

at t° . Where the experimental data for this computation were not known, the values for W'_{18} were interpolated. A_{gas} indicates the molecular heat of combustion of the substances in the gaseous state at t° and $p = \text{const.}$

A comparison of Zubow's data with those of other authors will be made in the next paper.

WARSAW, POLAND.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY.]

THE CRYSTAL STRUCTURE OF CESIUM DICHLORO-IODIDE.¹

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Purpose of the Investigation.—The crystal structure of the alkali halides, sodium and potassium chlorides, has been determined.² It has seemed of particular interest to ascertain the modifications in this structure which result when more halogen atoms are introduced into the molecule with the formation of alkali polyhalides.

The real nature of these compounds has long been in doubt and it was felt that a knowledge of the crystal structure of a typical polyhalide might aid in removing this uncertainty. Formerly it was customary to consider these compounds as "double salts" or "addition compounds," for instance the trihalides as compounds of RX and $XX'(CsCl \cdot ICl)$ where R is an alkali metal and X and X' are halogens, and the pentahalides as compounds of RX and $XX'_3(CsCl \cdot ICl_3)$.³ The ease with which such compounds as $R(ICl_4)$ are decomposed into normal halide and complex halogen (RCl and ICl_3) by carbon tetrachloride⁴ supported this view. By some the halogen atoms were considered to be grouped about the positive atom but as Werner⁵ has pointed out, this point of view is quite untenable. The view which seems to agree best with the properties of these compounds considers them to be compounds of metal ion or group and complex halogen anion.⁵ More recent studies, especially upon the polyiodides, have strengthened this view.⁶

Cesium dichloro-iodide ($CsCl_2I$) was chosen for this study of crystal structure because of its supposed dimorphism, and because experience had shown that good crystals of one of these forms at least could be readily prepared.

¹ This article is based upon a portion of the thesis presented to the Faculty of the Graduate School of Cornell University by Ralph W. G. Wyckoff in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² W. H. Bragg and W. L. Bragg, "X-Rays and Crystal Structure," 1918. Chap. VII.

³ Wells and Penfield, *Am. J. Sci.*, [3] **43**, 29 (1892) discuss possible structures for the trihalides.

⁴ Weinland and Schlegelmilch, *Z. anorg. Chem.*, **30**, 134 (1902).

⁵ A. Werner, "New Ideas on Inorganic Chemistry" (Hedley, translator), 1911, p. 86.

⁶ R. Abegg u. F. Auerbach, "Handbuch d. anorg. Chem.," Bd. IV, *Abt.*, **2**, 432 et seq. (1913).

Preparation of the Specimens.—Cesium dichloro-iodide is described as crystallizing in 2 forms, a hexagonal and a rhombic modification. The hexagonal cesium dichloro-iodide is obtained from solutions which are rather weak in cesium chloride (CsCl). If cesium chloride is present in larger quantities, the rhombic form is said to result.¹

Rhombohedral (hexagonal) cesium dichloro-iodide was obtained by dissolving about 10 g. of cesium chloride in 50 cc. of water, adding 8 g. of iodine, and passing chlorine through the hot solution until all the iodine had dissolved.² Six-sided plates (less than a millimeter in thickness, but nearly a centimeter in diameter) formed upon slow cooling. The edges of these plates reflect light well but the 2 large faces are invariably dull and pitted.

All attempts to prepare the rhombic modification by increasing the amount of cesium chloride failed. When the concentration recommended by Wells and Penfield³ was used, small crystals that were apparently of the rhombic system appeared. But when these crystals were examined by the X-rays the pattern that was obtained clearly indicated that the crystals were not simple, but twinned. On breaking the crystals they were frequently found to be hollow. Usually all of the faces appearing upon these crystals reflected light fairly well. Attempts to grow rhombic crystals by slow evaporation over sulfuric acid in a room of constant temperature also failed. Under these conditions twined crystals were always obtained. Crystals were grown from solutions, the cesium chloride content of which varied by small steps from a solution containing one molecule of cesium chloride to 5 molecules of water, from which rhombohedral plates of cesium dichloro-iodide were obtained, to the point where cesium chloride itself crystallized out.

Because of the failure to produce true rhombic cesium dichloro-iodide the special rhombohedral arrangement, which shows only in this particular polyhalide, has alone been determined.

The cesium chloride used in preparing the cesium dichloro-iodide was very pure. It was originally obtained from pollucite, and an arc spectrum photograph showed the presence of no other alkalis.

The Method of Crystal Structure Determination.—The method of study is similar to that used by Nishikawa in studying the structure of the spinels.⁴ This method may be considered as made up of 2 parts.

1. The study of the X-ray spectrum obtained from the anticathode of an X-ray bulb using the crystal under investigation as a grating. From

¹ Wells and Penfield, *loc. cit.*, p. 17.

² If an excess of chlorine is used, cesium tetrachloro-iodide (CsCl_4I) is produced (Wells and Penfield, *loc. cit.*).

³ *Loc. cit.*

⁴ S. Nishikawa, *Tokyo Sugaku-Buturigakkwai Kizi*, [2] 8, 199 (1915).

this spectrum the distance between like planes in the crystal can be ascertained and information can be obtained concerning the kind of unit which by repetition of itself builds up the crystal.

2. The study of the Laue patterns obtained by passing X-rays through a section of the crystal.

Part 1. The Study of the X-ray Spectrum.—The X-ray spectrum of tungsten from a Coolidge tube was obtained by reflection from the large (111) face of a crystal. The distances measured upon the photographic plate from the image of the slit to the principal tungsten lines are:

Line.	Wave Length. ^a Å. U.	Plate Distance. Cm.
α_1	1.471	8.6
β_1	1.278	6.9
β_2	1.241	6.7
γ_1	1.095	5.6

^a M. Siegbahn, *Jahrb. Radioakt. Elektronik.*, [3] 13, 296 (1916).

