Rotating crystal X-ray photographs.

By Gilbert Greenwood, M.Sc.

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SINCE the original experiments of M. von Laue on the diffraction of X-rays by crystals, other and more suitable methods of research have been devised. The Bragg ionization-chamber method and the Debye-Scherrer powder method are now quite well known. The newest technique is that of the so-called 'rotating crystal', which is based essentially on some experiments of M. de Broglie.[1] This method was first employed and developed in the Kaiser Wilhelm Institut für Faserstoffchemie in Berlin. It has recently been extended by the work of J. D. Bernal [2] in the Royal Institution in London.

There are two methods of making this type of photograph. In both a small crystal is rotated in a beam of X-rays and the reflected beams recorded photographically, in one case on a flat plate, and in the other on a cylindrical film the axis of which coincides with the axis about which the crystal is rotated. Usually the crystal is rotated about an important zone-axis. In the first case, the spots on the plate lie on hyperbolae, whilst in the second case the spots are arranged along straight lines running horizontally round the film. These lines have been called 'Schichtlinien'—'layer-lines'. In this paper the latter type of photograph only is considered.

This method seems to be particularly well adapted for the study of more purely crystallographic problems, in distinction to determinations of crystal-structure. The difference lies essentially in the fact that this method measures so easily the identity period (or true unit-cell dimension) in the direction of the axis of rotation, whilst in the other methods a spacing is measured. In these cases the unit-cell dimensions must be

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[1] M. de Broglie, Compt. Rend. Acad. Sci. Paris, 1913, vol. 157, pp. 924 and 1413; 1914, vol. 158, p. 177.

[2] J. D. Bernal, Proc. Roy. Soc. London, Ser. A, 1926, vol. 113, p. 117.

obtained indirectly. The indices of the reflecting planes, giving rise to the spots on the photographs, can be found, and from statistical data obtained in this way the space-group in which the substance crystallizes can often be determined. Cases frequently occur where only the crystal-system and not the particular class can be determined by crystallographic measurements. If, in such cases, the space-group can be fixed unequivocally, then the crystal-class and at the same time the symmetry-elements of the crystal are determined. A further instance of the rotating crystal photograph as an aid in the investigation of symmetry may be given. Consider an axis of n-fold symmetry, where a certain doubt exists as to the value of n. Arranged round this axis are n equivalent faces $(h\ k\ l)$ and, if the crystal is rotated about this axis, the spot on the photograph to which the indices $(h\ k\ l)$ are assigned consists of n superimposed spots. Now let the crystal be rotated about a direction which nearly but not quite coincides with this axis. Then each spot on the film is split up into its n constituents, and the order of the axis is found by counting the number of these constituent spots.

The identity period is very simply related to the distance between the 'layer-lines'. This relationship seems to have been first obtained in a somewhat complicated manner in a series of papers by M. Polanyi and K. Weissenberg.[1] It may be obtained as follows, by a simple type of reasoning which, when applied to spacings, gives the Bragg equation. Here it is applied to identity periods. In fig. 1 let $a\,b\,c$ be the direction of rotation and let a, b, c, &c., be the lattice points which are equivalent along this line, i.e. the distances between these points are equal to the primitive translation in this direction. Let it be I. Let X-rays of wave-length λ fall on this string of points. Radiation is diffracted from the points in all directions. Consider the direction cd which makes an angle μ with the incident beam. The phase-difference between the rays from b and c is ec, and a reflected beam is obtained in the direction cd when this difference is a multiple of λ. Hence

$$n\lambda = ec = bc \sin \mu = I \sin \mu, \text{ or } I = n\lambda/\sin \mu.$$

If the beam cd gives rise to the first layer-line, then $n = 1$. For the second layer-line $n = 2$, and so on.

Let the vertical dotted line be the section of the cylindrical film of radius r, and let $2e$ represent the distance between the layer-line and the corresponding one on the lower half of the film. Then $\tan \mu = e/r$. Hence I can be determined.

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[1] M. Polanyi, Zeits. Physik, 1921, vol. 7, p. 149; M. Polanyi and K. Weissenberg, ibid., 1922, vol. 9, p. 123; 1922, vol. 10, p. 44.

J. D. Bernal has carried out a complete mathematical investigation of the reflection of X-rays by rotating crystals, under the various forms of experiment, by the use of the conception of the reciprocal or polar lattice, an idea which seems to date back to the time of Bravais.[1] On pages 133, 134, and 148 of his paper the above results appear in a slightly different form.

