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## THE CRYSTAL STRUCTURES OF THE CUPROUS HALIDES.

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### Introduction.

This determination of crystal structure will outline the manner of application of the general method of study based upon the results of the theory of space groups<sup>1</sup> to cubic compounds of the type  $RX$  (where  $R$  and  $X$  are atoms of the same valence) when all of the diffraction data are furnished by a study of the powder photograph from the crystal under investigation.

In order to arrive at a definite structure for such a crystal it is necessary to make the assumption that its structure is simple, since the present lack of precise knowledge concerning the laws which govern the scattering of X-rays by different atoms makes it impossible to eliminate with certainty the one or more complicated structures which can be equally well brought into qualitative agreement with the observed diffraction data from any crystal. Because no crystals of this type have as yet been found for which it is necessary to assign a structure containing more than 4 molecules within the unit cell in order to arrive at a qualitative agreement with the experimental results, discussion will be here limited to possible structures having not more than 4 molecules in the unit.

**The Crystalline Material.**—The cuprous halides were prepared in the ordinary fashion, the chloride and bromide by the reduction of the corresponding cupric salts with sulfur dioxide, the iodide by the reaction between a cupric salt and potassium iodide. The copper iodide prepared in this fashion was sufficiently fine grained so that it could be immediately formed into a suitable film with collodion. Some difficulty was experienced in preparing films of the other two salts because of the readiness with which they undergo oxidation. They were finally obtained in suitable films by the use of molten Canada balsam.

Several unsuccessful attempts were made to grow crystals of the iodide of sufficient size so that reflection photographs from a known crystal face might be made to give the number of molecules to be associated with the unit cube. Several large and externally well-formed dodecahedrons (more than 0.5 cm. in diameter) of the cuprous chloride<sup>2</sup> were available for study. Attempts to prepare Laue photographs with sections from several of these specimens invariably led to photographs showing only a few scattered and much distorted spots. Several efforts to obtain reflection spectra by the usual rotating crystal method from both the cube and the dodecahedral faces and using both the L-radiation of tungsten and the K-radiation of molybdenum were likewise failures.

<sup>1</sup> Niggli, "Geometrische Krystallographie des Discontinuums," Gebrüder Borntraeger, Berlin, 1919.

Ralph W. G. Wyckoff, *Am. J. Sci.*, **1**, 138 (1921), etc.

<sup>2</sup> These crystals were provided through the courtesy of H. E. Merwin of this laboratory.

The reflections from the powder films that were made in the way already outlined were, however, satisfactory. The powder spectrograph was the same as that previously used by one of us<sup>3</sup> and resembles, though it is of smaller size and does not possess so many arrangements for the shielding from secondary radiation, a spectrograph recently described.<sup>4</sup> Satisfactory results were achieved by using simply a zirconium oxide filter which was in contact with and covered the entire face of the photographic film. This screen thus served the double purpose of rendering the primary rays monochromatic and of absorbing secondary radiation from both the spectrometer and the crystalline film. Such a filter in contact with the photographic plate is a necessity if any diffraction is to be recorded in the case of the cuprous bromide because of the very large amount of secondary radiation emitted, for the most part, by the bromine of the salt.

Because of discrepancies in the recorded values redeterminations of the *density* of cuprous chloride and cuprous iodide were made by a pycnometer method.<sup>5</sup> The density of the chloride at 30° against water at 4° was thus found to be 4.136, for the iodide 5.667. The only recorded value of the bromide,<sup>6</sup>  $\rho = 4.72$  is in good agreement with the diffraction measurements.

The *symmetry* of the crystals of the cuprous halides is described as that of the tetrahedral class (hemimorphic hemihedry) of the cubic system. The arrangement of the atoms in the unit cells of these crystals must therefore be defined by special cases of one of the space groups,  $T_d^1 - T_d^7$ , having tetrahedral symmetry.