The order of the spectrum which appears upon the plate is not known. But from the above data the value of the ratio d/n (where d is the distance between like planes of this face and n is the order of the spectrum) can be calculated. The well-known expression, $n\lambda = 2d \sin \theta$, where n and d have the meanings already given, $\lambda =$ the wave length of the X-rays, $\theta =$ the angle of the reflection,¹ holds in this case. From this equation $d/n = \lambda/(2 \sin \theta)$ results. The distances measured upon the photographic plate from the particular lines to the position of zero deflection are equal to the distances from the crystal to the plate (9.25 cm. approximately) multiplied by the $\tan 2\theta$. Calculations from the above data lead to the following values for d/n :

Line.	d/n .
α_1	2.01
β_1	2.015
β_2	2.01
γ_1	2.03

A more accurate determination of this ratio can be made, using the reference spectrum from sodium chloride. In making this comparison spectrum, crystals of cesium dichloro-iodide and sodium chloride were mounted together, one above the other. The spacing for sodium chloride is accurately known² so that by the use of this sodium chloride spectrum it is possible to get the distance from the crystal to the plate with greater accuracy. The following table gives measurements upon this second photograph:

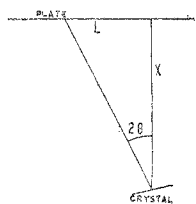


Fig. 1.

¹ W. H. Bragg and W. L. Bragg, *loc. cit.*, Chap. II.

² W. H. Bragg and W. L. Bragg, *ibid.*, p. 71.

Line.	Distance upon the plate from slit image to line for.		Wave Length. Å. U.
	NaCl. Cm.	CsCl ₂ I. Cm.	
α_1	5.55	8.65	1.471
β_4	4.75	7.20	1.296
β_1	4.68	7.05	1.278
β_3	4.58	6.90	1.258
β_2	4.50	6.75	1.241
γ_1	3.92	5.75	1.095

The distance from the crystal to the plate, x , is given by $\sin \theta = n\lambda/2d$, $\tan 2\theta = m/x$ or $x = m/\tan 2\theta$, where m is the distance of the spectrum line from the undeviated line. This leads to the following values for x :

Line.	Cm.
α_1	9.44
β_4	9.43
β_1	9.44
β_3	9.47
β_2	9.4
γ_1	9.43

	9.44

This value of x , when used for the more accurate evaluation of d/n for cesium dichloro-iodide leads to

Line.	d/n .
α_1	2.03
β_4	2.02
β_1	2.03
β_3	2.02
β_2	2.03
γ_1	2.02

	2.02×10^{-8} cm.

The Density of Cesium Dichloro-iodide.—In order to know the number of molecules associated with the unit of structure and the shape of this unit, the density of the salt must be known. As no determinations were to be found in the literature, the following measurements were made. Great accuracy in this determination was not needed for the present purpose. The density was found by observing the buoyant effect of benzene upon definite weights of cesium dichloro-iodide. Most of the air could be removed from the particles of the solid by keeping the salt during the determination in a small bottle which could be placed in boiling benzene. A number of determinations gave a mean density for cesium dichloro-iodide of 3.86.

The Unit of Structure.—Cesium dichloro-iodide belongs to the rhombohedral division of the hexagonal system. Two lattices, or units of struc-

ture, are fundamental to this division—the hexagonal lattice (Γ_h) and the rhombohedral lattice (Γ_{rh}).¹ The spacing (d) between like planes of either of these units can be obtained in terms of the crystallographic data, the density (ρ), the weight of one molecule of the salt (M), the number of molecules associated with the unit of structure (m), and the order of the reflection spectrum (n). In the case of the rhombohedral unit (Γ_{rh})

$$V = \frac{c^3}{3\sqrt{3}} \frac{1 - \cos \alpha}{1 + 2 \cos \alpha},$$

where c = the body diagonal of the unit, α = the angle between the rhombohedral axes, and V = the volume of the unit rhombohedron.

$$c = \sqrt[3]{3} \sqrt[3]{V \frac{1 + 2 \cos \alpha}{1 - \cos \alpha}},$$

$$d = c/3 = \frac{1}{\sqrt{3}} \sqrt[3]{V \frac{1 + 2 \cos \alpha}{1 - \cos \alpha}}, \quad V = mM/\rho.$$

$$d^3 = \frac{mM}{3\sqrt{3} \rho} \frac{(1 + 2 \cos \alpha)}{(1 - \cos \alpha)},$$

$$d^3/n^3 = \frac{M}{3\sqrt{3} \rho} \frac{(1 + 2 \cos \alpha)}{(1 - \cos \alpha)} \frac{m}{n^3}$$

$$n^3/m = \frac{M}{\rho \times (d/n)^3 \times 3\sqrt{3}} \times \frac{1 + 2 \cos \alpha}{1 - \cos \alpha}.$$

$M = 330.7 \times 1.64 \times 10^{-24}$ g., where 1.64×10^{-24} g. is the weight of one atom of hydrogen.²

$$\rho = 3.86$$

$$\alpha = 98^\circ 22'3$$

$$d/n = 2.03 \times 10^{-8} \text{ cm.}$$

$$n^3/m = 2.001.$$

Since n , the order of the spectrum, is not known with certainty, the number of molecules associated with the unit cell cannot be evaluated directly. The value of n^3/m , however, is seen to agree very closely with the value it would have if 4 molecules were associated with the unit of structure and the reflection were of the second order. A consideration of the other possible unit, the hexagonal prism, makes Γ_h seem highly improbable as the fundamental lattice for cesium dichloro-iodide. The results from these spectra measurements point then to a rhombohedral unit containing 4 molecules. The later study of the Laue photographs confirms this conclusion.

