of the Sb-atoms; the arrangement, therefore, is such, that in each layer each Ni-atom is surrounded by *six* Sb-atoms (fig. 1).
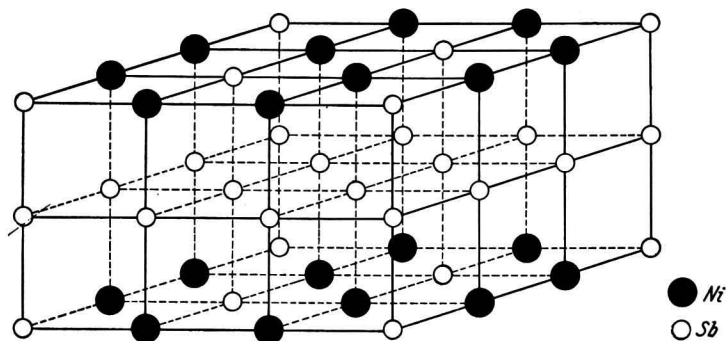

Fig. 1. Elementary cell of nickel antimonate. The O-atoms have been omitted in order to demonstrate the positions of the Ni- and Sb-atoms.

§ 8.   In order to determine the positions of the O-atoms, attention must be paid to the special symmetry, characteristic of the positions occupied by the Sb- and Ni-atoms; for these atoms presumably may be supposed to be the central atoms of co-ordinative complexes. The position occupied by the Ni-atoms, only possesses a single symmetry element: a vertical plane of symmetry. The Sb-atoms are situated in positions which partially have the symmetry S, partially the symmetry D_3, partially the symmetry D_{3d}. **The** structure of the antimonate-ions may be supposed to be the same, independent of their position in the crystal. The minimum symmetry of these ions, therefore, is D_{3d}. The Sb-atom is evidently surrounded by *six* O-atoms, situated in the corners of an octahedron, which may be more or less deformed in the direction of one of its four triad axes; this direction then must be that parallel to the principal axis of the crystal. This is in full accordance with PAULING's supposition that these compounds contain the ions $\{Sb(OH)_6\}$. Indeed, the univalent negative charge of the antimonate-ions can hardly be explained in another way than by supposing the *six* O-atoms surrounding the central atom actually to be present as *six OH*-groups.

§ 9.   As to the Ni-atoms, the fact that these atoms and the Sb-atoms occupy such analogous positions in the crystal structure, seems to indicate, that the Ni-atoms too are present as the central atoms of co-ordinative complexions, that have a structure analogous to that of the $Sb(OH)_6$-ions. In these ions, therefore, the Ni-ion must be surrounded by *six* octahedrally arranged water-molecules. This supposition really seems to be in full agreement with the structural results hitherto obtained. Moreover, the water-content of the compound completely agrees with the formula: $Ni(H_2O)_6\{Sb(OH)_6\}_2$.

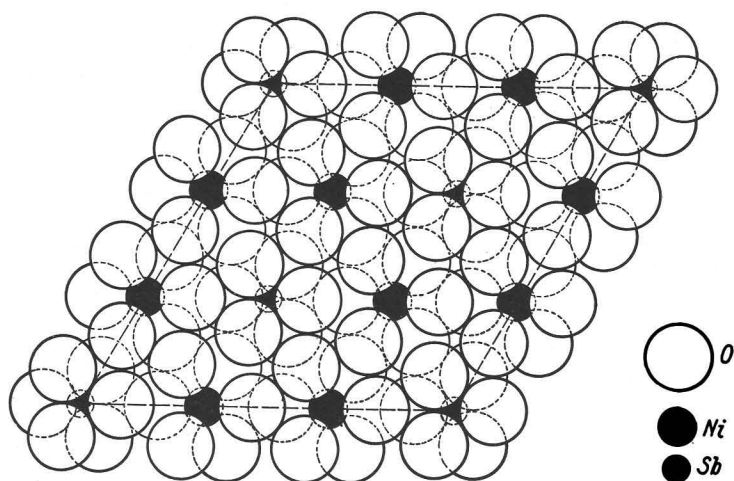It may be seen from fig. 2, in which such a layer of the elementary cell

Fig. 2. A layer of the elementary cell, containing $Ni(H_2O)^{..}$ -ions and $Sb(OH)'_6$-ions.

containing complex cations as well as complex anions is represented, that the H_2O-molecules and the OH-groups together form approximately a hexagonal very closely packed arrangement. If the assumption be made that the positions of the O-atoms are exactly conform to this packing, the distance between two neighbouring O-atoms can be readily calculated. The distance in a horizontal direction is 3.08_3 Å, in another direction 3.02_1 Å; these values are only slightly greater than twice the radius $(2.90$ Å$)$, according to Pauling[1]), of the water-molecule.

