

Chemistry. — “*On the Crystalstructure of Germanium-tetraiodide*”.
By Prof. Dr. F. M. JAEGER, Dr. P. TERPSTRA and Mr. H. G. K.
WESTENBRINK.

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§ 1. In the following the results of the determination of the crystal-structure of *Germaniumtetraiodide*: GeI_4 are published, of which a small quantity was kindly presented to us by Prof. DENNIS¹⁾. At the same time a small quantity of the corresponding optically-uniaxial *Di-iodide*: GeI_2 was received, the crystals of which were, however, unsuitable for an investigation in its full extent. We hope, however, yet to be able within a short time to compare the structures of both these compounds in connection with the results of a study of some derivatives isomorphous with GeI_2 .

In the first instance a number of diffraction-images were obtained after the method of HULL and DEBIJE, the source of radiation in this case being a copper-anticathode. The type of ROENTGEN-tube used was a dismantable gas-tube of cylindrical shape of the form used in Sir W. H. BRAGG's laboratory, and provided with an aluminium-window. The radiation used (at 50 K. V.; current: in mean 9 m.Amp.) consisted of copper-*K*-radiation of the wave-lengths: $\lambda_\alpha = 1,537$ A.U. and $\lambda_\beta = 1,388$ A. U., $\frac{\lambda_\alpha}{\lambda_\beta} = 1,107$. Occasionally a nickelfilter was made use of; however, afterwards this was dropped, because of the weakening of intensity, especially, as it appeared that the diffraction-images which belonged to each of these wave-lengths, could easily be discerned from each other. In these experiments the very finely powdered iodide was smeared upon a thin silk thread stretched along the axis of the cylindrical camera.

As an instance the values are given in the following table, measured by means of a comparator on one of the best films (N^o. 18) obtained in this way; the radius of the camera was 24,76 m.M.

Evidently the line N^o. 1 is the β -line corresponding to N^o. 2; N^o. 3 that corresponding to the β -line N^o. 4; N^o. 6 the β -line of N^o. 7; N^o. 8 that corresponding to the α -line N^o. 9. Moreover, $\frac{\sin^2 \theta}{\Sigma(h^2)}$ is, for λ_α equal to: 0,00418 and for λ_β equal to: 0,00341; these numbers are, indeed, to each other in the proportion of $\left(\frac{\lambda_\alpha}{\lambda_\beta}\right)^2$. Although, if the two first values

¹⁾ L. M. DENNIS, Journ. Amer. Chem. Soc., **44**, 2856, (1922).

are not considered, the indices: (111), (200), (220), (311), (222), (331), (240) and (224) may be calculated directly from these measurements, it will become clear from the following determinations, that the line N^o. 4 corresponds to the *second* order reflection on {111}. If the values N^o. 1 and N^o. 2 are also taken into account, it follows from these, that $\Sigma(h)^2$ for them is equal to 6, and the other forms observed will then obtain the values indicated in the table; evidently the images N^o. 1 and 2 represent the first order images on {112}, line N^o. 13 thus being the fourth order of them. In this connection it may be remarked also, that on Film N^o. 12 a rather intense line was found for $\theta/2 = 28^\circ 17'$, on Film N^o. 7a one for $\theta/2 = 25^\circ 16'$, corresponding to the third order reflections on {112} for λ_α en λ_β ; the theoretical angles are here: $28^\circ 22'$, resp.: $25^\circ 24'$. On the contrary. the corresponding images of the second order were nowhere observed with certainty.

Analysis of Film N ^o . 18.								
Number of the lines from the centre	Distance l of the images on both sides in m.m.	Wave-length	Estimated intensity	2θ	$\theta/2$	$\sin \theta/2$	$\sin^2 \theta/2$	Indices
1	$l/2 = 7.17$	λ_β	extremely weak	$\theta = 16^\circ 36'$	$8^\circ 18'$	0.1444	0.0208	(112)
2	$l/2 = 7.88$	λ_α	very weak	$\theta = 18^\circ 14'$	$9^\circ 7'$	0.1584	0.0251	(112)
3	20.29	λ_β	5	$47^\circ 16'$	$23^\circ 48'$	0.203	0.0412	(222)
4	22.49	λ_α	10	$52^\circ 4'$	$26^\circ 2'$	0.225	0.0506	(222)
5	26.00	λ_α	7	$60^\circ 12'$	$30^\circ 6'$	0.260	0.0676	(400)
6	33.31	λ_β	3	$77^\circ 8'$	$38^\circ 4'$	0.333	0.1089	(440)
7	37.11	λ_α	9	$85^\circ 56'$	$42^\circ 58'$	0.366	0.1340	(440)
8	39.33	λ_β	1	$91^\circ 4'$	$45^\circ 4'$	0.387	0.1497	(622)
9	43.85	λ_α	8	$101^\circ 32'$	$50^\circ 46'$	0.429	0.1840	(622)
10	$l/2 = 22.97$	λ_α	3	$106^\circ 20'$	$53^\circ 10'$	0.448	0.2007	(444)
11	59.18	λ_α	3	$137^\circ 0'$	$68^\circ 30'$	0.563	0.3169	(662)
12	60.92	λ_α	3	$141^\circ 4'$	$70^\circ 4'$	0.577	0.3329	(480)
13	67.64	λ_α	2	$156^\circ 36'$	$78^\circ 18'$	0.631	0.3981	(448)

From these measurements it can be deduced, that here a cubic space-lattice is present in the structure: from $\frac{\lambda_\alpha^2}{4a^2} = 0.00418$ and $\frac{\lambda_\beta^2}{4a^2} = 0.00341$, the edge a of the elementary cubic cell is calculated:

$$a = 11.89 \text{ A.E.}$$

As the volume V of this cell is $1679 \text{ cubic A.U.} = 1679 \cdot 10^{-24} \text{ ccm.}$, and as DENNIS¹⁾ determined the specific weight d of the crystals (in sulphuric acid) at 26° C. on: 4,3215, the number N of the molecules GeJ_4 ($M=580,18$) in this cell is calculated as: $N = \frac{V \cdot d}{M \cdot 1,64 \cdot 10^{-24}} = 7,63$; evidently, therefore, the cell contains 8 molecules GeJ_4 , and the true specific weight²⁾ of the crystals must be: $d_{40} = 4,534$.

Besides the films mentioned here, also some photographs were prepared after HULL's method on flat films; although very faint, also in this case the lines of $\{112\}$ were observed here. One of these radiograms proved, moreover, without any doubt, that the line $N^0. 3$ is indeed no other than the line for λ_{β} , corresponding to $N^0. 4$.

