

Chemistry. — “*The Crystalstructure of Gallium*”. By Prof. F. M. JAEGER, P. TERPSTRA and H. G. K. WESTENBRINK.

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§ 1. In this paper the results of the structure-determinations are published, which by means of the ROENTGEN-spectrographic method were obtained in studying the pure crystallized *gallium*-metal. The *gallium* used in these investigations was prepared in a spectroscopically pure condition from a residue, which was obtained in 1915 at the *Bartlesville Zinc-Company* in *Oklahoma* as an exsudation-product of the *zinc-lead*-plates ready for refining. This residu is left in the repeated distillation of the impure *zinc*: 12000 kilograms of raw material yield about 60 kilograms of the *lead*-containing residue, which do not contain more than a few grammes of *gallium*¹⁾. The final mixture contains, moreover, less than 8 % *indium*, less than 1 % *zinc* and only traces of *copper* and *cadmium*²⁾. It was solved in pure hydrochloric acid, then potassiumhydroxide added until almost neutral reaction, and the boiling solution treated with freshly precipitated copper-hydroxide, prepared from the sixfold weight of coppersulphate by means of the necessary quantity of *KOH*. When all hydroxide is solved and a white, gelatinous precipitate is settled, the liquor is filtered and repeatedly treated in the same way, until no precipitate any longer appears to be formed. The collected gelatinous residue is now thoroughly washed, then solved by hydrochloric acid and the copper still present in the solution eliminated by means of hydrogensulphide. After expelling the excess of hydrogensulphide, the solution is boiled with an excess of *KOH*, with the purpose to eliminate *indium* and traces of *iron* eventually present: both metals will then be precipitated, while the *gallium* remains in the solution and may be separated from the filtered liquor by means of carbonic acid³⁾. The precipitate thus obtained is thoroughly washed, converted on the waterbath by means of a slight excess of pure, strong sulphuric acid into *gallium-sulphate* (+ 16 H_2O), and then the calculated quantity of ammoniumsulphate is added. After evaporation of the solvent into a small volume, the solution is precipitated by means of its fivefold volume of 98 %-

¹⁾ W. F. HILLEBRAND and J. A. SCHERRER, Journ. of Industr. and Engin. Chemistry, **8**, 225, (1916).

²⁾ P. E. BROWNING and H. S. UHLER, Amer. Journ. of Science, **41**, 351, (1916).

³⁾ All filtrates may be treated with potassiumferrocyanide and the precipitate eventually formed be decomposed by means of *KOH* or strong H_2SO_4 at higher temperature, to regain traces of *gallium* contained in it.

alcohol. The ammoniumgallium-alum thus prepared is solved in water, slightly acidified by some free sulphuric acid; this precipitation is repeated four or five times. The pure *gallium*-alum is solved in caustic potash, the ammonia driven out and the alkaline solution electrolyzed between platinum-electrodes. The metal thus obtained is once more converted into its hydroxide, solved in sulphuric acid, the solution, after addition of diluted sulphuric acid of 1,4 s.g., being brought to a volume of 350 ccm.; then it is electrolyzed with a current of 4 Amp. ¹⁾ After eventually separated *indium* being eliminated, the *gallium* obtained is anodically brought to solution in diluted (1 : 10) sulphuric acid (by a current of originally 1 Amp., later of 0,1 Amp. and 12 Volt) between a wire-shaped anode and a plate-shaped cathode. The solution is evaporated till a dry residue is formed; this is solved in water and, under continuous stirring by means of a stream of gas, now electrolyzed with 4 Amp. between a plate-shaped anode and a wire-shaped cathode. *Zinc* eventually present is thus totally eliminated; the solution is again during some hours electrolyzed with 0,6 or 0,8 Amp., the consecutive fractions of separated metal are successively eliminated and after having done this about seven times, all pure *gallium* is very slowly separated from the remaining solution by means of the electric current.

The already very pure metal thus obtained is now converted into its chloride: $GaCl_3$ after the method indicated by DENNIS and BRIDGMAN ²⁾ and this subjected to a fractional distillation at 230°—240° C. In this way the last traces of other metals were removed, even of *zinc* and *indium*, whose chlorides boil only at much higher temperatures ³⁾. The pure, distilled $GaCl_3$ was then again converted into the hydroxide, this solved in caustic potash and the solution again electrolyzed between platinum-electrodes. In the spectrum of the metal thus obtained neither the *indium*-lines, nor those of *zinc* or of any other of the accessory metals originally present in the raw material, could be observed any more now. ⁴⁾

§ 2. The pure *gallium* is a beautiful, silver-white metal, melting at 30°,2 C., and once molten, remains liquid far below that temperature, it being most susceptible to undercooling-phenomena. At about 0° C. it solidifies, depending on the particular conditions of the experiment, into aggregates of larger or smaller octahedral-shaped or flattened crystals.

¹⁾ LECOQ DE BOISBAUDRAN, Ann. de Chim. et Phys., **10**, 100, (1877); H. S. UHLER and P. E. BROWNING, Amer. Journ. of Science, **42**, 389, (1916).

²⁾ L. M. DENNIS and J. A. BRIDGMAN, Chem. News, **118**, 248, 256, 270, 281, 290, (1919).

³⁾ The boilingpoint of $ZnCl_2$ is 730° C., that of $GaCl_3$ is 215°—220° C. $InCl_3$ is volatile at 440°, but distills very slowly only at 600° C.; about the apparatus, cf. p. 257 of the paper mentioned.

⁴⁾ About the analytical determination of *Ga*, cf: L. E. PORTER and PH. E. BROWNING, Journ. Amer. Chem. Soc. **41**, 361, (1919); Chem. News **119**, 251, (1919).

It is very tough and cannot be powdered finely enough, so that the powder-method of HULL-DEBIJE originally seemed to promise very few results. However, it appeared possible to obtain easily somewhat larger and very good crystals of the metal, so that the crystal-structure could be investigated in details by BRAGG's spectrographic method, as well by means of rotation-spectrogramms (after SCHIEBOLD).

Crystals of *gallium* were for the first time obtained by LECOCQ DE BOISBAUDRAN ¹⁾, the discoverer of this element. He considered them as being monoclinic, but DESCLOIZEAUX got the conviction, that they possessed tetragonal symmetry. According to WYCKOFF ²⁾, a powder-spectrogram obtained by him, would indicate that the crystals are at least *not cubic*, as this appears to be the case with *aluminium* ³⁾, which belongs to the same group of elements and which has a face-centred cubic grating with 4 atoms in each fundamental cell. As far as concerns the other elements of this group of the periodic system, the element *indium* would, according to SACHS ⁴⁾, crystallize in regular octahedra; but HULL and DAVEY ⁵⁾ demonstrated that *indium* possesses a tetragonal grating with face-centred fundamental cells, whose dimensions were found to be $a_0 = 4,58$ A.U. and $c_0 = 4,86$ A.U., the axial ratio $a : c$ therefore being: $1 : 1,06$; this proves that the crystals are pseudo-cubic. By means of a LAUE-spectrogram, LEVI ⁶⁾ recently was able to prove that *thallium* possesses hexagonal symmetry.

§ 3. *The Crystalform of Gallium.*

From the molten, strongly undercooled metal rather large, very lustrous crystals of the shape reproduced in Fig. 1a were obtained by inoculation of the molten mass and removing the rapidly grown individuals at the right moment. If, however, the crystals are allowed to grow *slowly* from the only slightly undercooled liquid, flat, often curved crystals, which are much poorer in limiting forms are deposited, as shown in Fig. 1b. Afterwards we will draw attention once more to this remarkable fact, as it will appear to be intimately connected with the typical crystalstructure of this metal.

Ditetragonal-bipyramidal.

$$a : c = 1 : 1,6753.$$

Forms observed: $o = \{111\}$, predominant, very lustrous and in general

¹⁾ LECOCQ DE BOISBAUDRAN, Compt. rend. Paris, **83**, 1044, (1876).

²⁾ R. W. G. WYCKOFF, The Structure of Crystals, (1924), 243. These data are until now not published.

³⁾ Cf. the corr. literature in P. P. EWALD, *Krystalle und RÖNTGENstrahlen*, (1923), 292. The edge of the cubic cell would be: 4,07 A.U.

⁴⁾ A. SACHS, Zeitschr. Kryst., **38**, 495, (1904).

⁵⁾ A. W. HULL and W. P. DAVEY, Phys. Rev., **17**, 571, (1921).

