

The crystal-structures of the sulphides of mercury.

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Introductory.

MERCURIC sulphide, HgS , occurs in nature as two well-known modifications, cinnabar and metacinnabarite. The latter is somewhat rare and occurs as black cubic crystals possessing the symmetry of the zinc-blende, i. e. the ditesseral polar class. It is considered to be identical with chemically precipitated black mercuric sulphide, the density of both being 7.81. Cinnabar is of more common occurrence and is found as well-defined crystals and in the massive state. The crystals are assigned to the trigonal holoaxial class. The rhombohedral angle¹ is $92^{\circ}30'$ corresponding to an axial ratio c/a of 1.1453. The crystals possess a very good cleavage parallel to the prism $(2\bar{1}1)=(10\bar{1}0)$. The rotation of the plane of polarization, for red light traversing the crystal in a direction parallel to the optic axis, is 315° per millimetre, a value roughly eighteen times that of a similar thickness of quartz. The birefringence of cinnabar is double that of calcite; thus $\epsilon=3.201$, $\omega=2.854$, $\epsilon-\omega=0.347$. The density of cinnabar is 8.09, a value rather higher than that of the cubic form. There is probably an intimate relationship between the structures in these two modifications, judging by the ease with which either modification can be obtained from the other. Heat is developed when metacinnabarite is converted to cinnabar, so that the latter possesses less potential energy and is the more stable form. In view of the remarkable properties possessed by cinnabar, the exact determination of the positions of the atoms in the crystal is of great interest.

Since this work was begun, the results of two other investigations have

¹ Data from the compilation of P. Groth, *Chem. Kryst.*, 1906, vol. 1, p. 151.

been published. Mauguin¹ investigated cinnabar spectrometrically and confirmed the trigonal holoaxial symmetry assigned to the crystal. He showed that the positions of the mercury and sulphur atoms must be those of the sodium and chlorine atoms in sodium chloride. The cinnabar structure may be pictured as derived from that of sodium chloride by a slight compression of the latter, parallel to a trigonal axis, and displacements, which he showed must be small, of the atoms from the positions at the corners of the unit cells. The axial ratio c/a was found to have a value 2.291, which is double that given by Groth. N. H. Kolkmeijer, J. M. Bijvoet, and A. Karssen² have published two papers. In the first of these, the crystal-structure of cubic mercuric sulphide was determined and found to be similar to that of zinc-blende, with $a=5.85\text{\AA}$. They also made some measurements on cinnabar, and showed that the length of the a -axis in this crystal is identical with the shortest distance between two mercury atoms in metacinnabarite. In the second paper, they extended the observations on cinnabar and found that the results obtained by Mauguin were substantially correct. Their value for a of cinnabar (4.14\AA .) is slightly lower than that obtained by Mauguin (4.15\AA .) and by the present authors (4.16\AA .). Their determination of the structure of cubic mercuric sulphide is in agreement with that which had been obtained by us. We had found that it has a zinc-blende arrangement of the mercury and sulphur atoms, with practically the same dimensions for the side of the unit cell. The present paper describes our results on cubic mercuric sulphide, and in addition an examination of cinnabar. In the case of the latter crystallized substance, the results confirm the general arrangement of the atoms suggested by Mauguin, and, in addition, make it possible to assign positions to the mercury and sulphur atoms by determining with some accuracy their displacements from the lattice corners of the simple structure.

Experimental.

The powders used were, in the case of cinnabar, the finely powdered massive mineral, and in the case of the cubic modification, some chemically precipitated sulphide, well washed and dried. The powders were separately mounted on a hair and exposed in a cylindrical camera to the radiation of a copper anticathode. A nickel

¹ C. Mauguin, *Compt. Rend. Acad. Sci. Paris*, 1923, vol. 176, pp. 1483. [*Min. Abstr.*, vol. 2, p. 330.]