§ 10. The influence of the thus grouped O-atoms upon the intensities of the reflexed X-ray-beams may also be computed. If these atoms are situated in the positions: $1/9$, 0, $1/8$; etc. their calculated influences are as follows:

$(30\bar{3}0)$ **0** $(60\bar{6}0)$ **0** $(90\bar{9}0)$ **+100 %** $(12.0.\bar{12}.0)$ **0** $(33\bar{6}0)$ **—50 %** $(6\bar{3}90)$ **0** $(9.3.\bar{12}.0)$ **0** $(6.6.\bar{12}.0)$ **—50 %**

(0002) **0** $(30\bar{3}2)$ **0** $(60\bar{6}2)$ **0** $(90\bar{9}2)$ **0** $(12.0.\bar{12}.0)$ **0** $(33\bar{6}2)$ **—87 %** $(\bar{3}\bar{3}62)$ **+87 %**

$(6\bar{3}92)$ **0** $(\bar{6}392)$ **0** $(9.3.\bar{12}.2)$ **0** $(\bar{9}.\bar{3}.12.2)$ **0** $(6.6.\bar{12}.2)$ **+87 %** $(\bar{6}.\bar{6}.12.2)$ **—87 %**

(0004) **—100 %** $(30\bar{3}4)$ **0** $(60\bar{6}4)$ **0** $(90\bar{9}4)$ **—100 %** $(12.0.\bar{12}.4)$ **0** $(33\bar{6}4)$ **+50 %**

$(\bar{3}\bar{3}64)$ **+50 %** $(6\bar{3}94)$ **0** $(\bar{6}394)$ **0** $(9.3.\bar{12}.4)$ **0** $(\bar{9}.\bar{3}.12.4)$ **0** $(6.6.\bar{12}.4)$ **+50 %** $(\bar{6}.\bar{6}.12.4)$ **+50 %**.

(N.B. In this table a decrease of the intensity of a reflected beam with for instance 87 % of the total diffracting power of the O-atoms is denoted by: —87 %).

Such reflections proved, indeed, to have very high intensities. On the oscillation-spectrograms they all showed a nearly maximal blackening of the film, so that the spectrograms were not suited for the study of the disparities occurring in the spots above mentioned. Therefore, still another oscillation-spectrogram was prepared with a shorter time of exposure, during which the crystal was oscillated round the direction [0001] through an angle of 60°. This spectrogram showed the following reflection-spots with the intensities indicated:

$(30\bar{3}0)$**8** $(33\bar{6}0)$**3** $(60\bar{6}0)$**6** $(6\bar{3}90)$**7** $(90\bar{9}0)$**7** $(6.6.\bar{12}.0)$**6** $(9.3.\bar{12}.0)$**7** $(12.0.\bar{12}.0)$**5**

$(33\bar{6}1)$**5** $\left.\begin{array}{c}(63\bar{9}1)\\(\bar{6}391)\end{array}\right\}$**2** $(6.6.\bar{12}.1)$**1** $(\bar{6}.\bar{6}.12.1)$**1** $\left.\begin{array}{c}(9.3.\bar{12}.1)\\(\bar{9}.\bar{3}.12.1)\end{array}\right\}$**1**

$(30\bar{3}2)$**8** $\left.\begin{array}{c}(41\bar{5}2)\\(\bar{4}\bar{1}52)\end{array}\right\}$**5** $(33\bar{6}2)$**5** $(\bar{3}\bar{3}62)$**7** $(60\bar{6}2)$**8** $\left.\begin{array}{c}(52\bar{7}2)\\(\bar{5}\bar{2}72)\end{array}\right\}$**2** $\left.\begin{array}{c}(6\bar{3}92)\\(\bar{6}392)\end{array}\right\}$**8** $(90\bar{9}2)$**7**

$(6.6.\bar{12}.2)$**5** $(\bar{6}.\bar{6}.12.2)$**5** $\left.\begin{array}{c}(9.3.\bar{12}.2)\\(\bar{9}.\bar{3}.12.2)\end{array}\right\}$**7**

[1]) L. Pauling, Z. Krist. **72**, 482 (1930).