⁶⁾ G. R. LEVI, Nuovo Cimento, Ottobre, (1926); cf. also: Zeits. f. Kryst., **61**, 561. (1925). Although the symmetry is right, the structure indicated by this author is apparently not so, a new investigation being, therefore, necessary.

well developed; $c = \{001\}$, well developed and yielding excellent reflections; $s = \{121\}$, small, but well reflecting, mostly with only part of its faces present; $\omega = \{115\}$, extremely narrow, but measurable; $r = \{101\}$, scarcely visible, just as $\varepsilon = \{313\}$ also; the indices could, however, be

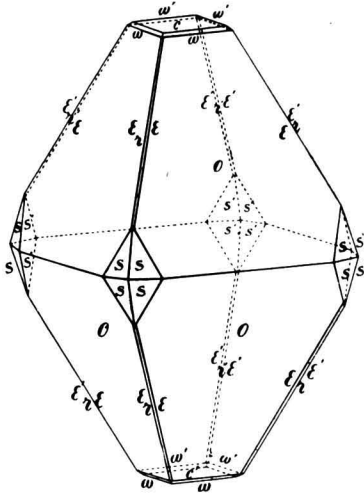


Fig. 1a.

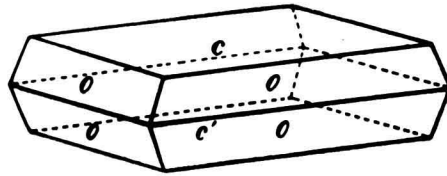


Fig. 1b.

determined by approximative measurements and ascertained by means of the general zone-relations. The habitus of the crystals is that of steep bipyramids, or short-prismatic according to an edge of the zone $[(001):(111)]$. The slowly developed crystals were thick tables parallel to $\{001\}$.

Angular values :	Observed :	Calculated :
$c : o = (001) : (111) =$	*67	7
$o : o = (111) : (\bar{1}\bar{1}\bar{1}) =$	*81	3 81° 18'
$o : o = (111) : (\bar{1}\bar{1}\bar{1}) =$	45	35 45 46
$s : s = (121) : (\bar{1}\bar{2}\bar{1}) =$	51	6 51 12
$s : s = (121) : (\bar{1}\bar{2}\bar{1}) =$	29	30 29 53 ¹ / ₂
$s : s = (121) : (\bar{1}\bar{2}\bar{1}) =$	—	— 119 34
$o : s = (111) : (121) =$	19	41 19 8
$c : s = (001) : (121) =$	75	7 75 3 ¹ / ₄
$o : r = (111) : (101) =$	ca. 40 ¹ / ₂ °	40 39
$\varepsilon : o = (313) : (111) =$	ca. 24°	24 40 ² / ₃
$\varepsilon : r = (313) : (101) =$	ca. 16°	15 58 ¹ / ₃
$c : \omega = (001) : (115) =$	ca. 24 ¹ / ₂ °	25 21
$o : \omega = (111) : (115) =$	ca. 42 ¹ / ₂ °	41 46

A stereographical projection of the forms observed is reproduced in Fig. 2.

The value of the angle $c : a$ is the mean value of five measurements and of four measurements of the angle $(111) : (\bar{1}\bar{1}\bar{1})$. The smallest value

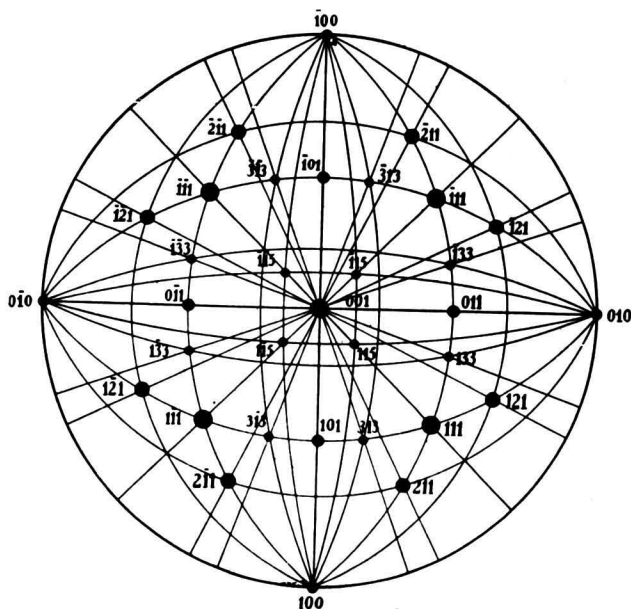


Fig. 2.

observed was $66^{\circ}45'$; from this last value, which differs only $22'$ with the fundamental angle used in the calculation of the axial ratio, this ratio would be found to be: $a : c = 1 : 1,646$.

§ 4. In the first place spectrograms after BRAGG's method were prepared by means of the K -radiation of a copper-anticathode on a face (001) of the basis and on a face of the bipyramid $\{111\}$. At the same time the spectrum of a piece of rocksalt on a face of the cube $\{100\}$

TABLE I.							
	$\frac{\theta}{2} :$		$\sin^2 \frac{\theta}{2} :$		Spacings d in A. U. :		
	for $\lambda = Cu_{\alpha}$	for $\lambda = Cu_{\beta}$	for $\lambda = Cu_{\alpha}$	for $\lambda = Cu_{\beta}$	from : $\lambda = Cu_{\alpha}$	from : $\lambda = Cu_{\beta}$	Mean values:
Basis	$11^{\circ}51'$	$10^{\circ}39\frac{1}{2}'$	0.0422	0.0342	3.75	3.76	3.75 ⁵
Bipyramid	$15^{\circ}13'$	$13^{\circ}41\frac{1}{2}'$	0.0689	0.0560	2.93	2.93	2.93

was photographed, with the purpose of having a spectrum for comparison, from which the true distances could be derived. The results of these measurements are given in Table I: with a distance of 60 mm between crystal and photographic plate, the accuracy of these data is about 0,02 A.U.

§ 5. Complete rotation-spectrograms were prepared with the purpose to determine 1. the identity-distances of the fundamental grating in different directions; 2. the symbols (indices and orders) of the diffracting planes in an accurate way. These spectrograms were obtained by using a modified theodolite-goniometer after GOLDSCHMIDT; this instrument is excellently adapted to this purpose, as a rotation in all desired directions may easily be effected by means of it. In most cases the crystal was moved round the axis of revolution to and fro to both sides over an angle of about 25° . In these experiments use was made of a flat photographic plate, which was suitably fixed at a distance of 40 or 50 mm. from the rotating crystal. The time of exposure was, on applying a copper-anticathode and a tension of about 50 K.V., ordinarily about 90 minutes.

To determine the identity-distance in the direction of the c -axis, a rotation-spectrogram was prepared, while the crystal was oscillating round this crystallographical axis; the distance from plate to crystal in this case was 40,5 mm. A distance of 16 mm was measured on the plate between the 1st positive and the 1st negative hyperbola; from this follows, in using the formula: $I = \frac{\lambda}{\sin \mu}$, — in which formula I is the identity-distance required, $\lambda = Cu_\alpha = 1,540$ A. U. and $\mu = \text{arc tg } \frac{8}{40,5}$, — that the dimension I_c in the direction of the c -axis is: 8,00 A.U. In connection with the data of the spectrogram after BRAGG's method, mentioned above in Table I, the conclusion must be drawn that the diffraction-image observed there is really one of the 2nd order, the spacings between the planes parallel to (001) being actually halved. The accurate value for the identity-distance I_c in the direction of the c -axis is, therefore, evidently: $I_c = 2 \times 3,75^5$ A.U. = 7,51 A.U.

A preliminary determination of the identity-distance I_a in the direction of the a -axis was made by means of a rotation-spectrogram, the crystal being rotated round the a -axis. Here the distance of the plate from the crystal was: 38,5 mm; the distance of the first positive to the first negative hyperbola on the image was: 26,5 mm, from which data the required distance I_a is calculated to be: 4,7 A.U. The final accurate determination of I_a was executed as follows.

