2. The advantages of this method over others and methods of rendering the determinations more accurate, are discussed.

Moscow, Russia

[Contribution from the Gates Chemical Laboratory, California Institute of Technology, No. 59]

THE CRYSTAL STRUCTURES OF CESIUM TRI-IODIDE AND CESIUM DIBROMO-IODIDE

By Richard M. Bozorth and Linus Pauling

Received February 19, 1925 Published June 5, 1925

Introduction

About two years ago Clark and Duane[1] announced the discovery of certain peaks in a spectrometric study of the reflection of X-rays from crystals which they interpreted as due to X-rays characteristic of elements in the crystals and produced by such elements under the influence of the impinging beam, and reflected from the crystals at angles given by the relation $n\lambda = 2\,d \sin \theta$. They have since developed[2,3] a new method of crystal analysis based on this effect. The phenomena reported and the interpretations suggested are of interest from many view-points.[4] A further study by other investigators of the production and properties of these characteristic reflections seems therefore highly desirable.

One research of this character has already been published by Pauling and Dickinson.[5] The orthorhombic crystal of uranyl nitrate hexahydrate, $UO_2(NO_3)_2.6H_2O$, which had been investigated by Clark[3] and the results interpreted by the new method was further studied by means of spectral and Laue photographs with the aid of the theory of space-groups. This investigation led to the conclusions that the structure is not that given by Clark, and that his observed peaks were not produced by characteristic uranium L-radiation in the way designated by him. These results indicated the desirability of still further investigation.

Among the analyses reported in Ref. 2 are those of the orthorhombic crystals, cesium tri-iodide, CsI_3, and cesium dibromo-iodide, $CsIBr_2$. These crystals, are described by Groth[6] as orthorhombic bipyramidal,

---

[1] Clark and Duane, *Proc. Nat. Acad. Sci.*, **9**, 126 (1923).

[2] Clark and Duane, *J. Opt. Soc.*, **7**, 455 (1923).

[3] Clark, This Journal, **46**, 372 (1924).

[4] For example, R. W. G. Wyckoff in his monograph on "The Structure of Crystals" (The Chemical Catalog Co., New York, **1924**, p. 80) makes the following statement: "As yet the properties of this 'characteristic reflection' are incompletely understood; but its very existence and the opportunity it offers of producing distinctive diffraction effects from only a part of the atoms of a crystal make it of immediate interest and probably of great future value to crystal analysis."

[5] Pauling and Dickinson, This Journal, **46**, 1615 (1924).

[6] Groth, "Chemische Krystallographie," Engelmann, Leipzig, **1906**, vol. 1, p. 306.

with axial ratios 0.6824:1:1.1050 and 0.7203:1:1.667, respectively. Spectrometer measurements of X-radiation from a tube with tungsten anticathode reflected from the plane (100) of cesium tri-iodide were interpreted as showing the reflection of the general radiation with a strong cesium absorption edge and the characteristic lines cesium Kα and Kβ in the first, second, third and fourth orders, and also in one order the characteristic lines iodine Kα and Kβ. The authors then say, "From the angles and wave lengths substituted in the equation $n\lambda = 2\,d \sin \theta$, d_{100} for cesium is 4.50×10^{-8} cm., and for iodine 1.12×10^{-8} cm. Hence, planes containing iodine atoms are $^1/_4$ as far apart as those containing cesium atoms. The spectra of the 010 and 001 planes duplicate the spectrum of the 100 planes, except that the peaks occur at different angles......Since the iodine planes lie $^1/_4$ as far apart as the planes containing cesium atoms in all three directions, there is only one space distribution possible in the unit parallelepiped containing one molecule of cesium tri-iodide. This unit contains cesium atoms at each corner, and the three iodine atoms on the body diagonal at distances of $^1/_4$, $^1/_2$ and $^3/_4$ of its length; in other words, an iodine atom lies at the center of the parallelepiped, and one on each side of it, equidistant half-way between the center and a corner cesium atom. There is no evidence that the diagonals are all unidirectional in a crystal."