The value of m or m_1 , the number of molecules associated with the unit of structure cannot be told directly because n cannot be evaluated

¹ A. Schönflies, "Krystallsysteme und Krystallstruktur.," p. 459.

² W. H. Bragg and W. L. Bragg, *loc. cit.*, p. 110.

³ P. Groth, "Chemische Krystallographie," I, 305 (1906).

with certainty. It can, however, be obtained in the following indirect fashion. All possible values of the ratio n^2/m are shown in the following table:

m	1	2	3	4	6	12
n						
1	1	0.50	0.33	0.25	0.16	0.08
2	8	4.00	2.67	2.00	1.33	0.67
3	27	13.50	9.00	6.75	4.50	2.25
4	64	32.00	21.33	16.00	10.67	5.33

From an inspection of this table it is evident that 4 molecules are associated with the unit cell, which is a rhombohedron. The spectrum obtained upon the photographic plate is of the second order.

Part 2. The Study of the Laue Patterns.—A symmetrical Laue photograph made by passing the X-rays in a direction normal to the (111) face of a crystal and several unsymmetrical photographs when the rays were not exactly perpendicular to this face were prepared. Stereographic projections of these photographs were made and the indices of the planes producing the various spots in the figures were determined. The manner of drawing this projection is given by the following data for the symmetrical case (Fig. 1a).

XYZ is the plane of the photographic plate,

O is the position of the crystal,

$XZ = XY = YZ$,

$OI = 5$ cm., $YXI = 30^\circ$,

$b \sin \alpha/2 = 1/2 XY = x \cos 30^\circ = x\sqrt{3}/2$,

therefore

$$b = \frac{x\sqrt{3}}{2 \sin \alpha/2}.$$

Also

$$x^2 + 5^2 = \frac{3x^2}{4 \sin^2 \alpha/2}, \text{ and } x = 8.98 \text{ cm.}$$

If an attempt is made to construct the diagram using a base built upon this value of x , there is no simple correspondence between the calculated and observed positions of the spots. This agreement, however, is obtained by taking as axes the face diagonals of the figure (as z). These new axes rather than the old are to be considered as the axes of the unit rhombohedron. The necessary calculations follow:

$$x \sin 30^\circ = u,$$

$$z^2 = 5^2 + u^2,$$

$$z = \sqrt{5^2 + [8.98 \sin 30^\circ]^2} = 6.72 \text{ cm.},$$

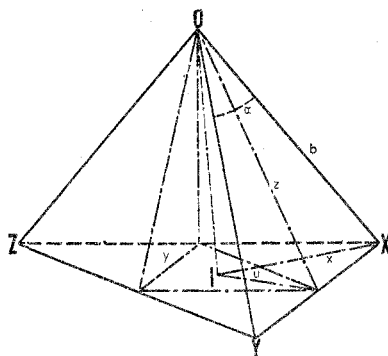


Fig. 1a.

$$y = x \cos 30^\circ = 7.77 \text{ cm.},$$

$$\beta \text{ (the new face angle)} = \sin^{-1} (y/2)/z \times 2 = 70^\circ 42',$$

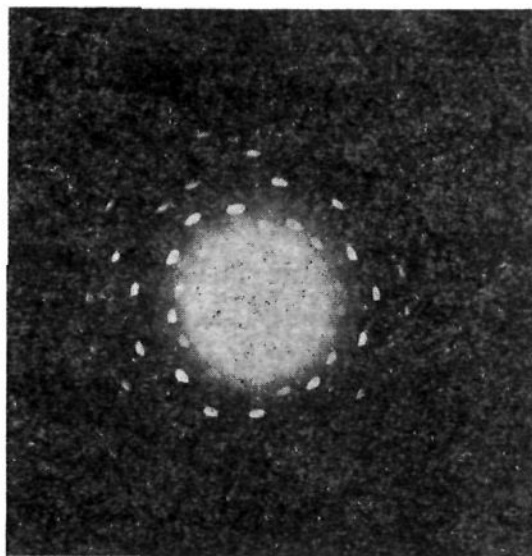


Fig. 2.

The distance¹ between a plane (*hkl*) and a parallel plane through a point (*x₁y₁z₁*) in a rhombohedral lattice is

$$\frac{(hx_1 + ky_1 + lz_1 - 1) \sqrt{1 + \cos^3 \beta - 3 \cos^2 \beta}}{\sqrt{(h^2 + k^2 + l^2) \sin^2 \beta + 2(hk + hl + kl) (\cos^2 \beta - \cos \beta)}}$$

where *h, k, l* are the Miller indices of the plane. β , the angle between

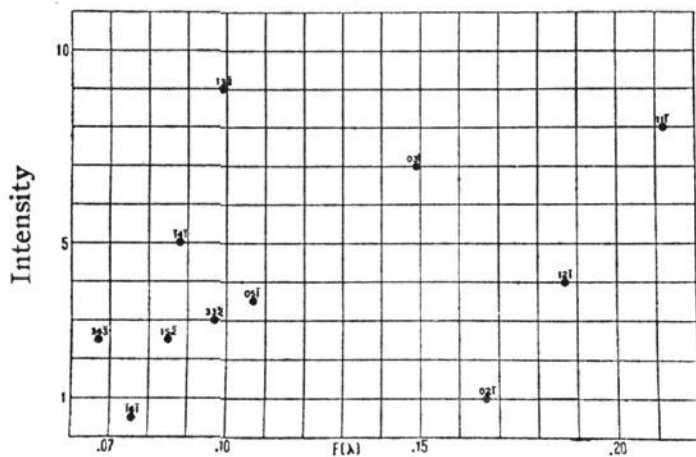


Fig. 3.

the crystallographic axes, $\approx 70^\circ 42'$. *x₁, y₁, z₁* are the coordinates of the point of reference. From this *d* (the spacing) is seen to vary with

$$\frac{1}{\sqrt{(h^2 + k^2 + l^2) \sin^2 \beta + 2(hk + hl + kl) (\cos^2 \beta - \cos \beta)}}$$

