THE DETERMINATION WITH X-RAYS
OF THE
STRUCTURES OF CRYSTALS

Thesis

by

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THE CRYSTAL STRUCTURE OF MOLYBDENITE

By Roscoe G. Dickinson[1] and Linus Pauling

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The mineral molybdenite, MoS_2, is described[2] as occurring in hexagonal crystals with a very complete basal cleavage. A study of its crystal structure has been carried out using X-ray spectral photographs and Laue photographs treated as previously described.[3] Since the crystals bend very easily and inelastically, some difficulty was experienced in obtaining good Laue photographs. However, the following procedure resulted in very satisfactory photographs: a crystal considerably thicker than the desired section was selected and one surface cleaved away; the cleavage face was then cemented to a cover glass and the specimen thus supported cleaved to the desired thickness and photographed without removal from the glass. A Laue photograph taken with the incident beam normal to the basal plane possessed a hexagonal axis and 6 symmetry planes. Several photographs were made with the beam somewhat inclined to this position.

The Unit of Structure

Angles of reflection of the molybdenum Kα radiation from the faces (0001), $(10\bar{1}0)$, and $(11\bar{2}0)$ are given in Table I. The reflections from the last two faces were obtained by transmission of the beam through the crystal; in these cases the α doublet was not resolved. A density determination carried out with a pycnometer using benzene gave the value 4.92 g./cc. From this the number of molecules in a unit having $d_{0001} = 6.15$ Å. and $d_{10\bar{1}0} = 2.73$ is found to be 0.988. The axial ratio of this unit is 1.95; correspondingly the angle between the faces $(20\bar{2}1)$ and (0001) should be 77° 28.6′. Direct observations[2] have given values from 70° 28′ to 77° 13′, the last being the usually accepted value.

Table I

Reflection Data from Molybdenite

$h\ i\ k\ l$	λ	Observed angle of reflection	$\frac{I}{n} \times d_{hikl}$	Relative intensities	S $u = 0.621$
(0001)	0.7078	3° 18′	$\frac{1}{2} \times 12.32$	strong	5.05
....	....	6° 37′	$\frac{1}{4} \times 12.28$	weak	1.27
....	....	9° 56′	$\frac{1}{6} \times 12.32$	medium	5.85
....	....	13° 19′	$\frac{1}{8} \times 12.28$	med. strong	9.17
....	....	16° 43′	$^1/_{10} \times 12.30$	med. weak	4.26
$(10\bar{1}0)$	0.7085	7° 27′	$^1/_1 \times 2.73$	....	..
$(11\bar{2}0)$	0.7085	13° 25′	$^1/_1 \times 1.53$	....	..

When indices were assigned to the Laue spots on a basis of this unit, values of $n\lambda$ as low as 0.13 Å. were found. As the minimum wave length

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[1] National Research Fellow in Chemistry.

[2] Hintze, "Handbuch der Mineralogie," Viet and Co., Leipzig, **1904,** vol. 1, p. 410.

[3] Dickinson, This Journal, **44,** 276 (1922).

present was about 0.24 Å., this unit is not possible. A unit having d_{0001} = 12.30 Å. and an axial ratio 3.90 and containing, therefore, 2 MoS_2 gave no impossible values of $n\lambda$; this unit is the smallest one possible and all of the indices used in the remainder of this paper refer to its axes.

The Arrangement of the Atoms

Reference to a tabulation[4] of the coördinates of equivalent points in space groups isomorphous with the point-groups D_{3h}, C_{6v}, D_6, and D_{6h} shows that there is a variety of ways of arranging 2 MoS_2 in an hexagonal unit in such a way that the molybdenum atoms are in equivalent positions, and likewise the sulfur atoms. Some of these arrangements can be obtained by placing 1 MoS_2 in the smaller unit shown to be impossible. Excluding these, the following distinct arrangements remain.

	Mo at	S at
1.	$(\frac{1}{3}\frac{2}{3}0)$ $(\frac{2}{3}\frac{1}{3}0)$	$(\frac{1}{3}\frac{2}{3}u)$ $(\frac{1}{3}\frac{2}{3}\bar{u})$ $(\frac{2}{3}\frac{1}{3}u)$ $(\frac{2}{3}\frac{1}{3}\bar{u})$
2.	$(00v)$ $(00\bar{v})$	$(\frac{1}{3}\frac{2}{3}u)$ $(\frac{1}{3}\frac{2}{3}\bar{u})$ $(\frac{2}{3}\frac{1}{3}u)$ $(\frac{2}{3}\frac{1}{3}\bar{u})$
3.	(000) $(00\frac{1}{2})$	$(\frac{1}{3}\frac{2}{3}u)$ $(\frac{2}{3}\frac{1}{3}\bar{u})$ $(\frac{1}{3},\frac{2}{3},\frac{1}{2}-u)$ $(\frac{2}{3},\frac{1}{3},\frac{1}{2}+u)$
4.	$(00\frac{1}{4})$ $(00\frac{3}{4})$	$(\frac{1}{3}\frac{2}{3}u)$ $(\frac{2}{3}\frac{1}{3}\bar{u})$ $(\frac{1}{3},\frac{2}{3},\frac{1}{2}-u)$ $(\frac{2}{3},\frac{1}{3},\frac{1}{2}+u)$
5.	$(\frac{1}{3}\frac{2}{3}\frac{1}{4})$ $(\frac{2}{3}\frac{1}{3}\frac{3}{4})$	$(00u)$ $(00\bar{u})$ $(0,0,\frac{1}{2}+u)$ $(0,0,\frac{1}{2}-u)$
6.	$(\frac{1}{3}\frac{2}{3}\frac{1}{4})$ $(\frac{2}{3}\frac{1}{3}\frac{3}{4})$	$(\frac{1}{3}\frac{2}{3}u)$ $(\frac{2}{3}\frac{1}{3}\bar{u})$ $(\frac{1}{3},\frac{2}{3},\frac{1}{2}-u)$ $(\frac{2}{3},\frac{1}{3},\frac{1}{2}+u)$

Arrangements 1 and 2 make it difficult to account for the absence of odd orders from (0001), and the absence of all first orders from planes having $\frac{1}{3}(h + 2i)$ integral and l odd. Any of the remaining arrangements accounts for the above observations.

The value of $S = \sqrt{A^2 + B^2}$ for planes having $\frac{1}{3}(h + 2i)$ not integral and l odd is always 2 $\overline{\text{Mo}}$ for Arrangement 3; therefore, at a given wave length such planes should always reflect more weakly the smaller the value of d/n. This is not at all in accord with the Laue photographic data, hence Arrangement 3 is impossible.

From (0001) the eight order was slightly stronger than the sixth and much stronger than the fourth. Assuming that a molybdenum atom has at least twice the reflecting power of a sulfur atom (the respective atomic numbers are 42 and 16) it can readily be shown that these (0001) intensities necessitate giving u a value between 0.11 and 0.15 or between 0.61 and 0.65 in Arrangements 4, 5, and 6. On Laue photographs, planes of the forms $\{31\bar{4}5\}$ and $\{31\bar{4}3\}$ were found to reflect much more strongly than $\{31\bar{4}1\}$ in spite of their smaller spacings. The value of S for these planes is given by $S = 2\,\bar{S}[\cos 2\pi(\frac{1}{3} + lu) + \cos 2\pi(\frac{1}{3} - lu)]$ for either Arrangment 4 or 5. The possible values of u make S differ only moderately for these 3 forms and never in such a way that the first 2 are both greater than the third. Hence Arrangements 4 and 5 are impossible.

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[4] Wyckoff, "The Analytical Expression of the Results of the Theory of Space-Groups," *Carnegie Inst. Publ.*, **318** (1922).

For Arrangement 6 the values of S are given by the following equations.

Class 1: $\frac{1}{3}(h + 2i)$ integral, l even.

$$n = 1;\ S = 2\,\overline{\text{Mo}} + 4(-1)^{\frac{l}{2}}\,\overline{\text{S}}\cos 2\pi l\,\text{u}$$

Class 2: $\frac{1}{3}(h + 2i)$ not integral, l even.

$$n = 1;\ S = \overline{\text{Mo}} - 2(-1)^{\frac{l}{2}}\,\overline{\text{S}}\,[\cos 2\pi(\tfrac{1}{3} + l\,\text{u}) + \cos 2\pi(\tfrac{1}{3} - l\,\text{u})]$$

Class 3: $\frac{1}{3}(h + 2i)$ integral, l odd.

$$n = 1;\ S = 0.$$

$$n = 2;\ S = 2\,\overline{\text{Mo}} - 4\,\overline{\text{S}}\cos 4\pi\,l\,\text{u}$$

Class 4: $\frac{1}{3}(h + 2i)$ not integral, l odd.

$$n = 1;\ S = \sqrt{3}\,\overline{\text{Mo}} + 2(-1)^{\frac{l+1}{2}}\,\overline{\text{S}}\,[\cos 2\pi(\tfrac{1}{3} + l\,\text{u}) - \cos 2\pi(\tfrac{1}{3} - l\,\text{u})]$$

For $0.11 < \text{u} < 0.15$ the calculated value of S for $\{31\bar{4}1\}$ is much greater than for $\{31\bar{4}5\}$ and $\{31\bar{4}3\}$, but is much less in the range $0.61 < \text{u} < 0.65$; this range, then, contains the only possible values of u. The value of u may be more closely fixed by the consideration of other data.

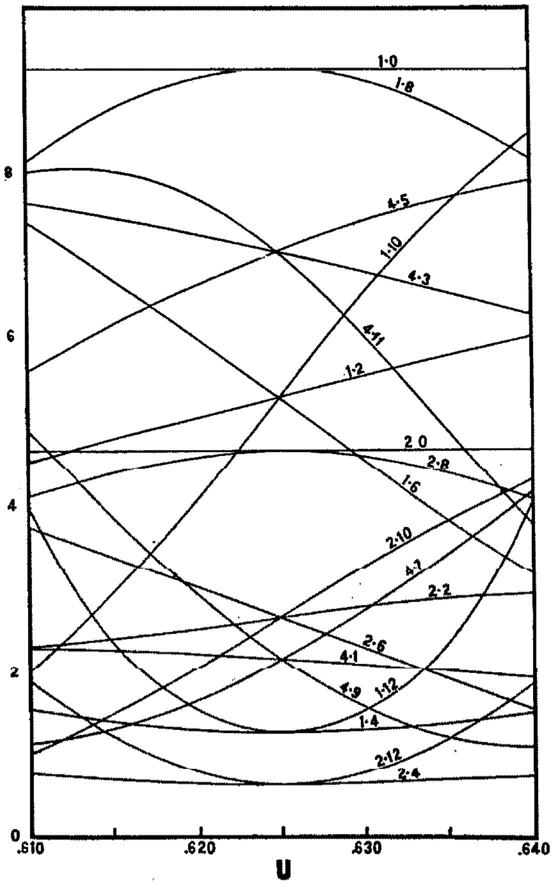

Fig. 1.—Values of S for values of u between 0.61 and 0. 64 calculated for Arrangement 6, placing $\overline{\text{S}} = 1$. The first number on each curve indicates the class of plane and the second the value of l. Thus 4 – 5 is the curve for any plane of Class 4 having $l = 5$.

In Fig. 1 are shown values of S for various planes plotted against values of u in the range $0.61 < \text{u} < 0.65$; in the calculation of these, $\overline{\text{Mo}}$ and $\overline{\text{S}}$ have been taken proportional to the respective atomic numbers. It was found that $\{33\bar{6}.10\}$ reflected considerably more strongly than $\{14\bar{5}.12\}$; therefore, u is appreciably greater than 0.614. Also $\{23\bar{5}9\} \geq \{23\bar{5}7\}$; therefore, u is probably slightly less than 0.625. From these and similar data the value of u is taken as 0.621 ± 0.004. All of the Laue photographic data treated in the above manner were found to be in agreement with the values of S calculated using $\text{u} = 0.621$; when, however, comparisons were made between planes of different classes, requiring a more accurate knowledge of $\overline{\text{Mo}}$ and $\bar{\text{S}}$, the agreement was not so good, although on the whole satisfactory. The extent of this agreement is illustrated by typical data given in Table II.