Film $N^0. 18$ was tested, moreover, by the aid of a photometer-arrangement with a thermoelectrical cell and mirror-galvanometer with respect to its differences in intensity. In fig. 1 the results of these measurements on one half of the film are plotted graphically. Besides the images already mentioned above, the presence of the images of the first order (for α - and β -radiation): $\{111\}$, $\{221\}$, $\{421\}$, $\{411\}$, $\{432\}$, $\{731\}$, etc., although comparatively weak, was revealed, as well as that of those of $\{112\}$.

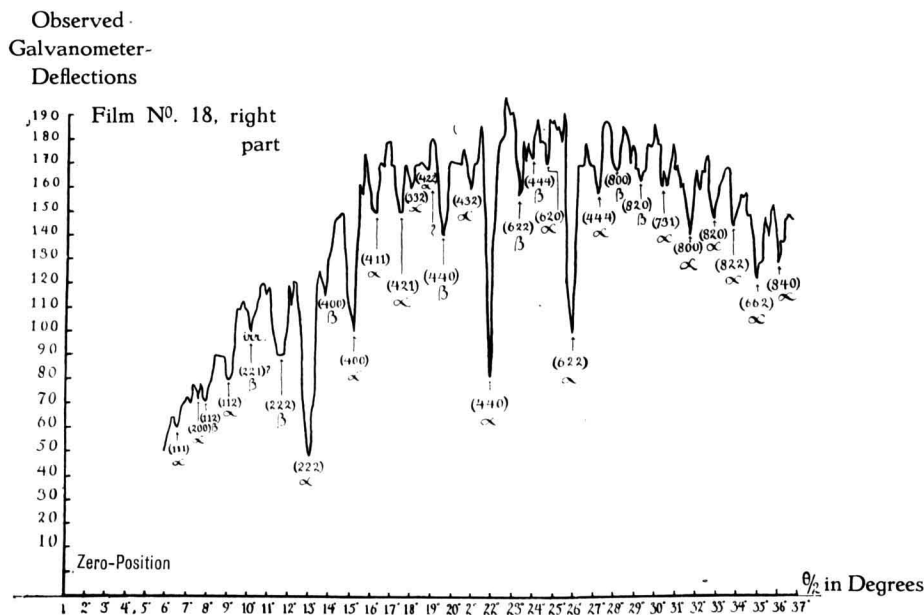


Fig. 1. Photometrical curve of Film $N^0. 18$.

1) Loc. cit., p. 2856. As GeJ_4 in contact with solvents is extremely easily decomposed, so it is probable, that in reality no solvents will be without action upon this substance, — the deviations in d thus being explicable.

2) From the measurements on the other films a value for a is deduced, not appreciably deviating from 12 A.U. In this case, d_{40} would be: 4,405.

Because of the general veil superimposed upon all these lines, it is, however, impossible to determine the absolute intensity of these lines. The most intense lines correspond to $\{111\}$, $\{331\}$ and $\{311\}$ in the *second* order; to $\{100\}$, $\{110\}$ and $\{210\}$ in the *fourth* order; to $\{100\}$ in the *eighth* order etc.

Further confirmation of this was again obtained by means of a rotation-radiogram, a perpendicular to the edge of one of the triangular octahedron-planes being chosen here as vertical axis of revolution. Besides some other images, those of $\{222\}$, $\{444\}$, $\{622\}$, $\{440\}$ and $\{662\}$ appeared to be present upon it; but there was, for instance, no indication of $\{100\}$ or $\{110\}$.

§ 2. For the purpose to obtain full certainty about the orders of the diffraction-images mentioned above, measurements were made on a plate parallel to $\{111\}$, after BRAGG's spectrographic method. The crystalplates parallel to $\{111\}$ were obtained by slow evaporation of a solution of the iodide in carbondisulphide in a vacuum. The very thin triangular plates thus obtained were mounted carefully on thin glass-plates, put upon the *X-ray-spectrometer* and given a slow oscillating motion along the axis of the instrument by means of a clock-work. To determine accurately the distance between the crystal-plate and the central spot on the photographic plate, two photograms were made on the same film, this being placed in parallel positions at two different distances a_1 and a_2 . The shift $a_2 - a_1 = w$ was measured very accurately; by measuring also on the film the distances s_1 and s_2 of two corresponding lines, e.g. that of the lines for λ_x of λ_3 , in both cases, the distance x , where the plate stood in the first experiment, can be easily calculated; for:

$$\frac{x}{x+w} = \frac{s_1}{s_2}.$$

If θ is the glancing angle, at which the diffraction takes place, then evidently $\operatorname{tg} 2\theta = \frac{s_1}{2x}$, so that, θ being now determined, the spacing $d_{(111)}$ of the reticular planes may be calculated from the formula: $2d_{(111)} \cdot \sin \theta = n \cdot \lambda$.

In this way for $x = 45,82$ mm. and for $\lambda_x = 1,54$ A.U.¹⁾, s_1 was found to be: 44,10 mm.; therefore, $\theta_x = 12^\circ 51'$; in the same way, for $\lambda_3 = 1,389$ A.U. and $x = 45,40$ mm., s_1 was found to be: 39,09 mm., θ_3 thus being: $11^\circ 39'$. If these spectra be *second* order spectra, $d_{(111)}$ becomes: 6,924 A.U., resp.: 6,879 A.U., in mean: 6,901 A.U. Indeed, if in a cubic space-lattice the edge a be really equal to 11,9 A.U., $d_{(111)} = \frac{1}{3} a \sqrt{3}$ must be: 6,90 A.U. The intensive image N^0 . 4 film 18 thus corresponds really to (222). The spectrum of the fourth order must,

¹⁾ Actually in the *K*-radiation of copper; : $\lambda_{x_1} = 1,537$ A.U. and $\lambda_{x_2} = 1,543$ A.U.; on an average therefore, $\lambda_x = 1,540$ A.U. For λ_3 the value: 1,389 A.U. was used; θ is here equivalent to $\theta/2$ in the table above.

therefore, be situated at a distance from the central spot (for λ_x), equal to: 60,34 mm., when x again is 45,82 mm. ($2\theta = 52^\circ 48'$). With an exposure during 10 minutes (8 to 10 milli-Amp.), this image was really found at its right place on the films X and X', and that very intensive. For the spectrum of the first order, the distance to the central spot for λ_x should be: 10,38 mm. and for λ_3 : 9,31 mm. Indeed, both these spectra could be stated, be it extremely faint, on film III; their intensities are incomparably fainter than those of the second and fourth order¹⁾. Even if (on film III') the spectrum of the first order was exposed during 37 minutes, that of the second order during only 5 minutes, the intensity of the first image appeared to be very much smaller than that of the last image.