But $d = \frac{n\lambda}{2 \sin \theta}$, consequently $\frac{n\lambda}{2 \sin \theta}$ varies with the value of the

¹ A. W. Hull, *Phys. Rev.*, [2] 10, 661 (1917).

above expression and the wave length, λ , of the X-rays producing a spot is a function of

$$\frac{\sin \theta}{\sqrt{h^2 + k^2 + l^2} \sin^2 \beta + 2(hk + hl + kl) (\cos^2 \beta - \cos \beta)} = f(\lambda).$$

The distance of a spot from the undeviated position, as measured upon the photographic plate, divided by the distance from the crystal to the plate is the tangent of twice the angle of reflection, θ . The relative intensities given in the following tables are from estimations made upon

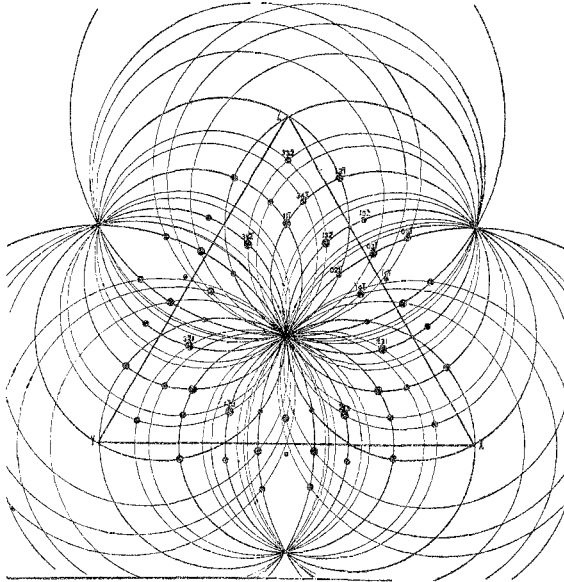


Fig. 4.

the negative. The value of $f(\lambda)$ for the various spots which appear are plotted against intensities in Fig. 3. The stereographic projection of this symmetrical photograph (Fig. 2) is shown in Fig. 4.

TABLE I.—DATA FROM THE SYMMETRICAL LAUE PHOTOGRAPH.

hkl .	Distance from central spot.	$2f(\lambda)$.	Intensity.
$02\bar{1}$	1.90	0.3339	1.0
$11\bar{1}$	2.55	0.424	8.0
$12\bar{1}$	4.03	0.373	4.0
$03\bar{1}$	2.80	0.298	7.0
$05\bar{1}$	3.75	0.214	3.5
$13\bar{2}$	2.30	0.198	9.0
$\bar{1}4\bar{1}$	1.95	0.177	5.0
$\bar{1}6\bar{1}$	2.85	0.152	0.5
$15\bar{2}$	3.40	0.170	2.5
$33\bar{2}$	4.30	0.193	3.0
$34\bar{3}$	3.15	0.134	2.5

Similar measurements were made upon 3 unsymmetrical photographs and the data thus obtained are contained in the accompanying Tables (II, III and IV). In all cases the distance from the crystal to the photographic plate was 5 cm.

TABLE II.—DATA FROM THE FIRST UNSYMMETRICAL LAUE PHOTOGRAPH.

hkl .	Distance from central spot.	$f(\lambda)$.	Intensity.
02 $\bar{1}$	1.40	0.0592	2.5
$\bar{1}20$	1.15	0.0492	2.0
$\bar{1}02$	1.50	0.0630	2.0
0 $\bar{1}2$	1.95	0.0805	3.5
2 $\bar{1}0$	2.53	0.1000	6.0
20 $\bar{1}$	2.35	0.0948	5.5
11 $\bar{1}$	2.50	0.131	5.5
$\bar{1}\bar{1}1$	3.15	0.158	2.0
$\bar{1}11$	1.78	0.103	8.0
12 $\bar{1}$	3.72	0.131	2.0
$\bar{1}21$	3.05	0.113	3.0
$\bar{1}12$	3.25	0.118	2.7
1 $\bar{1}2$	4.55	0.150	0.5
2 $\bar{1}1$	5.10	0.161	0.2
21 $\bar{1}$	4.4	0.147	0.5
03 $\bar{1}$	2.25	0.066	6.5
$\bar{1}30$	2.10	0.062	7.0
$\bar{1}03$	2.50	0.072	3.0
0 $\bar{1}3$	2.95	0.083	1.0
3 $\bar{1}0$	3.60	0.096	0.7
30 $\bar{1}$	3.40	0.092	0.7
05 $\bar{1}$	3.10	0.0545	5.5
$\bar{1}50$	2.95	0.0526	6.0
$\bar{1}05$	3.50	0.0588	2.5
0 $\bar{1}5$	3.75	0.0628	2.0
5 $\bar{1}0$	4.70	0.0789	0.4
50 $\bar{1}$	4.60	0.0800	0.4
13 $\bar{2}$	2.00	0.0495	8.0
$\bar{2}31$	1.55	0.0393	4.0
$\bar{2}13$	1.75	0.0437	7.0
1 $\bar{2}3$	2.60	0.0624	3.5
3 $\bar{2}1$	3.00	0.0700	3.0
31 $\bar{2}$	2.60	0.0624	3.5
$\bar{1}4\bar{1}$	1.35	0.0304	0.5
$\bar{1}\bar{1}4$	1.85	0.0404	2.5
4 $\bar{1}\bar{1}$	2.60	0.0547	4.5
$\bar{1}\bar{1}6$	2.5 =	0.0372	0.1
6 $\bar{1}\bar{1}$	3.65	0.0498	2.5
15 $\bar{2}$	2.90	0.0480	4.0
$\bar{2}51$	2.55	0.0430	4.0
$\bar{2}15$	2.90	0.0480	3.7
125	3.65	0.0568	1.0
52 $\bar{1}$	4.30	0.0639	0.5
51 $\bar{2}$	3.95	0.0603	0.7

