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THE CRYSTAL STRUCTURE OF CADMIUM IODIDE

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Introduction

The purpose of this work was to determine by means of X-rays the positions of the atoms in crystalline cadmium iodide, CdI₂.

The crystals were prepared by spontaneous evaporation of a saturated solution at room temperature. The crystals are light yellow hexagonal tablets, described crystallographically by Groth² as belonging to the hexagonal system.

The X-ray data were obtained (1) from photographs of line spectra from the principal faces, using rhodium as the target, and (2) from Laue photographs taken with the beam approximately perpendicular to a (001) plane.

Spectral Photographs and the Unit of Structure

Photographs were taken of line spectra reflecting from (001), (100) and (110) planes. The first was taken by reflecting the X-rays from the (001) face, while for the other two measurements the X-rays were passed through a thin crystal in such a way that the (100) or (110) planes could reflect. The angles of reflection and the estimated intensities of the reflected beam are given in Table I. Measurements are for the rhodium α_1 line of wave length 0.6121 Å.³

TABLE I
DATA FROM THE SPECTRAL PHOTOGRAPHS

Reflecting plane	Angle of reflection	d/n	Estimated intensities
(001)	2° 34'	6.83	Medium strong
	5° 9'	3.410	Strong
	7° 43'	2.280	Medium
	10° 19'	1.709	Very strong
	12° 56'	1.367	Weak
	15° 34'	1.140	Medium weak
	18° 14'	0.978	Very weak
	20° 55'	0.857	Medium weak
(100)	14° 26'	1.228
(110)	8° 18'	2.120	Strong
	16° 53'	1.054	Weak

The value of d/n , where d is the interplaner distance and n the order of reflection, may be calculated from these data. If the reflections occurring

¹ Du Pont Fellow in Chemistry.

² P. Groth, "Chemische Krystallographie" Leipzig, 1906, vol. 1, p. 213.

³ Duane, *Nat. Research Council Bull.*, 1, No. 6 (1920).

at the smallest angles from the (001) and (110) planes be regarded as first-order reflections, the dimensions of the corresponding hexagonal unit of structure are found to be 6.84 Å. in height and 4.24 Å. along one side of the base. (See Fig. 2.) Combining these measurements with the density, 5.644 as quoted by Groth,² this unit is found to contain 0.995 molecule. On this basis the (001) reflections are of the first to eighth orders, the (110) reflections of the first to third orders, and the (100) reflection of the third order.

Discussions of the Possible Structures

A symmetrical Laue photograph showed that cadmium iodide is not hexagonal, but trigonal. An examination of all the spots showed that the symmetry⁴ of the photograph corresponds to that of the point group, D_3^d , and that, therefore, the arrangement of the atoms is given by one of the space groups isomorphous with the point groups D_3^d and C_3^v . If there is but one molecule in the unit, the possible arrangements are all included in the following:

- | | |
|----------------------------|---|
| 1. Cd at $00\frac{1}{2}$, | I at $\frac{1}{3} \frac{2}{3} u, \frac{2}{3} \frac{1}{3} \bar{u}$. |
| 2. Cd at $00u$, | I at $\frac{1}{3} \frac{2}{3} 0, \frac{2}{3} \frac{1}{3} 0$. |
| 3. Cd at 000 , | I at $00u, 00\bar{u}$. |

Arrangement 3, places the 3 atoms in a straight line parallel to the axis of the crystal in such a way that the spectrum from any prism face would show a regular decline of intensity with order of reflection. Since the (100) spectrum shows a third order much stronger than the first or second orders, this arrangement may be ruled out.

To distinguish between Arrangements 1 and 2, use was made of the intensities of the (001) reflections. For the intensity, I , of reflection of a given wave length from any plane we may write: $I = f(d/n) \cdot S^2$, where for Arrangement 1,

$$S = \bar{C}d \cos \pi nl + 2I \cos 2\pi n \left(\frac{h+2k}{3} + lu \right). \quad (1)$$

$\bar{C}d$ and \bar{I} , the reflecting powers of the atoms, were taken to be proportional to their atomic numbers, and were put equal to 10 and 11, respectively. It is assumed that $f(d/n)$ is a function decreasing continually with decreasing values of d/n . H , k , and l are the Bravais-Miller indices of the reflecting plane.