² N. H. Kolkmeijer, J. M. Bijvoet, and A. Karssen, *Proc. Sect. Sci. K. Akad. Wetensch. Amsterdam*, 1924, vol. 27, pp. 390, 847; *Recueil Trav. Chim. Pays-Bas*, 1924, vol. 43, pp. 677, 894. [*Min. Abstr.*, vol. 2, p. 511.]

screen was used to intercept the K_{β} radiation so that the lines on the film were due to the K_{α} beam alone, with $\lambda = 1.5374 \text{ \AA}$. The authors also obtained one film from cinnabar with the apparatus described by A. J. Bradley,¹ for the purpose of testing the dimensions obtained by their own camera. There was a very satisfactory agreement between the two.

The Structure of Cubic Mercuric Sulphide.

A series of six films were measured on a travelling-stage microscope and the average results are shown in Table I. An inspection of the lines in Table I shows that only those lines whose indices are all even or all odd are present. This is typical of all cubic structures whose basic lattice is the face-centred cube. Considerations of density assign four molecules of HgS to the unit cube. If the number of molecules in the unit cube were larger, other lines than those actually observed would have appeared on the film. The structure must consist of two interpenetrating face-centred cubic lattices, these being the familiar 'rock-salt' and 'zinc-blende' arrangements. It is required, therefore, to find a means of distinguishing between these two types.

The method used throughout this research is as follows. The lines observed on the films are arranged as near as possible in descending order of magnitude, the strongest line being 1. Calculated intensities for any arrangement may be similarly arranged in descending order, and the two orders may then be placed side by side and compared. That structure is chosen as the closest approximation to the truth, for which the agreement between calculated and observed orders of intensity is best. The method of selection adopted in practice has been to add the difference between calculated and observed orders for each line, for it has been found that the sum shows a marked minimum for a certain set of values of the parameters. The difference is generally less than one unit per line for the structure which gives the best agreement. In the case of cubic mercuric sulphide, there are only two structures to choose between, viz. the rock-salt and the zinc-blende structures. Table II shows the observed and calculated orders of intensity for the two arrangements. They are based upon the assumption that the ions of Hg^{++} and S^{--} reflect in the ratio of 78:18, and that the falling off of intensity with increasing glancing angle θ is represented by a factor¹ $\frac{1}{\sin^2 \theta}$. A reference to Table II will show that

¹ A. J. Bradley, The crystal structure of metallic arsenic. *Phil. Mag.*, 1924, ser. 6, vol. 47, pp. 657-671. [*Min. Abstr.*, vol. 2, p. 331.]

TABLE I. *Precipitated cubic mercuric sulphide (HgS).*

[With K_{α} copper radiation, $\lambda = 1.5374 \text{ \AA.}$]

Average distance (mm.).	θ .	$\sin \theta$.	$\sin^2 \theta$.	$K \times (h^2 + k^2 + l^2)$.	(hkl.)	Observed order of intensity.
11.6	13° 4'	0.2262	0.05117	0.01706 × 3	(111)	1
13.57	15 17	0.2635	0.06944	0.01736 × 4	(200)	10
19.37	21 51	0.3721	0.1385	0.01736 × 8	(220)	3
23.0	25 57	0.4376	0.1915	0.01741 × 11	(311)	1
24.0	27 1	0.4543	0.2064	0.01720 × 12	(222)	12
28.1	31 36	0.5241	0.2747	0.01720 × 16	(400)	11
31.05	34 59	0.5734	0.3288	0.01734 × 19	(331)	7
31.95	35 59½	0.5877	0.3452	0.01726 × 20	(420)	7
35.5	39 59	0.6425	0.4128	0.01720 × 24	(422)	4
38.03	42 49	0.6795	0.4617	0.01710 × 27	(333) } (511) }	6
42.58	47 54	0.7419	0.5504	0.01721 × 32	(440)	13
45.15	50 46	0.7746	0.6000	0.01711 × 35	(531)	5
46.1	51 50	0.7862	0.6181	0.01720 × 36	(600) } (442) }	14
49.45	55 42	0.8261	0.6826	0.01707 × 40	(620)	9

TABLE II. *Precipitated cubic mercuric sulphide (HgS).*

Lines in order of intensity.