The assignment of indices to the individual spots was carried out in the German Laboratories in the following way. A measured value of $\sin^2\theta$ obtained from the film was compared with the values of $\sin^2\theta$ for the planes which could give rise to a reflection lying on the layer-lines in question. Let the direction of the axis of rotation be $[u\,v\,w]$, then it has been shown[2] that any plane $(h\;k\;l)$ which gives rise to a reflection spot on the nth layer-line must obey the relation $hu + kv + lw = n$.

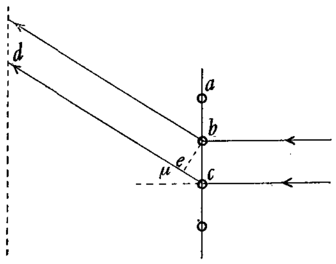

FIG. 1.

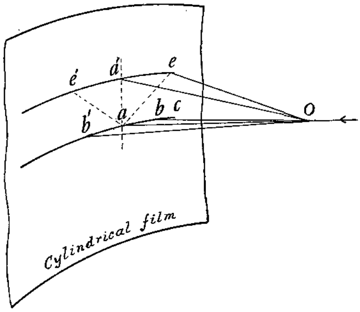

FIG. 2.

Knowing the possible planes and the unit-cell dimensions, the theoretical values of $\sin^2\theta$, where θ is the glancing angle, can be calculated. The measurement of the experimental value of $\sin^2\theta$ is as follows. Let $a\;b\;c$, fig. 2, represent the equatorial line of spots, i.e. reflections from planes parallel to the axis of rotation. At the point O, the centre of the camera, is the crystal, and reflection occurs here. Consider a particular spot at b and the corresponding one on the other side at b', then the angular distance $b\,b'$ is equal to $4\,\theta$. Now consider a spot e in the first layer-line. Let the angle $e\,a'$, which is easily measured on the film (equal to half $e\,e'$), be α. The angle $a'\,o\,a$ is equal to μ, whilst the angle between the primary beam oa and the reflected beam $o\,e$ equals $2\,\theta$. These angles form the sides of a right-angled spherical triangle, and we

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[1] A. Bravais, Études cristallographiques, Paris, 1866, p. 103.

[2] Perhaps the most satisfactory proof of this fact is that given by J. D. Bernal on p. 148 of his paper.

obtain $\cos 2\theta = \cos a \cos \mu$. Remembering that $\sin^2\theta = \frac{1}{2}(1-\cos 2\theta)$ and calculating in tabular form, $\sin^2\theta$ is very easily got from the length ee'.

J. D. Bernal has developed a method of assigning indices by projecting the film or flat plate, magnified up to the correct size, on to suitably constructed charts, when the indices can be read off. Accurate crystal adjusting arrangements and precision cameras have been devised, and the spots then fall exactly on the correct places on the charts.

In making the photographs about to be described, a Hadding tube was used. This type of tube was found to work very well. The anticathode is easily interchangeable, and in some photographs Cu- and in others Fe-radiation was used. The high voltage applied to the tube was obtained from a transformer working in conjunction with a mechanical rectifier. Both the anticathode and cathode were water-cooled; the latter, being at a high potential, required an insulated system. The camera was an ordinary Debye-Scherrer camera of the original pattern. Instead of a rod of crystal powder being supported inside, the small crystal was mounted on a goniometer head, attached to a spindle, which was arranged so as to be rotated by an external motor. The diameter of the camera was 5·72 cm.

Tetra-methyl-ammonium iodide $N(CH_3)_4I$.

According to F. Slavík[1] this substance crystallizes in the tetragonal system with an axial ratio of $a : c = 1 : 0{\cdot}723$, and although the crystal-class is usually said to be bipyramidal, no very definite proof of this has been given.

Rotation photographs were made, in which the directions, about which the crystals were rotated, were [001], [100], and [110]. The first two photographs were made with Cu-radiation and the third with Fe-radiation. The results obtained for the identity periods, from measurements of the layer-lines, are given in the following table.

Table I.