Finally these experiments were executed once more with a silver-anticathode, which gives a radiation of $\lambda = 0,565$ A.U. Now the spectrum of the second order appeared at: $2\theta = 9^\circ 24'$; the distance of both images to the central spot now being: 7,52 mm., with $x = 45,5$ mm. ($s_1 = 15,1$ mm.); in the same way the spectrum of the fourth order appeared at a distance from the central spot of: 15,52 mm. ($s_1 = 31,4$ mm.) and with an appreciable intensity ($2\theta = 18^\circ 50'$). The spectrum of the third order must be found at: $2\theta = 39^\circ 6'$, i. e. at a distance from the central spot of; 36,97 mm., if copper-radiation of $\lambda 1,540$ A.U. be used; its distance from the *second* order spectrum (see above) therefore being: $36,97 - 22,05 = 14,9$ mm. The experiment was made in such a way, that the spectrum of the second order was exposed only 5 minutes, but that of the third order 30 minutes (film VI), and notwithstanding this, an extremely faint image appeared to be hardly visible in the calculated place.

By all these experiments it is convincingly proved, that on (111) diffraction occurs in such a way, that the spectra of the first and third order are extremely faint, those of the second and fourth order, however, very intensive.

§ 3. In trying to solve the problem: to which of the 230 space-groups do the crystals of GeI_4 really belong?, — it is necessary also to keep in mind, that the specific diffracting influence of the *I*-atoms, which are four times as numerous, is very different from that of the *Ge*-atoms, and also, that the absorption of ROENTGEN-rays is very different for both²⁾.

¹⁾ During the preparation of film III the aluminium-window of the tube appeared to be gradually covered with volatilized copper. Because of the unequal absorption thus taking place, the lines corresponding to λ_3 appeared now to be more intensive than those for λ_x .

²⁾ The strong absorptive power of iodine in this salt, manifested itself also in preparing the radiograms after VON LAUE: it was only possible to get them, if extremely thin plates were made use of.

A first step towards this solution of the problem was the determination of the crystallographical symmetry. With some small crystals obtained from a solution in benzene, a number of very small facets were observed at the corners of one of the planes of the octahedron. The crystal was measured by means of a goniometer with two circular divisions; the plane (112) being taken as polar facet. The following reflexes were localised:

Face	φ	ρ	Kind of reflection:	Index of Crystal-plane
α	0°	19° 38'	sharp	(111)
β	129	23 57	very sharp	(102)
γ	0	90 10	sharp	(11 $\bar{1}$)
δ	34	34	faint	(211)
ε	25	57	very faint	(210)
ζ	184	69	very faint	$\bar{(112)}$
η	204	56 35	sharp	$\bar{(102)}$
θ	209	27	very faint	?
ι	294 $\frac{1}{4}$	42 37	sharp	(021)
κ	330	35	very faint	(121)
λ	34	32	faint	(211)
μ	124	37	faint	?
ν	114	62 15	sharp	($\bar{111}$)
\omicron	182	34 59	very sharp	(001)
σ	313	65	very faint	(010)
τ	34	31	very faint	(211)

τ , μ and δ are parts of the same facet; $\varphi = (112)$

A stereographic projection of the forms observed is reproduced in Fig. 2. Evidently is a combination present of an *octahedron* {111}, a *hexahedron* {100}, an *icositetrahedron* {211} and a *pentagonal dodecahedron* {210}; the zonal relations in the projection-figure make this sufficiently clear.

The symmetry of the crystals can, therefore, only be that of the *tetrahedral-pentagonal dodecahedral* class ($3A_2$; $4L_3$; $0L_2$; $0II_4$; $0P$; $0C$), or that of the *dyakis dodecahedral* class ($3A_2$; $4L_3 (= \bar{L}_6)$; $0L_2$; $3II_2$; $0P$; C).

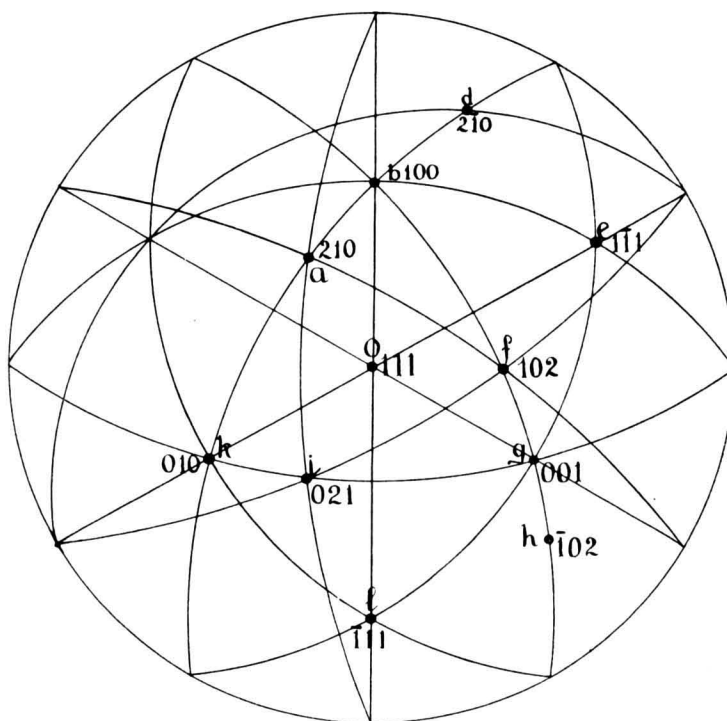


Fig. 2. Stereographical Projection of the observed Forms on a plane of $\{111\}$.

§ 4. It is *a priori* excluded to make a final choice between these two classes of symmetry by means of a LAUE-photograph of a crystal-plate cut parallel to (111); other plates were, moreover, not at our disposition. For, as one of us¹⁾, in collaboration with H. HAGA, was able to prove formerly, such LAUE-radiograms must always show the same symmetry as a similarly orientated plate of a crystal, whose symmetry is that of the crystal under investigation after a centre of symmetry has been added to it. But as in both classes mentioned *no* axes of twofold symmetry perpendicular to the faces of the rhombododecahedron do occur, these faces can *never* appear as planes of symmetry in the LAUE-radiogram on (111), if a centre of symmetry is thought to be added to the tetrahedral-pentagonaldodecahedral symmetry, nor will this be the case with a dyacisdodecahedral crystal, because this does already possess such a centre of symmetry. The LAUE-radiogram obtained by radiation perpendicular through a plane of (111) can, therefore, in both cases only show an axis of threefold symmetry, *without* any symmetrical arrangement of its spots with respect to three planes intersecting along this axis under 120° (60°). Notwithstanding this fact, such a LAUE-radio-

¹⁾ H. HAGA and F. M. JAEGER, These Proceedings 17, 18, 19.