(hkl).	Observed.	Calculated for zinc-blende structure.	Calculated for rock-salt structure.
(111)	1	1	4
(200)	10	10	1
(220)	3	3	1
(311)	1	2	6
(222)	12	13	7
(400)	11	11	12
(331)	7	7	10
(420)	7	4	3
(422)	4	5	5
(333) } (511) }	6	8	11
(440)	13	12	12
(531)	5	6	9
(600) } (442) }	14	14	14
(620)	9	9	8

Σ (14 lines) = 9.

Σ (14 lines) = 44.

the structure is that of zinc-blende. This is in agreement with the external symmetry of metacinnabarite crystals. The value of the unit cell length a is 5.854 \AA ., that calculated from the density being 5.83 \AA .. The distance between adjacent Hg and S atom-centres is $\frac{5.854\sqrt{3}}{4} = 2.54 \text{ \AA}$.. These dimensions are in good agreement with the value obtained by Kolkmeijer, Bijvoet, and Karsen ($a=5.85 \text{ \AA}$.).

The Structure of Cinnabar.

The average results of six films of cinnabar are included in Table III. The spacings correspond with a hexagonal space-lattice, with three molecules per unit cell. The unit cell dimensions are:

$$\begin{aligned} a &= 4.160 \text{ \AA} \\ c &= 9.540 \text{ \AA} \end{aligned}$$

The dimensions calculated from the density and accepted axial ratio give $a=4.165 \text{ \AA}$ and $c=9.540 \text{ \AA}$.

If the atoms were arranged on a 'rock-salt' lattice, slightly compressed along a trigonal axis in the manner explained above, the co-ordinates of points would be:

$$\left. \begin{array}{l} \text{Mercury atoms at } (000), (\frac{2}{3} \frac{1}{3} \frac{1}{3}), (\frac{1}{3} \frac{2}{3} \frac{2}{3}) \\ \text{Sulphur atoms at } (00\frac{1}{2}), (\frac{2}{3} \frac{1}{3} \frac{5}{6}), (\frac{1}{3} \frac{2}{3} \frac{1}{6}) \end{array} \right\} \dots \dots \dots (1)$$

This arrangement cannot be far from the truth, because a comparison of the observed order of intensity with that calculated for such an arrangement, shows quite a good general agreement (see Table III). That the actual structure is more complex is shown by the appearance of certain lines which would not be given by the simple structure, viz.:

$$\left. \begin{array}{l} (10\bar{1}0), \quad (10\bar{1}3), \quad (11\bar{2}2) \quad (10\bar{1}9) \\ \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad (3035) \\ \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad (1128) \\ \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad (22\bar{1}2) \end{array} \right\} \dots$$

The simple rhombohedral structure is therefore ruled out. As the (0001) planes are thirdded, the only other types to be considered belong to the trigonal holoaxial classes, represented by the symbols D_3^3 and D_3^4 . This is in agreement with Mauguin's work mentioned earlier in this paper. In D_3^4 there is a possible movement of atoms from positions on the simple rhombohedron, in a direction *parallel* to the a -axis of the hexagonal lattice. Each sulphur atom will tend to move nearer to two adjacent mercury atoms situated in planes at a distance equal to $c/6$ above and

TABLE III. *Cinnabar (HgS)*.
 [With K_{α} copper radiation, $\lambda = 1.5374 \text{ \AA}$.]