An arrangement similar to that given cesium tri-iodide is ascribed to cesium dibromo-iodide on the basis of similar data.

Particular importance attaches to the problem of proving or disproving the correctness of the interpretation of the experimental data for cesium tri-iodide, since these data afford one of the principal evidences of the reality of this phenomenon of characteristic reflection by crystals.[7] The problem has therefore been further investigated in this Laboratory by the usual X-ray methods.

The first research was made by one of the present authors (R. M. Bozorth) alone, in the first part of 1923. He studied cesium tri-iodide by means of spectral and Laue photographs, and determined its density. His results led to the conclusions that the unit of structure contains 4 CsI_3 (instead of 1 CsI_3 as concluded by Clark and Duane), and does not provide interplanar distances corresponding to those of Clark and Duane. No spots were found on the Laue photographs not consistent with this unit of structure. Moreover, the determined density, which was in good agreement with his own X-ray measurements, was much greater than that calculated from the data of Clark and Duane.

In view of the discordance of these results and conclusions with those of Clark and Duane, it was thought desirable to check them before publication, by independent measurements. Consequently, the other author of

---

[7] See, for example, Ref. 4, p. 159.

this paper (L. Pauling) in the spring of 1924 (after R. M. Bozorth had left this Laboratory) repeated and extended the X-ray investigations of cesium tri-iodide, and made a similar study of cesium dibromo-iodide. Pauling's work on cesium tri-iodide was done on a new preparation, and Bozorth's data were not available to him until after his measurements had been made and interpreted, and his results prepared, only the general nature of Bozorth's conclusions being known to him. The complete agreement in the data obtained and the conclusions drawn was not disclosed until December, 1924, when Bozorth submitted a report on his work to the Director of this Laboratory. Hence, the work reported in this paper represents the results of two distinct researches. To save space, the description of the experiments, the data, and their discussion have been incorporated in a single article.

We wish to express our thanks for financial aid received from a grant made by the Carnegie Institution of Washington to Professor A. A. Noyes, and to him for his assistance in the preparation of this article for publication.

The Experimental Method

Closely similar experimental methods were used in the two researches; the following detailed description of the crystals used refers to the second. Cesium hydroxide, prepared by adding an excess of freshly precipitated silver oxide to a solution of pure cesium chloride and filtering, was neutralized with hydriodic acid; the resulting cesium iodide solution was found to contain no silver or chlorine. Crystals of cesium tri-iodide were obtained by the slow evaporation over sulfuric acid of a solution in water and alcohol of this cesium iodide and about one-half of the stoichiometric amount of iodine.[8] These crystals were found on goniometric examination to show the forms {100}, {110}, {011} and {001}, to be tabular on {100}, elongated in the direction of the c-axis, and to have a pronounced cleavage on {001}, as described by Groth. Crystals of cesium dibromo-iodide obtained similarly from an aqueous solution of cesium iodide and bromine showed the forms {100}, {110} and {102}, were tabular on {100} and cleaved along {001}. Extinction of polarized light was observed in the direction of the three axes.

Spectral photographs were taken of the K-radiation of molybdenum either by reflection from a developed face or by transmission through a crystal plate less than 0.1 mm. thick. The data in Table I were made with the spectral apparatus equipped with a slotted screen rotating at twice the angular velocity of the crystal in order to prevent reflections from all planes but one from striking the photographic plate. Laue photographs were taken with the incident beam at various small angles with the normal

---

[8] Wells and Penfield, *Am. J. Sci.*, (3) **47**, 463 (1894).

to (100) (Pauling), (001), (110), etc. (Bozorth), using the general radiation from a tube with a tungsten anticathode operated at a peak voltage of 52 kv., corresponding to a minimum wave length of about 0.24 Å. for X-rays in the spectrum. Indices were assigned to the Laue spots with the help of gnomonic projections.