The quadratic form for $\sin^2 \frac{\theta}{2}$ in the tetragonal system can be written as:

$$\sin^2 \frac{\theta}{2} = \frac{\lambda^2}{4a^2} (h^2 + k^2) + \frac{\lambda^2}{4c^2} l^2,$$

where a and c represent the identity-distances I_a and I_c mentioned above, in the directions considered. Now $c = I_c = 7,51$ A.U.; therefore $\frac{\lambda^2}{4c^2}$ has the value: 0,0105. The value for $\sin^2 \frac{\theta}{2}$ for planes parallel to (111) can

be taken from Table I. If the diffraction-image after BRAGG's method is supposed to be of the 1st order, it follows from the quadratic form:

$$\sin^2 15^\circ 13' = \frac{(1,540)^2}{4a^2} \times (1 + 1) + 0,0105 \times 1;$$

or:

$$\frac{(1,540)^2}{4a^2} = 0,0292, \text{ from which is deduced: } a = I_a = 4,51 \text{ A. E.}$$

From the rotation-spectrogram the conclusion was already drawn, that this value for I_a needed not to be multiplied; therefore, it follows from $a = 4,51$ A.U. and $c = 7,51$ A.U., that the axial ratio $a:c =$ equal to: $1:1,667 (= \frac{5}{3}$ almost exactly). This value is in plain agreement with the results of the angular measurements of the *gallium*-crystals, by which $a:c$ was found to be: $1:1,6753$; for the fundamental angle $c:o$ in the latter case being: $67^\circ 7'$, it would be $67^\circ 2'$ for the axial ratio deduced in the above, — the difference being only $5'$.

The quadratic formula for $\lambda = 1,540$ A.U. takes, therefore, the form:

$$\sin^2 \frac{\theta}{2} = 0,0292 (h^2 + k^2) + 0,0105 l^2,$$

and thus for the wave-length $Cu_\alpha = 1,389$ A.U. in the same way:

$$\sin^2 \frac{\theta}{2} = 0,0238 (h^2 + k^2) + 0,0086 l^2.$$

§ 6. The dimensions of the elementary cell of the grating now being exactly known, the number N of atoms lying in each cell can be immediately computed from the formula:

$$N = \frac{V \times s}{A \times 1,64 \cdot 10^{-24}},$$

in which formula V is the volume of the cell in cm^3 , this being $(4,51)^2 \times (7,51) \cdot 10^{-24} \text{ cm}^3$; $s =$ specific weight of crystallized *gallium*¹⁾, this number being: 5,904 and $A =$ atomic weight of the element, i.e. 69,9. From these numbers N is calculated as: 7,85; it must be supposed, therefore, that in each fundamental cell *eight* atoms of *gallium* must find their places.

§ 7. The other rotation-spectrograms²⁾, in the preparation of which the crystal was rotated round a diagonal of the upper face of the parallelepipedon or respectively round a diagonal of one of the lateral faces of the elementary cell³⁾, enabled us to draw the conclusion, that the fundamental BRAVAIS' grating of the crystalstructure, must necessarily be a *simple tetragonal grating*⁴⁾, so that neither one of the faces of it is centred, nor the centre of the cell is occupied by an atom.

1) TH. W. RICHARDS and S. BOYER, Journ. Amer. Chem. Soc. **43**, 274, (1921).

2) Cf. Tables V and VI.

3) These directions are resp. indicated by the zone-symbols: $[110]$ and $[\bar{1}01]$; i.e. round the basic, resp. the polar edge of the bipyramid $\{111\}$ as axes.

4) This will be confirmed by the detailed study of the symbols of the diffracting planes.

a. *Rotation-spectrogram with revolution round the zone-axis* [110].

The distance of crystal and photographic plate was: 41 mm.; the distance of the 1st hyperbola to the centre of the plate was: 10 mm., $tg \mu$ therefore being: $\frac{10}{41} = 0,2439$. From this follows: $I_{[110]} = 6,5$ A.U., while from the true value for $I_a (= 4,51$ A.U.), the diagonal of the basal face of the elementary cell is calculated to be: $4,51 \sqrt{2}$ A.U. = 6,38 A.U., which is in good agreement with the experimental result.

b. *Rotation-spectrogram with rotation round* $[\bar{1}01]$ (polar edge of {111}).

The distance of the crystal and the plate was here: 45 mm.; the distance of the 1st hyperbola to the centre of the plate was: 17 mm.; therefore: $tg \mu = \frac{17}{45} = 0,3777$ and $I_{[\bar{1}01]} = 8,2$ A.U. Calculation, on the other side, shows, that the diagonal of the lateral face of the elementary cell is: $\sqrt{(4,51)^2 + (7,51)^2}$ A.U. = 8,7 A.U. Here also there is a perfect agreement between calculated and observed value.

§ 8. With the aid of the quadratic formula found in the foregoing pages, it was now further possible to make a complete analysis as well of the different rotation-spectrograms, as of the powder-spectrogram finally obtained in the following way. As was said already, by the specific properties of the *gallium*-crystals, which are very tough and which probably possess, moreover, gliding-faces, — it was almost impossible to grind them down into a powder of sufficiently fine grains. A thin silk thread rubbed with this powder was covered with it, but if stretched along the axis of the camera, no interference-images after HULL-DEBIJE'S method could be obtained on the film. We succeeded, however, by grinding the *gallium* in a mortar under liquid air and smearing the silk thread,¹⁾ also under liquid air, with the finest *gallium*-dust in the mortar. *Gallium* gets very brittle at the temperature of liquid air and can be ground then easily into very fine powder; in the subsequent rising of the temperature, the original grating is preserved in the dust sticking to the silk thread, and now a real powder-spectrogram could be observed, only locally marred by small black patches, showing that some grains of the powder were not yet fine enough. However, the film could readily be made use of for the estimation of the relative intensities of the diffraction-lines.

The results of the analysis of the powder-spectrograms, as well of that of the different rotation-spectrograms already mentioned in § 5 are reviewed in the Tables II till VI. If necessary, besides the indices h , k and l with respect to the ordinary crystallographical axes, also the indices h' , k' and l' are mentioned, which are related to axes of which

¹⁾ It is remarkable, that the silk preserves its plasticity also at the temperature of the liquid air.

one coincides with the axis of rotation of the crystal in each case. The purpose of these last indices is to prove, that the indices h , k and l , as derived from the quadratic equation, are *not* contradictory to the sequence-numbers of the successive hyperbolae on the films, on which hyperbolae the corresponding interference-image is arranged. The necessary transformation-equations, by which h' , k' and l' are calculated from h , k and l , are also given in the tables.

§ 9.

TABLE II.						
Analysis of the Powder-spectrogram of Gallium.						
(Radius of the camera: 25 mm)						
Distance $2l$ in m.m.:	Wave- length:	$\frac{\theta}{2}$:	$\sin \frac{\theta}{2}$:	$\frac{\sin^2 \frac{\theta}{2}}{2}$ (observed):	$\frac{\sin^2 \frac{\theta}{2}}{2}$ (calculated):	Symbols ($h k l$):
19.70	Cu_{β}	11°23'	0.1970	0.0387	} 0.0324	(002)
						0.0324
20.10	Cu_{α}	11°38'	0.2016	0.0408	0.0420	(002)
23.48	..	13°56'	0.2351	0.0554	0.0562	(111)
26.24	Cu_{β}	15°11'	0.2619	0.0686	0.0689	(111)
30.80	Cu_{α}	17°49'	0.3060	0.0936	0.0952	(200)
34.48	Cu_{β}	19°50'	0.3393	0.1151	0.1166	(200)
39.22	Cu_{α}	22°42'	0.3859	0.1490	} 0.1460	(210) *)
						0.1529
40.25	..	23°18'	0.3956	0.1565	} 0.1565	(211)
						0.1588
44.04	..	25°30'	0.4305	0.1853	0.1880	(212)
49.71	..	28°46'	0.4812	0.2316	0.2336	(220)
51.18	Cu_{β}	29°37'	0.4942	0.2442	} 0.2466	(311)
						0.2486
55.09	Cu_{α}	31°53'	0.5282	0.2792	0.2756	(222)
57.63	..	33°21'	0.5498	0.3023	} 0.3025	(311)
						0.3048

About ten weak lines, following the last mentioned one, were omitted here, as they have no significance for our purpose. The tension was here 55000 Volts; the time of exposure: 3 hours.

§ 10.

TABLE III.					
Rotation-spectrogram with revolution round the <i>c</i> -axis.					
(The distance from plate to crystal was: 41 mm)					
Number of the hyperbolae:	Distance of Spots from the centre in mm:	$\frac{\theta}{2}$:	$\sin^2 \frac{\theta}{2}$ (observed):	$\sin^2 \frac{\theta}{2}$ (calculated):	Symbols (<i>h k l</i>):
0	62.5	28°22'	0.2257	0.2336	(220)
1	24.0	15°10'	0.0684	0.0689	(111)
1	42.4	22°59'	0.1524	0.1565	(211)
— 1	24.0	15°10'	0.0684	0.0689	(111)
2	48.6	25°19'	0.1810	0.1880	(212)
— 2	50.1	25°21'	0.1833	0.1880	(212)
3	40.3	22°15'	0.1434	0.1529	(113)

§ 11.