TABLE II (continued).

hkl .	Distance from central spot.	$f(\lambda)$.	Intensity.
$3\bar{3}\bar{2}$	3.40	0.0641	1.5
$\bar{2}33$
$3\bar{2}3$	4.30	0.0762	0.3
$2\bar{3}\bar{3}$
$\bar{3}23$	2.25	0.0434	4.2
$2\bar{3}3$	2.35	0.0451	4.5
$3\bar{3}\bar{2}$	2.10	0.0407	0.1
$14\bar{3}$	1.30	0.0241	0.1
$\bar{1}\bar{3}4$	2.00	0.0359	0.2
$4\bar{3}\bar{1}$	2.30	0.0406	0.6
$34\bar{3}$	2.8±	0.0435	0.2
$\bar{3}34$	3.70	0.0536	2.0
$3\bar{3}4$	3.85	0.0552	2.0
$4\bar{3}3$	3.30	0.0492	3.0
$4\bar{3}\bar{3}$	3.00	0.0457	3.0
$2\bar{5}\bar{3}$	2.70	0.0395	0.2
$\bar{3}5\bar{2}$	2.15	0.0446	0.1
$2\bar{3}5$	3.30	0.0463	2.0
$5\bar{3}\bar{2}$	3.70	0.0505	2.5
$5\bar{2}\bar{3}$	3.25	0.0458	2.0

TABLE III.—DATA FROM THE SECOND UNSYMMETRICAL LAUE PHOTOGRAPH.

hkl .	Distance from central spot.	$f(\lambda)$.	Intensity.
010	6.75	0.342	7.0
$\bar{1}01$	3.25	0.109	20.0
$\bar{1}20$	2.55	0.0547	3.0
$\bar{1}02$	7.15	0.147	4.0
$\bar{1}30$	3.80	0.0597	8.5
$\bar{1}03$	9.05	0.130	3.3
$03\bar{1}$	2.30	0.0359	7.0
$04\bar{1}$	3.35	0.0406	0.5
$\bar{1}40$	4.50	0.0544	0.2
$05\bar{1}$	3.90	0.0384	6.0
$\bar{1}50$	4.90	0.0477	8.0
$\bar{1}05$	10.85	0.095	1.5
$06\bar{1}$	4.35	0.0361	0.8
$\bar{1}60$	5.22	0.0431	1.4
$07\bar{1}$	4.80	0.0400	0.3
$\bar{1}70$	5.42	0.0377	1.1
$\bar{1}07$	11.65	0.0724	0.2
140	9.07	0.1134	1.2
150	8.63	0.0852	3.5
170	8.10	0.0589	3.0
710	8.95	0.0635	3.0
190	7.80	0.0442	1.0
910	8.50	0.0474	0.9
$\bar{3}41$	3.20	0.0299	0.8
$\bar{6}31$	4.25	0.0305	0.1

TABLE III (continued).

hkl .	Distance from central spot.	$f(\lambda)$.	Intensity.
$\bar{2}11$	1.85	0.0349	15.0
$\bar{2}21$	3.54	0.0561	0.5
$\bar{2}31$	4.47	0.0582	7.0
$\bar{2}51$	5.44	0.0483	7.2
$\bar{2}61$	5.70	0.0437	1.0
$\bar{2}71$	5.88	0.0393	1.0
$\bar{2}12$	5.15	0.081	1.5
$\bar{2}13$	7.35	0.0913	4.0
$\bar{2}15$	9.80	0.0806	3.8
$\bar{3}12$	2.40	0.0306	6.0
$\bar{3}13$	4.60	0.0500	0.2
$\bar{3}14$	6.15	0.0560	5.6
$\bar{3}16$	8.25	0.0558	2.5
$\bar{2}03$	5.63	0.0723	0.1
$22\bar{1}$	4.87	0.0852	6.0
$23\bar{1}$	5.85	0.0768	7.5
$24\bar{1}$	6.30	0.0716	2.0
$\bar{2}5\bar{1}$	6.58	0.0627	7.0
$27\bar{1}$	6.75	0.0477	3.0
$12\bar{1}$	3.10	0.0892	9.0
$13\bar{1}$	4.30	0.0670	2.2
$14\bar{1}$	4.95	0.0600	8.5
$15\bar{1}$	5.32	0.0525	1.8
$16\bar{1}$	5.55	0.0462	6.0
$33\bar{2}$	3.30	0.0358	4.5
$34\bar{2}$	4.15	0.0399	0.2
$35\bar{2}$	4.75	0.0402	4.0
$55\bar{2}$	6.00	0.0429	3.5
$57\bar{2}$	6.70	0.0371	0.1
$33\bar{1}$	6.85	0.0825	2.7
$34\bar{1}$	7.35	0.0761	6.3
$36\bar{1}$	7.68	0.0594	4.3
$38\bar{1}$	7.70	0.0467	3.5
$45\bar{1}$	8.30	0.0669	5.0
$47\bar{1}$	8.45	0.0549	3.0
$56\bar{1}$	8.38	0.057	3.5
$58\bar{1}$	9.00	0.0499	1.0
$\bar{3}22$	3.68	0.0421	0.3
$\bar{3}32$	4.55	0.0464	6.5
$\bar{3}52$	5.63	0.044	4.5
$\bar{3}23$	5.65	0.0565	6.0
$\bar{1}11$	6.45	0.175	3.5
$\bar{3}43$	6.97	0.0568	3.2
$\bar{2}32$	7.16	0.0800	0.1
$\bar{3}53$	7.28	0.0530	0.1
$\bar{1}21$	7.50	0.147	6.0
$\bar{2}52$	7.60	0.0641	0.1
$\bar{1}31$	7.63	0.113	4.0
$\bar{1}41$	7.60	0.0885	4.5