For the reflections from the (001) face S becomes $10 + 22 \cos 2nu$ for Arrangement 1, while for Arrangement 2, $S = [(10 \cos 2nu + 22)^2 + (10 \sin 2nu)^2]^{1/2}$. Plots were constructed showing the value of S for all distinct values of the parameter u for each of these arrangements.

Consideration of the comparative intensities of the different orders of reflection given in Table I and of the nature of the intensity function leads to

⁴ Notation of Schönflies, "Krystallsysteme u. Krystallstruktur," Teubner, Leipzig, 1891.

the conclusion that certain inequalities exist in the values of S . If S_n be the value of S for the n th order, $S_2 > S_1$, $S_4 > S_2$, $S_4 > S_3$, $S_6 > S_5$, $S_8 > S_6$, and $S_8 > S_7$. It was determined from the plots that these conditions are never satisfied for Arrangement 2, and therefore this arrangement is impossible. These conditions are satisfied for Arrangement 1 only in the region between $u = 0.23$ and 0.253 . Because the sixth order reflection is several times as strong as the seventh, and since S_6 is calculated as described above to be greater than S_7 only above 0.248 , the best value of u is considered to be 0.250 . Deviations of the reflecting powers of the atoms from strict proportionality to their atomic numbers would not require the value of u to lie within these limits, but even a large deviation would not permit a value of u very far removed from 0.25 .

Confirmation of the Structure by the Laue Photographs

Unsymmetrical Laue photographs were examined to confirm the structure given by Arrangement 1. Several photographs showed a 6-fold symmetry axis, but it was concluded that the crystals producing them were twinned and in some cases re-entrant angles were actually observed under the microscope. Two photographs having only a 3-fold symmetry axis showing over 150 spots each were analyzed, the intensity of each spot estimated and its wave length calculated on the basis of the unit previously chosen. The smallest wave length found for any spot was 0.26 \AA , a value consistent with the voltage applied to the tube, about $53,000$ volts. Figure 1 is a gnomonic projection of one of the photographs; the area of each spot being proportional to the intensity estimated from the photographic plate. Table II includes some of the most useful data of the other photograph.

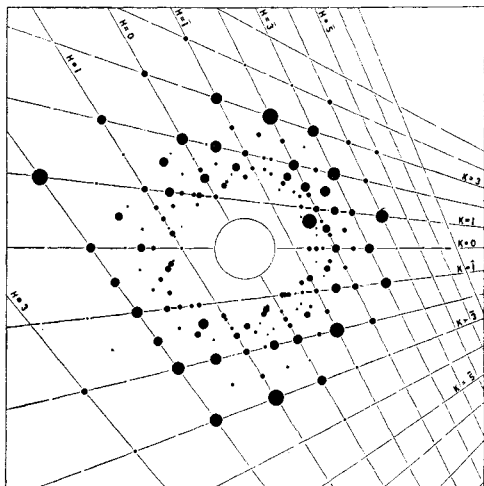


Fig. 1.—Gnomonic projection from a Laue photograph taken through a (001) face of cadmium iodide. The distance from the crystal to the photographic plate was 5 cm. The diameter of the circle in the center of the projection was 10 cm. on the original.

photographic plate. Table II includes some of the most useful data of the other photograph.

The structure was tested most satisfactorily by comparing the intensities of spots produced by planes having the same interplaner distances and reflecting with the same wave length. Forms as $\{hkl\}$ and $\{khl\}$ have the same calculated value of S when $(h + 2k)/3$ is an integer, but otherwise

S is usually different for the two forms. In no case where $(h + 2k)/3$ is an integer could differences in intensities be established when comparisons were made in the manner just described. When $(h + 2k)/3$ is not an integer, the intensities never failed to correspond, with the usual degree of accuracy, to the values of S calculated by means of Equation 1 for $u = 0.25$. Comparisons were also made between all forms having interplaner distances nearly equal, and found to be satisfactory. Many of these comparisons may be made with the data given in Table II. The critical absorption frequencies of cadmium and iodine must be taken account of.