TABLE IV.					
Rotation-spectrogram with revolution round the <i>a</i> -axis.					
(The distance from plate to crystal was: 40.5 mm)					
Number of the hyperbolae:	Distance of Spots from the centre in mm:	$\frac{\theta}{2}$:	$\sin^2 \frac{\theta}{2}$ (observed):	$\sin^2 \frac{\theta}{2}$ (calculated):	Symbols (<i>h k l</i>):
0	17.8	11°52'	0.0423	0.0420	(002)
0	43.8	23°37'	0.1605	0.1680	(004)
				0.1588	(022)
1	40.3	22°4'	0.1452	0.1460	(120) *
				0.1529	(113)
1	64.0	28°50'	0.2326	0.2405	(123)
				0.2264	(114)
2	50.0	25°30'	0.1854	0.1880	(122)

§ 12.

TABLE V. Rotation-spectrogram with the revolution round the direction [110]. (The distance from plate to crystal was: 41 mm)						
Number of the hyperbolae:	Distance of Spots from the centre in mm:	$\frac{\theta}{2}$:	$\sin^2 \frac{\theta}{2}$ (observed):	$\sin^2 \frac{\theta}{2}$ (calculated):	Symbols ($h k l$):	($h' k' l'$) (Reduced on the axis):
0	45.5	24°0'	0.1665	0.1680	(004)	(004)
0	18.6	12°12'	0.0447	0.0420	(002)	(002)
1	53.5	26°16'	0.1959	0.1972	(104)	(1 $\bar{1}$ 4)
1	25.5	15°56'	0.0754	0.0712	(102)	(1 $\bar{1}$ 2)
2	42.5	23°1'	0.1529	0.1529	(113)	(203)
3	51.0	25°36'	0.1867	0.1880	(212)	(3 $\bar{1}$ 2)
Transformation-formulae: $h' = h + k$; $k' = k - h$; $l' = l$. The index h' belongs to the axis of revolution.						

§ 13.

TABLE VI. Rotation-spectrogram with the revolution round the direction $[\bar{1}01]$. (The distance from plate to crystal was: 45 mm)						
Number of the hyperbolae:	Distance of Spots from the centre in mm:	$\frac{\theta}{2}$:	$\sin^2 \frac{\theta}{2}$ (observed):	$\sin^2 \frac{\theta}{2}$ (calculated):	Symbols ($h k l$):	($h' k' l'$) (Reduced on the axis):
0	26.6	15°17'	0.0695	0.0689	(111)	(110)
0	39.5	20°38'	0.1242	0.1168	(020)	(020)
1	56.5	25°44'	0.1885	0.1880	(122)	(121)
-1	47.6	23°19'	0.1567	0.1565	(211)	(21 $\bar{1}$)
2	46.5	22°58'	0.1522	0.1529	(113)	(112)
-2	26.6	15°17'	0.0695	0.0689	(1 $\bar{1}$ $\bar{1}$)	(11 $\bar{2}$)
-2	72.0	29°0'	0.2350	0.2336	(220)	(2 $\bar{2}$ $\bar{2}$)
-3	47.7	23°20'	0.1569	0.1569	(21 $\bar{1}$)	(21 $\bar{3}$)
-3	58.5	26°13'	0.1952	0.1972	($\bar{1}$ 04)	($\bar{1}$ 0 $\bar{3}$)
4	51.5	24°26'	0.1711	0.1680	(004)	(004)
-4	49.0	23°43'	0.1618	0.1588	(20 $\bar{2}$)	(20 $\bar{4}$)
Transformation-formulae: $h' = h$; $k' = k$; $l' = l - h$. The index l' belongs to the axis of revolution.						

§ 14. For the determination of the space-group the tables of ASTBURY and YARDLEY¹⁾ were made use of. From the spectrograms described above, it is evident, that interference-images belonging to atomic planes with the symbols of the type: $(h k 0)$, in which $(h + k)$ is *odd*, and of the type: $(0 k l)$, in which l is *odd*, were *not* observed with certainty. Such uncertain symbols were indicated by an asterisk *) in the tables. All other combinations of indices were observed; but in the case of the symbols thus indicated with an asterisk, always another combination of indices appeared to be possible also.

As *gallium*, according to the crystallographical measurements, very probably possesses ditetragonal-bipyramidal symmetry, — as becomes evident, for instance, from the fact, that some crystals, as in Fig. 1a, manifest the full number of faces of each form in perfectly well-balanced development, — the four only space-groups possible here amongst the twenty groups belonging to this crystal-class, are, in WYCKOFF's notation²⁾:

D_{4h}^1 : no halving of spacings between atomic planes what so ever;

D_{4h}^7 : halving of spacings between atomic planes of the type: $(h k 0)$, in which $(h + k)$ is *odd*;

D_{4h}^{10} : halving of spacings between atomic planes of the type: $(0 k l)$, in which l is *odd*;

D_{4h}^{16} : halving of spacings between atomic planes of the types: $(h k 0)$, in which $(h + k)$ is *odd*, and of the type: $(0 k l)$, in which l is *odd*.

To fix the choice between these, it is, therefore, of the highest importance now, to determine with full certainty the yet problematic indices of those interference-images, for which from the quadratic equation alone, hitherto no choice could be made between e.g. (101) (Cu_α) and (002) (Cu_β), or between (210) and (113) ; etc. The rotation-spectrograms, described in the tables III till VI, were principally prepared with the purpose of determining the identity-distances in the directions of revolution: but now it appeared necessary to prepare some others, with the intention to exclude with absolute certainty those indices, which were yet doubtful; the choice between the four space-groups mentioned can only be made, if the indices-triples really present, be determined beyond any doubt.

In the way followed up till now, it was, as already said, not possible to fix the choice between some of the symbols, as calculated from the quadratic equation, because the values of $\sin^2 \frac{\theta}{2}$ thus computed, did not differ sufficiently from each other. Therefore, in preparing the new rotation-spectrograms, which are reviewed in the tables VII till XI following here-after, — it was in each case necessary to determine accurately,

1) W. T. ASTBURY and K. YARDLEY, "Tabulated data for the Examination of the 230 Space-groups by homogeneous X-rays", London, (1924), Proceed. Royal Soc., A, 224, 221—257.

2) R. W. G. WYCKOFF, "The Analytical Expression of the Results of the Theory of Space-groups", Washington, (1922), Carnegie-Publ. N^o. 318.

between what extreme angular limits in both directions the rotation round the axis of revolution really took place during the experiment. It was possible, by making a stereographical projection of the scattering planes with the aid of a WULFF's plot and rotating that projection through the same limiting angles as were used in the case of the rotating crystal, — to ascertain, whether these planes had really been in such positions, as possibly to give the diffraction-images of the symbols, which were supposed to have been observed in each special case. In this way it could be verified rigorously, whether atomic planes, to which simple indices were attributed, really had been in such favourable positions for giving interference-images or not, and whether some of them were absent, although those atomic planes might have been in the right positions for scattering the incident X -rays.

§ 15. In the spectrogram, to which table VII refers, the crystal was rotated round the direction $\bar{[101]}$ in such a way, that in both directions an angle of 29° was covered, starting with a position, in which the primary pencil of X -rays was parallel to (111). By means of the stereographical projection it could be stated, that the atomic planes mentioned in table VII, had really been in the required „reflecting” positions. As

TABLE VII.						
Rotation-spectrogram with revolution round the direction $\bar{[101]}$.						
(Distance between crystal and plate: 54.5 mm)						
Number of the hyperbolae:	Distance of Spots from the centre in mm:	$\frac{\theta}{2}$:	$\sin^2 \frac{\theta}{2}$ (observed):	$\sin^2 \frac{\theta}{2}$ (calculated):	Symbols ($h k l$):	Symbols ($h' k' l'$) (reduced):
0	32.1	$15^\circ 15'$	0.0691	0.0689	(111)	(110)
0	45.5	$19^\circ 56'$	0.1162	0.1168	(020)	(020)
1	57.5	$23^\circ 16'$	0.1560	0.1565	$\bar{(211)}$	$\bar{(211)}$
—1	33.0	$15^\circ 36'$	0.0723	0.0712	$\bar{(102)}$	$\bar{(101)}$
2	45.5	$19^\circ 56'$	0.1162	0.1168	$\bar{(200)}$	$\bar{(202)}$
—2	25.0	$12^\circ 19'$	0.0455	0.0420	(002)	(002)
—2	55.5	$22^\circ 46'$	0.1499	0.1529	$\bar{(113)}$	$\bar{(112)}$
3	58.0	$23^\circ 23'$	0.1575	0.1565	$\bar{(211)}$	$\bar{(213)}$
4	56.0	$22^\circ 53'$	0.1512	0.1529	$\bar{(113)}$	$\bar{(114)}$
—4	61.0	$24^\circ 7'$	0.1667	0.1680	(004)	(004)