gram was yet prepared, because it seemed of interest for the further determination of the crystalstructure. A very thin plate parallel to (111) was for this purpose stuck to a thin glass-plate and a diffraction-image made in the usual manner by means of a MÜLLER-gas-tube with a platinum-anticathode and an osmotic pressure-regulation (60 K. V.). The glass-plate was orientated as accurately as possible by means of a goniometer-arrangement; the time of exposition was 5 hours (with 4 milli-Amp.). The image appeared, however, yet to be not completely symmetrical, as a consequence of a slight deviation in the direction of the X -rays from the normal on (111); notwithstanding this, however, it could be clearly shown, that the LAUE-radiogram was undoubtedly symmetrically built with respect to three diameters intersecting at 120° (60°). The cause of this abnormal behaviour must doubtlessly be attributed to the great differences in diffracting power, already mentioned, of the numerous iodine-atoms on the one hand, in comparison with that of the germaniums-atoms on the other hand, which are four times as scanty, in connection with a particular kind of mass-distribution of both atomic species throughout the structure as a whole. Here, indeed, is found a

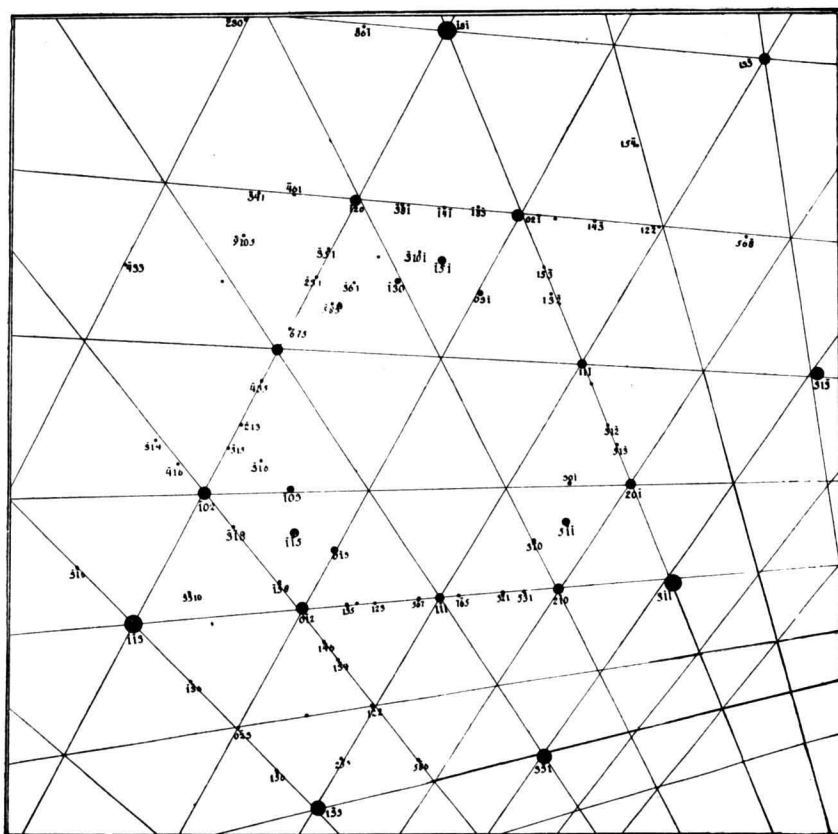


Fig. 3. Gnomonic Projection of the LAUE-radiogram on $\{111\}$.

new instance of the already known phenomenon, that the symmetry of such LAUE-radiograms can occasionally be deceptive in so far, as symmetry-elements may be apparently present, which are incompatible with the proper crystallographical symmetry, but only manifest themselves as a consequence of accidental peculiarities of the atomic arrangement.

A gnomonic projection of this LAUE-radiogram is reproduced in Fig. 3. The distance l of the spots from the central one and that ($s = 4$ c.m.) of the film and the crystal-plate being known, — the indices of the diffracting planes and the sinus of the angles θ could be calculated from the relation: $l = s \cdot \operatorname{tg} 2\theta$; at the same time the intensities of these spots were approximately estimated. As the edge a of the cubic cell ($= 11,89$ A.U.) is known, the distances d between the diffracting planes (hkl) can be directly calculated¹⁾ in A.U. and by these values for d it is possible to determine the product $n \cdot \lambda$ in the formula: $2d \cdot \sin \theta = n\lambda$ or in $\frac{2a \cdot \sin \theta}{\sqrt{h^2 + k^2 + l^2}} = n\lambda$. Now the voltage of the gas-tube in these experiments was 60 K.V.; the maximal intensity of the polychromatic platinum-radiation, therefore, must be situated in the neighbourhood of 0,4 or 0,5 A.U.²⁾ On this supposition it appears possible, by comparison of the relative intensities, to estimate with a high degree of probability the values of n , i. e. of the orders of the observed spots: inversely, the sequence of the intensities³⁾ for each value of λ thus calculated, gives a control with respect to the right choice of the multipliers n . In this way the data could be obtained, which are collected in the table on page 756.

If the estimated intensities are graphically plotted against the deduced wave-lengths⁴⁾, a graph is obtained as reproduced in Fig. 4. The sequence of the observed, relative intensities for the faces of the same form $\{hkl\}$ appears really to be just the same, as might be expected in connection with the shape of the curve for the energy-distribution in the ROENTGEN-spectrum, if a voltage of 60 K.V. be applied to the tube.

¹⁾ R. W. G. WYCKOFF, *The Structure of Crystals*, (1924), p. 452; P. P. EWALD, *Ann. der Physik*, **44**, (1914), p. 257. Also here θ is equivalent to $\theta/2$ in the above.

²⁾ In WYCKOFF's book is given a graph of the intensity-distribution for the different wave-lengths λ of the tungstene-spectrum, as shown on the photographic plate, if a voltage of 60 K.V. is applied. The intensity increases from the shorter wave-lengths rapidly until a maximum at about 0,484 A.E., this being the characteristic limit of absorption for silver. As platinum in the periodic table is close to wolframium, the energy-distribution in the platinum-spectrum under 60 K.V. will *grosso modo* show great analogy with that of the other metal. It is this supposition, which is made use of in the determination of the numbers n of the spots considered.

³⁾ It need hardly to be said again, that the estimations of the relative intensities (10 for the most intensive, 1 for the faintest spots) can have no other significance than as rough indications of the existing differences. The numbers attributed to the spots only will express, that one spot is darker than another.

⁴⁾ R. W. G. WYCKOFF, *Amer. Journal of Science*, **50**, (1920), 318, P. P. EWALD, *Krystalle und Roentgenstrahlen*, p. 115.