TABLE II
DATA FROM ONE OF THE LAUE PHOTOGRAPHS

Plane	Interplaner distance Å.	Wave length of X-rays Å.	Intensity of spot	Calculated amplitude, for $u = 0.25$
$\bar{2}21$	2.09	0.46	0.4	10
$\bar{3}11$	2.01	0.47	1.6	29
$\bar{4}31$	2.01	0.48	0.8	9
132	1.95	0.47	1.3	21
312	1.95	0.39	0.8	21
$\bar{2}52$	1.64	0.42	0.4	21
$\bar{3}52$	1.64	0.46	0.5	21
$\bar{5}11$	1.59	0.35	0.05	10
$\bar{5}41$	1.59	0.33	0.05	10
$\bar{4}12$	1.56	0.49	0.3	12
$\bar{5}42$	1.56	0.49	0.3	12
$\bar{1}53$	1.51	0.50	0.05	10
153	1.51	0.49	0.05	10
$\bar{5}42$	1.45	0.49	0.4	32
414	1.45	0.49	0.4	32
$\bar{5}02$	1.44	0.44	0.2	21
$\bar{5}52$	1.44	0.41	0.2	21
053	1.40	0.40	0.03	9
$\bar{0}53$	1.40	0.45	0.2	29
$\bar{3}32$	1.38	0.37	0.0	12
$\bar{5}54$	1.35	0.43	0.0	1
504	1.35	0.41	0.0	1
$\bar{6}55$	1.19	0.42	0.02	9
515	1.19	0.41	0.05	29
$\bar{7}24$	1.11	0.47	0.05	32
754	1.11	0.45	0.05	32

Discussion of the Structure

The arrangement to which the foregoing considerations lead is shown in Fig. 2. In this arrangement the shortest distance between the centers of cadmium and iodine atoms is 3.00 Å., which is exactly the sum of the Bragg radii⁵ for these atoms. Because of the nature of the structure the

⁵ W. L. Bragg, *Phil. Mag.*, **40**, 180 (1920).

iodine atoms are also "in contact" on the Bragg hypothesis. The shortest distance between their centers is 4.21 Å., while Bragg's value of the "diameter" of this atom is 2.80. This separation indicates that atoms which are presumably charged with the same sign may be expected to be farther apart than Bragg's hypothesis requires.

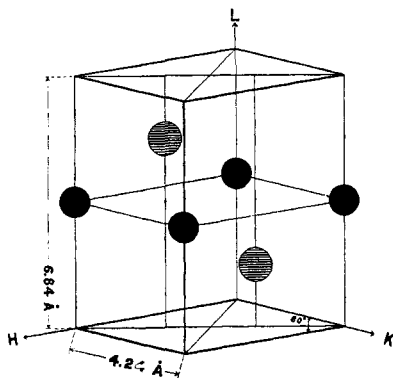


Fig. 2.—This parallelepiped, if repeated parallel to itself in the directions of its edges, will show the crystal structure of cadmium iodide. The black circles represent cadmium atoms, the striped circles iodine atoms.

This structure may be divided into electrically neutral layers by passing planes parallel to the base midway between the cadmium atoms. This may well account for the excellent basal cleavage of the crystal.

It is interesting to note that this arrangement is that found for pyrochroit, $Mn(OH)_2$, by G. Aminoff,⁶ who estimates the value of u for that compound to be $2/9$.

Summary

All the data obtained from 3 spectral photographs and 2 unsymmetrical Laue photographs confirm the structure of cadmium iodide represented in Fig. 2. The positions of the iodine atoms were determined by comparing observed intensities of reflections with the intensities predicted on the assumption that the reflecting powers of the atoms are proportional to their atomic numbers; but with any reasonable assumption regarding reflecting powers the atoms would be placed close to the positions that have been chosen. This arrangement has been shown to be the only possible one if there is only one molecule in the unit.

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⁶ Aminoff, *Z. Kryst. Mineralog.*, **56**, 127 (1921).