Rotation about [001] using Cu-radiation.			Rotation about [100] using Cu-radiation.			Rotation about [110] using Fe-radiation.		
$2e$.	μ.	I.	$2e$.	μ.	I.	$2e$.	μ.	I.
1·6 cm.	15·6°	5·73 Å.	1·1 cm.	10·9°	8·14 Å.	1·0 cm.	9·9°	11·3 Å.
3·6	32·2	5·78	2·35	22·4	8·08	2·1	20·2	11·2
			4·1	35·7	7·92	3·5	31·5	11·1
	Mean = 5·75			Mean = 8·05			Mean = 11·20	

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[1] F. Slavík, Zeits. Kryst. Min., 1902, vol. 36, p. 273.

The axial ratio as calculated from these values is $a : c = 1 : 0{\cdot}715$, which agrees with the above crystallographic data.

In all tetragonal crystals there are two alternative orientations possible for the a-axis. This depends on the fact that the translation group Γ_t may be regarded either as a simple or as a base-centred tetragonal prism, according to whether the side or the diagonal of the square base is made the a-axis. In exactly the same way the translation group Γ'_t may be regarded as a centred, or a face-centred tetragonal prism. In the tables of Astbury and Yardley[1] these four possibilities are made clear by comparison with the analogous orthorhombic groups Γ_o, Γ_o', Γ_o''', and Γ_o''. In most space-group tables the shortest identity period in the plane (001) is chosen as a-axis, i. e. the translation-groups are regarded either as a simple or a centred tetragonal lattice. Crystallographic measurements give no criterion for fixing the axial directions, and if necessary the axes chosen and the indices assigned by the crystallographer must be altered. A difficulty arises, however, with regard to the scalenohedral space-groups. From the external symmetry the axial directions are taken as fixed, and this causes the groups V_d^5 to V_d^8 to be based on a base-centred lattice, and V_d^9 and V_d^{10} on a face-centred lattice. In the determination of space-groups from reflection data, this must not be overlooked.

The second and third photographs show that the identity periods in the crystallographic directions [100] and [110] are 8·05 Å. and 11·20 Å. Hence the crystallographic axes coincide with the structural axes used in mathematical crystallography, and no changes are required. The value of $I_{[110]}$ calculated from $I_{[100]}$ is 11·30 Å. Using the known value of the density 1·835, the molecular weight of the substance, and the size of the unit-cell, it is possible to calculate the number of molecules in this unit. It is found to be *two*. A further analysis of the photographs was now carried out, and the indices of the reflecting planes assigned to the appropriate spots on the photographs. The glancing angle θ is given by the quadratic form, which in the case of tetragonal crystals is:

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

For the photographs made with Cu-rays it becomes:

$$\sin^2\theta = 0{\cdot}0093\,(h^2+k^2)+0{\cdot}0179\,l^2$$

whilst in the case of Fe-radiation it is:

$$\sin^2\theta = 0{\cdot}0147\,(h^2+k^2)+0{\cdot}0284\,l^2.$$

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[1] W. T. Astbury and K. Yardley, Phil. Trans. Roy. Soc. London, Ser. A, 1924, vol. 224, p. 221.

In tables II, III, and IV the results from the films obtained by rotating about the directions [001], [100], and [110] are given. In all cases the value $\sin^2 \theta$ for the particular reflection is calculated as described in the introductory section, and this is compared with the theoretical value calculated from the quadratic form and thus the indices are found. In some cases the measured value agrees equally well with the $\sin^2 \theta$ calculated for two planes ; if this occurs both indices are given. Sometimes, especially in systems with a high degree of symmetry, two different planes may have the same spacing, and then the interference spots will coincide. The two indices are again given.

Table II.

Rotation about [001]. Cu-radiation.

	Points without alternative indices.	Points with alternative indices.
Equator. $l = 0$.	200, 220, 130, 400, 240, 440. 350, 600, 260, 460, 370, 800. 280, 660, 480, 190, 390.	(140, 330), (550, 170). (380, 570), (500, 340, 150). (10.0.0, 680, 1.10.0).
1st Layer-line. $l = 1$.	101, 111, 201, 121, 221, 301. 131, 231, 401, 141, 241, 251. 351, 601, 261, 701, 461, 371. 281, 481, 191, 581.	(501, 341), (381, 571). (801, 471, 181). (671, 291).
2nd Layer-line. $l = 2$.	202, 232, 402, 252, 602, 362. 702, 462, 562, 802, 662. 582.	(222, 302), (502, 342). (262, 452) (482, 902). (672, 292).

Table III.

Rotation about [100]. Cu-radiation.