Table of Diffraction-spots in the LAUE-radiogram

Distance of the Spot from the centre in m.m.:	Index of the diffracting planes:	$\sin \theta$	n. λ in A.U.	Orders n:	λ in A.U.	Estimated intensity:
32.5	(111)	0.335	4.65	8	0.58	5
26.0	($\bar{1}\bar{1}\bar{1}$)	0.284	3.94	8	0.49	6
34.5	(111)	0.348	4.83	8	0.60	4—5
25.2	(201)	0.278	2.98	4	0.74	5—6
22.5	(012)	0.253	2.71	4	0.68	6—7
18.0	($\bar{1}20$)	0.210	2.25	4	0.56	6(+)
26.0	(210)	0.284	3.04	4	0.76	5—6
20.0	($\bar{1}02$)	0.230	2.47	4	0.62	7(—)
20.0	(021)	0.230	2.47	4	0.62	6—7
27.8	($\bar{1}51$)	0.300	1.40	2	0.70	4—5
36.0	(511)	0.359	1.66	2	0.83	4(—)
29.0	($\bar{1}\bar{1}5$)	0.310	1.43	2	0.71	5(—)
13.3	($\bar{1}\bar{1}3$)	0.158	1.14	2	0.57	10
17.5	(311)	0.206	1.50	2	0.75	8
11.0	($\bar{1}31$)	0.134	0.97	2	0.49	10
40.0	(301)	0.383	2.91	4	0.73	2
35.1	(013)	0.353	2.68	4	0.67	3—4
30.4	($\bar{1}30$)	0.320	2.43	4	0.61	3
41.5	(310)	0.391	2.96	4	0.74	2
32.4	($\bar{1}03$)	0.335	2.55	4	0.64	3—4
33.5	(031)	0.342	2.59	4	0.65	3
15.2	(586)	0.181	0.39	1	0.39	1
13.2	(568)	0.158	0.34	1	0.34	1(—)
9.8	(133)	0.120	0.66	2	0.33	6
12.0	($\bar{1}33$)	0.145	0.80	2	0.40	8(—)
13.6	(331)	0.162	0.89	2	0.45	8
12.0	(313)	0.145	0.80	2	0.40	7—8

This result may serve as an argument for the correctness of the calculated values of λ for each spot, and consequently for those of the numbers n . All the sections of curves in this graph are evidently parts

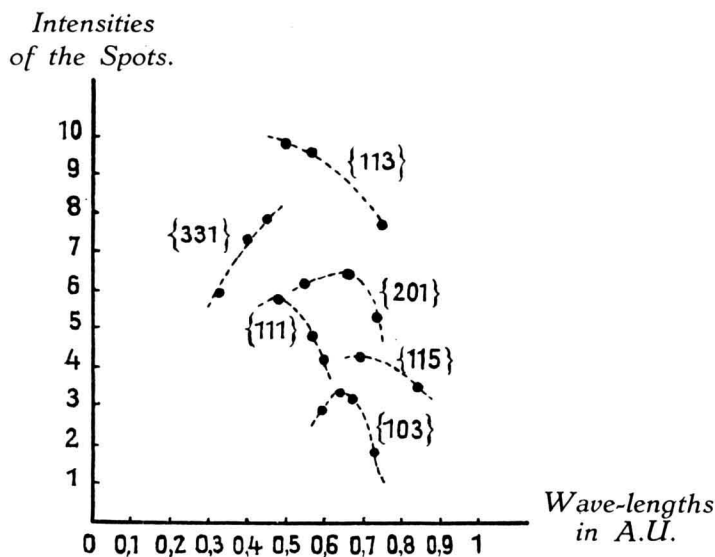


Fig. 4. Distribution of Intensities in the LAUE-radiogram.

of intensity-curves showing a maximum in the vicinity of 0.5 A.U. In connection with this, it may be, moreover, remembered, that in the DEBIJE-films the image of $\{201\}$ has indeed but an appreciable intensity in the *fourth* order; also $\{331\}$ appears in it only in the *second* order with a measurable intensity. By the BRAGG-method it was found, that $\{111\}$ only shows a considerable intensity for *even* orders, while $\{113\}$ has the greatest intensity as well in the DEBIJE- as in the LAUE-radiogram, etc. Moreover, the results obtained in the rotation-radiogram mentioned before, are also in best concordance with all this.

§ 5. If now it be considered that in the powder-radiograms a faint image of $\{111\}$ and of $\{112\}$ of the first order was found, as well, although very faint, of $\{221\}$, $\{441\}$ and $\{432\}$, while it appears now from the discussion just given, that among the spots of the LAUE-image there is present also a first order image of $\{586\}$, — then it must be clear, that images of the *first* order are possible in this structure of planes having *three* odd, *two* odd, or *two* even indices. This fact, — combined with the evidence brought in the foregoing pages, that the spectra on $\{111\}$ are very intensive in the second and fourth, but very faint in the first and third order, — enables us with a high degree of probability to make our choice between the twelve space-groups, which only are compatible with the two symmetries possible in this case.

If the three fundamental translation-groups (BRAVAIS' space-lattices) of the space-groups considered are discerned as follows: Γ_c for the simple cubic, Γ_c'' for the body-centred, and Γ_c' for the face-centred cubic space-lattice, — then the twelve space-groups here only of interest, can be tabulated as follows ¹⁾:

Symbol of the Space-groups of dyacisdodecahedral and of tetrahedral-pentagonal-dodecahedral symmetry	Corresponding translation-group :	Number of points equivalent to each point of the Space-group :
T_1	Γ_c	12
T_2	Γ_c'	48
T_3	Γ_c''	24
T_4	Γ_c	12
T_5	Γ_c''	24
T_h^1	Γ_c	24
T_h^2	Γ_c	24
T_h^3	Γ_c'	96
T_h^4	Γ_c'	96
T_h^5	Γ_c''	48
T_h^6	Γ_c	24
T_h^7	Γ_c''	48

In the last column the number of equivalent points is indicated, corresponding to each arbitrarily chosen point of the group. If through each of these corresponding equivalents molecular planes be passed parallel to each other, their sequence will appear to be such, that the diffraction-images of definite orders must be cut out by interference. It can be foreseen ²⁾, that :

a. if the fundamental translation-group is Γ_c , there will appear diffraction-images of *all three* kinds of planes $\{hkl\}$ in *all* orders ;

b. if the translation-group is Γ_c' , there will appear in *odd* orders only images of planes $\{hkl\}$ with *three odd indices* ;

c. if the translation-group is Γ_c'' , there will appear in *odd* orders only

¹⁾ R. W. G. WYCKOFF, *The analytical Expression of the Results of the Theory of Space-groups*, p. 33 and 34.

²⁾ R. W. G. WYCKOFF, loc. cit., IV, (1922), p. 175, 181, 183 ; W. T. ASTBURY and K. YARDLEY, Phil. Trans. R. Soc. London, A **224**, (1924), p. 222.

images of planes $\{hkl\}$ with *two even* indices and one *odd* index; in all these cases *zero* being considered as *even* index.

With respect to the facts mentioned above, it must be clear now, that, as among the images of *odd* order such appear not only of $\{111\}$ and $\{731\}$, but also of $\{221\}$, $\{421\}$, $\{432\}$, $\{568\}$, and of $\{112\}$ and $\{411\}$, the fundamental translation-group can only be I_c , i. e. the *simple cubic space-lattice*. For I_c'' is excluded by the first order of $\{111\}$ and I_c' by that of $\{112\}$, while the presence of the first order spectrum of $\{568\}$ is in full agreement with the presence of I_c . Of the twelve space-groups mentioned, thus only *five*: T^1 , T^4 , T_h^1 , T_h^2 , and T_h^6 need to be further considered here.