#### The Possible Arrangements of the Atoms in the Unit Cells.

*One Chemical Molecule within the Unit.*—There is but one way of placing a single molecule of a compound RX within the unit so that the arrangement possesses cubic symmetry. These two special cases having a single equivalent position within the unit are special cases of the space group  $T_d^1$ . On the basis of the arrangement of its equivalent positions (or atomic positions) the symmetry of this possible grouping is that of the holohedry of the cubic system. Any lower degree of symmetry, such as is evident in the case of crystals of the cuprous halides, would be attributed to some lack of symmetry in the atoms themselves. This possible structure<sup>7</sup> for the crystals under investigation is as follows.

<sup>3</sup> Wyckoff, *Am. J. Sci.*, **2**, 244 (1921).

<sup>4</sup> Hull, *Phys. Rev.*, [2] **17**, 571 (1921).

<sup>5</sup> Johnston and Adams, *THIS JOURNAL*, **34**, 566 (1912).

<sup>6</sup> Groth, "Chemische Krystallographie," Wilhelm Engelmann, Leipzig, 1906, Vol. 1, p. 199.

<sup>7</sup> The results in this paper dealing with all of the possible arrangements for the atoms in these crystals are based upon a complete analytical expression of the results of the theory of space groups prepared by one of the present writers but as yet unpublished.

Cu: 000.

X:  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ .

*Two Molecules within the Unit Cell.*—There is no possible way of arranging 2 molecules of a compound of the type RX within a unit cell so that the resulting structure will exhibit cubic symmetry.

*Three Molecules within the Unit Cell.*—But one way of placing 3 molecules of a compound RX within a unit cube is possible. This arrangement, also a special case of the space group  $T_d^1$ , is as follows.

(3a) Cu:  $\frac{1}{2}\frac{1}{2}0$ ;  $\frac{1}{2}0\frac{1}{2}$ ;  $0\frac{1}{2}\frac{1}{2}$ .

X:  $00\frac{1}{2}$ ;  $0\frac{1}{2}0$ ;  $\frac{1}{2}00$ .

In this arrangement again a degree of symmetry lower than that of the holohedry of the cubic system must be accounted for by some dissymmetry in the shape of the atomic fields of force.

*Four Molecules within the Unit Cell.*—Two space groups exhibiting tetrahedral symmetry have special cases with 4 equivalent positions in the unit cell. The possible structures derived from one of these,  $T_d^2$ , are

(4a) Cu: 000;  $\frac{1}{2}\frac{1}{2}0$ ;  $\frac{1}{2}0\frac{1}{2}$ ;  $0\frac{1}{2}\frac{1}{2}$ .

X:  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ ;  $00\frac{1}{2}$ ;  $0\frac{1}{2}0$ ;  $\frac{1}{2}00$ .

This, the "sodium chloride arrangement," has in the grouping of its atoms holohedral symmetry.

(4b) Cu: 000;  $\frac{1}{2}\frac{1}{2}0$ ;  $\frac{1}{2}0\frac{1}{2}$ ;  $0\frac{1}{2}\frac{1}{2}$ .

X:  $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ ;  $\frac{1}{4}\frac{3}{4}\frac{3}{4}$ ;  $\frac{3}{4}\frac{1}{4}\frac{3}{4}$ ;  $\frac{3}{4}\frac{3}{4}\frac{1}{4}$ .

The symmetry of the arrangement of the atoms in this, the "zinc sulfide structure," is tetrahedral.

The arrangement of the atoms in the third of the possible structures<sup>8</sup> containing four molecules in the unit also gives tetrahedral symmetry. This structure is derived from the space group  $T_d^1$ . It is as follows:

(4c) Cu: uuu;  $u\bar{u}\bar{u}$ ;  $\bar{u}u\bar{u}$ ;  $\bar{u}\bar{u}u$ .

X: vvv;  $v\bar{v}\bar{v}$ ;  $\bar{v}v\bar{v}$ ;  $\bar{v}\bar{v}v$

The values of the coördinates u and v can lie anywhere between zero and unity.