TABLE I

SPECTRAL DATA FOR CESIUM TRI-IODIDE. (BOZORTH)

(*hkl*)	Order of reflection	Line[a]	Angle of reflection	d/n	Estimated intensity[b]
(100)	n	γ	5° 11′	3.43 Å.	
	n	β	5 18	3.415	ms
	n	α	5 57	3.415	
	$2n$	β	10 39	3.415	
	$2n$	α_1	11 59	3.41	m
	$2n$	α_2	12 3	3.41	
	$3n$	β	16 7	3.41	
	$3n$	α_1	18 8	3.41	w
	$3n$	α_2	18 14	3.415	
(001)	n	α	3 44	5.46	vw
	$2n$	γ	6 28	5.50	
	$2n$	β	6 36	5.49	m
	$2n$	α	7 24	5.51	
	$3n$	α	11 8	5.51	w
(110)	n	α	3 40	5.55	w
	$2n$	α	7 16	5.61	mw
	$3n$	β	9 42	5.62	
	$3n$	α_1	10 53	5.62	m
	$3n$	α_2	10 57	5.62	
	$4n$	..	....	..	a
	$5n$	α_1	18 19	5.63	
	$5n$	α_2	18 28	5.62	w

[a] In this and following tables the following X-ray lines are indicated: γ, Mo Kγ, λ = 0.6197 Å.; β, Mo Kβ, λ = 0.6311 Å.; α_1, Mo Kα_1, λ = 0.7078 Å.; α_2, Mo Kα_2, λ = 0.7121 Å.; α, mean of α_1 and α_2, λ = 0.710 Å.

[b] The abbreviations signify: s, strong; ms, medium strong; m, medium; mw, medium weak; w, weak; vw, very weak; a, absent. In this table the estimated intensities refer to the Mo K spectrum as a unit.

The Units of Structure

Spectral data for cesium tri-iodide are given in Tables I and II. In the second research, Table II, at least two reflections from different crystals were taken from each pinacoid. These data lead to values of d/n of 3.40 Å. for (100), 5.00 for (010), and 5.51 for (001). Similarly, the spectral data in Table III lead to values of d/n for cesium dibromo-iodide of 3.285 Å. for (100), 4.59 for (010), and 5.33 for (001). It will be noticed that there is a pronounced similarity between the spectra from the tri-iodide and those from the dibromo-iodide.

It was found that, in order to account for the production of observed

Table II

Spectral Data for Cesium Tri-iodide. (Pauling)

(*hkl*)	Order of reflection	Line	Angle of reflection	*d*/*n*	Estimated intensity
(100)	*n*	β	5° 20.3′	3.392 Å.	mw
	n	α	5 59.3	3.403	s
	2*n*	γ	10 30.6	3.398	vw
	2*n*	β	10 41	3.401	w
	2*n*	α_1	12 0.3	3.403	m
	2*n*	α_2	12 4.5	3.405	mw
	3*n*	α_1	18 11	3.403	vw
	3*n*	α_2	18 17.6	3.403	vw
(010)	*n*	β	3 37	5.000	w
	n	α	4 4	5.008	m
	2*n*	β	7 15	4.998	vw
	2*n*	α	8 9	5.006	mw
(001)	*n*	α	3 42	5.505	vw
	2*n*	β	6 35	5.506	w
	2*n*	α_1	7 23	5.509	m
	2*n*	α_2	7 24.6	5.518	mw
	4*n*	α_1	14 54.6	5.500	vw

Table III

Spectral Data for Cesium Dibromo-iodide. (Pauling)