Transformation-formulae:
 $h' = h ; k' = k ; l' = l - h.$
 The index l' refers to the axis of revolution.

the indices attributed to them appeared to be in full agreement with the subsequent hyperbolae on the film, as well with the quadratic equation, *their exactness is sufficiently assured in this case.*

§ 16. In the same way table VIII gives a review of the results obtained on rotating the crystal round the *c*-axis. If the position in which the primary pencil of *X*-rays is parallel to the plane (110), is called the position for which $\frac{\theta}{2} = 0^\circ$, — then the crystal appeared in this case to be rotated from $\frac{\theta}{2} = -11^\circ$ till $\frac{\theta}{2} = +35^\circ$. The plane (110) should have given a diffraction-image of the 1st order for $\frac{\theta}{2} = \text{circa } 14^\circ$, and a 2nd order image at about $\frac{\theta}{2} = +28^\circ$; but a 1st order image was *not* observed in this case.

TABLE VIII.					
Rotation-spectrogram with revolution round the <i>c</i> -axis.					
(Distance between crystal and plate: 42.5 mm)					
Number of the hyperbolae:	Distance of Spots from the centre in mm:	$\frac{\theta}{2}$:	$\sin^2 \frac{\theta}{2}$ (observed):	$\sin^2 \frac{\theta}{2}$ (calculated):	Symbols (<i>h k l</i>):
0	67.0	28°48'	0.2321	0.2336	(220)
0	35.0	19°44'	0.1140	0.1168	(200)
1	25.0	15°14'	0.0691	0.0689	(111)
1	44.0	23°0'	0.1527	0.1565	(211)

§ 17. The table IX refers also to a rotation-spectrogram with revolution round the *c*-axis. But now the crystal was rotated between the

TABLE IX.					
Rotation-spectrogram with revolution round the <i>c</i> -axis.					
(Distance between crystal and plate: 42 mm)					
Number of the hyperbolae:	Distance of Spots from the centre in mm:	$\frac{\theta}{2}$:	$\sin^2 \frac{\theta}{2}$ (observed):	$\sin^2 \frac{\theta}{2}$ (calculated):	Symbols (<i>h k l</i>):
0	26.7	19°47'	0.1146	0.1166	(200)
0	66.3	28°50'	0.2326	0.2336	(220)
1	43.9	23°16'	0.1561	0.1565	(211)
3	43.5	23°0'	0.1527	0.1529	(113)

limits: $\frac{\theta}{2} = -15^\circ$ and $\frac{\theta}{2} = +31^\circ$, if $\frac{\theta}{2} = 0$ is now the position, in which the plane (100) is parallel to the primary beam. The atomic planes (101), (100) and (210) will now all come into positions favourable for the occurrence of interference-images of the 1st order. Notwithstanding this, however, no such images were observed here.

§ 18. In table X the results are collected, which refer to a rotation-spectrogram with revolution round the a -axis. In the mean position the primary beam was parallel to the plane (001), and from this position the rotation took place in both directions through an angle of 23° . An interference-image of the plane (013) could now be expected, but on the film no trace of it could be discovered. The other planes of $\{013\}$ do not come into positions favourable for "reflection". Moreover, no interference-images of atomic planes can occur with the symbols: (102), (10 $\bar{2}$), (202), (20 $\bar{2}$) and neither of the planes of $\{210\}$; the indices given in table X, therefore, must be the only possible ones.

Another spectrogram of this kind was made, moreover, in which the only difference with the preceding case consisted in this, that the crystal, — having its mean position, when (001) was parallel to the primary pencil of X -rays, — was first turned 60° in the direction of this primary beam and then rotated from this new position over 23° to both sides of it. In this case it might namely have been possible for (210), to give a diffraction-image; but even now, this image was *not* present on the film. In this experiment the planes of $\{113\}$ could not give any confusion in the decision about the presence or absence of the image from (210), because the images belonging to this form would be situated on other hyperbolae; moreover, of all its planes, only (11 $\bar{3}$) could arrive in a "reflecting" position, and its image was really observed on the film. Also an image from (110) could be expected in this case; but it was absent once more in the spectrogram obtained.

TABLE X.					
Rotation-spectrogram with revolution round the a -axis.					
(Distance between crystal and plate: 45 mm)					
Number of the hyperbolae:	Distance of Spots from the centre in mm:	$\frac{\theta}{2}$:	$\sin^2 \frac{\theta}{2}$ (observed):	$\sin^2 \frac{\theta}{2}$ (calculated):	Symbols ($h k l$):
0	20.0	11°59'	0.0431	0.0420	(002)
1	27.0	15°29'	0.0712	0.0689	(111)
1	46.0	22°49'	0.1504	0.1529	(113)
2	48.5	23°36'	0.1603	0.1565	(211)

TABLE XI.					
Rotation-spectrogram with revolution round the <i>a</i> -axis.					
(Distance between crystal and plate: 46 mm)					
Number of the hyperbolae:	Distance of Spots from the centre in mm:	θ : 2 :	$\sin^2 \frac{\theta}{2}$ (observed):	$\sin^2 \frac{\theta}{2}$ (calculated):	Symbols (<i>h k l</i>):
0	39.0	20°9'	0.1187	0.1168	(020)
0	49.0	23°24'	0.1577	0.1588	(022)
1	27.0	15°18'	0.0696	0.0689	(111)
-1	47.6	23°0'	0.1527	0.1529	($\bar{1}$ 13)
2	50.0	23°42'	0.1616	} 0.1588 0.1565	(202)
					(21 $\bar{1}$)

§ 19. After the analysis and study of the spectrograms reviewed in the tables VII till XI, the conclusion can be drawn with sufficient certainty, that really no other space-groups than D_{4h}^1 , D_{4h}^7 , D_{4h}^{10} and D_{4h}^{16} are possible in the case of the *gallium*-crystals, while all other space-groups can readily be excluded. On the other hand it becomes highly probable, that amongst those D_{4h}^{16} is the right one, because of the fact, that the interference-images corresponding with atomic planes having the symbols $\{h k 0\}$ and $\{0 k l\}$, in which respectively $(h + k)$ or l are *odd*, appear to have systematically an intensity equal to zero, at least in so far as this could be proved. However, it is advisable to investigate by means of calculating the relative intensities, whether perhaps one of the other space-groups might also be taken into account in this respect, so that the 8 atoms were arranged in such a way within each elementary cell, that a sufficient agreement between the calculated intensities and those observed in the powder-spectrogram were obtained. The powder-spectrogram is much better suited for this purpose than the rotation-spectrograms, for which an accurate calculation of the intensities is hardly possible.

The calculation of the intensities in the powder-spectrogram was effectuated by means of the well-known formula:

$$I = \frac{1 + \cos^2 \theta}{2 \cos \frac{\theta}{2} \cdot \sin^2 \frac{\theta}{2}} \cdot n \cdot |S|^2,$$

in which n is the number of planes of the complete crystalform $\{h k l\}$, and $|S|$ signifies the absolute value of the structural factor, in such a way, that:

$|S|^2 = |\sum e^{2\pi i(hm + kn + lp)}|^2 = |\sum \cos 2\pi(hm + kn + lp)|^2 + \sum |\sin 2\pi(hm + kn + lp)|^2$ is¹⁾.

The estimated intensities of the lines of the powder-spectrogram are reviewed in the 2nd column of table XII. A practically unobservable small intensity was found to be present for lines, corresponding with (001), (100), (110), (101), (103) and (120); with exception of (110), all these symbols belong really to one of the types: $\{h k 0\}$ or $\{0 k l\}$, with respectively $(h + k)$, or $l = \text{odd number}$.

A review of all possible combinations of 8 equivalent points compatible with these space-groups, is given in WYCKOFF's tables. (Cf: *Analytical Expression*, etc., (1922), p. 89–102).

A. Space-group D_{4h}^1 .

In this case *five* combinations of 8 equivalent points are possible, which cases are discerned by the author as p , q , r , s and t (loco cit. p. 90).