### The Choice of the Correct Structures.

Using the customary expression<sup>9</sup> for the calculation of the intensity of reflection from any arrangement of atoms, and taking A as the sum-

<sup>8</sup> If as is conceivable, though not probable perhaps, in the light of the existing crystallographic studies of these crystals, their symmetry is really tetrahedral, then one more structure which likewise contains four molecules within the unit cube is possible. This grouping, which is isomorphous with the space group  $T^4$ , is as follows:

(4d) Cu: uuu;  $u+\frac{1}{2}, \frac{1}{2}-u, \bar{u}$ ;  $\bar{u}, u+\frac{1}{2}, \frac{1}{2}-u$ ;  $\frac{1}{2}-u, \bar{u}, u+\frac{1}{2}$ .

X: vvv;  $v+\frac{1}{2}, \frac{1}{2}-v, \bar{v}$ ;  $\bar{v}, v+\frac{1}{2}, \frac{1}{2}-v$ ;  $\frac{1}{2}-v, \bar{v}, v+\frac{1}{2}$ .

A discussion of this possible structure in relation to the X-ray diffraction data will be given in a footnote at a later point.

<sup>9</sup> Wyckoff, *Am. J. Sci.*, 50, 317 (1920).

mation of its cosine terms and B as the summation of the corresponding sine terms, the diffraction effects to be expected from copper and halogen atoms placed in each of these possible groupings can be readily calculated. They are for

Arrangement (1a):

When the indices of the reflecting plane are *two odd* and *one even*  $A = \bar{R} + \bar{X}$  for all values of  $n$ , where  $\bar{R}$  and  $\bar{X}$ , the scattering powers of the atoms of R and of X, are to be taken as roughly proportional to the atomic numbers and where  $n$  is the order of the reflection.

For indices *two even* and *one odd*, or *all odd*,  $A = \bar{R} - \bar{X}$  when  $n$  is odd,  $A = \bar{R} + \bar{X}$  when  $n$  is even. In all cases  $B = 0$ .

Arrangement (3a):

For indices *two odd* and *one even*,  $A = \bar{R} + \bar{X}$  when  $n$  is odd,  $A = 3(\bar{R} + \bar{X})$  when  $n$  is even. For indices *two even* and *one odd*,  $A = \bar{R} - \bar{X}$  when  $n$  is odd,  $A = 3(\bar{R} - \bar{X})$  when  $n$  is even. For indices *all odd*  $A = 3(\bar{R} - \bar{X})$  when  $n$  is odd,  $A = 3(\bar{R} + \bar{X})$  when  $n$  is even. In all cases  $B = 0$ .

Arrangement (4a):

For indices *two even* and *one odd*, or *two odd* and *one even*,  $A = 0$  when  $n$  is odd,  $A = 4(\bar{R} + \bar{X})$  when  $n$  is even. For indices *all odd*,  $A = 4(\bar{R} - \bar{X})$  when  $n$  is odd,  $A = 4(\bar{R} + \bar{X})$  when  $n$  is even. In all cases  $B = 0$ .

Arrangement (4b):

For indices *two even* and *one odd*,  $A = 0$  when  $n$  is odd,  $A = 4(\bar{R} \pm \bar{X})$  when  $n$  is even, + when  $n = 4, 8, \dots$ , - when  $n = 2, 6, \dots$ . For indices *two odd* and *one even*,  $A = 0$  when  $n$  is odd,  $A = 4(\bar{R} + \bar{X})$  when  $n$  is even. In both of these cases  $B = 0$ . For indices *all odd*,  $A = 4\bar{R}$ ,  $B = 4\bar{X}$  when  $n$  is odd,  $A = 4(\bar{R} \pm \bar{X})$  when  $n$  is even, + when  $n = 4, 8, \dots$ , - when  $n = 2, 6, \dots$ ,  $B = 0$ .

Arrangement (4c):

$A = R[\cos 2\pi nu(h+k+1) + \cos 2\pi nu(h-k-1) + \cos 2\pi nu(k-h-1) + \cos 2\pi nu(1-h-k)] + \bar{X}$  [a similar term in  $v$ ].  $B =$  a sine term similar to the cosine term.