TABLE III (*continued.*)

<i>hkl.</i>	Distance from central spot.	$f(\lambda).$	Intensity.
$\bar{1}5\bar{1}$	7.52	0.0716	0.3
$\bar{1}6\bar{1}$	7.48	0.0602	4.5
$\bar{1}8\bar{1}$	7.32	0.0449	0.5
$\bar{4}1\bar{5}$	5.50	0.0397	0.2
$\bar{4}3\bar{5}$	7.10	0.0470	2.0
$\bar{4}5\bar{5}$	8.00	0.0465	0.2
$\bar{3}\bar{1}4$	3.60	0.0335	0.5
$\bar{3}34$	7.95	0.0638	4.5
$\bar{3}54$	8.70	0.0583	1.5
$2\bar{1}\bar{3}$	3.70	0.0470	20.0
$\bar{2}3\bar{3}$	9.25	0.0917	3.4
$\bar{3}4\bar{5}$	9.60	0.0629	1.0
$\bar{3}2\bar{5}$	8.37	0.0629	4.0
$\bar{1}\bar{1}2$	10.05	0.187	3.3
$\bar{3}0\bar{5}$	6.20	0.0514	5.5
$\bar{1}0\bar{2}$	7.15	0.147	4.5
$\bar{3}0\bar{7}$	7.75	0.0466	1.5
$\bar{1}0\bar{3}$	9.00	0.129	3.5
$\bar{1}0\bar{5}$	10.85	0.0948	2.8
$3\bar{1}\bar{6}$	6.00	0.0497	0.5
$\bar{2}\bar{1}\bar{5}$	6.65	0.0678	4.0
$\bar{2}\bar{1}\bar{7}$	8.25	0.0512	2.5
$\bar{1}\bar{1}2$	3.80	0.074	13.0
$\bar{1}\bar{1}\bar{3}$	6.10	0.085	1.5
$\bar{1}\bar{1}4$	7.65	0.0835	4.5
$\bar{1}\bar{1}6$	9.30	0.0679	4.0

TABLE IV.—DATA FROM THE THIRD UNSYMMETRICAL LAUE PHOTOGRAPH.

<i>hkl.</i>	Distance from central spot.	$f(\lambda).$	Intensity.
$52\bar{3}$	3.61	0.0495	1.0
$43\bar{3}$	3.37	0.0550	1.8
$31\bar{2}$	2.95	0.0693	1.5
$41\bar{3}$	2.30	0.0401	0.5
$32\bar{3}$	2.00	0.0388	0.5
$11\bar{1}$	2.50	0.1305	2.5
$34\bar{3}$	2.90	0.0446	1.5
$12\bar{1}$	3.30	0.1195	2.0
$13\bar{1}$	3.55	0.0946	1.0
$14\bar{1}$	3.62	0.0760	1.0
$16\bar{1}$	3.70	0.0535	1.0
010	3.55	0.3210	2.0
$\bar{1}6\bar{1}$	3.05	0.0465	1.8
$\bar{1}4\bar{1}$	2.80	0.0628	3.5
$15\bar{2}$	2.25	0.0335	0.6
$05\bar{1}$	2.20	0.0408	3.5
$13\bar{2}$	1.58	0.0399	3.0
$03\bar{1}$	1.50	0.0455	8.0
$\bar{1}30$	1.15	0.0355	2.0

TABLE IV (continued).

hkl .	Distance from central spot.	$f(\lambda)$.	Intensity.
$\bar{1}11$	0.95	0.0528	2.5
$\bar{2}13$	1.20	0.0310	1.5
$\bar{1}02$	1.20	0.0513	1.5
$\bar{1}21$	2.00	0.0782	3.2
$\bar{2}53$	3.05	0.0464	2.0
$\bar{2}33$	2.40	0.0485	5.0
$\bar{1}22$	3.40	0.1035	1.5
$\bar{2}35$	3.55	0.0518	2.0
$\bar{2}15$	2.45	0.0414	3.0
$\bar{1}13$	3.40	0.0915	1.0
$\bar{1}05$	3.30	0.0569	2.0
$\bar{1}03$	2.30	0.0671	4.0
$\bar{1}14$	1.85	0.0404	2.0
$0\bar{1}1$	0.72	0.0482	20.0
$0\bar{1}2$	2.30	0.0929	4.5
$0\bar{1}3$	3.15	0.0870	1.5
$0\bar{1}5$	4.00	0.0657	1.0
$1\bar{3}2$	1.20	0.0310	1.8
$1\bar{2}1$	1.28	0.0485	15.0
$2\bar{3}1$	1.45	0.0358	1.5
$1\bar{3}4$	2.45	0.0429	2.2
$1\bar{2}5$	4.20	0.0626	1.0
$1\bar{2}3$	3.30	0.0754	1.0
$2\bar{3}5$	4.10	0.0542	0.5
$2\bar{3}3$	3.05	0.0559	1.6
$3\bar{4}3$	2.75	0.0417	0.7
$3\bar{3}2$	3.35	0.0599	1.4
$2\bar{2}1$	2.90	0.1010	0.5
$1\bar{1}0$	1.55	0.1010	15.0
$4\bar{3}1$	3.35	0.0549	1.0
$3\bar{2}1$	1.50	0.0364	2.0
$5\bar{3}0$	3.10	0.0452	1.0
$2\bar{1}0$	3.70	0.136	0.7
$5\bar{2}1$	3.10	0.0482	1.0
$4\bar{1}1$	3.60	0.070	10.0
$2\bar{1}\bar{1}$	1.35	0.0512	15.0
$3\bar{1}\bar{2}$	1.20	0.0300	2.0
$5\bar{1}2$	2.80	0.0447	1.5
$20\bar{1}$	3.05	0.1175	1.8