The arrangement of the atoms according to the coordinates mentioned sub p is excluded, because of the fact that the spacing of the atomic planes parallel to (001) would not be halved, while experiment shows that this actually takes place. The same argumentation is valid for an arrangement of the atoms according to the coordinates mentioned sub q . Moreover, the combination r , s and t appear to be excluded, because if the parameter v in the direction of the c -axis be taken equal to $\frac{1}{4}$, the spacing, between the planes parallel to (001) is, indeed halved, but the identity-distance I_c appears to be shortened simultaneously to half its true value: then the cell would no longer contain 8, but only 4 atoms, what is in contradiction with experience. Therefore, the whole space-group D_{4h}^1 must be excluded.

B. Space-groups D_{4h}^7 .

Here *four* cases are possible of 8 equivalent places symmetrically arranged, which by the author are discerned as the cases g , h , i and j (loco cit., p. 93). The combinations g and h are excluded according the same arguments, which in the previous case led to the exclusion of the cases p and q . The combinations mentioned sub i and j are impossible, because the intensities of (110) and (001) must be both zero, which only occurs if $u = v = \frac{1}{4}$. But then the intensity of (101) in case i would be very great, while it is zero in reality; in case j the intensities of (113) and (212) become also zero, which is not in accordance with experience, as may be seen from the results formerly discussed. The space-group D_{4h}^7 is, therefore, also excluded.

C. Space-group D_{4h}^{10} .

Five cases, discerned in the tables as k , l , m , n and o , are possible

¹⁾ The question, several times already discussed in recent days, whether the intensity I may be supposed to be really proportional to $|S|^2$, or whether it be more in conformity with the actual situation, in supposing a proportionality to $|S|^n$, in which n lies between 1 and 2, — is now left out of consideration here.

here for arrangements of 8 equivalent points in a way compatible with the special symmetry of this space-group (loco cit., p. 95).

The case mentioned sub k must be excluded, because the mutual arrangement in this case would be such, that halving of spacings would occur, if l be odd; for in this case the sums ($hm + kn + lp$) differ pairwise just with an exact amount of $\frac{l}{2}$, so that in the structural factor S always sinus and cosinus of angles will appear combined, which differ from each other with the value π , with the result that these numbers will totally annihilate each other. For $l = \text{odd}$, all corresponding intensities, therefore, will get the value zero, which is contradictory to experience, because e.g. (111) and (113) are certainly observed with measurable intensity. The case k is thus excluded, and the same argumentation is valid for the combinations mentioned sub l and m ; the cases being, therefore, also impossible here. Considering the cases n and o , it may be remarked, that the intensities of (100), (110) and (210) must be zero, which only takes place, if $u = v = \frac{1}{4}$. But then the intensity of (211) appears also to become zero, which is contradictory to the experimental results. From this follows, that both cases n and o are excluded, and therewith the whole space-group D_{4h}^{10} .

D. The space-group D_{4h}^{16} .

Within this group four cases of 8 equivalent positions must be discerned, which in the tables are indicated sub f , g , h and i (loco cit., p. 98). The combination mentioned sub f is excluded beforehand, because the coördinates corresponding to h and k are not variable here: thus, e.g. the intensity of (110) cannot get the value $= 0$, while experiment reveals this fact with certainty. The combinations of points mentioned sub g and h are equally excluded, because in these cases p must be taken equal to zero or to $\frac{1}{2}$. The sum of the sinus and that of the cosinus in the structural factor S must be equal to zero, therefore, not only for $l = 0$, but also if l be even, because in that case, for $p = \frac{1}{2}$, the corresponding angle is increased with a whole number, multiple of 2π . Now the intensity of (210) appears really to be zero, as might be expected in the space-group D_{4h}^{16} ; but according to what was said above, also the intensity of (212) should be zero in that case, while experiment has taught the contrary.

It therefore appears, that only the case mentioned sub i remains possible here. The parameters of the 8 equivalent points in this case are:

$$\left[u, \left(u + \frac{1}{2} \right), v \right]; \left[u, \left(\frac{1}{2} - u \right), \left(v + \frac{1}{2} \right) \right]; \left[-u, \left(\frac{1}{2} - u \right), v \right]; \left[u, \left(u + \frac{1}{2} \right), \left(v + \frac{1}{2} \right) \right]; \\ \left[\left(u + \frac{1}{2} \right), u, -v \right]; \left[\left(u + \frac{1}{2} \right), -u, \left(\frac{1}{2} - v \right) \right]; \left[\left(\frac{1}{2} - u \right), -u, -v \right]; \text{en} \left[\left(\frac{1}{2} - u \right), u, \left(\frac{1}{2} - v \right) \right].$$

The symmetry of this atomic arrangement is characterized by the presence of tetragonal screw-axes: $[001]_{0,1/2}$ and $[001]_{1/2,0}$; diagonal rotation-axes: $[001]_{0,0}$ and $[001]_{1/2,1/2}$; eight symmetry-centra:

$$\left[\frac{1}{4}, \frac{1}{4}, 0 \right], \left[\frac{3}{4}, \frac{1}{4}, \frac{1}{2} \right], \left[\frac{3}{4}, \frac{3}{4}, 0 \right], \left[\frac{1}{4}, \frac{3}{4}, \frac{1}{2} \right], \left[\frac{1}{4}, \frac{1}{4}, \frac{1}{2} \right], \left[\frac{3}{4}, \frac{1}{4}, 0 \right], \left[\frac{3}{4}, \frac{1}{4}, \frac{1}{2} \right] \text{ and } \left[\frac{1}{4}, \frac{3}{4}, 0 \right];$$

gliding-mirror planes $(001)_0$ and $(001)_{1/2}$, with translations in (001) ; idem such: $(110)_0$, $(\bar{1}\bar{1}0)_0$, $(100)_0$, $(100)_{1/2}$, $(010)_0$, and $(010)_{1/2}$, with translations parallel to the c -axis; rotation-mirrorplanes: $(001)_{1/4}$ and $(001)_{3/4}$; and mirrorplanes: $(110)_{1/2}$ and $(\bar{1}\bar{1}0)_{1/2}$.

It could be shown, that indeed a sufficient agreement between the observed and calculated intensities could be obtained (cf. table XII), if for u the value: $\frac{8}{40}$ or $\frac{9}{40}$, and for v the value $\frac{6}{40}$ or $\frac{7}{40}$ be substituted.

A more accurate calculation of the parameters is impossible, while the observed, or rather: the estimated intensities are known only too inaccurately. It may be remarked, that in this case the smallest distance of two Ga -atoms appears to be: 2,56 A.U., while, according to W. L. BRAGG, the "atomic radius" of the Ga -atom should be 1,3 A.U., which is as perfect an agreement as one could desire.

Fig. 3, 4 and 5 may give an image of the structure of the elementary cell in perspective and in orthogonal projection on a face of (001) ; in Fig. 3 the four successive layers atoms A , B , C and D and the places of their centres are drawn and the different dimensions in the direction of the c -axis indicated. In each layer the atoms are arranged as indicated

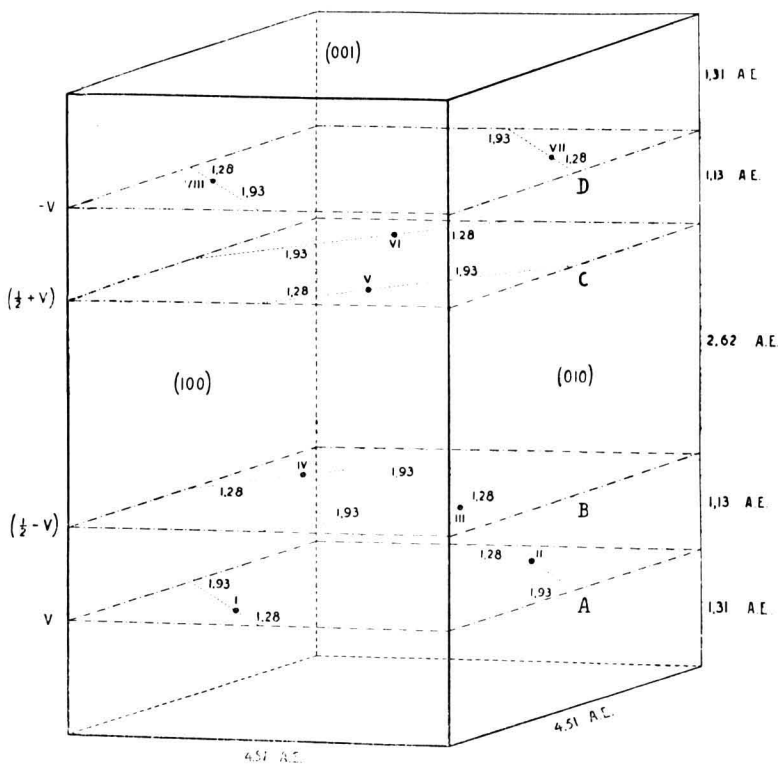


Fig. 3.