	Points without alternative indices.	Points with alternative indices.
Equator. h (or k) = 0.	200, 201, 102, 400, 303, 104.	(204, 600).
1st Layer-line. h (or k) = 1.	111, 102, 112, 150, 151.	(103, 141).
2nd Layer-line. h (or k) = 2.	211, 220, 240, 233, 224.	—
3rd Layer-line. h (or k) = 3.	321, 331, 333, 352.	(303, 332), (342, 350).

Table IV.

Rotation about [110]. Fe-radiation.

	Points without alternative indices.	Points with alternative indices.
Equator. $h-k=0$.	110, 111, 220, 221, 331, 441. 442, 115, 551, 552, 444.	(223, 332).
1st Layer-line. $h-k=1$.	211, 320, 213, 430, 104. 324, 105, 543.	(432, 214).
2nd Layer-line. $h-k=2$.	201, 311, 204, 531, 423. 532, 205, 641.	(315, 642).
3rd Layer-line. $h-k=3$.	$2\bar{1}0$, 411, 303, $2\bar{1}4$, 522. 414, $2\bar{1}5$.	—

A certain amount of difficulty is experienced in the investigation of this substance, owing to the iodine in the molecule, which liberates fluorescent iodine radiation. This fluorescent radiation gives rise to a general blackening and fogging of the film. In the second film (Table III) this was especially marked, in fact the two ends of the film were so black that it was impossible to make any measurements of the large angles of deflection that occur in this region.

The following table has been constructed as a summary of the preceding data, and gives details of the halvings of different types of planes. None of the points to which alternative indices could be assigned have been used.

Table V.

(hkl)	All normal, even when $(h+k+l)$, $(h+k)$, $(k+l)$, or $(k+h)$ is odd.
(hhl)	All normal whatever value of h, l, or $(h+l)$.
$(hh0)$	Normal.
$(hk0)$	All normal, even when $(h+k)$ is odd, except 280. The first order, however, of this plane—140—occurs as a possible index for another interference point.
(100)	Halved. The reflections 200, 400, 600; and 800 occur. No trace of 100, 300, 700, or 900 could be found.
(001)	No data could be found. A spectrometer investigation was therefore made for me by Mr. R. W. James, to whom I take this opportunity of expressing my thanks. A reflection 100 was found, whilst no trace of 200 could be found. This plane is therefore normal.

Consideration must now be given to the points with alternative indices. In all cases except a possible 500 the conclusion of the above table *that*

(100) only is halved is not contradicted. There are, however, two possible alternatives to account for this reflection and neither of these contradicts the statement of halving.

Tetra-ethyl-ammonium iodide, $N(C_2H_5)_4I$.

F. Slavík[1] describes this substance as crystallizing in the scalenohedral class of the tetragonal system, i. e. having ditetragonal alternating symmetry. The value given for the axial ratio is $a:c = 1:0{\cdot}5544$. Crystals exhibit a well-marked scalenohedral form. According to conventional crystallographic usage the axial directions are therefore fixed, coinciding with the directions of the twofold symmetry axes which are determined by the scalenohedral symmetry. Identity periods in the crystallographic directions [001], [100], and [110] were measured with the following results.

Table VI.

Rotation about [001] using Fe-radiation.			Rotation about [100] using Cu-radiation.			Rotation about [110] using Cu-radiation.		
2*e*.	μ.	*I*.	2*e*.	μ.	*I*.	2*e*.	μ.	*I*.
1·7 cm.	16·6°	6·78 Å.	0·72 cm.	7·2°	12·30 Å.	1·0 cm.	9·9	8·97 Å.
3·7	34·3	6·87	1·5	14·7	12·15	2·15	20·6	8·75
			2·3	21·9	12·40			
			3·3	30·0	12·30			
	Mean = 6·82			Mean = 12·29			Mean = 8·86	

This shows that, using the crystallographic axial directions, the type of lattice underlying the structure is a base-centred one. If, however, the [100] and [110] directions were to be interchanged, the structure would be based on a lattice with a simple square base. It is usual in tetragonal space-groups to refer the structure to such axes, but in this case, since there is strong evidence from the symmetry of the crystal that the crystallographic axes are correct, these axes will be adopted in the evaluation of the diagrams.