$(30\bar{3}3)\,2$ $(33\bar{6}3)\,5$ $(60\bar{6}3)\,2$ $\left.\begin{array}{c}(63\bar{9}3)\\[-2pt]\overline{(\bar{6}393)}\end{array}\right\}1$ $(90\bar{9}3)\,2$

$(30\bar{3}4)\,7$ $(31\bar{4}4)\,1$ $(40\bar{4}4)\,1$ $(\bar{3}144)\,1$ $(32\bar{5}4)\,1$ $(\bar{3}254)\,1$ $\left.\begin{array}{c}(41\bar{5}2)\\[-2pt]\overline{(\bar{4}152)}\end{array}\right\}2$ $(33\bar{6}4)\,7$

$(\bar{3}\bar{3}64)\,7$ $(60\bar{6}4)\,6$ $(63\bar{9}4)\,5$ $(6.6.\bar{1}\bar{2}.4)\,4$ $(\bar{6}.\bar{6}.12.4)\,4$ $(9.3.\bar{1}\bar{2}.4)\,5$

$(\bar{9}.\bar{3}.12.4)\,5$ $(9094)\,5$

These intensities generally seem to agree rather well with those which one might expect in accordance with the arrangement of the O-atoms suggested. The intensities of the reflections (3030), $(60\bar{6}0)$, $(90\bar{9}0)$, and $(12.0.\bar{1}2.0)$, being 8, 6, 7 and 5 respectively clearly show the increase in intensity of the reflection $(90\bar{9}0)$. Equally $(33\bar{6}2)$ has a perceptibly lower intensity than $(\bar{3}362)$. The intensity of $(33\bar{6}0)$ is very small, whilst $(6.6.\bar{1}2.0)$ too is less intensive than for instance $(9.3.\bar{1}2.0)$; etc. By another oscillation-spectrogram the small intensity of (0004) had already previously been proved. All these facts to a certain degree corroborate the very closely packed arrangement of the O-atoms supposed. At greater reflection-angles, however, this specific influence of the atoms was hardly any more noticeable. This may be partly accounted for by the more rapid decrease of the diffracting power of the O-atoms with increasing reflection-angles, compared to that of the Ni- and Sb-atoms, owing to the greater extension of the O-atoms. Besides this, also small deviations from the ideal arrangement will show their influence especially at great reflection-angles. Most probably these deviations also cause the remarkable difference in intensity of the beams reflected by $(33\bar{6}1)$ and $(\bar{3}361)$, of which the latter could *not* be detected, even on spectrograms which had been exposed during a long time.

§ 11. According to PAULING [1]), who supposes the distance between the centres of the Ni-atom and the surrounding H_2O-molecules to be equal to the distance Ni—NH_3 in the $Ni(NH_3)_6$-complex [2]), this distance may be assumed to be 2.40 Å. If the structure of the $Ni(H_2O)_6$-complex be rigourously octahedral, the distance between two adjacent H_2O-molecules belonging to the same complex then would be: 3.40 Å; the distance between two such molecules belonging to different complexes, however, would be 2.94 Å, — which value agrees very well with the radius of the water-molecule: 1.45 Å theoretically deduced.

The dimensions of the $Sb(OH)_6$-complex are not known as yet. If the structure of the complex be assumed as exactly octahedral, only one parameter: the distance Sb—O within the complex has to be determined. If

[1]) L. PAULING, Z. Krist. **72**, 482 (1930).

[2]) R. W. G. WYCKOFF, J. Am. Chem. Soc. **44**, 1239 (1922).

this distance were the same as that between *Ni* and *O* in the $Ni(H_2O)_6$-complex, the intensity of the reflections, excepted those of the type: ($3m$, $3n$, $2p$), would not be affected by the *O*-atoms. However, the great difference of intensity of the reflected beams of, for instance, ($33\bar{6}1$) and

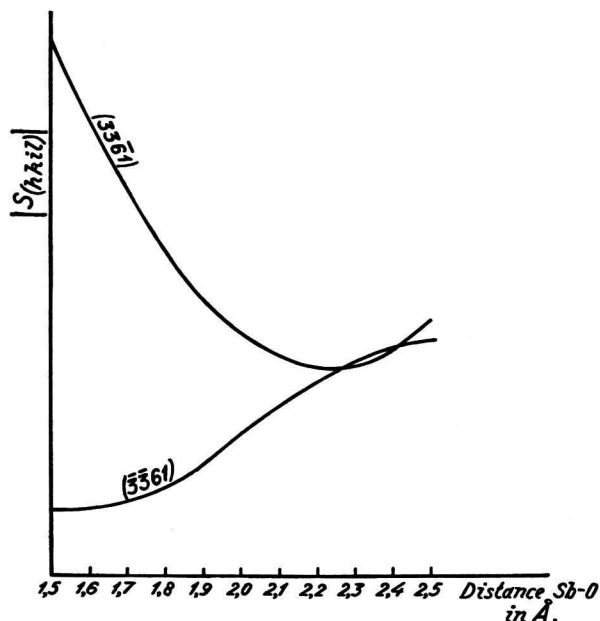Fig. 3. Structure-amplitude of the reflections ($33\bar{6}1$) and ($\bar{3}3361$) as a function of various values of the distance *Sb-O* within the $Sb(OH)_6$-complex.