TABLE XII.					
Symbols (<i>h k l</i>):	Estimated intensities:	Calculated intensities ($\times 10000$):			Mean calculated intensities $\times \frac{1}{250}$:
	($\lambda = Cu_2$)	for: $u = \frac{8}{40}; v = \frac{6}{40}$:	for: $u = \frac{8}{40}; v = \frac{7}{40}$:	for: $u = \frac{9}{40}; v = \frac{7}{40}$:	
(110)	0	30	30	0	0.08
(002)	6	300	1100	1100	3 à 4
(111); (102)	8	2000 + 600	1100 + 200	1400 + 100	7 à 10
(200)	6	1250	1250	1700	5.5 à 6
(113)	7	1300	2200	2500	8
(211)	7	1100	1350	300	3 à 4
(212)	2	250	170	200	0.7 à 1
(220)	2	350	350	650	1.4 à 2.6
(222)	2	60	200	370	0.2 à 1.5
(311); (302)	4	80 + 700	170 + 500	370 + 160	2 à 2.5

Dividing the calculated values by 250 (column 6), numbers are obtained, which clearly show that the sequence of the relative intensities, as calculated, is principally the same as that of the estimated ones.

in Fig. 4, and 5; evidently the centres of each pair are distant from each other 2,56 A.U., while the distance of a next pair in the same straight line is 3,86 A.U.; etc. Although the arrangement of two immediately consecutive layers, such as *A* and *B* or *C* and *D* is essentially the same, each layer appears with respect to its neighbour turned round the *c*-axis over 90° and simultaneously shifted along a diagonal of (001) over a certain distance. As already mentioned, the smallest distance of the atomic centres is exactly that, which follows from W. L. BRAGG's values for the atomic radius of the *gallium*-atom: $2 \times 1,3 \text{ A.U.} = 2,6 \text{ A.U.}$ after BRAGG, while experimentally measured: 2,56 A.U. Four neighbouring atoms of one layer (cf. Fig. 5) are situated in the corners of a trapezium; just in its centre fits the *Ga*-atom of the immediately adjacent layer. If in the way indicated by BRAGG, round the atomic centres spheres be described with a radius $R = 1,3 \text{ A.U.}$, then the five spheres just mentioned appear to touch each other, so that in each double layer as *AB* or *CD*, all spheres are so closely packed, that the double layer could be thought to be built up completely by means of closest packed,

massive spheres¹⁾. It may be remarked, moreover, that the atomic planes of $\{110\}$ consist of three parallel ones, two of which have an identical atomic arrangement, the third being, however, at a different distance and having a somewhat different arrangement. If one considers the two

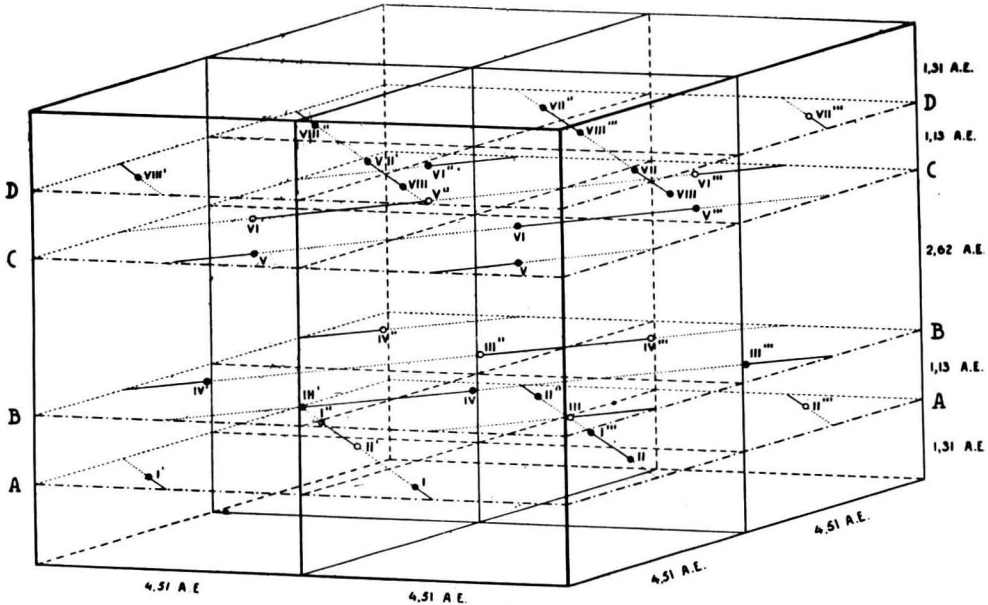


Fig. 4.

first, very closely approaching planes as a single one, the whole situation can also be described by saying, that in the directions (110) , $(\bar{1}\bar{1}0)$, etc. one *flat* plane of atoms interchanges with a plane, which appears to be slightly bent up and down in a regular way. It is this circumstance, which causes the intensities of $\{110\}$ to get *not exactly* the value zero; calculation teaches, that there remains an extremely small intensity of the corresponding diffraction-images.

The atomic planes parallel to the basis $\{001\}$ are, amongst all planes of the structure, those whose occupation by atoms is the densest.

¹⁾ Fig. 5 gives an orthogonal projection on (001) of two successive layers every time: Fig. 5a of A and B; Fig. 5b of C and D, which are identical with AB, but with respect to them turned round the c -axis over exactly 90° . The distance of two consecutive layers is:

$$\left(\frac{20}{40} - 2v\right) c_0 = \frac{6}{40} c_0 = 1,13 \text{ A.U.}$$
 The distance of an atomic centre in B to each of the nearest four centra in A is, in projection 2,3 A.U.; therefore, the true distance is: $\sqrt{(1,13)^2 + (2,3)^2} = 2,56 \text{ A.U.}$ From this follows, that the atomic spheres with a radius of 1,28 A.U. (according W. L. BRAGG) are situated in both layers in the way indicated in Fig. 5.

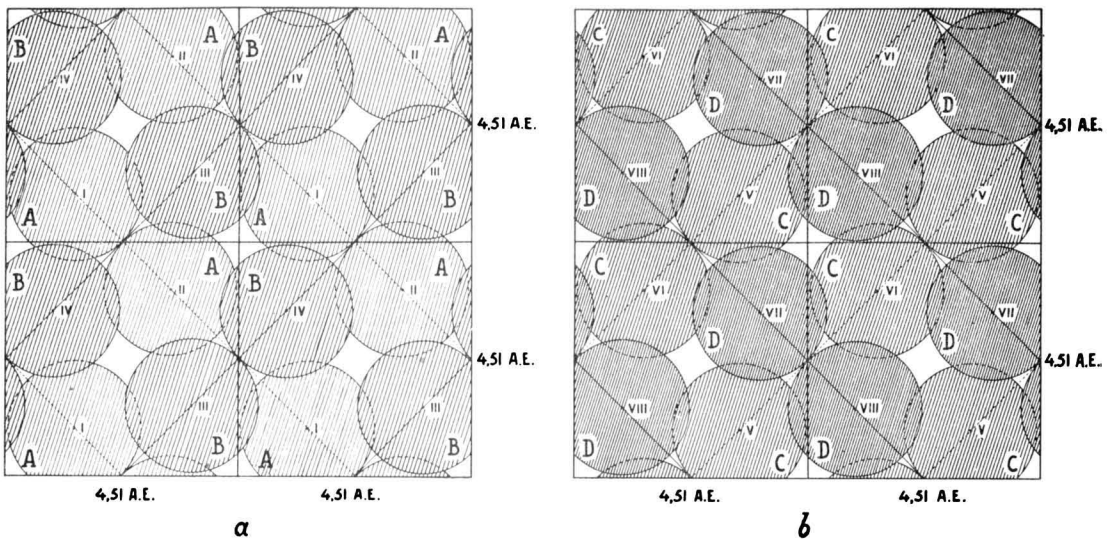


Fig. 5.

§ 20. It is remarkable, and highly in favour of the exactness of the here proposed structure of the metal, that from this structure several of the peculiarities of the solid *gallium* may be deduced.