Table II

Laue Photographic Data from Molybdenite

Incident beam 8° 20′ from normal to (0001). Crystal thickness 0.23 mm.

h i k l	Class	$n\lambda$	*d*	Estimated intensity	*S* u = 0.621
$\bar{2}021$	4	0.37	1.36	3.2	2.17
$\bar{1}\bar{2}31$	4	.40	1.03	1.4	2.17
$3\bar{1}\bar{2}2$	2	.38	1.02	0.8	2.53
$\bar{3}213$	4	.34	1.00	6.0	7.18
$\bar{2}3\bar{1}4$	2	.37	0.98	0.15	0.64
$03\bar{3}5$	3	.37	.85	0.0	0
$4\bar{2}\bar{2}3$	3	.36	.77	0.0	0
$3\bar{4}12$	2	.38	.75	0.3	2.53
$\bar{4}225$	3	.39	.75	0.0	0
$\bar{3}\bar{1}43$	4	.36	.74	2.6	7.18
$31\bar{4}5$	4	.34	.72	2.0	6.68
$24\bar{2}7$	3	.40	.72	0.0	0
$\bar{4}316$	2	.38	.71	0.3	2.93
$\bar{1}4\bar{3}7$	4	.36	.70	0.3	1.70
$2\bar{5}33$	4	.36	.62	1.0	7.18
$5\bar{3}\bar{2}5$	4	.37	.61	1.0	6.68
$1\bar{5}43$	3	.34	.59	0.0	0
$\bar{5}237$	4	.37	.59	0.15	1.70
$\bar{1}\bar{4}54$	1	.37	.59	0.15	1.27
$\bar{5}328$	2	.37	.58	0.2	4.58
$\bar{4}\bar{1}56$	1	.37	.57	0.6	5.85
$23\bar{5}9$	4	.36	.57	0.2	2.71
$\bar{5}147$	3	.36	.56	0.0	0
$41\bar{5}8$	1	.34	.56	0.8	9.17
$\bar{4}5\bar{1}.10$	1	.34	.54	0.3	4.26
$\bar{1}5\bar{4}.12$	1	.39	.52	faint	0.72
$3\bar{6}35$	3	.36	.51	0.0	0
$2\bar{6}45$	4	.35	.50	0.3	6.68
$\bar{6}33.10$	1	.34	.48	0.15	4.26
$\bar{6}24.11$	4	.37	.47	0.2	7.58

Discussion of the Structure

The arrangement found to account for X-ray data from molybdenite is shown in Fig. 2. This arrangement is derivable from the space group D_{6h}^4 as well as from the space groups D_{3h}^4, D_6^6, C_{6h}^2, and D_{3d}^2. Considering the atoms as points or spheres, the structure then has holohedral hexagonal symmetry.

Small, very thin crystals of molybdenite may be made by fusing together ammonium molybdate, sulfur and potassium carbonate.[5] We have ex-

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[5] Guichard, *Ann. chim. phys.*, [7] 23, 552 (1901). Hintze, Ref. 2, p. 418, also mentions trigonal artificial crystals.

amined crystals made by this method and have found them to be frequently triangular rather than hexagonal plates. Such a face development is not to be expected if the symmetry is that of the hexagonal holohedry. Several explanations of this apparent discrepancy are possible: (1) The artificial crystals may have a structure different from that of the natural mineral; satisfactory Laue photographs from the artificial crystals were not obtainable to decide this point. (2) The structure may be the same in both cases and the natural crystals twinned so as to simulate the higher symmetry; however, we have not found it possible to account for the X-ray data on this hypothesis. (3) Although the structure found has holohedral symmetry for the positions of the atoms, it may have a 3-fold symmetry axis when the shapes of the atoms or the bonds between them are considered. That this is a possible explanation follows immediately from the fact that the structure is derivable from the space group D_{3h}^4 or D_{3d}^2.

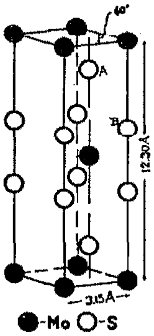

Fig. 2.—Arrangement of the atoms in molybdenite, MoS_2.

In the structure found, each sulfur atom is equidistant from 3 molybdenum atoms, and each molybdenum atom is surrounded by six equidistant sulfur atoms at the corners of a small triangular prism whose altitude is 3.17 ± 0.10 and whose edge is 3.15 ± 0.02. The distance from the molybdenum atom to these nearest sulfur atoms is then 2.41 ± 0.06. This distance is in good agreement with Bragg's hypothesis of constant atomic radii.[6] Taking the radius of molybdenum as 1.36, which is half the distance between the atoms in the metal (Wyckoff[7] has shown this to be consistent with the distances in silver molybdate, Ag_2MoO_4), and the radius of sulfur 1.05 as given by Bragg, the sum is 2.41. On the other hand, the 2 sulfur atoms marked A and B in Fig. 2, which should also be in contact on Bragg's hypothesis, are at a distance of 3.49 Å., while constant radii require 2.10. These relations are analogous to those found in cadmium iodide,[8] and in tin tetra-iodide.[9] This great distance between sulfur atoms is undoubtedly connected with the excellent basal cleavage of molybdenite.

Summary

The mineral molybdenite has been investigated by means of spectral and Laue photographs and, with the aid of the theory of space groups, the simplest structure capable of accounting for the X-ray data has been derived. This structure, which is of a new type, contains 2 MoS_2 in an hexagonal unit having d_{0001} = 12.30 Å. and an axial ratio 3.90. The molyb-

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[6] W. L. Bragg, *Phil. Mag.*, **40,** 180 (1920).

[7] Wyckoff, *Proc. Nat. Acad. Sci.*, 9, 35 (1923).

[8] Bozorth, THIS JOURNAL, **44,** 2235 (1922).

[9] Dickinson, *ibid.*, **45,** 961 (1923).

denum atoms are at $(\frac{1}{3}\frac{2}{3}\frac{1}{4})$ $(\frac{2}{3}\frac{1}{3}\frac{3}{4})$ and the sulfur atoms at $(\frac{1}{3}\frac{2}{3}u)$ $(\frac{2}{3}\frac{1}{3}\bar{u})$ $(\frac{1}{3},\frac{2}{3},\frac{1}{2}-u)$ $(\frac{2}{3},\frac{1}{3},\frac{1}{2}+u)$ where $u = 0.621 \pm 0.004$.

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THE CRYSTAL STRUCTURE OF MAGNESIUM STANNIDE

By Linus Pauling

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Introduction

The temperature-composition diagram[1] of the binary system, magnesium-tin, shows a pronounced maximum corresponding to the composition Mg_2Sn. This compound is described[2] as cubic with octahedral habit and complete octahedral cleavage. For the purpose of obtaining information regarding the nature of intermetallic compounds, crystals of magnesium stannide, Mg_2Sn, have been investigated by means of X-rays, resulting in a complete determination of their structure. No crystal structure determination for an intermetallic compound has been previously reported.

By melting the calculated amounts of magnesium and tin in an iron crucible under a mixture of potassium and magnesium chlorides, and cooling slowly, a mass of magnesium stannide was obtained from which individual crystals could be cleaved. The X-ray data were obtained from Laue and spectral photographs, treated as described by Dickinson.[3] I wish to express my thanks to Dr. Roscoe G. Dickinson for his advice and active interest in this research.

The Determination of the Structure

Spectral data from a (111) face of a crystal of magnesium stannide are given in Table I. Using the value of 3.591 for the density,[2] these data place $n^3/m = 0.248$ for the first reflection. No reflections were found on the Laue photographs with values of $n\lambda$ less than 0.26 Å. U., calculated for the unit containing four Mg_2Sn, with $n = 1$, and $d_{100} = 6.78 \pm 0.02$ Å. U.

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[1] Kurnakow and Stepanow, *Z. anorg. Chem.*, **46**, 177 (1905).

[2] Sustschinsky, *Z. Krist.*, **38**, 265 (1904).

[3] Dickinson, This Journal, **44**, 276 (1922).

As the lower limit of X-rays present in the spectrum was 0.24 Å. U., a larger unit of structure is not indicated.

A symmetrical Laue photograph through the (111) face showed a trigonal axis and three reflection planes; consequently only arrangements derived from point-groups T_d, O and O_h were treated. No planes but those with all indices odd gave values of $n\lambda$ less than 0.50, although a large number of other planes were in positions favorable for reflection, so treatment was given only to arrangements based on a face-centered lattice. There are three ways[4] of arranging $4Mg_2Sn$ with these restrictions, irrespective of any assumptions regarding the equivalence of atoms of one element. These are

I Sn at 000, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$
Mg at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, $\frac{1}{4}\frac{1}{4}\frac{3}{4}$, $\frac{1}{4}\frac{3}{4}\frac{1}{4}$, $\frac{3}{4}\frac{1}{4}\frac{1}{4}$, $\frac{3}{4}\frac{3}{4}\frac{3}{4}$, $\frac{3}{4}\frac{3}{4}\frac{1}{4}$, $\frac{3}{4}\frac{1}{4}\frac{3}{4}$, $\frac{1}{4}\frac{3}{4}\frac{3}{4}$
II Sn at 000, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$
Mg at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, $\frac{3}{4}\frac{1}{4}\frac{3}{4}$, $\frac{1}{4}\frac{3}{4}\frac{3}{4}$, $\frac{3}{4}\frac{3}{4}\frac{1}{4}$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}00$, $0\frac{1}{2}0$, $00\frac{1}{2}$
III Sn at 000, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$
Mg at $\frac{3}{4}\frac{3}{4}\frac{3}{4}$, $\frac{3}{4}\frac{1}{4}\frac{1}{4}$, $\frac{1}{4}\frac{1}{4}\frac{3}{4}$, $\frac{1}{4}\frac{3}{4}\frac{1}{4}$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}00$, $0\frac{1}{2}0$, $00\frac{1}{2}$

The intensity of the third order (111) reflection is greater than that of the second order, and the structure factor, $S = \sqrt{A^2 + B^2}$, must be greater for the third order. For Arrangements II and III, the corresponding values are

$$n = 2, \quad A = 4\overline{\mathrm{Sn}}, \quad B = 0; \quad n = 3, \quad A = 4\overline{\mathrm{Sn}} - 4\overline{\mathrm{Mg}}, \quad B = \pm 4\overline{\mathrm{Mg}}.$$

On the very safe assumption that an atom of tin scatters X-rays more strongly than an atom of magnesium, the value of S for the third order is less than that for the second order, eliminating these two arrangements.

For Arrangement I reflecting planes may be divided into three classes, which have the following values of S.

Class I: *hkl* one odd, two even; $n = 1$, $S = 0$; $n = 2$, $S = 4\overline{\mathrm{Sn}} - 8\mathrm{Mg}$
Class II: *hkl* all odd; $n = 1$, $S = 4\overline{\mathrm{Sn}}$
Class III: *hkl* two odd, one even; $n = 1$, $S = 0$; $n = 2$, $S = 4\overline{\mathrm{Sn}} + 8\overline{\mathrm{Mg}}$.

On the previously made assumption regarding relative reflecting powers, the values for the structure factor of the classes of planes increase in this

Table I

Reflection Data for Mg_2Sn, (111) Face

X-rays reflected Å. U.	Angle of reflection	$\frac{d_{111}}{n}$ Å. U.	I_{observed}	S
$Mo\beta_1 = 0.6311$	4° 37′	3.918	strong	$4\overline{\mathrm{Sn}}$
$Mo\alpha_1 = 0.7078$	5° 11′	3.921		
$Mo\beta_1$	9° 16′	$^1/_2 \times 3.920$	weak	$4\overline{\mathrm{Sn}} - 8\overline{\mathrm{Mg}}$
$Mo\alpha_1$	10° 20′	$^1/_2 \times 3.913$		
$Mo\beta_1$	14° 3′	$^1/_3 \times 3.899$	medium	$4\overline{\mathrm{Sn}}$
$Mo\alpha_1$	15° 46′	$^1/_3 \times 3.913$		
$Mo\beta_1$	18° 52′	$^1/_4 \times 3.902$	medium	$4\overline{\mathrm{Sn}} + 8\overline{\mathrm{Mg}}$

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[4] Wyckoff, "The Analytical Expression of the Results of the Theory of Space Groups," *Carnegie Inst. Pub.*, 1922.

order: I, II, III. Intensity data showing the extent of the agreement with this structure are given in Tables I and II. In comparing intensities of two planes reflecting at the same wave length, if the intensity of the plane with the smaller value of d/*n* is larger than that of the other, the structure factor of the first must be greater than that of the second. No intensity relations not accounted for by the above arrangement were observed.