(*hkl*)	Order of reflection	Line	Angle of reflection	*d*/*n*	Estimated intensity
(100)	*n*	γ	5° 24′	3.294 Å.	w
	n	β	5 30	3.294	m
	n	α_1	6 10.7	3.290	s
	n	α_2	6 12.4	3.293	ms
	2*n*	γ	10 53.5	3.279	vw
	2*n*	β	11 5.2	3.281	mw
	2*n*	α_1	12 26.6	3.284	ms
	2*n*	α_2	12 31.4	3.286	m
	3*n*	β	16 45.4	3.283	vw
(010)	*n*	β	3 56.3	4.593	m
	n	α	4 26	4.592	s
	2*n*	β	7 54.7	4.585	vw
	2*n*	α	8 53.7	4.591	mw
(001)	*n*	β	3 24	5.322	vw
	n	α	3 48.7	5.339	w
	2*n*	β	6 48	5.329	m
	2*n*	α	7 38.3	5.341	s
	3*n*	α	11 34	5.315	vw

Laue spots by X-rays known to be present in the incident beam, one must assign a value of 2 to *n* for each pinacoid of each crystal. The resultant unit of structure in each case contains four molecules; the density of cesium tri-iodide from X-ray measurements is 4.51 g. per cc., and that of the dibromo-iodide is 4.29, in agreement with the carefully determined value 4.47 g. per cc. for the tri-iodide (Bozorth) and the approximate value 4.2 for the dibromo-iodide, both obtained by pycnometer methods.

The spectral data for cesium tri-iodide in Table I (first research), combined with Laue data, require that the unit of structure have $d_{100} = 6.83$ Å., $d_{010} = 9.89$ and $d_{001} = 11.00$. The value given for d_{010} was obtained indirectly from the data from (100) and (110), and is probably less accurate than the others.

No reflection occurred on any of the eight or ten completely analyzed Laue photographs that was not accounted for by these units of structure. Representative Laue data for the two crystals are given in Tables IV,

TABLE IV

LAUE PHOTOGRAPHIC DATA FOR CESIUM TRI-IODIDE; REFLECTIONS FROM BIPYRAMIDAL FORMS. (BOZORTH)

hkl	d_{hkl} Å.	$n\lambda$ Å.	Estimated intensity	*hkl*	d_{hkl} Å.	$n\lambda$ Å.	Estimated intensity
156	1.33	0.43	0.6	183	1.17	0.43	2.5
147	1.31	.42	.9	190	1.10	.40	0.2
165	1.31	.42	.6	1.0.10	1.10	.41	1.0
128	1.31	.42	.15	1.1.10	1.09	.40	0.02
138	1.26	.42	2.5	191	1.09	.40	.15
182	1.20	.41	1.3	192	1.08	.39	.4

TABLE V

LAUE PHOTOGRAPHIC DATA FOR CESIUM TRI-IODIDE; REFLECTIONS FROM BIPYRAMIDAL PLANES. (PAULING)

(Photograph No. 2. Incident beam 3.5° from normal to (100). Crystal thickness, 0.06 mm.)

hkl	d_{hkl} Å.	$n\lambda$ Å.	Estimated intensity	*hkl*	d_{hkl} Å.	$n\lambda$ Å.	Estimated intensity
$14\bar{7}$	1.31	0.36	0.5	$1\bar{2}9$	1.17	0.50	0.5
$1\bar{4}\bar{7}$	1.31	.46	2.5	$18\bar{3}$	1.17	.27	.3
$1\bar{2}\bar{8}$	1.30	.41	0.2	183	1.17	.35	.4
$14\bar{8}$	1.19	.29	.4	$1\bar{8}\bar{3}$	1.17	.44	3
$1\bar{4}\bar{8}$	1.19	.37	1.2	1.3.11	0.95	.32	0.1
148	1.19	.45	3.5	$1.\bar{3}.11$	.95	.35	.2
129	1.17	.47	0.8	297	.88	.43	.1

TABLE VI

LAUE PHOTOGRAPHIC DATA FOR CESIUM DIBROMO-IODIDE; REFLECTIONS FROM BIPYRAMIDAL PLANES. (PAULING)

