Physics. — *"The Crystal Structure of Mercuric Sulphide. I."* By N. H. KOLKMEIJER, J. M. BIJVOET and A. KARSSEN. (Communication Nr. 14 from the Laboratory of Physics and Physical Chemistry of the Veterinary College). (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated at the meeting of May 3, 1924).

§ 1. *Introduction.* Some modifications are known of HgS; so far as we know only one of these — the hexagonal cinnaber [1]) — has been investigated with X rays. We intend to examine the different black and red modifications mentioned in the literature [2]). Here we give the results regarding the so called amorphous black HgS; in this form mercury is precipitated out of solution by a sulphide.

§ 2. *The apparatus.* The apparatus was of the ordinary type used in the powder method [3]). A tin diaphragm, length 60 mm. diameter 2 mm., reduced the black central spot. Besides, as in the experiments of DE SMEDT and KEESOM [4]), a little tube of calculated dimensions formed the lengthening piece of the diaphragm in the camera in order to protect the film from the secondary rays excited at the diaphragm. The radius of the camera was 27,2 mm. The sample was in a thinwalled glasstube of 1 mm. diameter. By a Ni-filter all but the $CuKa$-rays were for the greater part absorbed.

§ 3. *Röntgenograms and Calculation.* In columns 1 and 2 of the table are recorded the distances on the film from the middle of the image to the interference lines and the estimated intensities; in column 3 these values are diminished by $\frac{r}{2}(1 + \cos \vartheta)$, the approximate correction for the thickness of the rod according to GERLACH and PAULI [5]). Column 4 contains the corresponding values of $10^3 . \sin^2 \frac{\vartheta}{2}$

[1]) CH. MAUGUIN, C R. **176**, 1483, 1923.

[2]) I.a. E. T. ALLEN and J. L. CRENSHAW, Zs. anorg. Chem. **79**. 155, 1913.

[3]) Cf. A. J. BIJL and N. H. KOLKMEIJER, these Communications Nr. 1, these Proceedings **21**, 405, 1918.

[4]) J. DE SMEDT and W. H. KEESOM, these Communications Nr. 10, these Proceedings **25**, 118, 1922.

[5]) W. GERLACH and O. PAULI, Zs. f. Physik **7**, 116, 1921.

showing the common factor 17.35. Column 5 gives the values of Σh^2 following from this factor and column 6 the calculated values of $10^3 . sin^2 \frac{\vartheta}{2}$. The agreement with the observed values of column 4 is very good. Column 7 gives the indices of the reflecting planes.

Therefore the "amorphous" HgS crystallizes in the cubic system.

From the mentioned value of the common factor the lattice parameter is found to be

$$a = 5.85 . 10^{-8} \text{ cm.}$$

In combination with the value of the density this gives about 4 for the number n of HgS-groups per unit-cell. Starting from $n = 4$ we find for the density

$$d = 7{,}69$$

in good agreement with the highest of the values given in LANDOLT-BÖRNSTEIN-ROTH 1912 (7.55—7.70).

"AMORPHOUS" HgS.

Distances in mm.	Intensity estim	Distanc. corr.	$10^3 . sin^2 \vartheta/2$ observed	Σh^2	$10^3 . sin^2 \vartheta/2$ calculat.	$h_1 h_2 h_3$	Intensities calculated
1	2	3	4	5	6	7	8
13,3	vs	12,6	53	3	52	111	6
15,0	w	14,5	67	4	69	200	2
21,3	vs—	20,9	141	8	139	220	12
24,9	vs	24,5	190	11	191	311	17
26,2	vw	25,8	209	12	208	222	3
30,5	vw	30,1	277	16	278	400	6
33,6	m	33,3	330	19	330	331	17
34,6	wm	34,3	348	20	347	420	10
38,5	m	38,2	418	24	416	422	24
41,4	m	41,1	470	27	468	333 511	23
45,9	w—	45,7	554	32	555	440	12
48,6	s	48,4	603	35	607	531	34
49,9	w	49,7	626	36	624	442 600	12

The positions of the particles in the cell are yet to be determined by the consideration of the intensities of diffraction. Column 7 shows that the mixed indicesplanes are absent, from which it is obvious that the *Hg*- and the *S*-particles are arranged in face-centered cubes. Now two relative positions of these lattices are possible (NaCl- and ZnS-structure resp.); of these only the latter (space group T_d^2; relative displacement along the diagonal over a quarter of its length) is adequate. In calculating the intensities all the continuous factors are suppressed, the intensity I being taken proportional to $v\,|S|^2$; here v is the number of planes-factor and

$$S = (1 + e^{\pi i(h_2+h_3)} + e^{\pi i(h_3+h_1)} + e^{\pi i(h_1+h_2)})\,(Hg + Se^{\pi i(h_1+h_2+h_3)})$$

where $Hg = 78$ (number of electrons in the *Hg*-ion) and $S = 18$ (idem in the *S*-ion). So only the observed and calculated intensity ratios of neighbouring lines are to be compared; columns 2 and 8 show very good agreement.

From the given structure the sum of the radii of the atomic domains of *Hg* and *S* follows to be 2,53 Å; according to BRAGG the radius of the atomic domain of *S* amounts to 1,02 Å; the radius of *Hg*, which, so far as we know, was not till yet determined, then appears to be 1,51 Å.

§ 4. *Summary.*

Black precipitated *HgS* is of *ZnS* structure. Lattice parameter $5.85.10^{-8}$ cm. Density 7.69, radius of the atomic domain of *Hg* $1.51.10^{-8}$ cm.

Utrecht
Amsterdam, April 4, 1924.