TABLE II

LAUE PHOTOGRAPHIC DATA FOR Mg_2Sn. INCIDENT BEAM 12° 30′ FROM NORMAL TO (111)

hkl	$\frac{d_{kkl}}{n}$ Å. U.	λ Å. U.	I_{observed}	Class	*hkl*	$\frac{d_{kkl}}{n}$ Å. U.	λ Å. U.	I_{observed}	Class
$13\bar{3}$	1.52	0.28	2.8	II	$41\bar{2}$	0.74	0.29	0.08	I
$\bar{1}\bar{1}2$	1.38	.30	8	III	$91\bar{3}$	.71	.32	.3	II
$\bar{5}11$	1.30	.31	2.4	II	$\bar{7}71$	.68	.34	.2	II
$\bar{1}5\bar{3}$	1.15	.36	2.4	II	$50\bar{1}$	.67	.33	.4	III
$30\bar{1}$	1.07	.33	2.6	III	$\bar{1}9\bar{5}$	.66	.28	.14	II
$03\bar{2}$	0.94	.33	0.5	I	052	.63	.45	.4	I
$2\bar{3}1$	.91	.26	.4	III	$\overline{11}.1.\bar{1}$	.61	.32	.12	II
$35\bar{5}$	.88	.26	.2	II	$11.1.\bar{1}$	.61	.46	.5	II
$71\bar{3}$	.88	.31	.6	II	$11.1.\bar{3}$	.59	.31	.10	II
$\bar{3}7\bar{3}$	.83	.30	.5	II	$\bar{4}33$	.58	.48	1.0	III
$17\bar{5}$	.78	.30	.4	II					

Discussion of the Structure

The structure determined for magnesium stannide is the one known as the calcium fluoride arrangement.[5] It places eight magnesium atoms around each tin atom at the corners of a cube, and four tin atoms around each magnesium atom at tetrahedron corners. The sum of the atomic radii of magnesium[6] and tin[7] obtained from the distance between atoms in the metals is 3.01 Å. U. (from gray tin) or 2.80 (from white tin); the closest approach of tin and magnesium atoms in magnesium stannide is 2.94 ± 0.01. There is no similarity in the way in which an atom of tin or magnesium is surrounded by other atoms in the metals and in this compound.

Crystals of sodium cadmide, $NaCd_2$, reported from goniometrical measurements as cubic, were prepared by the method of Kurnakow.[8] Each of several Laue photographs taken from three different crystals with the beam perpendicular to an octahedral face showed a 3-fold symmetry axis lying in three symmetry planes. The photographs were, however, so complicated that it was not found possible to assign indices with certainty to many of the spots even on the symmetrical photographs. It was accordingly not possible to determine the apparently very complex structure.

[5] W. H. and W. L. Bragg, *Proc. Roy. Soc.*, **89A**, 474 (1913).

[6] Hull, *Phys. Rev.*, [2] **10**, 661 (1917).

[7] Bijl and Kolkmeier, *Proc. Acad. Sci. Amsterdam*, **21**, 494 (1919).

[8] Kurnakow, *Z. anorg. Chem.*, **23**, 459 (1900).

In view of the lack of a simple valence relation between the atoms, complex atom-groups may be formed in sodium cadmide in a way similar to the formation of Pb_2^- ions in a solution of sodium plumbide, $NaPb_2$, in liquid ammonia,[9] preventing a simplicity of structure.

Summary

Crystals of the intermetallic compound magnesium stannide, Mg_2Sn, have been prepared and investigated by means of Laue and spectral photographs with the aid of the theory of space-groups. The intermetallic compound has been found to have the calcium fluoride structure, with $d_{100} = 6.78 \pm 0.02$ Å. U. The closest approach of tin and magnesium atoms is 2.94 ± 0.01 Å. U.

PASADENA, CALIFORNIA

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[9] Kraus, THIS JOURNAL, 29, 1557 (1907).

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THE CRYSTAL STRUCTURE OF URANYL NITRATE HEXAHYDRATE

By Linus Pauling and Roscoe G. Dickinson

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Introduction

Uranyl nitrate hexahydrate, $UO_2(NO_3)_2.6H_2O$, readily forms rhombic bipyramidal crystals whose axial ratios are given[1] as 0.8737:1:0.6088. The reflections from three faces of this crystal of the X-radiation from a tube with a tungsten anticathode have been investigated by Clark[2] using an ionization spectrometer. From the face (010) he obtained superposed on the general radiation a number of peaks which he interpreted as being due to the characteristic L-radiation of uranium excited in the crystal and reflected by it. For instance, when the incident beam made the angle 1°32′ with the crystal face he found a peak which he takes as $L\gamma_1$ (wave length 0.61283 Å.). Substituting these values in the equation $n\lambda = 2d\sin\theta$, one obtains $d_{010}/n = 11.45$ Å. This distance, 11.45 Å., Clark takes as the length of one of the edges of the unit parallelopiped. He obtained in a similar manner 7.93 and 13.01 Å. for the other two edges. He states that "the unit parallelopiped contains four molecules, as calculated from the density, 2.807. The uranium atoms are, therefore, at the corners and at the center of the faces....."

The conclusion that the structure is face-centered simply because there are four molecules in the unit is, however, unjustified; for the theory of space groups shows that numerous other arrangements with this number of molecules in the unit and with the requisite symmetry are possible. Moreover, this conclusion is not in agreement with Clark's assignment of wave lengths to his peaks. For, if the structure is face-centered, only odd orders of reflection can appear from the pinacoids; and if $d_{010} = 11.45$ Å., the smallest angle of reflection that can occur with a given wave length from (010) will be obtained from $n\lambda = 2d \sin\theta$ by placing $d = 11.45$ and $n = 2$; and for $\lambda = 0.61283$ Å. this smallest angle is 3°4′, not 1°32′.

Two possible reasons for this discrepancy suggest themselves: (1) the origin of the peaks may be other than that supposed by Clark, or (2) the structure may not be that given by him. Our own results, described below, indicate that both of these reasons are valid.

The investigation has been aided on the financial side from a grant made by the Carnegie Institution of Washington.

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[1] Groth, "Chemische Kristallographie," Engelmann, Leipzig, **2**, 142 (1908).

[2] Clark, This Journal, **46**, 379 (1924).

The Experimental Method

Crystals of the pure salt, $UO_2(NO_3)_2.6H_2O$, were dissolved in a small amount of water, and the solution was allowed to evaporate over sulfuric acid in a desiccator. For the identification of the faces on the resulting crystals interfacial angles were measured on a reflection goniometer, and the extinction directions observed in a polarizing microscope. The forms observed were those previously reported;[1] our crystals were, however, usually tabular on a $\{100\}_G$, rather than on b $\{010\}_G$. The subscript G is here placed on all indices which are based on the crystallographic axes given by Groth.[1]

Using the method of reflection from the face of a rotating crystal, spectral photographs of the radiation from a molybdenum target X-ray tube were obtained from the three pinacoids; (since $\{001\}_G$ was not developed on the crystals, the crystal was ground with fine carborundum in a plane normal to $\{100\}_G$ and $\{010\}_G$). The tube was operated at a peak voltage of 60 kv. At least two spectral photographs were made from each pinacoid with the crystal in different orientations.

Using a tungsten target tube operated at a peak voltage of 52 kv, Laue photographs were taken with the incident beam making small angles with the normals to $(100)_G$ and $(010)_G$. The indices corresponding to the spots occurring on these photographs were obtained from gnomonic projections.[3]

The density of the salt was determined by finding with a pycnometer the density of a liquid in which a small crystal remained suspended. Two such determinations gave for the density 2.744 and 2.740 g. per cc.

The Unit of Structure

The spectral data given in Table I lead to the following values of d/n: $(100)_G$, 5.71; $(010)_G$, 6.575; $(001)_G$, 2.005 Å. Examination of the indices and angles of reflection of a number of Laue spots showed that the smallest values which can be assigned to n to give an integral number of molecules in the unit and not to require that the Laue spots be produced by wave lengths below those known to be present in the general radiation are: $(100)_G$, $n = 2$; $(010)_G$, $n = 2$; $(001)_G$, $n = 4$. The smallest possible unit of structure accordingly has these values[4] of d: $(100)_G$, 11.42; $(010)_G$, 13.15; $(001)_G$, 8.02 Å., and contains 4 molecules. From the density, 2.742, the calculated number of $UO_2(NO_3)_2.6H_2O$ per unit is 3.90.

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[3] Wyckoff, *Am. J. Sci.*, **50**, 322 (1920).

[4] It will be observed that Clark's values can be brought into approximate agreement with ours by making a suitable permutation of indices. Whether this permutation is permissible is not clear. However, the facts described subsequently in this paper make this approximate agreement appear fortuitous.

TABLE I

SPECTRAL DATA FROM $UO_2(NO_3)_2.6H_2O$

$(hkl)_G$	Line	Observed angle of reflection	$\frac{d}{n}$	Relative intensities[a]
$(100)_G$	Mo$K\beta$	3° 10.4′	$^1/_2 \times 11.40$	m
	α	3 33.5	$^1/_2 \times 11.44$	s
	β	6 21.2	$^1/_4 \times 11.40$	vw
	α	7 7.6	$^1/_4 \times 11.43$	m
	β	9 33.0	$^1/_6 \times 11.42$	mw
	α_1	10 43.0	$^1/_6 \times 11.42$	ms
	α_2	10 45.2	$^1/_6 \times 11.44$	m
	β	12 45.7	$^1/_8 \times 11.42$	vw
	α_1	14 19.7	$^1/_8 \times 11.43$	mw
	α_1	18 2.7	$^1/_{10} \times 11.42$	w
$(010)_G$	β	2 44.5	$^1/_2 \times 13.17$	mw
	α	3 5.8	$^1/_2 \times 13.15$	s
	β	5 31.4	$^1/_4 \times 13.12$	m
	α	6 10.7	$^1/_4 \times 13.19$	vs
	β	8 16.8	$^1/_6 \times 13.15$	mw
	α	9 18.5	$^1/_6 \times 13.16$	ms
	β	11 4.3	$^1/_8 \times 13.14$	w
	α	12 27.7	$^1/_8 \times 13.16$	m
	β	13 53.5	$^1/_{10} \times 13.14$	w
	α_1	15 37.0	$^1/_{10} \times 13.16$	m
	α_1	15 43.4	$^1/_{10} \times 13.15$	mw
	β	16 47.0	$^1/_{12} \times 13.12$	vw
	α_1	18 53.3	$^1/_{12} \times 13.12$	w
$(001)_G$[b]	γ	8 53.6	$^1/_4 \times 8.02$	vw
	β	9 4.0	$^1/_4 \times 8.01$	m
	α_1	10 11.0	$^1/_4 \times 8.01$	s
	α_2	10 13.2	$^1/_4 \times 8.02$	ms

[a] The abbreviations are: vs, very strong; s, strong; ms, medium strong; m, medium; mw, medium weak; w, weak; vw, very weak.

[b] On several spectral photographs from $(001)_G$ taken with the crystal in different orientations, reflections were observed in the plane of the $(001)_G$ reflections which could not be accounted for as ordinary reflections from $(001)_G$; for example, a line of medium intensity at $\vartheta = 5° 22.2'$ and a weak line at 4° 47′. These reflections have been shown to be similar in their origin to the diffuse spots near the central image observed on some Laue photographs [Dickinson, *Phys. Rev.*, **22**, 199 (1923)]; these phenomena and their explanation will be the subject of a later paper.