Calculations from the Laue Photographs.—The symmetry of cesium dichloro-iodide is that of the point group D_3^d .¹ The spectrum measurements indicate that the fundamental lattice is Γ_{rh} . There are 2 groups of D_3^d which have Γ_{rh} as the lattice, D_{3d}^5 and D_{3d}^6 . The fact that planes having two odd and one even indices are effective in the first order shows that the cell must be body-centered. The simplest body-centered cell which possesses the new face diagonal axes contains one molecule. The

¹ A. Schönflies, *loc. cit.*, pp. 95, 475.

arrangement of the atoms within a unit rhombohedron containing one molecule of cesium dichloro-iodide is shown in Fig. 5, the cesium atom being placed at the origin, the iodine atom in the center and the 2 chlorine atoms along the diagonal joining them. This arrangement may be considered as a special case of D_{3d}^5 . The coördinates of these points will be: Cs (0, 0, 0); I ($a/2$, $a/2$, $a/2$); Cl (α/a , α/a , α/a); ($-\alpha/a$, $-\alpha/a$, $-\alpha/a$); where α/a is some fractional part of a , the length of a side of the rhombohedron.

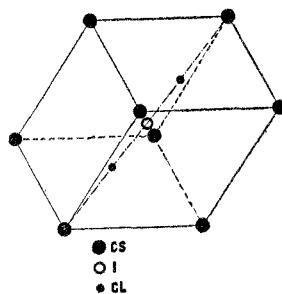


Fig. 5.

Assuming this arrangement for the atoms in the unit of structure for cesium dichloro-iodide, the intensity of reflection of the X-rays from any plane can be considered as proportional to the sum of the squares of 2 terms:

$$A^2 + B^2 \propto \text{Intensity.}$$

$$A = \text{Cs} \cos 2\pi n(hx + ky + lz) + \text{I} \cos 2\pi n(hx_1 + ky_1 + lz_1) + \text{Cl} \cos 2\pi n(hx_2 + ky_2 + lz_2) + \text{Cl} \cos 2\pi n(hx_3 + ky_3 + lz_3).$$

$$B = \text{Cs} \sin 2\pi n(hx + ky + lz) + \text{I} \sin 2\pi n(hx_1 + ky_1 + lz_1) + \text{Cl} \sin 2\pi n(hx_2 + ky_2 + lz_2) + \text{Cl} \sin 2\pi n(hx_3 + ky_3 + lz_3),$$

where n is the order of the reflection, hkl are the Miller indices of the reflecting plane, $x_n y_n z_n$ are the coördinates of the various atoms in the unit, and Cs, I and Cl represent the atomic numbers (or atomic weights) of these elements.

Introducing the values for $x_n y_n z_n$, these become

$$A = \text{Cs} \cos 2\pi n(0) + \text{I} \cos \pi n(h + k + l) + 2\text{Cl} \cos 2\pi n\alpha/a(h + k + l),$$

$$B = \text{Cs} \sin 2\pi n(0) + \text{I} \sin \pi n(h + k + l) + 0;$$

and these immediately reduce to

$$A = \text{Cs} \mp \text{I} + 2\text{Cl} \cos 2\pi n\alpha/a(h + k + l),$$

$$B = 0.$$

Two general cases arise when $n = 1$:

(1) When $(h + k + l)$ is odd.

$$A = \text{Cs} - \text{I} + 2\text{Cl} \cos 2\pi\alpha/a(h + k + l).$$

Because cesium and iodine would be expected to have about the same diffracting power, the chlorine atoms should be very effective. This will be the case with points having either all odd or 2 even and one odd indices.

(2) When $(h + k + l)$ is even.

$$A = \text{Cs} + \text{I} + 2\text{Cl} \cos 2\pi\alpha/a(h + k + l).$$

Points having 2 odd and one even indices fall in this class.

If $n = 2$ the effects of the cesium and iodine atoms will always add together.

To Determine the Position of Chlorine.—A few points will be found in the first order which do not have 2 odd and one even indices. These points fall into 3 groups according to the value of $(h + k + l)$.

$$\begin{aligned}(h + k + l) &= 1. \quad \bar{3}22, \bar{1}20, \bar{1}11, \bar{3}13, \bar{2}21. \\ &= 3. \quad 0\bar{4}\bar{1}, 13\bar{1}. \\ &= 5. \quad 34\bar{2}, \bar{2}61, \bar{1}60, \bar{3}53, \bar{2}52, \bar{1}51, 140.\end{aligned}$$

They should be especially effective for the placing of chlorine because it is to be expected that cesium and iodine will practically neutralize one another.

If various values are assigned to α/a in the preceding equations, there will be changes in A (the amplitude of the reflected beam) which can be represented by the series of curves of Fig. 6. In preparing these curves

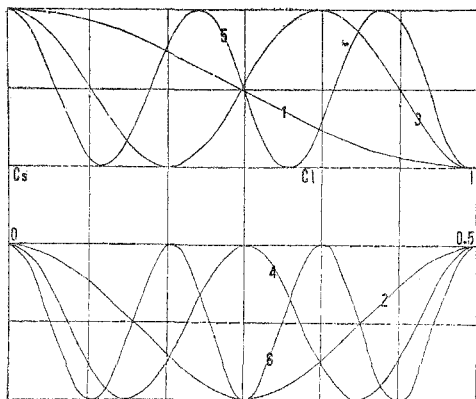


Fig. 6.

the constant value of $Cs - I$ has been neglected. The system of curves is thus symmetrical about its center point and consequently information derived from these curves will not be sufficient to settle between 2 possible positions of the chlorine atoms. In one of these positions the chlorine atoms will lie closer to the iodine atom than to the cesium atom; in the other this condition will be reversed. It will be assumed for the purposes

of calculation that the chlorine atoms lie closer to the iodine atom than to the cesium atom. If this is the case the curves show that the chlorine atoms must lie between $\alpha/a = 0.3$ and $\alpha/a = 0.4$ and between $\alpha/a = 0.6$ and $\alpha/a = 0.7$.