($\bar{3}3361$) can only be explained by the influence of the said atoms. In fig. 3 the structure-amplitude of these reflections is plotted as a function of different values for the distance *Sb—O*, when the diffracting power of the atoms is supposed to be proportional to the number of electrons contained in them. From this figure it may easily be seen, that the difference in intensity mentioned above seems to indicate that the distance *Sb—O* is considerably shorter than that between *Ni* and *O* in the $Ni(H_2O)_6$-complex. However, not too much value may be attached to this result, as the assumptions concerning the positions of the *O*-atoms cannot be rigorously true, for in this case the elementary cell would be a smaller one.

SUMMARY.

The structures of the *antimonates* of *nickel* and *magnesium*, crystallizing in the shape of hexagonal plates, — to which hitherto the formula: $Me(SbO_3)_2 . 12 H_2O$ or $Me(H_2SbO_4)_2 . 10 H_2O$ was attributed, were investigated by means of *X*-rays. It was demonstrated that in their structures the complex cations $\{Ni(H_2O)_6\}$ and $\{Mg(H_2O)_6\}$ respectively and the complex anions $\{Sb(OH)_6\}$ are present. The formulae of these

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compounds, therefore, must be considered to be:$\{Ni(H_2O)_6\}\{Sb(OH)_6\}_2$ and $\{Mg(H_2O)_6\}\{Sb(OH)_6\}_2$; these formulae were already previously suggested by PAULING, who based this hypothesis on the value of the co-ordination number of Sb in its O-compounds, as calculated from the ionic radii.

About the further particularities of the structure mentioned, all data can be found in this paper.

This investigation was carried out with the experimental resources and the means of the Laboratory for Inorganic Chemistry of the University.

<div align="right">Groningen, Laboratory for Inorganic
and Physical Chemistry of the University.</div>

Plantkunde. — *Het voortkweeken van Hippeastrum langs vegetatieven weg.* II. Door IDA LUYTEN. (Mededeeling N⁰. 46 van het Laboratorium voor Plantenphysiologisch Onderzoek te Wageningen.) (Communicated by Prof. A. H. BLAAUW).

(Communicated at the meeting of January 25, 1936).

In 1926 heb ik voor het eerst de methode om Hippeastrum langs vegetatieven weg voort te kweeken, besproken. Na de toen gepubliceerde onderzoekingen zijn nog vele proeven genomen: en wel over de optimale temperatuur waarbij de rokken moeten liggen om regeneratie te krijgen; over de beste wijze van oogsten der jonge bolletjes; over de breedte van de weefsel-zône die regeneratie laat zien; over den ouderdom der te hollen bollen, over het snijden in plaats van hollen; over den gunstigsten tijd van het jaar om de Hippeastrumbollen te hollen.

Deze gegevens wil ik alle hier bespreken, met de hoop, dat het zal kunnen bijdragen tot een groote zekerheid van de resultaten bij het hollen. Immers met deze gegevens moet het mogelijk zijn iederen bol vegetatief door holling voor te planten en wel zoo, dat men groote partijen van zuivere afstamming kan kweeken. Want niet alleen is het van belang, dat de door kruising verkregen mooie en waardevolle hybriden door vermeerdering vastgelegd en van een voortbestaan verzekerd worden en „op naam" verhandeld kunnen worden, maar ook voor de geheele Hippeastrum-cultuur is het van gewicht dat we groote partijen telkens ontstaan uit één bol, verkrijgen. Het is mij n.l. gebleken, dat door de temperatuur invloed kan uitgeoefend worden, op het bloeipercentage. Om zulk een invloed nauwkeurig te kunnen vastleggen is het noodig, dat men proeven doet met gelijksoortige en met even oude bollen, om zoodoende de beste behandelingswijze te kunnen vaststellen. De resultaten van den invloed der temperaturen op het bloeiprocent zullen in een latere mededeeling worden beschreven.