The Space Lattice

The space lattice underlying the entire atomic arrangement can be determined by a consideration of the character of the indices of the planes giving first order reflections; for no first order reflections can occur in the following cases:

Lattice Γ_0''', face-centered; h, k, or l even.
Lattice Γ_0'', body-centered; $h + k + l$ odd.
Lattice Γ_0', end-centered on (001); $h + k$ odd.

Lattice Γ_0', end-centered on (010); $k + l$ odd.
Lattice Γ_0', end-centered on (100); $k + l$ odd.

In Table II are given representative data from one Laue photograph. Reference to these data shows that planes of each of these types except the last (those having $k + l$ odd) gave first order reflections. This fact definitely eliminates the face-centered and body-centered lattices. If the lattice were the simple one, Γ_0, no such general types of planes would fail to give first-order reflections, and this lattice would not account for the observed absence in the first order of planes having $k + l$ odd, many of which were in positions favorable to reflection. These absences are, however, accounted for by the lattice Γ_0' end-centered on $(100)_G$.

TABLE II

LAUE DATA FROM $UO_2(NO_3)_2.6H_2O$; PHOTOGRAPH NO. 8, THROUGH $(100)_G$

$(hkl)_G$	(hkl)	$n\lambda$ Å.	d Å.	Estimated intensity[a]	S for $u = 0.13$
104	041	0.44	1.97	0.05	1.25
$1\bar{1}4$	$\bar{1}41$	.43	1.94	a	0
$1\bar{6}2$	$\bar{6}21$	.45	1.89	8	9.98
124	241	.42	1.88	0.25	1.25
$1\bar{2}4$	$\bar{2}41$	.38	1.88	.25	1.25
153	$\bar{5}31$	.38	1.84	3.5	6.37
$1\bar{7}1$	$\bar{7}11$	.45	1.79	2.5	7.29
144	441	.35	1.69	0.05	1.25
163	631	.40	1.67	a	0
$1\bar{8}0$	$\bar{8}01$	.39	1.62	a	0
182	821	.37	1.51	3.5	9.98
$1\bar{8}\bar{2}$	$\bar{8}\bar{2}1$	.41	1.51	3.5	9.98
191	911	.37	1.42	1.3	7.29
$19\bar{1}$	$9\bar{1}1$	.44	1.42	1.2	7.29
$1\bar{8}\bar{3}$	$\bar{8}\bar{3}1$	.37	1.39	a	0
$1\bar{5}\bar{5}$	$\bar{5}\bar{5}1$	.43	1.35	1.4	8.09
1.10.0	10.0.1	.35	1.30	a	0
$1\bar{2}\bar{6}$	$\bar{2}\bar{6}1$	.44	1.29	1.5	9.82
$1.10.\bar{1}$	$10.\bar{1}.1$	.36	1.29	a	0
$1\bar{6}\bar{5}$	$\bar{6}\bar{5}1$	.39	1.28	a	0
$19\bar{3}$	$9\bar{3}1$	.39	1.27	0.8	6.37
$1\bar{3}\bar{6}$	$\bar{3}\bar{6}1$	.41	1.27	a	0
$18\bar{4}$	$8\bar{4}1$	.40	1.26	a	1.25
$2\bar{6}5$	$\bar{6}52$	.40	1.26	a	0
$1.10.\bar{2}$	$10.\bar{2}.1$	.36	1.24	1.8	9.98
$1\bar{4}\bar{6}$	$\bar{4}\bar{6}1$	.38	1.23	1.8	9.82
$14\bar{6}$	$4\bar{6}1$	.42	1.23	1.8	9.82
$17\bar{5}$	$7\bar{5}1$	.39	1.21	0.9	8.09
275	752	.41	1.19	.6	5.88
$2\bar{7}5$	$\bar{7}52$	.35	1.19	.7	5.88
$15\bar{6}$	561	.39	1.18	a	0
$19\bar{4}$	$9\bar{4}1$	.36	1.17	a	0
$1.10.\bar{3}$	$10.\bar{3}.1$	.34	1.17	a	0

TABLE II (*Concluded*)

$(hkl)_G$	(hkl)	$n\lambda$ Å.	d Å.	Estimated intensity[a]	S for $u = 0.13$
$18\bar{5}$	$8\bar{5}1$	.35	1.14	a	0
$16\bar{6}$	$6\bar{6}1$	.36	1.13	1.6	9.82
$11\bar{7}$	$1\bar{7}1$	.36	1.13	0.35	5.36
285	852	.37	1.12	a	0
$2.\overline{11}.2$	$\overline{11}.2.2$	.36	1.12	a	0
$13\bar{7}$	$3\bar{7}1$	.35	1.10	0.2	5.36
$2.\overline{11}.\bar{3}$	$\overline{11}.\bar{3}.2$	.42	1.07	.6	7.71
$2\bar{9}\bar{5}$	$\bar{9}\bar{5}2$	.45	1.06	.25	5.88
$3\bar{5}7$	$\bar{5}73$	.41	1.01	.25	5.36
$2.13.\bar{1}$	$13.\bar{1}.2$	.39	0.99	.2	6.85
367	673	.41	.98	a	0
$2.13.\bar{2}$	$13.\bar{2}.2$	.39	.97	a	0
377	773	.38	.94	0.15	5.36
$2.\overline{11}.\bar{5}$	$\overline{11}.\bar{5}.2$	.35	.94	.15	5.88
$2.13.\bar{3}$	$13.\bar{3}.2$	.37	.93	.15	7.71
$3.\overline{12}.4$	$\overline{12}.4.3$	.37	.93	a	1.25
3.14.0	14.0.3	.46	.91	a	0
3.10.6	10.6.3	.38	.91	0.35	9.82
$3.\overline{14}.\bar{2}$	$\overline{14}.\bar{2}.3$	.40	.89	.2	9.98

[a] a signifies absent.

Discussion of Previous Conclusions

The complete absence of all odd orders of reflection from the pinacoids (Table I) makes it difficult to interpret any of Clark's[2] peaks as first-order reflections from these faces. Moreover, as shown above, the Laue photographic data definitely show that the underlying lattice is the end-centered one; and this again necessitates the absence of odd orders of reflection from two pinacoids. This makes it clear that at least some of the peaks observed by Clark did not arise from the excitation of the L-radiation of uranium within the crystal and its reflection by the pinacoids; for, as shown in the introduction, this explanation would necessitate interpreting some of the peaks as first-order reflections. The belief that[5] "the unit parallelopiped.....is face-centered" is, moreover, not substantiated by the work described in this paper. It is evident that for purposes of crystal structure analysis further investigation of the phenomenon reported by Clark and Duane[6] is desirable.

The Space Group

The holohedral space groups derived from the lattice Γ_0' are[7] V_h^{17}, V_h^{18}, V_h^{19}, V_h^{20}, V_h^{21}, V_h^{22}. Some of these may be definitely excluded

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[5] Ref. 2, p. 384.

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

[7] Wyckoff, "The Analytical Expression of the Results of the Theory of Space-Groups," Carnegie Inst. Pub., No. **318** (1922).

by a consideration of reflections from *prism* planes.[8] Prism planes having $h + k + l$ even cannot reflect in the first order if the space group is V_h^{18}, V_h^{21}, or V_h^{22}; those having $h + k + l$ odd cannot reflect in the first order if the space group is V_h^{20} or V_h^{22}. The presence of reflections of both of these types, as shown in Table III, definitely eliminates all of these space groups. Of the remaining two space groups V_h^{17} and V_h^{19} the former permits first-order reflections from planes of only two prism zones, while the latter permits such reflections from all three. No first-order reflections from planes of the type $(hk0)_G$ were observed on any photograph, although a number of such planes were in positions favorable to reflection. The evidence is thus in favor[9] of V_h^{17} as opposed to V_h^{19}.

For convenience in applying the theory of space groups, and in comparing structures with each other, it is desirable to assign the axes in agreement with the conventions adopted during the development of the theory of space groups. The coördinates of equivalent positions for V_h^{17} as tabulated[7] require that no first-order reflections take place from planes with $h + k$ odd or with $k = 0$. If the axes of $UO_2(NO_3)_2.6H_2O$ be chosen such that $d_{100} = 13.15$, $d_{010} = 8.02$, and $d_{001} = 11.42$ Å., the structure will be in agreement with this tabulation. The transformation from indices $(hkl)_G$ to those (hkl) conforming with space group usage is $h_G = l$, $k_G = h$, and $l_G = k$.

TABLE III

LAUE DATA FROM $UO_2(NO_3)_2.6H_2O$. PHOTOGRAPH NO. 6, THROUGH $(010)_G$

$(hkl)_G$	(hkl)	$n\lambda$ Å.	d Å.	Estimated intensity
$\bar{3}02$	$02\bar{3}$	0.40	2.76	8
$\bar{7}20$	$20\bar{7}$	.41	1.58	a
$0\bar{1}5$	$\bar{1}50$	.31	1.58	0.8
$03\bar{5}$	$3\bar{5}0$	.40	1.50	.6
$\bar{8}30$	$30\bar{8}$	.54	1.36	a
$0\bar{1}6$	$\bar{1}60$	.30	1.32	a
902	029	.40	1.21	1.2
$\bar{5}06$	$06\bar{5}$	.30	1.15	0.6
$0\bar{1}7$	$\bar{1}70$	.30	1.13	.3
$05\bar{7}$	$5\bar{7}0$	.40	1.04	.3
11.2.0	2.0.11	.54	1.03	a
11.0.2	0.2.11	.32	1.01	0.4
$\overline{11}.4.0$	$4.0.\overline{11}$	.37	0.98	a
13.2.0	2.0.13	.41	.87	a
$\overline{13}.6.0$	$6.0.\overline{13}$	.43	.82	a
$\bar{7}30$	$30\bar{7}$	2 × 0.37	2 × 0.76	0.15

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[8] Niggli, "Geometrische Kristallographie des Discontinuums," Borntraeger, Leipzig, **1919**, p. 497.

[9] The absence of all odd orders of reflection from the three pinacoids is further evidence in favor of V_h^{17}; for V_h^{19} can give odd orders of reflection from one pinacoid while V_h^{17} can give odd orders from none.

The Arrangement of the Uranium Atoms

In view of the large number of parameters involved, it seems at present impracticable to attempt a determination of the positions of all of the atoms in the unit of structure. However, information can be obtained concerning the positions of the uranium atoms. Uranium has the atomic number 92; the sum of the atomic numbers of the other atoms in $UO_2(NO_3)_2.6H_2O$ is 138 and the highest of these is 8. Consequently, especially in the case of planes having complicated indices and small interplanar distances, the intensity of reflection may be expected to be governed largely by the positions of the uranium atoms. We have, indeed, found it possible to assign positions to the uranium atoms which give a very consistent agreement between the general character of the observed intensities and the structure factors S calculated, neglecting all atoms but those of uranium.

There are the three following ways of arranging the four uranium atoms in a unit with the space-group symmetry V_h^{17}: (*a*) 000, $00\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; (*b*) $\frac{1}{2}00$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}0$, $0\frac{1}{2}\frac{1}{2}$; (*c*) $0u\frac{1}{4}$, $0\bar{u}\frac{3}{4}$, $\frac{1}{2}\frac{1}{2}+u\ \frac{1}{4}$, $\frac{1}{2}\frac{1}{2}-u\ \frac{3}{4}$. If the uranium atoms alone are considered, and these without reference to their own symmetry, then (*a*) differs from (*b*) only by a translation of the whole structure along the H-axis, and (*c*) with $u = 0$ differs from (*a*) or (*b*) only by a translation of the whole structure; hence, in the present case, (*a*) and (*b*) are included in (*c*) and only the last need be considered. For first-order reflections (*c*) gives: $A = 4\bar{U} \cos 2\pi(uk + l/4)$; $B = 0$. In Fig. 1 are curves giving values of $S = \sqrt{A^2 + B^2}$ for a number of planes plotted against u from $u = 0$ to $u = 0.25$; this interval includes all distinct arrangements of the uranium atoms. The planes are divided into two classes: (1) those with l odd, and (2) those with l even. All planes of a given class with the same value of k have the same structure factor.