In one photograph the 2 points $05\bar{1}$ and $1\bar{3}4$, having approximately the same spacing, are produced by X-rays of the same length. Of these 2 spots $05\bar{1}$ is much more intense. Consequently planes for which $(h + k + l) = 4$ give larger effects than planes having $(h + k + l) = 2$. A consideration of spots due to $\bar{2}33$ and $2\bar{3}3$ and of spots due to $6\bar{3}1$ and $\bar{4}15$ leads to the same conclusion. This means that α/a must have a value about 0.3 rather than near to 0.4.

It is difficult to find points having approximately the same values for the spacing and different values of $(h + k + l)$ produced by X-rays of the same wave length. In order to place the chlorine atoms more accurately it is necessary to make use of the assumption, generally assumed to be correct, that the amplitude of the reflected X-ray wave is inversely

proportional to the spacing of the reflecting plane. Accepting this assumption a reduction of the form

$$\text{spacing} \times (\text{Cs} = 1 + 2\text{Cl} \cos 2\pi n\alpha/a(h + k + l))$$

can be used in comparing the amplitudes of the beams reflected from planes of different spacings.

Results from the first unsymmetrical photograph show that the intensity of reflection of X-rays of the same wave length by different planes is as follows:

<i>hkl</i> .	Intensity.	Relative spacing.	Amplitude.
13 $\bar{2}$	3.2	0.262 \times (260 + 71 ϵ)	= 68.1 + 18.2 ϵ
05 $\bar{1}$	3.0	0.198 \times (260 + 71 ϵ')	= 51.5 + 13.8 ϵ'
$\bar{1}4\bar{1}$	2.0	0.229 \times (260 + 71 ϵ)	= 59.5 + 16.0 ϵ
15 $\bar{2}$	2.0	0.183 \times (260 + 71 ϵ')	= 47.6 + 12.6 ϵ'
32 $\bar{3}$	0.5	0.206 \times (260 + 71 ϵ)	= 53.6 + 14.4 ϵ
		$\epsilon = \cos 2\pi\alpha/a \times 2,$	$\epsilon' = \cos 2\pi\alpha/a \times 4.$

Results from the second unsymmetrical photograph confirm those from the first. If the relative amplitudes of the X-rays are determined by substituting various values for α/a around 0.3 (the approximately determined position of chlorine) it is found that the observed intensity relations can be obtained only when α/a has a value from about 0.312 to about 0.317.

The following points are due to X-rays of the same wave length. The order of intensity is the order of writing:

<i>hkl</i> .	Relative spacing.	<i>h+k+l</i> .
0 $\bar{1}5$	0.198	4
1 $\bar{2}5$	0.183	4
2 $\bar{3}3$	0.206	2
$\bar{1}16$	0.171	6
$\bar{1}38$	0.129	10
$\bar{1}27$	0.148	8
3 $\bar{4}5$	0.139	4
0 $\bar{3}7$	0.128	4
019	0.120	10
4 $\bar{5}6$	0.124	6

The very favorable conditions for planes having $(h + k + l) = 10$ indicate that the chlorine atoms must lie near to 0.312 rather than to 0.317.

It is thus seen that the chlorine atoms must lie close to 0.31 of the length of the diagonal of the unit rhombohedron on either side of the cesium atom. This, of course, is on the assumption that the chlorine atoms lie nearer to the iodine atom. Since cesium and iodine have atomic weights so nearly equal (133 and 127), they must reflect X-rays to nearly the same extent if the generally accepted law of proportionality between reflecting power and atomic number is true. It then will be a very diffi-

cult matter to determine whether the chlorine atoms really lie nearer to the cesium or to the iodine atom.

When the arrangement of atoms in the unit of structure of cesium dichloro-iodide which we have obtained above is used for calculating the amplitudes of the X-rays reflected by various planes, there is a qualitative agreement with the observed intensities of the spots. Certain difficulties are met, however, if it is attempted to make this agreement quantitative. These attempts require the use of those assumptions, generally supposed true, which give the relation between intensity of reflection and spacing of like planes¹ and intensity of reflection and mass of the atom.²

The qualitative agreement is, however, so uniformly good that there can be little doubt as to the truth of the determination given here. The fact that this agreement is not quantitative points to the necessity, so many times urged before, for a careful and accurate investigation of the fundamental relations connecting reflection and spacing and reflection and weight of the reflecting atom.

This structure for cesium dichloro-iodide may be considered as closely analogous to that of sodium chloride and the other alkali halides. From this point of view the group (ICl₂) may be thought of as replacing the halogen of the simple compound. As a result of this substitution the unit cube is deformed into a rhombohedron by extension along the body diagonal.

The author wishes to express his thanks to Professor L. M. Dennis, who suggested this investigation, and to the Department of Physics for the use of the necessary apparatus. Most especially he is under great obligation to Dr. S. Nishikawa, whose untiring advice and aid has made this determination possible.

Summary.

The crystal structure of cesium dichloro-iodide (rhombohedral) has been determined. The body-centered unit rhombohedron contains one molecule. The cesium atom is placed either at the center or the corner of this unit and the iodine atom either at the corner or the center. Two chlorine atoms lie on the long diagonal of the rhombohedron very close to 0.31 of its length from the corners. Because of the *supposedly* very nearly equal scattering powers of cesium and iodine, it is impossible at present to decide which of these 2 possibilities is correct.

ITHACA, N. Y.

¹ W. H. Bragg and W. L. Bragg, *loc. cit.*, Chap. XI.

² W. H. Bragg and W. L. Bragg, *ibid.*, Chap. VIII.