Using the dimensions $a = 12{\cdot}29$ Å. and $c = 6{\cdot}82$ Å. (which give an axial ratio of $a:c = 1:0{\cdot}555$) and the value 1·566 for the density,

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[1] F. Slavík, Zeits. Kryst. Min., 1902, vol. 36, p. 274.

calculation shows that this unit-cell contains *four* molecules. The quadratic forms for the two wave-lengths used become;

$$\text{Fe-rays} :\!-\!\sin^2\theta = 0{\cdot}0062\,(h^2+k^2)+0{\cdot}0201\,l^2.$$

$$\text{Cu-rays} :\!-\!\sin^2\theta = 0{\cdot}0039\,(h^2+k^2)+0{\cdot}0127\,l^2.$$

The results obtained by the measurements of the photographs are given in the following tables.

Table VII.

Rotation about [001]. Fe-radiation.

	Points without alternative indices.	Points with alternative indices.
Equator. $l = 0$.	220, 330, 400, 280, 570.	(700, 170, 550).
1st Layer-line. $l = 1$.	111, 131, 441, 371, 281. 481.	(400, 331), (551, 171, 701). (341, 501).
2nd Layer-line. $l = 2$.	222, 402, 332, 442.	(202, 122). (162, 262).

Table VIII.

Rotation about [100]. Cu-radiation.

	Points without alternative indices.	Points with alternative indices.
Equator. h (or k) = 0.	102, 400, 202, 204.	(801, 404).
1st Layer-line. h (or k) = 1.	112, 113, 153.	(152, 133, 161). (164, 135).
2nd Layer-line. h (or k) = 2.	260, 224, 225.	(240, 222), (242, 203). (263, 281).

In the interpretation of the third photograph an important and interesting point must be considered. The indices and the quadratic forms refer to a unit of size 6·82 × 12·29 × 12·29 Å. The diagonal of the base of such a unit is 17·38 Å. The diagonal is actually found to be half this. The result of this is that the 1st, 3rd, 5th, &c., layer-lines disappear. This must, however, not be overlooked in assigning indices to the interference points. The apparent first layer-line is really the second and the relation $hu+kv+lw = 2$ must be applied.

Table IX.

Rotation about [110]. Cu-radiation.

	Points without alternative indices.	Points with alternative indices.
Equator. $h-k = 0$.	111, 220, 221, 002, 442, 224. 661, 005.	(222, 331). (003, 332, 113).
1st Layer-line. $h-k = 2$.	200, 112, 202, 420, 113, 531. 314, 424, 643, 752.	(114, 641), (860, 425).
2nd Layer-line. $h-k = 4$.	221, 400, 223, 731, 404. 225.	(401, 222), (402, 511), (622, 513).
3rd Layer-line. $h-k = 6$.	511, 332, 422, 711, 334.	—

Summarizing the data obtained from the points without alternative indices we get the following table.

Table X.

(hkl).	Planes of this type do not occur in the first order, i.e. they have halved spacings when $(h+k)$ is odd.
(hhl).	All normal whatever values of h, l, or $(h+l)$.
$(hh0)$.	Normal.
$(hk0)$.	Halved if $(h+k)$ is odd ; this is a special case of (hkl).
(001).	Normal.
(100).	Halved ; again a special case of (hkl).

Considering now the points possessing doubtful indices, we find certain points—700, 701, 122, 162, and 161—which would contradict the conclusion to be drawn from Table X—*that planes* (hkl) *are halved when* $(h+k)$ *is odd.* In all these cases, however, one of the alternative interpretations can be found, which is in agreement with the above-stated condition. This condition is expressed in terms of a base-centred lattice : when expressed in terms of a simple tetragonal lattice it becomes *all spacings are normal.*

Determination of the Space-groups of $N(CH_3)_4I$ and $N(C_2H_5)_4I$.

Most of the space-group tables give the abnormalities of spacings in terms of simple and centred tetragonal lattices as fundamental units. Astbury, however, often gives these same abnormalities when the structure is referred to base-centred and face-centred units. This has not been done, however, for certain groups of the scalenohedral class. In order to complete the data on the halving of spacings in groups of the tetragonal system when referred to the simplest tetragonal unit, the peculiarities of groups V_d^5 to V_d^{10} referred to this simple unit are given in Table XI.

Table XI.

Space-group.	Abnormal spacing.
V_d^5	None.
V_d^6	$(h0l)$ when l is odd.
V_d^7	$(h0l)$ when h is odd.
V_d^8	$(h0l)$ when $(h+l)$ is odd.
V_d^9	(hkl) when $(h+k+l)$ is odd.
V_d^{10}	(hkl) when $(h+k+l)$ is odd. $(h0l)$ when l is odd.