From these values of A and B the approximate intensity of reflection ( $I'$ ) from any plane  $hkl$  can be calculated for each of these arrangements through the use of the customary expression

$$I' \propto (d/n)^2 (A^2 + B^2)$$

the spacing  $d_{hkl}$  of any plane being obtained as usual from the relation

$$d_{hkl} = \frac{d_{100}}{\sqrt{h^2 + k^2 + l^2}}.$$

The intensity ( $I$ ) of a line in a powder photograph, the product of this  $I'$  into the number of planes ( $s$ ) in the crystal form to which the plane  $hkl$  is assigned, has thus been written

$$I_{hkl} \propto \frac{1}{(h^2 + k^2 + l^2)n^2} \times (A^2 + B^2) \times s$$

$d_{100}$  being written as unity. The constants of the spectrometer being known from a standardization with sodium chloride, it is a simple matter to derive from the equation  $d_{100}^3 = mM/\rho$  (where  $m$  = the number of molecules in the unit cube,  $M$  = the mass of one molecule of the salt and  $\rho$  = its density) the positions upon a spectrogram of the reflections from any plane of atoms for each of the possible structures. The carrying out of these two calculations, one of the intensity, the other of the positions of the reflections from all atomic planes, furnishes the manner of completely predicting the diffraction effects that would be obtained from the atoms of the substance under investigation arranged according to each of the possible crystal structures.

The intensities of reflection and the positions of the four strongest spectrum lines<sup>10</sup> thus calculated for each of the possible arrangements, except (4c), and for each of the salts under investigation are given in Tables I—IV. The observed positions of the spectrum lines and an estimate of their relative intensities are given for these crystals in Table V. Because of the uncertain character of the assumed values of the scattering powers of the different atoms and the approximate nature of the assumption that  $I \propto (d/n)^2$ , no more than a qualitative agreement is to be expected between the observed estimations of intensity and those calculated for the correct structures. It will be observed that of these various possibilities the only one which presents any agreement with observation is grouping (4b), the "zinc sulfide structure." Furthermore it will be seen that the qualitative agreement in this case is good.<sup>11</sup> This leaves no doubt but that the correct structure for these cuprous halides is in each case either precisely the "zinc sulfide arrangement" or a close approach to it. A consideration of the other possible grouping, (4c), shows that it is not possible to assign such values to  $u$  and  $v$  that the resulting structure is an approach to (4b). It can then be definitely concluded that if their structures are simple ones and if their symmetry is really that of the tetrahedral class of the cubic system,<sup>12</sup> the crystal structures of cuprous chloride, cuprous bromide and cuprous iodide are in each case given by the "zinc sulfide arrangement." The lengths of the sides

<sup>10</sup> In this instance no more lines are necessary to establish the structures.

<sup>11</sup> It is known from the experimentally established "normal decline" of intensity with spacing that this decline is at a rate faster than the square, as here assumed. All of the discrepancies between the calculated and the estimated intensities both in the case of those lines which are discussed and for other lines observed in the spectra but not recorded are found to be in accord with this fact.

<sup>12</sup> If the structure were tetartohedral, then grouping (4d) becomes a possibility (see Ref. 11). If in this grouping  $u = 0$  and  $v = 1/4$  the structure that results is identical with (4b). It is evident that qualitative agreement with experiment would also be ensured for values of  $u$  close to but not exactly equal to 0 and for values of  $v$  close to  $1/4$ .

of the unit cube, as calculated from the three strongest lines in each spectrum are

	A. U.
Cuprous chloride.....	5.49
Cuprous bromide.....	5.82
Cuprous iodide.....	6.10

TABLE I  
ARRANGEMENT (1a)