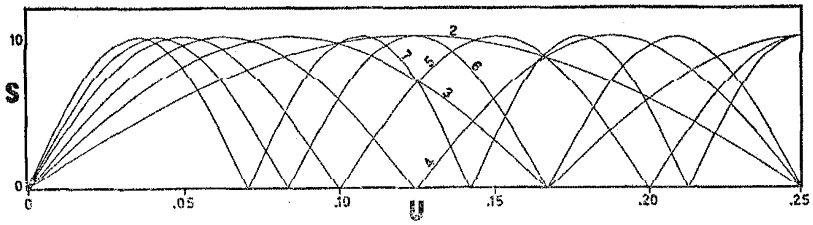

Fig. 1.—Values of S calculated for Arrangement *c*, with $4\bar{U} = 10$. The curves are for planes of Class 1, the number on the curve being the value of *k*. The curves also give values of S for planes of Class 2 with these values of *k* if *u* is made 0.25 at the left and 0 at the right of the figure.

Reference to the data of Table II shows that planes of Class 1 having $k = 4$ were found to reflect very weakly; those of Class 1 having $k = 2$ or

$k = 6$ reflected comparatively strongly. The structure factor due to the uranium atoms (Fig. 1) is in agreement with these facts only in the neighborhood of $u = 0.125$. A consideration of the reflections from other planes indicates for u a value near 0.13. Values of this structure factor for all planes of Table III are given in the 6th column. By comparing these values with the observed intensities it will be seen that this arrangement of the uranium atoms alone with $u = 0.13$ accounts satisfactorily for most of the abnormalities in intensity relations, and for all of the pronounced ones. If this value of u is altered by as much as 0.01 the agreement is in many cases destroyed.

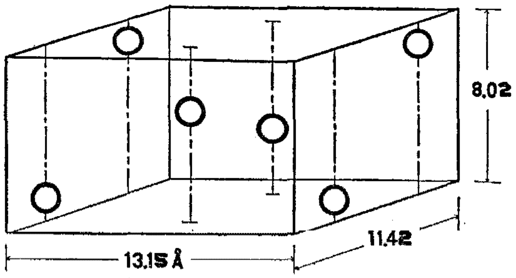

Fig. 2.—The arrangement of the uranium atoms in the unit of structure of uranyl nitrate hexahydrate, $UO_2(NO_3)_2.6H_2O$.

This arrangement of the uranium atoms in the unit of structure is shown in Fig. 2.

Summary

Crystals of uranyl nitrate hexahydrate, $UO_2(NO_3)_2.6H_2O$, have been investigated, using both spectral photographs of the molybdenum K-radiation and Laue photographs, and the data have been interpreted with the aid of the theory of space groups. The unit of structure, which contains four $UO_2(NO_3)_2.6H_2O$, has $d_{100} = 13.15$, $d_{010} = 8.02$, and $d_{001} = 11.42$ Å., and is end centered on (001). The data indicate that the space-group symmetry is V_h^{17}, and that the uranium atoms are at $(0u\frac{1}{4})$ $(0\bar{u}\frac{3}{4})$ $(\frac{1}{2}\frac{1}{2} + u\ \frac{1}{4})$ $(\frac{1}{2}\frac{1}{2} - u\ \frac{3}{4})$ with $u - 0.13$. Referred to the axes used by Groth,[1] the above-mentioned interplanar distances are for the planes $(010)_G$, $(001)_G$, and $(100)_G$, respectively.

These results make unjustifiable Clark's interpretation[2] of his observed peaks as due to a characteristic radiation of the uranium atoms reflected by the pinacoids.

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THE CRYSTAL STRUCTURES OF AMMONIUM FLUOFERRATE, FLUO-ALUMINATE AND OXYFLUOMOLYBDATE

By Linus Pauling

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Introduction

Crystals of ammonium fluo-aluminate $(NH_4)_3AlF$, fluotitanate $(NH_4)_3TiF_6$, fluovanadate $(NH_4)_3VF_6$, fluochromate $(NH_4)_3CrF_6$ and fluoferrate $(NH_4)_3FeF_6$, are described by Groth[1] as apparently isomorphous, optically isotropic octahedra. Ammonium oxyfluomolybdate $(NH_4)_3MoO_3F_3$ and oxyfluotungstate $(NH_4)_3WO_3F_3$, are also described[2] as forming similar small isotropic octahedra. The structures of ammonium chloroplatinate[3] $(NH_4)_2PtCl_6$, chlorostannate[4] $(NH_4)_2SnCl_6$ and fluosilicate[5] $(NH_4)_2SiF_6$, have been determined; it seemed of interest to investigate these complex fluorides for the purpose of finding, if possible, the changes in structure produced by the introduction of a third ammonium group. Moreover, the effect of replacing three of the six halogen atoms by oxygen could not be confidently predicted and it was thought that a study of these oxyfluorides also was desirable.

Crystals of ammonium fluoferrate were obtained by the slow evaporation of a solution of ammonium fluoride and ferric chloride. The light yellow crystals, less than 0.8 mm. on an edge, were found on analysis to contain only ammonia, iron and fluorine. Transparent plates of ammonium fluo-aluminate as large as 4 or 5 mm. on an edge were obtained similarly from a solution of ammonium fluoride and aluminum chloride and were also found to be free from impurities. Brilliant white crystals of ammonium oxyfluomolybdate about 1 mm. in diameter resulted from the slow evaporation of a solution of molybdic acid, ammonium hydroxide and ammonium fluoride. The crystals of all three substances were observed to be optically isotropic and to show the form $\{111\}$; subsidiary faces of $\{100\}$ were in some cases developed by ammonium fluo-aluminate.

Spectral, Laue and powder photographs were used in this investigation, the data so obtained being interpreted with the aid of the theory of space groups.[6] Spectral photographs of the K-radiation of molybdenum were made either by reflection from a developed face of the ro-

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[1] Groth, "Chemische Krystallographie," Engelmann, Leipzig, **1906**, vol. 1, p. 416.

[2] Ref. 1, p. 586.

[3] Wyckoff and Posnjak, This Journal, **43**, 2292 (1921).

[4] Dickinson, *ibid.*, **44**, 276 (1922).

[5] Bozorth, *ibid.*, **44**, 1066 (1922).

[6] See Refs. 3 and 4 for a more detailed description of the methods used.

tating crystal or, for small specimens, by reflection during the transmission of the beam through the crystal. Laue photographs were made with a tube with a tungsten anticathode operated at a peak voltage of 52,000 v., so that the minimum wave length of X-rays incident on the crystal was about 0.24 Å. The planes producing the Laue spots were identified with the aid of gnomonic projections. Powder photographs were made with an apparatus similar to that described by Davey,[7] using a molybdenum tube and having a zirconia filter directly in front of the film.

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The Structure of Ammonium Fluoferrate

In Table I are given data for ammonium fluoferrate leading to the value 4.55 Å. for d_{100}/n. It was found that in order to account for the production of the observed Laue reflections shown in Table II by means of X-rays present in the incident beam it would be necessary to place $n = 2$. No reflections remained unaccounted for by such a unit with $d_{100} = 9.10$ Å., which may accordingly be accepted as the correct one. This unit contains 4 $(NH_4)_3FeF_6$, corresponding to a calculated density of 1.96 g./cc. The density of a sample of precipitated ammonium fluoferrate obtained by pouring together solutions of ammonium fluoride and ferric chloride was found by means of a pycnometer with benzene to be 1.91. A powder photograph of this sample showed weak lines of ammonium chloride, the presence of which explains the slight disagreement in the densities. The value 9.10 Å. for d_{100} was verified by the powder photographic data, which are not given because they did not aid in determining the structure.

TABLE I

SPECTRAL DATA FROM (100) OF $(NH_4)_3FeF_6$

Order of reflection	Line[a]	Angle of reflection	d_{100}/n Å.	Estimated intensity[b]
n	β	3° 59.3′	4.53	m
n	α	4 28	4.56	s
$2n$	β	7 58	4.55	m
$2n$	α	8 57.7	4.56	s
$3n$	β	11 59	4.56	vw
$3n$	α	13 32.7	4.55	mw

[a] The symbol β denotes in this and subsequent tables the line MoK_β (0.6311 Å.); the symbol α, the line $MoK\alpha$ (0.710 Å.).

[b] Abbreviations used for all spectral intensities in this paper are: vs, very strong; s, strong; ms, medium strong; m, medium; mw, medium weak; w, weak; vw, very weak; a, absent.

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[7] Davey, *J. Optical Soc. Am.*, **5**, 479 (1921).

TABLE II

LAUE PHOTOGRAPHIC DATA FROM $(NH_4)_3FeF_6$

	hkl	d_{hkl} Å.	$n\lambda$ Å.	Estimated intensity	S for $u = 0.21$
Photograph No. 2, through (110)	104	2 × 1.10	2 × 0.45	0.3	0.76
	$\bar{5}71$	1.05	.44	.4	1.28
Photograph No. 3, through (110)	$01\bar{4}$	2 × 1.10	2 × .39	.05	0.76
	$3\bar{2}\bar{2}$	2 × 1.10	2 × .39	.15	2.07
Photograph No. 4, through (111)	$\bar{5}\bar{1}7$	1.05	.44	.3	1.28
	$\bar{7}35$	1.00	.44	.25	0.34
	$\bar{7}17$	0.91	.39	.15	0.66
	$\bar{3}40$	2 × .91	2 × .38	.20	1.57
	$\bar{1}59$	.88	.44	.25	3.03
	$93\bar{5}$	.85	.39	.15	2.09
	$\bar{4}32$	2 × .84	2 × .42	.10	1.10
	$\bar{2}5\bar{1}$	2 × .83	2 × .42	.20	3.08
	$5\bar{7}7$	.82	.41	.08	0.04
	$\bar{7}91$	.80	.40	.04	1.10
	$\bar{4}14$	2 × .79	2 × .41	.06	0.67
	$43\bar{3}$	2 × .78	2 × .41	.10	2.06
	$0\bar{3}5$	2 × .78	2 × .41	.15	4.36

No Laue spots correspond to first-order reflections except those from planes with all indices odd; this indicates that the arrangement of the atoms (with the possible exception of those of hydrogen) is based on a face-centered lattice. The coördinates of the positions of 12 N, 4 Fe, and 24 F for the only arrangements fulfilling these conditions are[8] as follows.