$N(CH_3)_4I$.—Certain space-groups can be definitely excluded owing to the occurrence of reflections, whilst other groups are only excluded by the absence of certain reflections. By means of the presence of reflections all groups are excluded except V_d^1, V_d^5, S_4^1, C_4^1, C_{4h}^1, C_{4v}^1, D_4^1, D_{4h}^1, D_4^2, and V_d^3. In the first eight of these, however, odd orders from (100) should occur: these were not found. Hence these groups may be eliminated, but this elimination is not so rigid as that based on the presence of certain reflections. Crystallographic evidence on the external symmetry does not help in the determination of the crystal-class, i. e. deciding between D_4 and V_d, since only holohedral forms have been observed. The corresponding tetra-ethyl-ammonium salt crystallizes (as will be shown in the next paragraph) in the class V_d. Hence, having regard to the similarities of the two substances, the evidence seems to be in favour of V_d^3 as the space-group in which tetra-methyl-ammonium iodide crystallizes.

As far back as 1917 an X-ray investigation of this substance was made by L. Vegard,[1] who measured the spacings of the planes (100), (110), (001), (101), and (111) and obtained a unit-cell of dimensions $a = 7{\cdot}88$, $c = 5{\cdot}69$ Å., in which the spacing of the (100) planes is halved. When this unit-cell is recalculated, using modern values of the wave-length of the X-rays, the size of the unit-cell becomes $a = 7{\cdot}97$ and $c = 5{\cdot}74$ Å. These experimental results are thus in agreement with those obtained from the rotation photographs. L. Vegard (loc. cit., p. 402), as a result of his measurements brings forward a structure which possesses 'the highest degree of symmetry'. The mathematical theory of space-groups, which was not well known to X-ray analysts at that early date, shows at once that any tetragonal crystal which gives the results described above,

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[1] L. Vegard, Phil. Mag., 1917, ser. 6, vol. 33, p. 395. [Min. Abstr., vol. 2, p. 507.]

cannot belong to the holohedral class. Hence the structure proposed by L. Vegard cannot be correct. Certain deductions as to the position of the atoms in the unit-cell can be made from space-group considerations, quite apart from any discussion of intensities. In the unit-cell are two nitrogen atoms, two iodine atoms, and eight CH_3 radicles. In the space-group V_d^3, a point in the general position repeats eight times in the unit. A nitrogen atom, therefore, cannot be in such a position. Points in special positions can be found so that they give rise to only one other equivalent point. In the space-group V_d^3 there are three such pairs of equivalent points and they have the co-ordinates (000), $(\frac{1}{2}\frac{1}{2}0)$; $(00\frac{1}{2})$, $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$; and $(0\frac{1}{2}\,u)$, $(\frac{1}{2}0\,\bar{u})$. Two out of these three pairs must be occupied by the nitrogen and the iodine atoms, whilst if we assume that the CH_3 radicles are equivalent—a somewhat natural assumption—they must occupy general positions in the unit. Cases are known, however, where chemically equivalent groups or atoms are not crystallographically equivalent.[1] This may happen here, since two sets of points can be found each of which consists of four equivalent points. In this case the CH_3 radicles would be of two types. The nitrogen atoms must, however, be of the same type since no point can be found, which by operation of the symmetry elements does not give rise to at least one equivalent point. The same also applies to the iodine atoms.

$N(C_3H_5)_4I$.—Using the simple tetragonal unit we find no abnormal spacings and conclude from the X-ray evidence that the possible space-groups are V_d^1, V_d^5, S_4^1, C_4^1, C_{4h}^1, C_{4v}^1, D_4^1, and D_{4h}^1. Crystallographic evidence is strongly in favour of scalenohedral symmetry and thus would point to the groups V_d^1 and V_d^5 as being most likely. All the groups except V_d^5 are based on a simple tetragonal lattice, and thus to produce a base-centred lattice the direction [110] must be taken as the new a-axis. The crystallographic data again produce strong evidence that the axial directions are two-fold axes of symmetry. An examination of the space-groups shows that in certain of them the axial directions do not coincide with two-fold axes. In this way groups S_4^1, C_4^1, V_d^1, C_{4h}^1, and C_{4v}^1, are seen to be very unlikely. The mass of evidence is therefore in favour of V_d^5 being the space-group concerned in the structure of tetra-ethyl-ammonium iodide.