For each of these five groups is the relation of the consecutive values of $\sin^2 \frac{\theta}{2}$ as follows ¹⁾:

For T_1 and T_h^1 : 1: 2: 3: 4: 5: 6: 8: 9: etc.
(100) (110) (111) (200) (201) (211) (220) (221)

For T_4 : 2: 3: 4: 5: 6: 8: 9: 10: etc.
(110) (111) (200) (201) (211) (220) (221) (301)

For T_h^2 : 2: 3: 4: 6: 8: 9: etc.
(110) (111) (200) (211) (220) (221)

For T_h^6 : 3: 4: 5: 6: 8: 9: etc.
(111) (200) (102) (211) (220) (221)

In the row of observed diffraction-images there are certainly absent those of the first order on (100) and (110); for this reason the four groups: T^1 , T_h^1 , T^4 and T_h^6 are excluded, — thus only T_h^6 remaining. For this group is true, that images of planes $\{h0l\}$, in which h is *even* and l is *odd*, or those of $\{0kl\}$, in which k and l are both *odd*, cannot appear in *odd* orders ²⁾. Indeed, among the observed images, that of $\{201\}$ is *not* present; in the LAUE-radiogram the *fourth* order spectra of $\{201\}$ and $\{102\}$ have about the same intensity, which indicates that the diffracting power of both these planes is about identical and explains also the absence of the first order of $\{102\}$, so that this absence needs not to be considered an argument against T_h^6 in this case. In favour of T_h^6 , on the other hand, it may be remembered, that besides the first order spectra on $\{100\}$ and $\{110\}$, also that of $\{031\}$ is absent, — which follows from the powder-radiogram, where the row of consecutive

$\sin^2 \frac{\theta}{2}$ was:

3 : 6 : 8 : 16 : 22 : 24 : 38 : 40 : 48;

¹⁾ Or of: $(h^2 + k^2 + l^2)$. Cf. i.a. P. NIGGLI, Zeits. f. Kryst. **57**, (1922), 261; *idem*, *Geometrische Kryst. des Diskontinuums*, Table X, p. 482.

²⁾ R. W. G. WYCKOFF, loc. cit., p. 183.

i.e. possesses even more scanty terms, as is postulated with respect to what has been said above.

It is now necessary to fit 8 molecules GeI_4 into the fundamental cell with its edges of 11,89 A.V., i.e. 8 Ge -atoms and 32 J -atoms. With respect to their *structural* function, these 32 J -atoms, although chemically equivalent, need *not* be all in the same condition: in general, the possible cases would be either that they have all (32) the same structural function, or that such is the case with 16 on the one hand and 16 on the other; moreover, it is possible to discern 16 atoms of one kind, 8 of a second kind and 8 of a third function in spatial respects; or to have 24 atoms of one and 8 of a second kind; or finally, there would be possible four groups of 8 atoms, each group differing from the others by its spatial relation in the space-group considered. But, as is seen from the table on page 758, the number of equivalent points in each of the five here possible space-groups can be no other than 12 or 24; in no case will it be possible, therefore, that the 32 J -atoms will have identical functions¹⁾ in the structure of GeI_4 , and neither will it be possible that 16 atoms of one and 16 atoms of a second kind are present in this structure. Moreover, groups of 8 equivalent atoms cannot be present in the space-groups T_1 and T_4 ($n = 12$); in T_h^1 , T_h^2 and T_h^6 an arbitrary number of 8 equivalent atoms of one kind and 24 of another kind may be present, but no group of 16 atoms. From this also follows, that T^1 and T^4 are excluded. T_h^1 also is highly improbable, because in this case $no \sin^{2\theta}/2$ will be excluded from the series of values observed, while, as was shown, the number of missing values in this row appeared to be rather great in the powder-radiograms obtained. As the fundamental translation-group now is certainly I_c' , and not I_c'' , the 32 J -atoms cannot be present in the structure in any other way than as: $24 + 8$. Regarding all these arguments, there can, in every case, only be a choice between T_h^2 and T_h^6 ; and this choice can be fixed only by consideration of the lack of certain diffraction-images of odd order.

The forms $\{103\}$ and $\{301\}$ for instance, can in T_h^2 give spectra as well in the even, as in odd orders; in T_h^6 , however, only in even orders. On no radiograms, indeed, occur images of these forms in the first or in the third order; but those of $\{602\}$ and $\{12.04\}$ are present. (Film XII). On the LAUE-radiograms also $\{12.04\}$ is present. This is in contradiction with T_h^2 , but in agreement with T_h^6 . In the same way $\{330\}$ is everywhere absent; but $\{440\}$ and $\{880\}$ are all observed together on the powder-radiograms. These facts also lead to the same conclusion with respect to the two space-groups considered here.

In T_h^2 the reflections on $\{201\}$ and $\{102\}$ may only occur in even orders, in T_h^6 however, those on $\{201\}$ only in even, but those of $\{102\}$ as well in even as in odd orders, as was already emphasized. The fact,

¹⁾ R. W. G. WYCKOFF, *The analytical Expression*, etc., p. 176.

that neither on $\{201\}$, nor on $\{102\}$ diffraction-images of odd orders are met with on the different photographs, need *not* be considered here as an argument against T_h^6 , if the LAUE-radiogram be also taken in account. Summarizing all evidences, we think it highly probable, that GeI_4 has a structure¹⁾ corresponding to T_6^h .

§ 6. The most simple supposition with respect to the arrangement of the eight GeI_4 -molecules, which can be made in concordance with all data acquired, leads to the structure reproduced in Fig. 5.