As becomes clear from the Fig. 3 and 4, the double layer AB parallel to $\{001\}$, is in the cell separated from the double layer CD , — which has the same structure as AB , but differs from it only by the fact that it is turned with respect to it round the c -axis over 90° , — by a free space between the atomic spheres. As the layer C is turned with respect to A over 90° , C cannot approach as near to the layer B , as A does: the atomic spheres would touch each other only, if the distance from C to B gets value: 2,48 A.U. (cf. Fig. 6; the sphere V must have the position V' to touch the layer B). In reality this distance is, however, 2,62 A.U., so that a free space of 0,14 A.U. remains open between AB and CD . To bring both double layers in touch with each other, the upper double layer would have to be pressed down over 0,14 A.U., — the height of the elementary cell then getting the value: $7,51 - 0,14 - 0,07 - 0,07 = 7,23$ A.U.

Now, as is already known since its discovery, the specific volume of solid *gallium* is *greater* than that of the liquid metal, — just as the specific volume of *ice* is greater than that of water at the same temperature. The idea is easily suggested now, that this peculiar behaviour of *gallium* is intimately connected with the decrease in volume, which the crystalline metal suffers in melting, because of the fact, that at the meltingpoint, the structure being broken up and the atoms regaining their free mobility, the free space between the atomic layers, mentioned above, will disappear at the same time.

Indeed, the specific weight of the *liquid gallium* can, on this supposition,

be calculated from that of the *solid metal*, this being known as: 5,904. For, as the height of the cell is diminished from 7,51 A.U. to 7,23 A.U., this specific weight must change to: $\frac{7,51}{7,23} \times 5,904 = 6,124$; on the other hand, the specific weight of the *liquid gallium* actually observed is: 6,095. The difference between the calculated and observed numbers is only 0,5 %, — this being an agreement, which may be called really perfect.

Recently EHRENFEST¹⁾ drew attention to the fact that some analogies in behaviour also occur in the case of such metals as *bismuthum*, *antimony*,

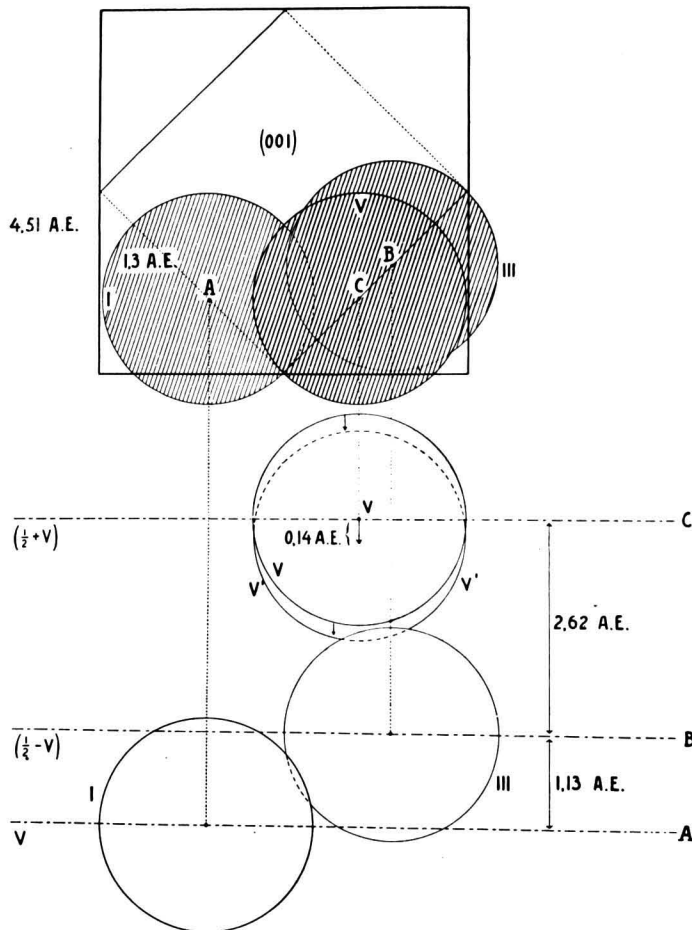


Fig. 6.

¹⁾ P. EHRENFEST, *Physica*, 5, (1925), p. 383.

From the fact that *bismuthum* shows an extraordinarily great diamagnetic susceptibility, the author concludes that the electronic orbits which cause this phenomenon, must surround more than one atom of the structure; because of this fact, the importance becomes clear of these layers of atoms approaching each other very nearly. In *gallium* the distance between two such atoms (2,56 A.U.) is even smaller than in *bismuthum*. All three metals (*antimony* included) have in common, that their electric conductivity increases, as they melt; all three have a specific volume in the solid state greater than in the liquid condition.

etc., whose crystalstructure is, like that of *gallium*, characterised by the occurrence of such double layers of atoms very nearly approaching each other. Perhaps the occurrence of these double layers might be related to the other fact, that, such metals as *bismuthum*, *antimony*, and *gallium* also, form oxides, which according to circumstances, may show a weak basic or a weak acid function ($Ga(OH)_3$ with *KOH* and *ammonia*; *antimonites*, *antimonates*, *bismuthites*; etc.): it is e.g. imaginable, that *two* modifications of the atoms, depending on their momentaneous electronic configuration, should really take part in building up these crystalstructures, of which modifications one kind had a more "metallic" character and the other a nature more tending to that of a "metalloid"; *together* they would then be able to form such double layers of atoms approaching very nearly to each other.

§ 21. But also in other respects the proposed structure enables us to give a satisfactory account of the special phenomena observed with the solid metal.

Attention has already been drawn to the fact, that the crystals of *gallium* show *two* different habits, according as they are formed *rapidly* or *slowly* from the more or less undercooled molten mass. (page 1196; Fig. 1a and 1b). This phenomenon must be interpreted in this way, that there exists evidently a great difference in crystallisation-velocity with these crystals in different directions perpendicular to the different sets of atomic planes. Evidently this velocity perpendicular to (001) is, under comparable circumstances, much smaller than in directions perpendicular to faces of {111} and {121}. As a consequence, if the crystal is only allowed sufficient time to develop, — i.e. in *slow* crystallisation, — the relative development of the faces of {001} will increase gradually in comparison with that of forms, like {111}, {121}, etc. According to BRAVAIS, the faces predominantly developed in the crystal are generally those of *greatest* atomic density. That this is really the case here also, may now be immediately seen from the structure derived for the *gallium*: for in (001) the eight metal-atoms appear to be distributed over *four* planes A, B, C and D of the structure, each layer containing *two* atoms (Fig. 5); therefore, the density $\Delta_{(100)}$ of these planes is: $\frac{2}{a_0^2} = \frac{2}{20,34} = 0,098$. On the other hand, for {111} e.g., those 8 atoms are distributed over *six* planes, of which *four* contain only *one* atom, and *two* layers which have *two* atoms in a parallelogram. For {111} the mean density of arrangement $\Delta_{(111)}$ is therefore: $\frac{4/3}{a_0 \sqrt{2c_0^2 + a_0^2}} = 0,026$ only. Thus it is evident ¹⁾ that, independent of the special values of the parameters *u*

¹⁾ It may be remarked, that the density of the atomic arrangement of {111} and {001} can only be *the same*, if the 8 atoms be distributed for {111} over only *two* atomic planes. This occurs, if to *u* the value $1/4$ is attributed. This parameter-value, however, is excluded here, because in that case the intensity of the diffraction-images on the planes parallel to (121), must be zero, the spacings then being halved for this form. Experience, however, proves, that the planes parallel to {121} have a great intensity.

and v , the density of the atomic arrangement parallel to (001) is about four times greater than that in the planes parallel to $\{111\}$. It is evident for this reason, that the velocity of growth perpendicular to the atomic planes parallel to (001) is so much smaller than that in directions perpendicular to the planes of the form $\{111\}$; which involves, that the faces of this form must finally disappear, making gradually place for the more and more predominant form $\{001\}$. The specific density of the planes parallel to $\{121\}$ is, moreover, again smaller, so that this form *à fortiori* will be absent in the crystals of Fig. 1^b. The bipyramidal habitus of the crystals of Fig. 1^a depends undoubtedly on the special properties of the strongly undercooled, liquid medium, from which they are generated; in many cases the degree of undercooling has, without any doubt, a great influence on the particular shape of the crystals, which are deposited from such a medium.

Hitherto we have not been able to obtain sufficient information about the cleavability, the cohesion, the presence of gliding-planes, etc. of the *gallium*-crystals, in order to test also these properties by means of the here indicated crystalstructure; and the same is valid for some other physical properties, as e.g. thermic and electric conductivity; etc. Perhaps, however, it will appear possible to obtain before long, the data required to elucidate these phenomena also in the light of the crystalstructure deduced.

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