Distance of line to centre (mm.).	θ .	Spacing in \AA . units.		(hkl) .	Obs. order of intensity.	Calc. order of intensity; $\phi = 45^{\circ}$.
		Observed.	Calculated.			
9.40	$10^{\circ} 35'$	$3.63 \pm$	3.61	(10 $\bar{1}$ 0)	28	28
10.13	11 25	3.368	3.376	(10 $\bar{1}$ 1)	2	2
10.74	12 $5\frac{1}{2}$	3.179	3.181	(0003)	19	18
11.90	13 24	2.869	2.879	(10 $\bar{1}$ 2)	1	1
14.65	16 30	2.383	2.370	(10 $\bar{1}$ 3)	28	28
16.40	18 29	2.080	2.083	(1120)	3	3
—	—	—	2.085	(1121)	—	—
17.14	19 19	1.990	1.990	(10 $\bar{1}$ 4)	4	3
17.83	20 $5\frac{1}{2}$	1.913	1.910	(1122)	25	28
—	—	—	1.806	(2020)	—	—
19.25	21 $41\frac{1}{2}$	1.772	1.773	(2021)	10	12
19.56	22 $2\frac{1}{2}$	1.744	1.744	(1123)	8	8
20.25	22 49	1.685	{ 1.688 1.689 }	{ (2022) (10 $\bar{1}$ 5) }	5	5
21.42	24 8	1.593	1.591	(0006)	19	20
—	—	—	{ 1.570 1.568 }	{ (2023) (1124) }	—	—
—	—	—	1.456	(10 $\bar{1}$ 6)	—	—
23.78	26 $47\frac{1}{2}$	1.435	1.439	(2024)	12	16
—	—	—	1.364	(1230)	—	—
25.22	28 25	1.353	1.351	(1231)	9	9
26.00	29 17	1.312	{ 1.312 1.312 }	{ (1232) (2025) }	6	6
26.94	30 20	1.267	{ 1.275 1.265 }	{ (10 $\bar{1}$ 7) (1126) }	6	6
—	—	—	1.254	(1233)	—	25
28.13	31 $41\frac{1}{2}$	1.213	1.204	(3030)	21	20
28.69	32 19	1.189	{ 1.185 1.185 1.185 }	{ (1234) (2026) (3031) }	14	12
—	—	—	1.166	(3032)	—	—
30.10	33 54	1.134	{ 1.141 1.133 }	{ (1127) (10 $\bar{1}$ 8) }	21	19
30.27	34 6	1.127	1.125	(3033)	17	14
30.82	34 43	1.107	1.110	(1235)	17	16
—	—	—	1.074	(3034)	—	—
32.20	36 16	1.060	1.061	(0009)	25	25
32.30	36 58	1.040	{ 1.041 1.036 1.036 }	{ (2240) (2241) (1236) }	23	24
33.11	37 17	1.031	1.032	(2027)	23	23
33.55	37 48	1.017	{ 1.020 1.018 1.018 1.017 }	{ (10 $\bar{1}$ 9) (3035) (1128) (2242) }	25	25

TABLE III—(continued):

Distance of line to centre (mm.), θ .	Spacing in Å. units. Observed.	Calculated.	(hkl) .	Calc. order		
				Obs. order of intensity.	of intensity $\phi = 45^\circ$.	
34.36	38° 43'	0.993	{ 1.00	10	11	
			{ 0.995			
			{ 0.990			
35.54	40 2½	0.960	{ 0.964	12	9	
			{ 0.960			
—	—	—	0.954	—	—	
37.10	41 47	0.920	0.920	(1.0.1.10)	16	20
—	—	—	0.915	(2215)	—	—
37.9	42 43	0.900	{ 0.902	14	14	
			{ 0.898			
			{ 0.898			
					Σ (39 lines) = 26.	