From space groups T_h^3, O^3, or O_h^5

4 Fe or 4 N at 4(b): $000;\ \frac12\frac12 0;\ \frac12 0\frac12;\ 0\frac12\frac12$

4 N or 4 Fe at 4(c): $\frac12\frac12\frac12;\ \frac12 00;\ 0\frac12 0;\ 00\frac12$

8 N at 8(e): $\frac14\frac14\frac14;\ \frac14\frac34\frac34;\ \frac34\frac14\frac34;\ \frac34\frac34\frac14;\ \frac34\frac34\frac34;\ \frac34\frac14\frac14;\ \frac14\frac34\frac14;\ \frac14\frac14\frac34$

24 F at 24(a): $u00;\ u+\frac12\ \frac12\ 0;\ u+\frac12\ 0\ \frac12;\ u\frac12\frac12;\ \bar{u}00;\ \frac12-u\ \frac12\ 0;\ \frac12-u\ 0\ \frac12;\ \bar{u}\frac12\frac12;$
$0u0;\ \frac12\ u+\frac12\ 0;\ \frac12\ u\ \frac12;\ 0\ u+\frac12\ \frac12;\ 0\bar{u}0;\ \frac12\ \frac12-u\ 0;\ \frac12\ \bar{u}\ \frac12;\ 0\ \frac12-u\ \frac12;$
$00u;\ \frac12\ \frac12\ u;\ \frac12\ 0\ u+\frac12;\ 0\ \frac12\ u+\frac12;\ 00\bar{u};\ \frac12\ \frac12\ \bar{u};\ \frac12\ 0\ \frac12-u;\ 0\ \frac12\ \frac12-u$

or at 24(c): $\frac14\frac14 0;\ \frac14\frac34 0;\ \frac34\frac14 0;\ \frac34\frac34 0;\ 0\frac14\frac14;\ 0\frac14\frac34;\ 0\frac34\frac14;\ 0\frac34\frac34;\ \frac14 0\frac14;\ \frac34 0\frac14;\ \frac14 0\frac34;\ \frac34 0\frac34;\ \frac12\frac34\frac14;\ \frac12\frac34\frac34;$
$\frac12\frac14\frac14;\ \frac12\frac14\frac34;\ \frac34\frac12\frac14;\ \frac14\frac12\frac14;\ \frac34\frac12\frac34;\ \frac14\frac12\frac34;\ \frac34\frac14\frac12;\ \frac34\frac34\frac12;\ \frac14\frac14\frac12;\ \frac14\frac34\frac12$

From space-groups T^2 or T_d^2

4 N or 4 Fe at 4(b)
4 N or 4 Fe at 4(c)
4 N or 4 Fe at 4(d): $\frac14\frac14\frac14;\ \frac14\frac34\frac34;\ \frac34\frac14\frac34;\ \frac34\frac34\frac14$
4 N or 4 Fe at 4(e): $\frac34\frac34\frac34;\ \frac34\frac14\frac14;\ \frac14\frac34\frac14;\ \frac14\frac14\frac34$

24 F at 24(a) or at 24(b): $\frac14\frac14 u;\ \bar{u}\frac34\frac14;\ u+\frac12\ \frac34\ \frac14;\ \frac34\ \frac12-u\ \frac34;\ \frac14\frac34\bar{u};\ u\frac34\frac34;\ \frac12-u\ \frac34\ \frac34;$
$\frac14\ u+\frac12\ \frac34;\ \frac34\frac14\bar{u};\ \frac14 u\frac14;\ \frac12-u\ \frac14\ \frac14;\ \frac34\ \frac14\ u+\frac12;\ \frac34\frac34 u;\ \frac34\bar{u}\frac14;$
$u+\frac12\ \frac14\ \frac34;\ \frac34\ \frac34\ \frac12-u;\ u\frac14\frac14;\ \frac14\bar{u}\frac34;\ \frac34\ u+\frac12\ \frac14;\ \frac14\ \frac14\ \frac12-u;$
$\bar{u}\frac14\frac34;\ \frac34 u\frac34;\ \frac14\ \frac12-u\ \frac14;\ \frac14\ \frac34\ u+\frac12$

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[8] Wyckoff, "The Analytical Expression of the Results of the Theory of Space-Groups," *Carnegie Inst. Pub.*, No. 318 (1922).

It will be noticed that no arrangement is possible in which all of the nitrogen atoms are in equivalent positions.

Any arrangement with the fluorine atoms at 24(c) will give the same structure factor to all first-order reflections from planes with all indices odd. The observation that, for example, {951} reflects more strongly than {771} at the same wave length despite its smaller interplanar distance accordingly eliminates this. The arrangement with Fe at 4(d), N at 4(b), 4(c), and 4(e), and F at 24(a) places six fluorine atoms at octahedron corners around an atom of nitrogen rather than one of iron. The chemical improbability of this structure provides considerable reason for not giving it further consideration; however, it was found possible to eliminate it definitely by means of X-ray data. It can be shown that, if this be the structure of the substance, the spectral data from (111) require that the parameter u should lie in the region between 0.20 and 0.30. Throughout this region the structure factor for {410} ($n = 2$) is greater than that for {322} ($n = 2$), except at u = 0.25, where they are equal. The experimental observation that {322} reflects much more strongly than {410} accordingly makes this structure impossible. The only remaining distinct arrangement can be derived from space groups T^2 or T_d^2 by placing Fe at 4(b), N at 4(c), 4(d), and 4(e), and F at 24(a), or from T_h^3, O^3, or O_h^5 by placing N at 8(e) instead of at 4(d) and 4(e).

Planes giving useful Laue reflections can be divided into three classes. These are, with corresponding values of the structure factor S, the following.

Class 1; all indices odd: $n = 1$, $S = 4\overline{\mathrm{Fe}} - 4\overline{\mathrm{N}} + 8\overline{\mathrm{F}}\,(\cos 2\pi \mathrm{u}h + \cos 2\pi \mathrm{u}k + \cos 2\pi \mathrm{u}l)$

Class 2; two indices odd, one even: $n = 1$, $S = 0$; $n = 2$, $S = 4\overline{\mathrm{Fe}} + 12\overline{\mathrm{N}} + 8\overline{\mathrm{F}}\,(\cos 4\pi \mathrm{u}h + \cos 4\pi \mathrm{u}k + \cos 4\pi \mathrm{u}l)$

Class 3; one index odd, two even: $n = 1$, $S = 0$; $n = 2$, $S = 4\overline{\mathrm{Fe}} - 4\overline{\mathrm{N}} + 8\overline{\mathrm{F}}\,(\cos 4\pi \mathrm{u}h + \cos 4\pi \mathrm{u}k + \cos 4\pi \mathrm{u}l)$

Comparison may be made, it will be seen, between planes in each class and between those of Classes 1 and 3 ($n = 2$) with only qualitative assumptions regarding relative reflecting powers; care must be used with planes with small values of S.

A spectral photograph from (111) showed five orders of reflection, with intensities strong, medium, weak, medium and weak. This shows that the structure factor is greater for $n = 4$ than for $n = 2$, and greater for $n = 5$ than for $n = 3$. Curves of these structure factors are shown in Fig. 1 for u = 0 to u = 0.50, which includes all distinct structures. In their calculation relative reflecting powers of different atoms have been assumed proportional to their atomic numbers; however, a considerable deviation from this would not invalidate the arguments given here. It will be seen that these spectral intensities limit u to the region between about 0.16 and 0.25. Similarly calculated curves of the structure-factors of some useful planes reflecting on Laue photographs for a range of values of u are given in Fig. 2. It was observed that {751} gave a stronger reflection than {410} (n = 2), requiring u to be less than 0.217, and that {953}, with considerably smaller interplanar distance, gave as strong a reflection as {771}, requiring u to be greater than 0.187. Further definite

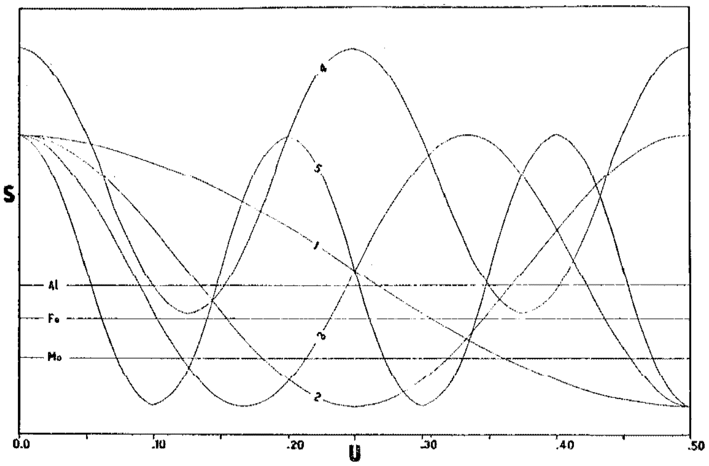

Fig. 1.—Structure-factor curves for (111). The order of reflection is given by the numbers on the curves. Positive values of S are to be read both above and below the horizontal lines, which have the value $S = 0$ for the substances indicated.

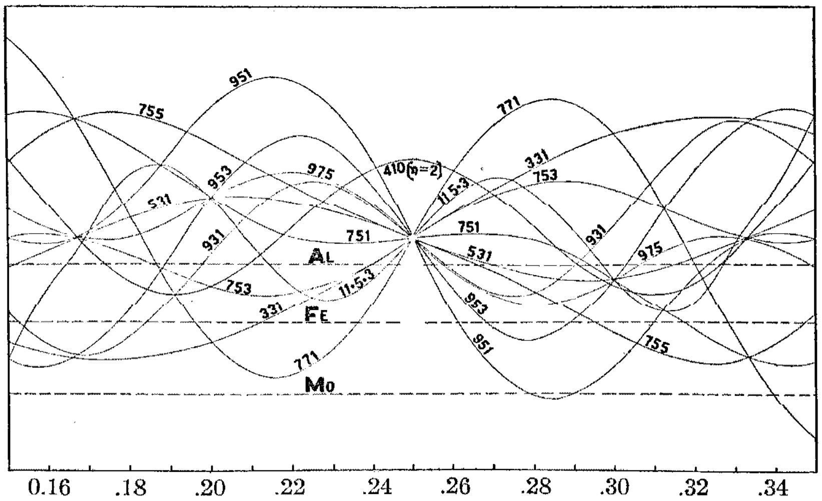

Fig. 2.—Structure-factor curves for the planes with the indices shown. Positive values of S are to be read both above and below the horizontal lines, which have the value $S = 0$ for the substances indicated.

limitation of possible values of u was not accomplished; values of S for $u = 0.21$, which seems to be the most probable value, are given in Table II for comparison with the observed Laue intensities; the agreement is good, except for a few planes for which S would be considerably affected by a small change in the relative reflecting powers of different atoms.

Chemical evidence strongly indicates that each nitrogen atom is surrounded by 4 hydrogen atoms. Space groups T^2 and T_d^2 provide the only way in which this can be accomplished. By assigning different values to the parameter v in 16(a), with coördinates,

$vvv;\ v+\tfrac{1}{2}\ v+\tfrac{1}{2}\ v;\ v+\tfrac{1}{2}\ v\ v+\tfrac{1}{2};\ v\ v+\tfrac{1}{2}\ v+\tfrac{1}{2};\ v\bar{v}\bar{v};\ v+\tfrac{1}{2}\ \tfrac{1}{2}-v\ \bar{v};$
$v+\tfrac{1}{2}\ \bar{v}\ \tfrac{1}{2}-v;\ v\ \tfrac{1}{2}-v\ \tfrac{1}{2}-v;\ \bar{v}v\bar{v};\ \tfrac{1}{2}-v\ v+\tfrac{1}{2}\ \bar{v};\ \tfrac{1}{2}-v\ v\ \tfrac{1}{2}-v;\ \bar{v}\ v+\tfrac{1}{2}\ \tfrac{1}{2}-v;$
$\bar{v}\bar{v}v;\ \tfrac{1}{2}-v\ \tfrac{1}{2}-v\ v;\ \tfrac{1}{2}-v\ \bar{v}\ v+\tfrac{1}{2};\ \bar{v}\ \tfrac{1}{2}-v\ v+\tfrac{1}{2}$

the 48 hydrogen atoms can be placed in such a way that each nitrogen atom is surrounded tetrahedrally by 4 hydrogen atoms. A probable arrangement of the hydrogen atoms results on giving v values of $\tfrac{1}{4} - d$, $\tfrac{1}{2} - d$, and $\tfrac{3}{4} + d$, in which d is the hydrogen-to-nitrogen distance; these positions are indicated by the corners of the tetrahedra in Fig. 4.

The Structure of Ammonium Fluo-aluminate

Spectral data for ammonium fluo-aluminate, given in Table III, show d_{111}/n to be 4.85 Å. If n were 1, the unit of structure would have d_{100} = 8.40 Å., and would contain $4(NH_4)_3AlF_6$. The calculated density 2.17 g./cc. is somewhat greater than 2.02, the value determined by a suspension method on small crystals, which showed considerable variation among themselves.