(Photograph No. 1. Incident beam 0.5° from normal to (100). Crystal thickness 0.06 mm.)

hkl	d_{hkl} Å.	$n\lambda$ Å.	Estimated intensity	*hkl*	d_{hkl} Å.	$n\lambda$ Å.	Estimated intensity
157	1.17	0.36	absent	$1\bar{4}\bar{8}$	1.14	0.44	0.5
$15\bar{7}$	1.17	.40	0.05	129	1.13	.36	absent
$1\bar{5}7$	1.17	.42	.05	$1\bar{2}9$	1.13	.38	0.1
148	1.14	.35	.15	$12\bar{9}$	1.13	.41	.1
$14\bar{8}$	1.14	.39	.5	297	0.84	.37	absent
$1\bar{4}8$	1.14	.40	.6	$29\bar{7}$	.84	.40	0.05

V and VI. The values of $n\lambda$ were calculated on the basis of these units of structure by means of the equation

$$n\lambda = 2\sin\theta \Big/ \sqrt{\left(\frac{h}{d_{100}}\right)^2 + \left(\frac{k}{d_{010}}\right)^2 + \left(\frac{l}{d_{001}}\right)^2}$$

The values given for d/n for these units are substantiated by the varying intensities of Laue spots produced by planes of the same form, which have, of course, the same structure factor. For example, in Table V the intensity of the spot produced by reflection from the plane (1.3.11) of X-rays of wave length 0.32 Å. is on account of absorption by cesium only one-half as great as that of the spot due to reflection from $(1.\bar{3}.11)$ at wave length 0.35 Å. Similar variations in intensity show the influence of the iodine absorption edge and the absorption edge of the silver on the photographic plate (silver K abs. at 0.4850 Å.).

Discussion of the Previous Investigation and the New Method of Crystal Analysis

The dimensions of the units of structure of cesium tri-iodide and cesium dibromo-iodide as given by Clark and Duane and as found in the present researches are these:

	Cesium tri-iodide			*Cesium dibromo-iodide*	
	Clark-Duane	Bozorth	Pauling	Clark-Duane	Pauling
d_{100}	4.50 Å.	6.83 Å.	6.80 Å.	4.26 Å.	6.57 Å.
d_{010}	6.43	9.89[a]	10.00	5.91	9.18
d_{001}	7.04	11.00	11.02	6.90	10.66

[a] Determined indirectly from d_{100} and d_{110}.

In each case our values are larger than those of Clark and Duane by a factor of about 1.55. This discrepancy appears inexplicable except on the basis of an error in the interpretation of experimental data. The crystals used in the present researches were prepared according to the directions of Wells and Penfield, and the interfacial angles agree with previous determinations. Values of d/n for the pinacoids were obtained in the usual way by reflection from faces previously identified goniometrically. The units of structure obtained from these values and Laue data are further verified by their explanation of the variation of intensity of Laue spots produced by planes of the same form. Moreover, completely concordant results have been obtained by two of us, working independently. It accordingly appears extremely improbable that any serious error has been made in the investigations reported in this paper. Some further confirmation of this conclusion is afforded by the pronounced disagreement between the directly determined value for the density of cesium tri-iodide, 4.47 g. per cc., and that, 4.18, calculated for the unit of structure of Clark and Duane.

If these results are accepted the conclusions must be drawn (1) that the units of structure previously given for cesium tri-iodide and the dibromo-iodide are not those actually possessed by these crystals; and (2) that the interpretation of the earlier observations as showing that there is reflection of characteristic radiation from the pinacoids of these crystals cannot be correct, since this interpretation necessitates interplanar distances for the pinacoids[9] which cannot be reconciled with those here reported.