Plane	<i>n</i>	Calculated Spacings			Calculated Intensity		
		CuCl	CuBr	CuI	CuCl	CuBr	CuI
110	(1)	2.40	2.60	2.69	12.670	24.420	40.000
112	(1)	1.39	1.50	1.55	8.480	16.350	26.800
132	(1)	0.91	0.98	1.02	7.270	15.090	22.900
130	(1)	1.07	1.16	1.20	5.090	9.830	16.100

TABLE II  
ARRANGEMENT (3a)

Plane	<i>n</i>	Calculated Spacings			Calculated Intensity		
		CuCl	CuBr	CuI	CuCl	CuBr	CuI
100	(2)	2.45	2.65	2.74	28.600	55.300	90.800
110	(2)	1.73	1.87	1.94	28.300	55.000	90.200
120	(2)	1.09	1.18	1.22	22.700	43.900	72.000
112	(2)	1.00	1.08	1.12	19.000	36.700	60.250

TABLE III  
ARRANGEMENT (4a)

Plane	<i>n</i>	Calculated Spacings			Calculated Intensity		
		CuCl	CuBr	CuI	CuCl	CuBr	CuI
100	(2)	2.70	2.92	3.02	50.700	98.000	161.300
110	(2)	1.90	2.06	2.13	50.300	97.300	160.100
120	(2)	1.20	1.30	1.35	40.300	77.900	128.000
112	(2)	1.10	1.19	1.23	33.600	65.200	107.200

TABLE IV  
ARRANGEMENT (4b)

Plane	<i>n</i>	Calculated Spacings			Calculated Intensity		
		CuCl	CuBr	CuI	CuCl	CuBr	CuI
110	(2)	1.90	2.06	2.13	50.500	98.000	160.000
111	(1)	3.12	3.37	3.49	47.900	88.000	146.500
113	(1)	1.62	1.76	1.82	39.300	72.000	119.500
112	(2)	1.10	1.19	1.23	33.750	65.300	107.000
133	(1)	1.23	1.31	1.38	22.700	41.500	69.200 <sup>13</sup>

<sup>13</sup> Though the calculated intensity of this line is less than that of two others (not given), it is more intense upon the photographs than even (112). This, however, is not unexpected because of its greater spacing. See Ref. 11.

TABLE V  
OBSERVED VALUES

Observed Spacings			Estimated Intensity (10 = the strongest line)		
CuCl <sup>14</sup>	CuBr	CuI	CuCl	CuBr	CuI
3.18	3.37	3.52	10	10	10
1.93	2.04	2.15	8	8	9
1.65	1.75	1.84	7	6	8
1.26	1.31	1.38	0.3	2	2
1.14	1.18	1.24	0.1	1	1

### The Chemical Significance of these Crystal Structures.

It has previously been pointed out<sup>15</sup> that with compounds of a certain type (the valence compounds, in which the chemical bonds are electrons shared by two atoms) there might be such a connection between the positions of the atoms and their chemical valence as would enable the prediction of the manner of combination of the atoms of a compound from the arrangement of its atoms. It was also shown that all of the structures thus far studied with the X-rays were in agreement with this idea. A "zinc sulfide arrangement" of the atoms of a compound of the type RX, where both R and X are monovalent atoms, is not to be anticipated, however, upon these simple grounds. As a consequence of this study of the cuprous halides, then, it will evidently be necessary to abandon these simple considerations and, when attempting to correlate crystal structure and the nature of chemical combination, to view such factors as the shapes and sizes of atoms as important in determining the arrangement of the atoms in crystals.

### Summary.

Cuprous chloride, cuprous bromide and cuprous iodide all have the "zinc sulfide arrangement" of their atoms in crystals. The lengths of the sides of the unit cubes in the three cases are 5.49 A. u., 5.82 A. u. and 6.10 A. u.

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<sup>14</sup> These values are uniformly higher than the calculated spacings so that there can be no doubt that the new determination of density is somewhat in error. Its value, calculated from the observed spacings, becomes = 3.93.

<sup>15</sup> Wyckoff, *J. Wash. Acad. Sci.*, 9, 565 (1919); *J. Franklin Inst.*, 191, 199 (1921).