TABLE III

SPECTRAL DATA FROM (111) OF $(NH_4)_3AlF_6$

Order of reflection	Line	Angle of reflection	d_{111}/n Å.	Estimated intensity
n	β	3° 43.6′	4.856	ms
n	α	4 11.5	4.861	vs
$2n$	β	7 29	4.845	ms
$2n$	α	8 25.5	4.847	vs
$3n$	β	11 15.3	4.846	vw
$3n$	α	12 40.6	4.851	mw
$4n$	β	15 6.5	4.844	vw
$4n$	α	17 0	4.855	mw

Values of $n\lambda$ as low as 0.095 Å., taking d_{100} = 8.40, were calculated for Laue reflections, indicating a unit with d_{100} = 25.20 Å., containing 256 molecules. However, there are the following reasons, other than the probable isomorphism with ammonium fluoferrate, for believing that this indication is illusory, namely, that the true unit has d_{100} = 8.40 Å., and that the Laue photographs were taken with crystals twinned on (111). (1) In Fig. 3 are plotted curves showing the relative intensities of {531} and

{13.11.5} ({531} on the twin) on two Laue photographs taken with crystals prepared at different times. It will be seen that there is pronounced disagreement, definitely indicating twinning. (2) All of the 20 lines observed on a powder photograph of the substance (Table IV) are accounted for by the small unit; these photographs are not influenced by twinning. The absence of any reflections requiring a larger unit makes it improbable that such a unit exists. (3) Only a few very complicated forms such as {25.17.7} gave low values of $n\lambda$. If indices $(h'k'l')$ based on the axes of the twin are calculated by means of the equations[9] $h' = 2l + 2k - h$, $k' = 2h + 2l - k$, and $l' = 2h + 2k - l$, no reflections remain unexplained by the small unit. Moreover, the ratio of intensities from the two individuals composing the twinned crystal whenever it can be determined is found to be about 8:1 for one crystal and 8:6 for the other.

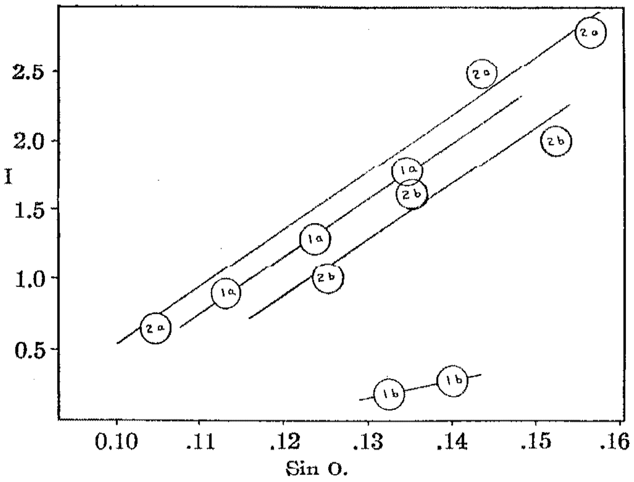

Fig. 3.—Relative intensities of reflection of 531; 1*a* and 1*b* are for the two individuals composing one twinned crystal of $(NH_4)_3AlF_6$ and 2*a* and 2*b* for another twinned crystal.

These indications were accepted as showing the unit of structure to be the small one with $4(NH_4)_3AlF_6$. It was found that some Laue spots were produced by the simultaneous reflection from one plane in one individual of the twinned crystal and from another in the other. In many cases, however, no reflection could occur from one of the two planes because wave lengths shorter than 0.24 Å. would have been required. These planes, free from ambiguity, could be compared with each other in the usual way. Only planes with all indices odd gave first-order reflections. Abnormal intensity relations occurred, eliminating any struc-

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[9] Tutton, "Crystallography," Macmillan and Co., London, 1911, p. 340.

Table IV

Powder Photographic Data from $(NH_4)_3AlF_6$; $d_{100} = 8.40$ Å.

hkl[a]	d_{hkl} calculated Å.	d_{hkl} observed Å.	Estimated intensity	Number of coöperating planes	S for $u = 0.197$
111	4.85	4.9	6	8	1.32
200	4.20	4.20	4	6	1.55
220	2.969	2.96	3	12	1.31
311	2.535	2.53	1.5	24	0.15
222	2.423	2.42	5	8	2.03
400	2.100	2.10	6	6	4.13
331	1.928	1.93	0.1	24	1.02
420	1.879	1.875	.2	24	0.78
422	1.717	1.720	.05	24	.55
333, 511	1.619	1.616	5	8, 24	2.19, 1.98
440	1.485	1.481	3	12	3.36
531	1.420	1.421	2	48	0.82
442, 600	1.400	...	..	24, 6	.02, 2.75
620	1.329	1.326	1	24	2.52
533	1.281	...	..	24	0.35
622	1.269	1.269	0.05	24	.82
444	1.213	1.210	0.1	8	2.60
711, 551	1.189	1.175	2	24, 24	0.26, 2.65
640	1.166	1.161	0.2–0.4	24	1.99
642	1.123	1.120	1	48	1.75
731, 553	1.093	1.094	1	48, 24	0.91, 1.49
800	1.050	...	..	6	3.00
733	1.028	...	..	24	2.08
820, 644	1.020	...	..	24, 24	0.34, 1.22
822, 660	0.991	0.985	0.2	24, 12	.58, 3.72
555, 751	.970	0.970	0.5	8, 48	3.32, 0.93
662	.964	...	..	24	0.37
840	.940	.940	0.2	24	2.24
911, 753	.922	...	..	24, 48	1.13, 0.24
842	.916	...	..	48	1.11
664	.895	.894	0.2	24	2.96

[a] In this table the second order of (211) is written (422), and similarly for all orders.

ture with F at 24(c); the second improbable arrangement was not eliminated by X-ray data on account of the similarity in reflecting powers of Al and N.

The value of u in the remaining arrangement can be closely limited. The spectral data show the structure-factor for $n = 2$ from (111) to be greater than for $n = 1$ and for $n = 4$ greater than for $n = 3$. The parameter u is accordingly limited to the region between 0.16 and 0.30 and that between 0.42 and 0.50. The latter can be eliminated by means of Laue data. Laue data from the two crystals for which the intensity ratios of twins are about 8:1 and 8:6 are given in Table V. Among the unambiguous intensity relations are these: $\{953\} >> \{753\}$, requiring u to be between 0.188 and 0.25; and $\{11.5.3\} > \{975\}$, requiring u to be less than 0.200. It will be observed that {531} reflected much more strongly than {331}, indicating the true position of the line $S = 0$ to be somewhat lower than drawn in Fig. 2 (corresponding to a greater reflecting power for Al). With this knowledge, the relation {931} > {753} places u above 0.194. The most probable value for u is 0.197; the complete agreement of this structure with the experimental data can be seen by reference to Tables IV and V. It is necessary to mention that

TABLE V

LAUE PHOTOGRAPHIC DATA FROM $(NH_4)_3AlF_6$, THROUGH (111)

CRYSTAL NO. 1; INTENSITY RATIO OF TWINS 8:1

Estimated intensity	hkl	d_{hkl} Å.	$n\lambda$ Å.	S for $u = 0.197$	$h'k'l'$	$d_{h'k'l'}$ Å.	$n'\lambda'$ Å.	S for $u = 0.197$
0.8	$3\bar{3}1$	1.92	0.35	1.02	$\bar{7}.11.\bar{1}$	0.64	0.12	..
.9	$\bar{3}\bar{1}5$	1.42	.32	0.82	$11.5.\overline{13}$	.47	.11	..
1.3	$\bar{1}5\bar{3}$	1.42	.35	.82	$5.\overline{13}.11$	.47	.12	..
1.8	$\bar{3}5\bar{1}$	1.42	.38	.82	$11.\overline{13}.5$	.47	.13	..
0.05	$2\bar{2}1$	2 × 1.40	2 × .43	.02	$\bar{4}8\bar{1}$	2 × .47	2 × .14	..
1.2	$03\bar{2}$	2 × 1.16	2 × .42	1.99	$2\bar{7}8$	2 × .39	2 × .14	..
0.05	$\bar{3}41$	2 × 0.83	2 × .43	0.63	$13.\bar{8}.1$	2 × .28	2 × .14	..
.3	$1\bar{5}9$	.81	.43	1.80	$7.25.\overline{17}$	.27	.14	..
.2	$\overline{13}.5.11$	.47	.12	..	$5\overline{13}$	1.42	.37	0.82
.3	$\overline{13}.11.5$	.47	.13	..	$5\overline{31}$	1.42	.39	.82

CRYSTAL NO. 2; INTENSITY RATIO OF TWINS 8:6; PHOTOGRAPH 1

Estimated intensity	hkl	d_{hkl} Å.	$n\lambda$ Å.	S for $u = 0.197$	$h'k'l'$	$d_{h'k'l'}$ Å.	$n'\lambda'$ Å.	S for $u = 0.197$
0.6	$1\bar{3}3$	1.92	0.34	1.02	$\bar{1}.11.\bar{7}$	0.64	0.11	..
.6	$\overline{31}5$	1.42	.29	0.82	$11.5.\overline{13}$	.47	.10	..
2.5	$\bar{1}5\bar{3}$	1.42	.41	.82	$5.\overline{13}.11$	.47	.14	..
2.8	$\bar{3}5\bar{1}$	1.42	.45	.82	$11.\overline{13}.5$	.47	.15	..
0.2	$\bar{5}33$	1.28	.33	.35	$17.\bar{7}.\bar{7}$	.43	.11	..
1.8	$\bar{5}51$	1.18	.32	2.65	$17.\overline{13}.\bar{1}$	.39	.11	..
0.7	$30\bar{2}$	2 × 1.16	2 × .32	1.99	$\bar{7}28$	2 × .39	2 × .11	..
.2	$22\bar{3}$	2 × 1.04	2 × .32	1.22	$\bar{4}.\bar{4}.11$	2 × .35	2 × .11	..
.5	$91\bar{5}$	0.81	.32	1.80	$\overline{17}.7.25$	.27	.11	..
.02	$\bar{3}.11.\bar{3}$	.71	.43	0.85	$19.\overline{23}.19$	.24	.14	..
.06	$11.1.\bar{5}$	.69	.43	2.16	$\overline{19}.11.29$	.23	.14	..
.4	$11.\bar{7}.\bar{1}$	.64	.10	..	$\bar{3}31$	1.92	.30	1.02
1.0	$5.11.\overline{13}$	.47	.12	..	$\bar{1}35$	1.42	.35	0.82
1.7	$\overline{13}.5.11$	.47	.13	..	$5\overline{13}$	1.42	.38	.82
2.0	$\overline{13}.11.5$	.47	.14	..	$5\overline{31}$	1.42	.43	.82
0.03	814	2 × .47	2 × .15	..	$\bar{2}12$	2 × 1.40	2 × .45	.02
.7	$\bar{1}.17.\overline{13}$	.39	.10	..	$1\bar{5}5$	1.18	.29	2.65
.3	$25.7.\overline{17}$	.27	.15	..	$\bar{5}19$	0.81	.44	1.80

CRYSTAL NO. 2; PHOTOGRAPH 2

Estimated intensity	hkl	d_{hkl} Å.	$n\lambda$ Å.	S for $u = 0.197$	$h'k'l'$	$d_{h'k'l'}$ Å.	$n'\lambda'$ Å.	S for $u = 0.197$
0.05	$37\bar{5}$	0.92	0.42	0.24	$1.\overline{11}.25$	0.31	0.14	..
.4	$9\overline{31}$	.88	.42	.04	$\overline{17}.19.13$	.29	.14	..
.5	$93\bar{5}$	.78	.43	.63	$\overline{13}.5.29$	.26	.14	..
.06	$11.\bar{3}.\bar{1}$	.73	.45	.32	$\overline{19}.23.17$	.24	.15	..
.05	$9\bar{7}5$	.68	.44	.75	$\overline{13}.35.\bar{1}$	.23	.15	..
.15	$11.3.\bar{5}$	.68	.43	.99	$\overline{15}.9.33$	.23	.14	..

an increase in the relative reflecting power of Al will increase S for some planes and decrease it for others.

After the structure of $(NH_4)_3AlF_6$ had been determined, a crystal showing re-entrant angles was found. This crystal was shown by goniometric measurements to be twinned with (111) as twinning plane and composition plane. Sections of each of the two individuals were made parallel to the twinning plane by cleaving; Laue photographs of these sections showed the crystal axes to correspond to the twinning described above. Moreover, *no reflections requiring the larger unit were produced by either individual.* The data from these photographs were in agreement with the structure deduced above. Subsequent careful examination of the face development of the small crystal giving photographs with the 8:6 intensity ratio showed it to consist of two individuals twinned on (111); their thicknesses were in the same ratio, about 8:6.