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[1] For example, the copper atoms and the zinc atoms in γ-brass, see A. J. Bradley and J. Thewlis, Proc. Roy. Soc. London, Ser. A, 1926, vol. 112, p. 678. The aluminium atoms in chrysoberyl are crystallographically of two types, see W. L. Bragg and G. B. Brown, Proc. Roy. Soc. London, Ser. A, 1926, vol. 110, p. 34.

In the base-centred unit-cell are four nitrogen atoms, four iodine atoms, and sixteen C_2H_5 radicles. From space-group theory we again find that all the nitrogen atoms must be equivalent, and also the iodine atoms. Three sets of four equivalent points occur, and have the co-ordinates $(00\,u)$, $(00\,\bar{u})$, $(\frac{1}{2}\frac{1}{2}\,u)$, $(\frac{1}{2}\frac{1}{2}\,\bar{u})$; $(0\frac{1}{2}\,u)$, $(0\frac{1}{2}\,\bar{u})$, $(\frac{1}{2}0\,u)$, $(\frac{1}{2}0\,\bar{u})$; $(\frac{1}{4}\frac{1}{4}\,u)$, $(\frac{3}{4}\frac{3}{4}\,u)$, $(\frac{1}{4}\frac{3}{4}\,\bar{u})$, $(\frac{3}{4}\frac{1}{4}\,\bar{u})$. Two out of these three sets must be occupied by the nitrogen and the iodine atoms. The C_2H_5 radicles may be in the sixteen general positions, or in two sets of eight equivalent positions.

The three substances, ammonium iodide, tetra-methyl-ammonium iodide, and tetra-ethyl-ammonium iodide, have been regarded as forming a series of closely related, if not strictly isomorphous compounds. Topic axes have been calculated for them, making the assumption that the same number of molecules occurred in the unit-cells, and on the basis of these topic axes P. Groth[1] has suggested hypothetical structures for the crystals. The results of X-ray analysis show that there is a different number of molecules in the units of the three substances. Ammonium iodide[2] has been found to have the rock-salt structure with four molecules in the unit. Tetra-methyl-ammonium iodide has two molecules in its unit, whilst in the large and more crystallographically correct unit of the tetra-ethyl salt there are four molecules. If the alternative small unit in which the base is not centred is considered, there are only two molecules in it. Making allowance for these different numbers of molecules in the units, the values shown in the table are obtained for the true topic axes. They are, of course, proportional to the actual unit-cell dimensions. The old topic axes are also shown in the table.

Table XII.

	Groth's Topic Axes.			True Topic Axes.			Unit-cell dimensions.	
	Mol. vol. V.	$\chi = \psi$.	ω.	V'.	$\chi = \psi$.	ω.	$a = b$.	c.
NH_4I.	57·51	3·860	3·860	220·04	6·04	6·04	7·20 Å.	7·20
$N(CH_3)_4I$.	108·70	5·319	3·842	217·4	6·72	4·84	8·05	5·75
$N(C_2H_5)_4I$ (*a*).	162·91	6·648	3·686	651·64	10·6	5·84	12·29	6·82
,, (*b*).	—	—	—	375·82	7·51	5·77	8·86	6·82

It is easily seen from the true topic axes that it is impossible to draw any conclusions as to the isomorphism of the three substances.

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[1] P. Groth, Chemische Krystallographie, 1906, vol. 1, p. 171; see also S. Kreutz, Elemente der Theorie der Krystallstruktur, 1916, p. 145.

[2] L. Vegard, Phil. Mag., 1917, ser. 6, vol. 33, p. 395.

In fact, these topic axes, the unit-cell dimensions, and the numbers of molecules in the unit-cells all show that the substances are not isomorphous even in a fairly wide sense of the term. It has been previously pointed out[1] that isomorphous replacement by organic radicles is by no means so common an occurrence as isomorphous replacement in the inorganic and mineral world. As a result of the crystallographic measurements on glyoxaline compounds and certain menthyl salts of a complicated carboxylic acid, it was concluded that isomorphous replacement only occurs in organic crystals when the replacement makes a comparatively small molecular change. The behaviour of the three substances here discussed is in agreement with this idea.

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[1] G. Greenwood, Min. Mag., 1925, vol. 20, p. 393.