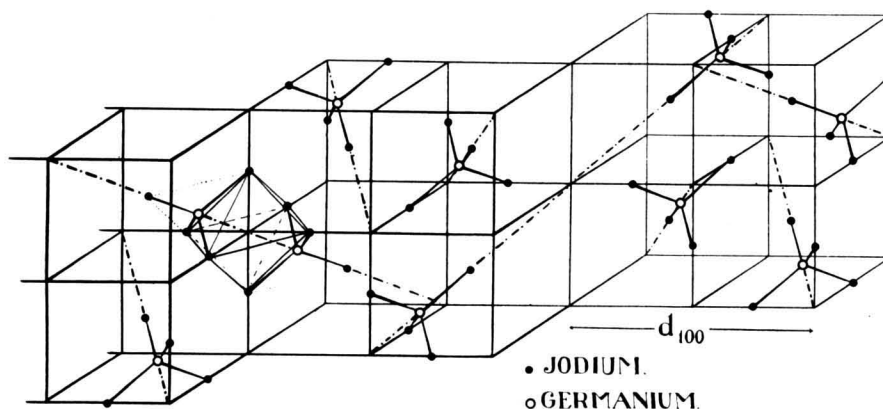


Fig. 5. *The Crystal-structure of Germaniumtetraiodide.*

Each Ge-atom in it appears as surrounded by four I -atoms, situated in the corners of a regular tetrahedron; from this it may be easily proved, that of the 32 I -atoms in each cell really 24 have equivalent positions in the structure and 8 a somewhat other structural function. For two GeI_4 -groups on each cube-diagonal of the fundamental cell can every time be thought to be combined in pairs, situated at equal distances of the centre to both sides of it; in such pairs evidently 6 I -atoms are always in equivalent positions with respect to each other, while 2 others have a somewhat different position, being directed more to the outsides of the combination. The I -atoms of such a pair are placed in the corners of a steep rhombohedron, the axis of which is a diagonal of the cubic cell; the nearest Ge-atoms, however, are then situated in the corners of an obtuse rhombohedron, coaxial with that of the I -atoms. In the combined pair of molecules both the Ge-atoms are placed in the centra of two diametrically opposed tetrahedra, the corners of which are occupied by the I -atoms. In the direction of a cube-diagonal planes of I -atoms alternate with such as are occupied by Ge-atoms in the way indicated in Fig. 6. Of course, this placing of the GeI_4 -molecules is somewhat

¹⁾ R. W. G. WYCKOFF, *The analytical Expression of the Results of the Theory of Space-Groups*, p. 127; P. NIGGLI, *Geom. Kryst. des Diskontinuums*, p. 367.

arbitrary, because the J -atoms may be thought shifted more or less along the cube-diagonal; in this case again 5 variable parameters must be

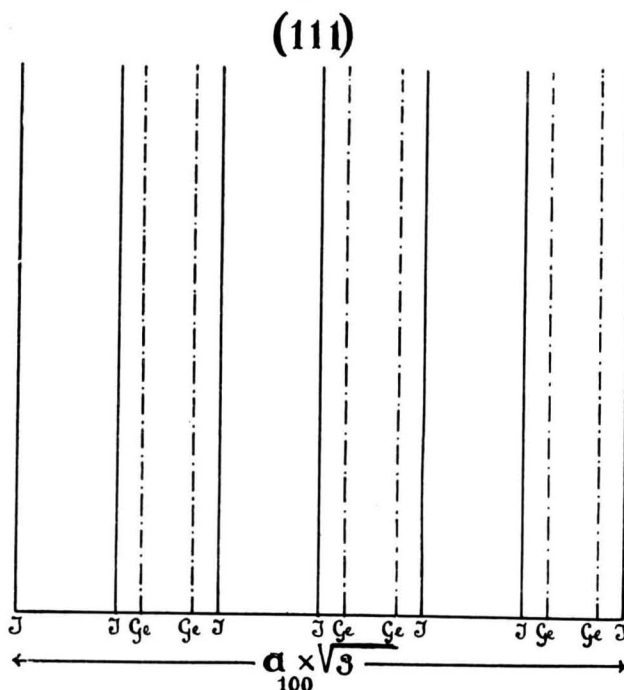


Fig. 6. Successive molecular Planes along a Perpendicular to $\{111\}$.

determined by comparison of observed and calculated intensities of the diffraction-images, — a task, which may safely be considered to be impracticable. In how far the here adopted structure can be considered to be in agreement with the observed relative intensities of the diffraction-images for the different planes on the DEBIJE-radiograms, may be seen from the data in the following table, in which the results are reviewed of the calculated values for a number of important crystal-planes.

If in the formula for the intensities:

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

in which n is the number of planes of the crystal form $\{hkl\}$ and $|S|$ is the absolute value of the structural factor, the function preceding $n \cdot |S|^2$ be called: $f(\theta/2)$, then the value of this function for different forms $\{hkl\}$ and for successive orders, may be immediately read from the existing tables¹⁾. Moreover, for Ge and I in the formula for $|S|$

¹⁾ L. WEBER, Zeitschr. f. Kryst. 57, 402, (1923).

are taken the atomic numbers 32 and 53 respectively ¹⁾ while the coordinates of the $24 + 8$ J -atoms and of the 8 Ge -atoms are the following:

I. 32 J -atoms; x, y, z and v -along the cube-edges.											
a. the 24 equivalent atoms :											
0	0	$1/4$	$1/2$	$1/2$	$-1/4$	0	$1/2$	$1/4$	$1/2$	0	$3/4$
$1/4$	0	0	$-1/4$	$1/2$	$1/2$	$1/4$	0	$1/2$	$3/4$	$1/2$	0
0	$1/4$	0	$1/2$	$-1/4$	$1/2$	$1/2$	$1/4$	0	0	$3/4$	$1/2$
0	0	$-1/4$	$1/2$	$1/2$	$1/4$	0	$1/2$	$3/4$	$1/2$	0	$1/4$
$-1/4$	0	0	$1/4$	$1/2$	$1/2$	$3/4$	0	$1/2$	$1/4$	$1/2$	0
0	$-1/4$	0	$1/2$	$1/4$	$1/2$	$1/2$	$3/4$	0	0	$1/4$	$1/2$
b. the 8 equivalent atoms; $v = 1/4$.											
$1/4$	$1/4$	$1/4$	$3/4$	$1/4$	$-1/4$	$-1/4$	$3/4$	$1/4$	$1/4$	$-1/4$	$3/4$
$-1/4$	$-1/4$	$-1/4$	$1/4$	$3/4$	$1/4$	$1/4$	$1/4$	$3/4$	$3/4$	$1/4$	$1/4$
II. 8 Ge -atoms; $v = 1/8$.											
$1/8$	$1/8$	$1/8$	$5/8$	$3/8$	$-1/8$	$-1/8$	$5/8$	$3/8$	$3/8$	$-1/8$	$5/8$
$-1/8$	$-1/8$	$-1/8$	$3/8$	$5/8$	$1/8$	$1/8$	$3/8$	$5/8$	$5/8$	$1/8$	$3/8$

If these values for p , q and r for all ($= m$) atoms within the fundamental cell be substituted in:

$$S = \sum_m \left(A_n \cdot e^{2i\pi(p_m h + q_m k + r_m l)} \right),$$

and if it be taken into account, that for the group T_h^6 all terms containing sinuses are equal to zero in the structural factor, — then it is possible to calculate directly for all planes $\{hkl\}$ the intensities of the diffraction-images for all orders.

These values are given in the table on the next page.

It will be clear from this, that there is a fairly good agreement between the calculated and observed intensities from a qualitative point of view, especially if the difficulty be taken into account of avoiding the attribution of a too great relative value in the estimation of the intensities of images, which eventually are excelling by their distinctness.