below it. The co-ordinates of points, in the general case where both sets of atoms move, are as follows:—

$$D_3^4 \left\{ \begin{array}{l} \text{Mercury atoms at } (0 - p_{\text{H}}, 0 - p_{\text{H}}, 0), (\frac{2}{3}, \frac{1}{3} + p_{\text{H}}, \frac{1}{3}), (\frac{1}{3} + p_{\text{H}}, \frac{2}{3}, \frac{2}{3}) \\ \text{Sulphur atoms at } (\frac{1}{3} + p_{\text{S}}, \frac{2}{3}, \frac{1}{6}), (0 - p_{\text{S}}, 0 - p_{\text{S}}, \frac{1}{2}), (\frac{2}{3}, \frac{1}{3} + p_{\text{S}}, \frac{5}{6}) \end{array} \right\} \quad (2)$$

where p_{H} and p_{S} are the parameters of mercury and sulphur atoms respectively. The symmetry of D_3^3 , on the other hand, necessitates a movement *normal* to the unit cell edge, so that each sulphur atom would tend to move in a direction towards one mercury atom. The co-ordinates of the D_3^3 arrangement are:

$$D_3^3 \left\{ \begin{array}{l} \text{Hg atoms at } (0 - 2p_{\text{H}}, 0 - p_{\text{H}}, 0), (\frac{2}{3} + p_{\text{H}}, \frac{1}{3} - p_{\text{H}}, \frac{1}{3}), (\frac{1}{3} + p_{\text{H}}, \frac{2}{3} + 2p_{\text{H}}, \frac{2}{3}) \\ \text{S atoms at } (0 - p_{\text{S}}, 0 + p_{\text{S}}, \frac{1}{2}), (\frac{1}{3} + 2p_{\text{S}}, \frac{2}{3} + p_{\text{S}}, \frac{1}{6}), (\frac{2}{3} - p_{\text{S}}, \frac{1}{3} - 2p_{\text{S}}, \frac{5}{6}) \end{array} \right\} \quad (3)$$

In each case there are two parameters, p_{H} and p_{S} , to be evaluated, and there is no limit fixed by the symmetry to the dimensions of either of these, which may vary independently of each other within a considerable range of values. It is necessary, therefore, to use some means of estimating the approximate values to be assigned to p_{H} and p_{S} . It can be readily shown that on the simple arrangement given by co-ordinates (1) the distance apart of mercury and sulphur atoms is greater than that obtained in the cubic sulphide, which is 2.54 Å. As a possible guide to the solution, we may try the effect of a displacement of the atoms which makes the distance apart of mercury and sulphur the same in the two structures. The amount of movement necessary to bring this about is roughly $a/8$ for the structure based on D_3^4 and $a/20$ for the structure based on D_3^3 . These values for p_{S} are fractions of the a -axis of the hexagonal space-lattice. It is convenient for purposes of calculation to replace the parameter p by

a parameter Φ where $\Phi = 360^\circ p$. The approximate values calculated above are then Φ_s (on D_3^4 type) = 40° – 45° . Φ_s (on D_3^3 type) = 18° . The authors used these values merely as guides to point to a possible solution of the parameters.

A test of the effect of moving the mercury and sulphur atoms from the symmetrical positions of the simple rhombohedral lattice brings out two points clearly. The calculated intensities are very sensitive to changes in the position of the mercury atoms. Quite a small movement destroys the general accord between calculated and observed values shown above to exist, and it is clear that these atoms must be almost exactly at the symmetrical positions, so that Φ_H has a very small value. On the other hand, a movement of the sulphur atoms in accord with either point-system can be made to improve considerably the agreement between calculated and observed orders of intensity. The movement consistent with point-system D_3^4 proves to be more effective in doing this than that associated with D_3^3 , and the best agreement is obtained when the sulphur atoms have moved to such an extent that the distance Hg—S in cinnabar is the same as that in cubic mercuric sulphide. Intensities for values of the parameter for the sulphur atom alone, ranging well on either side of the values obtained in the manner shown above, were calculated. Lines were arranged in order of magnitude downwards and these orders were compared with the observed order, shown in column six, Table III. The sum of errors, Σ , for each parameter was found and the results are shown in Table IV.