Now that investigations have, as we believe, shown the incorrectness of the structures of the three crystals uranyl nitrate hexahydrate, cesium tri-iodide, and cesium dibromo-iodide determined for the first time by the proposed method of crystal analysis utilizing characteristic secondary X-radiation, this method, in its present state at least, cannot be regarded as suitable for determining the structures of crystals.[10]

The Space Lattice and the Space Group

One observes by reference to the Laue data in Tables IV, V and VI that planes with one or two indices even, with the sum of all three indices even, and with the sum of any two indices even reflect in the first order. This shows[11] that the lattice underlying the structure cannot be face-centered, body-centered or end-centered, and is accordingly the simple orthorhombic lattice Γ_0. It is possible to distinguish between the holohedral space-groups V_h^1 to V_h^{16} (2 Di–1 to 2 Di–16) inclusive built on this lattice[12] by a consideration of the reflections from prism planes. A tabulation is given here of the types of prism planes which cannot give first-order reflections in the case of arrangements derived from each of these space groups.[13]

Space group	Odd order reflections do not occur from the following planes
V_h^1	....
V_h^2	$h = 0$ with $k + l$ odd; $k = 0$ with $h + l$ odd; $l = 0$ with $h + k$ odd
V_h^3	h or $k = 0$ with l odd
V_h^4	$h = 0$ with k odd; $k = 0$ with h odd; $l = 0$ with $h + k$ odd

---

[9] It might be contended that the indices assigned by Clark and Duane to the planes from which they obtained reflections are incorrect; but their data cannot be considered to show the reflection of characteristic radiation from *any* planes within these crystals, since there are no planes possessing the required interplanar distances.

[10] Since this article was submitted for publication, a paper has been published by Armstrong, Duane and Havighurst (*Proc. Nat. Acad. Sci.*, **11**, 218 (1925)) in which they conclude that the peaks reported by Clark and Duane were due to reflection in the usual ways from small crystals with axes slightly displaced from those of the main crystal. They state that no abnormal curves corresponding to the reflection of characteristic radiation of iodine, etc., were obtained with perfect crystals.

[11] Ref. 5, p. 1617.

[12] R. W. G. Wyckoff, "The Analytical Expression of the Results of the Theory of Space-Groups," *Carnegie Inst. Pub.*, No. 318, **1922**.

[13] Similar space-group criteria are given by (a) Niggli, "Geometrische Kristallographie des Discontinuums," Borntraeger, Leipzig, **1919**, p. 496, by (b) Astbury and Yardley, *Phil. Trans.*, **224A**, 221 (1924), and by (c) Wyckoff, *Am. J. Sci.*, 9, 145 (1925).

V_h^5 $k = 0$ with l odd
V_h^6 $h = 0$ with k odd; $k = 0$ with $h + l$ odd; $l = 0$ with $h + k$ odd
V_h^7 $k = 0$ with $h + l$ odd; $l = 0$ with h odd
V_h^8 $h = 0$ with k odd; $k = 0$ with l odd; $l = 0$ with k odd
V_h^9 $h = 0$ with k odd; $k = 0$ with h odd
V_h^{10} $h = 0$ with l odd; $k = 0$ with l odd; $l = 0$ with $h + k$ odd
V_h^{11} $k = 0$ with h odd; $l = 0$ with k odd
V_h^{12} $h = 0$ with $k + l$ odd; $k = 0$ with $h + l$ odd
V_h^{13} $l = 0$ with $h + k$ odd
V_h^{14} $h = 0$ with $k + l$ odd; $k = 0$ with l odd; $l = 0$ with h odd
V_h^{15} $h = 0$ with k odd; $k = 0$ with l odd; $l = 0$ with h odd
V_h^{16} $k = 0$ with $h + l$ odd; $l = 0$ with k odd