For it is easily seen, that the estimated intensities in the last column are placed in all cases in just the same sequence of increase, as occurs

¹⁾ Instead of Ge and J , also the values for Ge^{53} and J might have been taken; the differences, however, are not very appreciable in this case.

Table of calculated Intensities

Indices:	Order:	Structural-amplitudines:			Absolute value of $ S ^2$	Intensities	
		1st kind I -atoms:	2nd kind I -atoms:	Ge-atoms:		Calculated:	Estimated on DEBIJE-Film No. 18:
(111)	1	0	0	$64.\sqrt{2}$	0.8	1.6	— *)
(111)	2	— 1272	— 424	0	287.6	42.08	10
(111)	3	0	0	$-64.\sqrt{2}$	0.8	0.05	absent
(111)	4	1272	424	— 256	207.4	6.3	3
(111)	5	0	0	$64.\sqrt{2}$	0.8	0.01	absent
(111)	6	— 1272	— 424	0	287.6		—
(011)	1	0	0	0	0	0	—
(011)	2	— 424	+ 424	0	0	0	absent
(011)	3	0	0	0	0	0	„
(011)	4	1272	424	256	381.0	28.1	9
(011)	5	0	0	0	0	0	absent
(011)	6	— 424	+ 424	0	0	0	„
(001)	1	0	0	0	0	0	—
(001)	2	424	— 424	0	0	0	absent
(001)	3	0	0	0	0	0	„
(001)	4	1272	424	— 256	207.4	16.7	7
(112)	1	0	0	— 128	1.6	1.5	very faint
(112)	2	— 424	424	0	0	0	absent
(112)	3	0	0	— 128	1.6	0.1	„
(112)	4	1272	424	256	381.0	15.2	2
(311)	1	0	0	$-64.\sqrt{2}$	0.8	0.4	absent
(311)	2	— 1272	— 424	0	287.6	29.0	8
(331)	1	0	0	$64.\sqrt{2}$	0.8	0.2	absent
(331)	2	— 1272	— 424	0	287.6	14.5	3

*) If the line was situated outside the efficient part of the film, this is indicated by — in the last column.

with the calculated values; and everywhere the calculated intensities are equal to zero or to extremely small values, if among the observed intensities they were zero in reality. The here adopted structure, therefore, evidently completely accounts for all characteristics of the ROENTGEN-photograms of these crystals.

With respect to the intensity-distribution of the spots in the LAUE-image, which gives the illusion of an apparent symmetry after the planes of $\{110\}$, — it may be remarked that in the adopted structure three planes of $\{110\}$ containing each time 8 *J*-atoms and 2 *Ge*-atoms intersect along each cube-diagonal. In each of these planes the diffractive power of the *J*-atoms strongly dominate that of the *Ge*-atoms. In the structure as a whole, the other *J*-atoms are situated, moreover, symmetrically with respect to these three planes, which is not the case with the *Ge*-atoms, and for the last reason, therefore, the $\{110\}$ -planes are, in reality, *no* true symmetry-planes of the structure. But just because the diffractive power of the symmetrically distributed *J*-atoms is so strongly predominant in comparison with that of the much more scanty *Ge*-atoms, the influence of the last is practically lost in the LAUE-radiogram. It is for this circumstance, that the LAUE-image on $\{111\}$ appears to be symmetrical after three planes of $\{110\}$ and is, therefore, deceptive as a criterion for the symmetry-determination of the crystal.

Finally, we wish to draw attention to the fact, that the results here obtained are in full agreement with R. G. DICKINSON's determinations ¹⁾ of the also dyacidododecahedral *Tintetraiodide*: *Sn I₄*. According to GROTH's measurements this substance, which is isomorphous with *Ge I₄*, crystallizes from carbondisulphide in octahedral crystals, showing a combination of: $\{111\}$, $\{210\}$, $\{211\}$, $\{100\}$, and smaller: $\{110\}$, $\{120\}$ and a dyacidododecahedron of the zone $[(210):(111)]$, which could not be determined more precisely. Also NORDENSKJÖLD ³⁾ and RETGERS ⁴⁾ investigated this compound; the last author observed in crystals from a solution in methylene-iodide also a pentagonal-dodecahedron $\{210\}$. The structure deduced by DICKINSON is completely analogous to that adopted here for *Ge I₄*; even the dimensions of the fundamental cell (12,23 A.U.) are wholly comparable with those for *Ge I₄*. According to the American author a yet better agreement between calculated and observed intensities may be obtained in the case of *Sn I₄*, by a slight shift of the *Sn*- and *J*-atoms along a cube-diagonal.

On the contrary, the determinations of MARK and WEISSENBERG ⁵⁾ must be considered as quite insufficient. They also observed in their LAUE-radiograms a symmetry with respect to $\{110\}$ and, moreover, to $\{100\}$;

1) R. G. DICKINSON, Journ. Amer. Chem. Soc., **45**, 958, (1923).

2) P. GROTH, *Chemische Kristallographie*, **1**, p: 231.

3) N. G. NORDENSKJÖLD, Bihang K. Vet. Akad. Förh. Stockholm, **2**, N^o. 2, (1874).

4) J. W. RETGERS, Zeits. f. Kryst., **22**, 270, (1894).

5) H. MARK and K. WEISSENBERG, Zeits. f. Physik, **16**, 18, (1923).

for this reason, they exclude the space-group T_1^h . In the above we have discussed the cause of the appearance of those symmetry-planes parallel to $\{110\}$ and emphasized, that care must be taken not to be misled by this fact, as the phenomenon is solely a consequence of the predominant diffractive influence of the numerous *I*-atoms, symmetrically arranged with respect to $\{110\}$, in comparison with the much less powerful diffraction by the not symmetrically situated *Ge*-atoms. The authors also have taken a value for the cube-edge *a*, which is only half the true one: we have fully discussed, why the fundamental distance *a* needs to be taken twice as great. The measurements and determinations of both investigators are, therefore in full disagreement with the symmetry of SnI_4 , as determined by GROTH and others; in accordance with our experiences in the case of GeI_4 , there is no reason to doubt the exactness of these older crystallographical data.

Although there is no complete certainty as to the question, whether in the case of GeJ_4 there is present a structure formed by *ions* or not, — it is of interest, however, to draw attention to the fact, that throughout the whole structure tetrahedral groups ($Ge-J_4$) can clearly be discerned as more or less autonomous units in it. In this respect a very recent investigation of HANTZSCH and CARLSOHN¹⁾ may also be quoted here, in which paper the authors, by demonstrating a number of additive relations between the meltingpoints of the halogenides of the elements in the fourth group of the periodic table, also arrive at the result, that in the crystals of these compounds not the ions, but the molecules themselves are the real structural units.

*Groningen, Laboratory for Inorganic and
physical Chemistry of the University.*

¹⁾ A. HANTZSCH and CARLSOHN, Ber. d. d. chem. Ges., 58, 1741, (1925).