TABLE IV. *Cinnabar (HgS)*. With $\Phi_H = 0$.

D_3^4	{	Φ_s	...	0°	30°	40°	45°	50°	60°
		Σ	...	74	41	36	26	42	45
D_3^3	{	Φ_s	...	0°	15°	20°	—	25°	30°
		Σ	...	74	57	48	—	48	52

An inspection of Table IV shows (a) that the general agreement in D_3^4 type is better than in D_3^3 type (shown by the lower Σ values), and (b) that there is a minimum value for Φ_s in the neighbourhood of 45° on the D_3^4 arrangement. It is found, on the other hand, that if the effect of a slight movement of the mercury atoms is taken into consideration the value of Σ increases considerably. For instance, a displacement of 5° in the case of the ($\Phi_s = 45^\circ$) structure had the effect of raising Σ from 26 to 55. In addition, lines representing (1016), (1230), (2244), and (3032) ought to make their appearance, but these are not to be found on any of the films. A displacement of even $\frac{1}{2}^\circ$ from the above position would still bring in (3032), (1230), and possibly (2244). In a similar way, it can be

shown that on arrangements of the D_3^3 type, no improvement is obtained by postulating a displacement of mercury atoms. It may be concluded, therefore, that the experimental results are best explained by a structure possessing the symmetry of D_3^4 and with co-ordinates as follows:

Mercury atoms at (000) , $(\frac{2}{3} \frac{1}{3} \frac{1}{3})$, $(\frac{1}{3} \frac{2}{3} \frac{2}{3})$.

Sulphur atoms at $(\frac{1}{3} + p \cdot \frac{2}{3} \cdot \frac{1}{3})$, $(0 - p \cdot 0 - p \cdot \frac{1}{2})$, $(\frac{2}{3} \cdot \frac{1}{3} + p \cdot \frac{5}{6})$.

where $p = 45/360 = 0.125 \times a$.

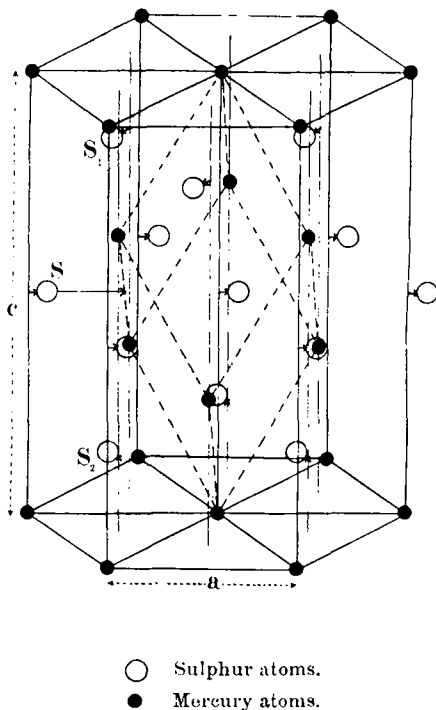


FIG. 1. The arrangement of atoms in cinnabar. Arrow-heads indicate directions of displacement of sulphur atoms. Dotted lines join mercury atoms on the same rhombohedron.

Description of Structure.—Cinnabar crystallizes on a point-arrangement whose symmetry D_3^4 agrees with the ascertained crystallographic symmetry of the mineral. As shown in figs. 1 and 2, mercury atoms are arranged on a simple rhombohedral lattice, while sulphur atoms are displaced in the (0001) planes parallel to the a -axis of the hexagonal lattice so that

each atom approaches two mercury atoms. A sulphur atom (S, fig. 1) displaced from a point $(11\frac{1}{2})$ moves into a position in contact with mercury atoms $(\frac{2}{3} \frac{1}{3} \frac{2}{3})$ and $(\frac{1}{3} \frac{2}{3} \frac{1}{3})$. The sulphur atoms, as for example those at S_1 , S, and S_2 , form spirals running parallel to the vertical axis. These are readily seen in fig. 2. The distances apart of sulphur atoms in the same spiral is 3.52 \AA ., agreeing with Bragg's value of 3.46 \AA .. In a rock-salt arrangement, each mercury atom would have six equidistant neighbours. In cubic mercuric sulphide each mercury atom has four equidistant neighbours at a distance of 2.54 \AA ., while in cinnabar, each mercury atom