TABLE VII

LAUE PHOTOGRAPHIC DATA FOR CESIUM TRI-IODIDE; PRISM REFLECTIONS. (PAULING)

hkl	d_{hkl} Å.	$n\lambda$ Å.	Estimated intensity	*hkl*	d_{hkl} Å.	$n\lambda$ Å.	Estimated intensity
Photograph No. 1				Photograph No. 2			
014	2.66	0.47	10	$10\bar{9}$	1.20	0.32	a
015	2.12	.44	10	$1.\overline{10}.0$	0.99	.33	a
043	2.07	.33	1	$2.0.\overline{11}$	.96	.46	a
150	1.92	.28	1.3	2.0.13	.82	.46	a
$10\bar{6}$	1.77	.36	3	$3.0.\overline{14}$	.75	.40	0.2
270	1.32	.46	a[a]	Photograph No. 3			
074	1.27	.28	0.2	$1\bar{6}0$	1.62	.32	a
$20\bar{9}$	1.15	.41	a	$2\bar{9}0$	1.06	.34	a
$0.\bar{3}.10$	1.05	.43	1	$3.\overline{10}.0$	0.92	.48	a
0.10.3	0.97	.30	0.2	1.11.0	.90	.48	0.3
$3.0.\overline{11}$	.92	.44	a	$3.\overline{11}.0$	.84	.39	0.1
1.0.13	.84	.45	a	1.12.0	.83	.42	a
1.0.14	.78	.41	0.2	1.13.0	.76	.38	0.1

[a] a signifies absent.

TABLE VIII

LAUE PHOTOGRAPHIC DATA FOR CESIUM DIBROMO-IODIDE; PRISM REFLECTIONS (PAULING)

hkl	d_{hkl} Å.	$n\lambda$ Å.	Estimated intensity	*hkl*	d_{hkl} Å.	$n\lambda$ Å.	Estimated intensity
$04\bar{1}$	2.34	0.40	0.2	019	1.17	0.32	0.6
$1\bar{5}0$	1.84	.56	2.5	$20\bar{9}$	1.11	.47	a
$10\bar{6}$	1.71	.46	4	1.0.10	1.05	.57	0.5
061	1.58	.41	2.5	190	1.05	.54	0.15
$1\bar{6}0$	1.55	.34	a	$2\bar{9}0$	1.02	.36	a
056	1.30	.43	1	1.0.11	0.96	.38	a
065	1.28	.42	2	$3.0.\overline{10}$	.96	.61	0.1

It will be seen from the Laue data for cesium tri-iodide given in Table VII that all types of planes with $h = 0$ reflect in the first order, planes with $k = 0$ do so only when l is even, and those with $l = 0$ only when $h + k$ is even. The types of planes observed to reflect definitely preclude the possibility of the space group being V_h^2, V_h^3, V_h^4, V_h^6, V_h^7, V_h^8, V_h^9,

V_h^{10}, V_h^{11}, V_h^{12}, V_h^{14} or V_h^{15}. Of the remaining space groups V_h^1 does not require any prism planes to give no first-order reflections and V_h^5 and V_h^{13} require this only of planes in one prism zone. It is accordingly probable[14] that the space group V_h^{16}, (2 Di$^-$16), which is in complete agreement with the observed reflections, is to be assigned to cesium tri-iodide. It is to be noted that the transformation $h = h_{SG}$, $k = l_{SG}$, and $l = k_{SG}$ is required to change from indices (hkl) based on the crystallographic axes given by Groth and used throughout this paper to those $(hkl)_{SG}$ based on the assignment of axes to V_h^{16} in the course of the development of the theory of space groups.

Laue data from cesium tri-iodide very similar to those in Table VII were obtained in the first research. On the basis of them exactly the same conclusions were previously independently drawn regarding the space-group symmetry of this crystal.

Prism reflections from cesium dibromo-iodide as given in Table VIII are seen to place this crystal in the same space-group as that of the tri-iodide; the same transformation equations are required to change the axes to those conforming to space-group convention.

Because of the number of parameters involved, it does not seem practicable at this time to attempt to determine the location of the atoms in the units of structure.