The Structure of Ammonium Oxyfluomolybdate

Spectral data for ammonium oxyfluomolybdate, given in Table VI, place d_{111}/n equal to 5.25 Å. If n is 1, the unit of structure has d_{100} = 9.10 Å. No reflections were found on any of three Laue photographs which required a larger unit (on each photograph there were a few scattered spots close to the central image to which it was difficult to assign indices; these were explained as produced by a crystal fragment with an orientation different from that of the main crystal). The density calculated from the X-ray data, assigning four molecules to the unit, is 2.23 g./cc.; a direct determination by means of a pycnometer of the density of a liquid in which a small crystal remained suspended gave the value 2.28.

TABLE VI

SPECTRAL DATA FROM (111) OF $(NH_4)_3MoO_3F_3$

Order of reflection	Line	Angle of reflection	d_{111}/n Å.	Estimated intensity
n	β	3° 26′	5.26	ms
n	α	3 53	5.25	vs
$2n$	..	...	..	a
$3n$	α	11 44	5.24	vw
$4n$	α	15 41	5.25	w

No planes were observed to give first-order reflections except those with all indices odd, indicating that the structure is based on a face-centered lattice. However, there are no arrangements of 4 Mo, 12 N, 12 O and 12 F based on this lattice,[8] nor any which are approximately face-centered. If the oxygen and fluorine atoms are considered crystallographically equivalent, the possible structures are those discussed for $(NH_4)_3FeF_6$. The presence of a number of abnormal intensity relations eliminates 24(c). If the substance had the second arrangement, the observed intensities of reflection from (111) would require that u be between 0.20 and 0.30. Throughout this region the structure factor for {551} is over twice as great as that for {320} ($n = 2$); the observation that the two forms reflect with about equal intensity accordingly eliminates this structure.

The spectral intensities from (111) limit the possible values of u for the third arrangement to the region between 0.15 and 0.30, with indications of a value near 0.20. The form {951} reflected on Laue photographs as strongly as {755}, despite its smaller interplanar distance; this limits u to between 0.194 and 0.25 and the further observation that {755} reflected more strongly than {931} shows u to be less than 0.220. The values of S given in Table VII are calculated for $u = 0.21$.

Table VII

Laue Photographic Data from $(NH_4)_3MoO_3F_3$, through (111)

hkl	d_{hkl} Å.	$n\lambda$ Å.	Estimated intensity	S for $u = 0.21$
$5\bar{5}\bar{1}$	1.27	0.28	0.20	4.09
$0\bar{2}3$	2 × 1.26	2 × .28	.20	3.42
$53\bar{7}$	1.00	.41	.08	1.23
$\bar{1}39$	0.95	.37	.04	2.28
$\bar{5}57$	.91	.38	.05	2.86
$\bar{5}75$	.91	.39	.05	2.86
$1\bar{5}9$	.88	.41	.05	3.92
$3\bar{7}7$	.88	.33	a	0.70
$\bar{5}93$	.85	.34	.04	2.98

Discussion of the Structures

The arrangement of the atoms in the units of structure of ammonium fluoferrate, fluo-aluminate and oxyfluomolybdate is shown in Fig. 4.

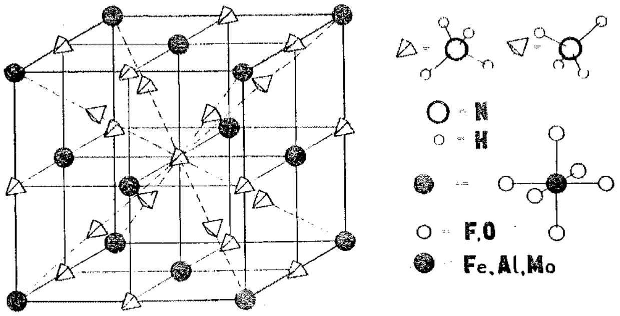

Fig. 4.—The arrangement of atoms in the units of structure of $(NH_4)_3FeF_6$, $(NH_4)_3AlF_6$ and $(NH_4)_3MoO_3F_3$.

This arrangement is the same as that of ammonium chloroplatinate, chlorostannate and fluosilicate, except that four additional ammonium groups are introduced at $^1/_2{}^1/_2{}^1/_2$, $00^1/_2$, $0^1/_20$ and $^1/_200$.

The sum of the Bragg radii[10] for iron and fluorine is 2.07 Å. The sum

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[10] Bragg, *Phil. Mag.*, 40, 180 (1920).

of the radii of molybdenum (taken[11] as 1.36) and fluorine is 2.03 Å., that of molybdenum and oxygen is 2.01. These distances are slightly larger than those tabulated in Table VIII. Moreover, the sum of the Bragg radii, 2.02 Å., is considerably larger than the Al to F distance in $(NH_4)_3AlF_6$. Bozorth has previously noted that the Si to F distance in $(NH_4)_2SiF_6$ is 1.72 Å., while the sum of the Bragg radii is 1.84. These deviations are illustrative of the lack of constancy of corresponding interatomic distances in crystals of different types.

Table VIII

Interatomic Distances for Complex Fluorides

Substance	d_{100} Å.	u	M–F distance Å.	F–F distance Å.
$(NH_4)_3FeF_6$	9.10	0.21	1.9	5.3
$(NH_4)_3MoO_3F_3$	9.10	.21	1.9	5.3
$(NH_4)_3AlF_6$	8.40	.197	1.66	5.08
$(NH_4)_2SiF_6$[a]	8.38	.205	1.72	4.94

[a] Ref. 5.

The introduction of a third ammonium group expands the structure only slightly. The F to F distance along the crystal axes is only 0.14 Å. greater for ammonium fluo-aluminate than for the fluosilicate, despite the fact that for the former there is an ammonium group between the fluorine atoms.

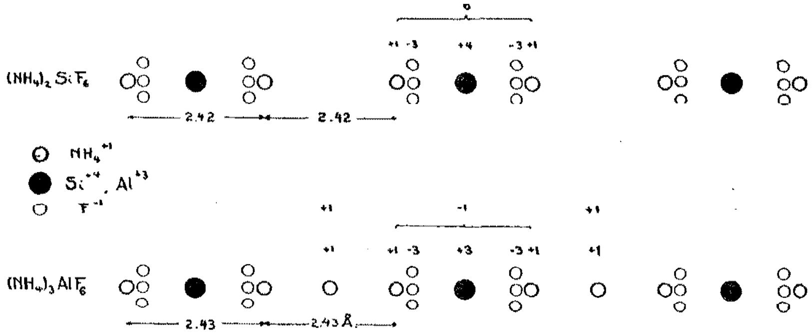

Fig. 5.—Diagrammatic representation of the sequence of planes of atoms along the normal to (111) of $(NH_4)_2SiF_6$ and $(NH_4)_3AlF_6$.

No statement concerning the cleavage of these crystals has been found in the literature. Upon trial, ammonium oxyfluomolybdate and fluoaluminate were found to have perfect octahedral cleavage. Crystals of the fluoferrate were not available for investigation. In the fluosilicate and isomorphous salts the atoms, presumably electrically charged to the extent indicated by their valences, are arranged in layers parallel to (111) as shown in Fig. 5. It is entirely reasonable to attribute the

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[11] Dickinson and Pauling, This Journal, 45, 1466 (1923).

very complete octahedral cleavage of these crystals to the presence of electrically neutral layers separated by a relatively large distance. In the fluo-aluminate and salts isomorphous with it the corresponding groups have negative charges and midway between them lie positively charged layers. This change might be expected to reduce the ease with which cleavage occurs; direct comparison, however, showed that the fluo-aluminate cleaved approximately as readily as the fluosilicate and the chlorostannate.

It was not found possible to arrange 4 $(NH_4)_3MoO_3F_3$ in a face-centered unit or in a unit approximately face-centered, except by assuming the oxygen and fluorine atoms to be in equivalent positions. These atoms probably have nearly but not exactly the same size. Moreover, their atomic numbers differ by one, so that if they have similar electron-shells the electrical charges on the entire atoms will differ by one. If they have not similar electron-shells, they differ in shape; they cannot be taken to be identical.

In the arrangement assigned to this crystal the MoO_3F_3 groups are at the intersection of four trigonal axes. But the group of three fluorine and three oxygen atoms around a molybdenum atom does not possess four trigonal axes. This apparent contradiction may have one of the following explanations.

(1) The true unit of structure may contain 32 molecules, or 256, or more. No Laue reflections were observed requiring a larger unit which, if it exists, must accordingly closely resemble a group of small units with the arrangement given. In view of this resemblance, it is difficult to understand how the MoO_3F_3 groups can, in the progress of crystallization, effect the proper orientation of other such groups depositing from solution 10 or 15 Å. away so as to arrange them in a manner completely concordant with the symmetry of the larger unit.

(2) It is conceivable, on the other hand, that the atoms of oxygen and of fluorine may be sufficiently similar to permit designating them as crystallographically equivalent in this case (not necessarily in all cases). The MoO_3F_3 group has approximately the form shown in Fig. 4. It is possible that in the formation of the crystals these groups are deposited with the oxygen and fluorine atoms directed at random along the crystal axes. Upon looking along a normal to an octahedral face of a crystal formed in this way one would see on the average the same number of oxygen atoms (and fluorine atoms) in the direction of each of the crystal axes. If this is the way in which a crystal of $(NH_4)_3MoO_3F_3$ is built, the unit of structure is that shown in Fig. 4. The crystal will at points within it show slight distortions; since these distortions are random ones, they will not affect the symmetry of the crystal as a whole.

Some justification for the belief in this hypothesis is afforded by the existence of solid solutions between isomorphous crystals. A bromine atom differs considerably from a chlorine atom; however, in the formation of solid solutions of potassium bromide and chloride, replacements of one by the other occur, apparently at random.[12] It is evident that in the case of such a solid solution distortions similar to those presumed to occur in $(NH_4)_3MoO_3F_3$ are present, and that the symmetry of the entire atomic arrangement is retained because of the random distribution of the distortions. For the solid solutions which show simple stoichiometrical relations between the amounts of the constituents present, the formation of larger units of structure may be invoked in explanation, as in (1), but this cannot be done in general.

Summary

Cubic crystals of ammonium fluoferrate, fluo-aluminate and oxyfluomolybdate have been prepared and their structures determined by means of data from spectral, Laue and powder photographs interpreted with the aid of the theory of space groups. The units of structure, based on a face-centered lattice, contain four molecules. The arrangement of atoms within the units is shown in Fig. 4 and the values determined for d_{100} and the parameter u are given in Table VIII.

The structures of these crystals are closely related to those of ammonium chlorostannate and isomorphous salts; the crystals likewise show very good octahedral cleavage.

In interpreting the data for ammonium oxyfluomolybdate, atoms of oxygen and fluorine were considered to be crystallographically equivalent, arguments being given in justification of this supposition.

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[12] Vegard, *Z. Physik*, 5, 17 (1921).

[Reprint from the Journal of the American Chemical Society, **47**, 1561 (1925).]

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 59]

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

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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

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[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

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[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	
	2*n*	β	10 39	3.415	
	2*n*	α_1	11 59	3.41	m
	2*n*	α_2	12 3	3.41	
	3*n*	β	16 7	3.41	
	3*n*	α_1	18 8	3.41	w
	3*n*	α_2	18 14	3.415	
(001)	*n*	α	3 44	5.46	vw
	2*n*	γ	6 28	5.50	
	2*n*	β	6 36	5.49	m
	2*n*	α	7 24	5.51	
	3*n*	α	11 8	5.51	w
(110)	*n*	α	3 40	5.55	w
	2*n*	α	7 16	5.61	mw
	3*n*	β	9 42	5.62	
	3*n*	α_1	10 53	5.62	m
	3*n*	α_2	10 57	5.62	
	4*n*	..	....	..	a
	5*n*	α_1	18 19	5.63	
	5*n*	α_2	18 28	5.62	w

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

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[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^5, 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.

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[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.

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