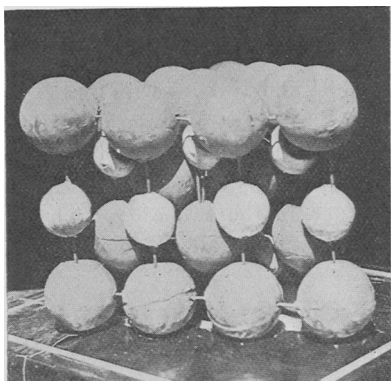


FIG. 2.

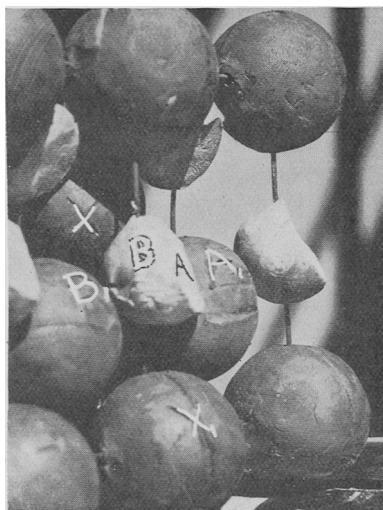


FIG. 3.

Models of the crystal-structure of cinnabar.

has two neighbours at 2.54 and two at 2.94 \AA .. These are shown in fig. 3, where the mercury atom is in close contact with sulphur atoms at A, A₁, and in more distant contact with atoms B, B₁. The distance of atoms A, A₁, is identical with that between these atoms in cubic mercuric sulphide.

Optical activity.—Sir Joseph Larmor¹ has shown that there exists a relationship between optical activity in the solid state and a certain type of crystal-structure, viz. one in which atoms are grouped together in spiral chains. He instances the classical example of quartz. Now

¹ J. Larmor, Proc. Roy. Soc. London, 1921, ser. A, vol. 99, pp. 1-10.

in quartz, there are spirals of atoms, or rather of ions which approximate to the 'neon' type; while in cinnabar the sulphur ions are arranged in spirals, but of the 'argon' type. This fact may provide an explanation for the much greater optical activity of cinnabar, when compared with quartz. As the radius of the spirals of sulphur atoms may be of use in subsequent calculations on the lines indicated in the paper quoted above, its value, as obtained by us, is given, viz. 0.87 \AA .

Eccentricity of the mercury atom.—As previously calculated, there are two values for the radius of combination of the mercury atom. If the radius of the sulphur atom be taken as 1.73 \AA ., in accordance with the latest observations of W. L. Bragg (to be published shortly), these values are 0.81 and 1.21 \AA . There is a difference of 0.40 \AA . between the two. These facts are substantiated by the results of Mauguin's¹ analysis of calomel, for here too the mercury atom is not truly spherical. The two radii of combination are found to be 0.94 and 1.37 \AA ., with a difference of 0.43 \AA ., i.e. practically the same as the difference between the two values obtained by us in cinnabar. The difference between the two sets of values, viz. in calomel and in cinnabar, is probably due to the difference in effective valency of the atom of mercury in the two cases. These observations may be worthy of consideration when a structure is being assigned to the mercury atom itself.

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¹ C. Mauguin, *Compt. Rend. Acad. Sci. Paris*, 1924, vol. 178, p. 1913. [*Min. Abstr.*, vol. 2, p. 510.]