Summary

Orthorhombic crystals of cesium tri-iodide and cesium dibromo-iodide have been studied by means of spectral and Laue photographs and interpreted with aid of the theory of space groups, by the two authors of this paper, working independently. The unit of structure of cesium tri-iodide was found to have $d_{100} = 6.83$ Å., $d_{010} = 9.89$ and $d_{001} = 11.00$ by the first research; and $d_{100} = 6.80$ Å., $d_{010} = 10.00$ and $d_{001} = 11.02$ by the second research. That of the dibromo-iodide was found to have $d_{100} = 6.57$ Å., $d_{010} = 9.18$ and $d_{001} = 10.66$. In the crystals of each substance there are four molecules in the unit.

The observed Laue reflections require that the structures be based on the simple orthorhombic lattice Γ_0; and a consideration of the reflections from prism planes makes it probable that the crystals are to be assigned to the space-group V_h^{16}.

The dimensions of the units of structure and the number of molecules in each as found for cesium tri-iodide and cesium dibromo-iodide in these researches are entirely different from those previously determined for them by Clark and Duane by means of their new method of crystal analysis.

---

[14] If the morphological evidence underlying the crystallographic assignment of CsI_3 to the orthorhombic holohedry is not conclusive, the criteria do not distinguish between V_h^{16} and C_{2v}^9, which requires that no first-order reflections occur with $h = 0$, $k + l$ odd and with $k = 0$, h odd. The criteria given by Niggli for C_{2v}^9 are incorrect.

Moreover, if the results of this paper are accepted, the experimental peaks observed by Clark and Duane cannot have been produced by the reflection of characteristic cesium and iodine radiation from planes of these crystals.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

A HYDROGEN LIQUEFYING CYCLE AND CRYOSTAT FOR THE MAINTENANCE OF LOW TEMPERATURES

BY WENDELL M. LATIMER, RALPH M. BUFFINGTON[1] AND HOWARD D. HOENSHEL

RECEIVED FEBRUARY 24, 1925 PUBLISHED JUNE 5, 1925

A combined hydrogen liquefier and cryostat of simple design has been developed in this Laboratory for carrying out such experiments as the measurements of specific heat, coefficients of expansion and electrical resistance at the temperatures of liquid and solid hydrogen. A brief description of the apparatus with the auxiliary liquefying system will be given in this paper.

When liquid hydrogen is used as a cooling agent by submerging an object in the liquid, the available cooling is due entirely to the heat of vaporization of the hydrogen. If, however, advantage is taken of the low heat content of the hydrogen evaporating from the liquid by passing this gas over the coils of the hydrogen liquefier, the effective cooling may be increased by the production of a larger amount of liquid hydrogen. The increased cooling which may be obtained amounts to the difference in temperature, 85–20°, multiplied by the average specific heat, 6 cal. per degree, or about 390 cal. per mole. The heat of vaporization of hydrogen is 240 cal. per mole, and the effective cooling is thus increased from 240 to 630 cal. For this reason it is advantageous when possible to build a small liquefier in connection with the object to be cooled. Such a system also obviates the necessity of storing liquid hydrogen and the losses which occur in transferring the liquid from the container to other vessels. It is such a combination[2] of liquefier and cryostat that is to be described.

Preparation and Purification of Hydrogen

The source of the greatest difficulties in the liquefaction of hydrogen is the maintenance of a supply of hydrogen free from small amounts of oxygen and nitrogen. The purity required depends upon the size of the valve orifice and the rate of flow of the high-pressure gas, but in general it has been our experience that with impurities in excess of 0.05% it is difficult to avoid plugging the orifice with solids. We have been unable to purchase pure hydrogen, due mainly to the fact that the commercial hydrogen obtainable in this locality is used for oxy-hydrogen torches and is mixed with coal gas to

---

[1] National Research Fellow in Chemistry.

[2] A similar combination of somewhat different design is described by Nernst, *Z. Elektrochem.*, **17**, 735 (1911).