Physios. — *"The Crystal Structure of Mercuric Sulphide"* II. By Dr. N. H. KOLKMEIJER, Dr. J. M. BIJVOET and Dr. A. KARSSEN. Communication N°. 15 from the Laboratory of Physics and Physical Chemistry of the Veterinary College at Utrecht. (Communicated by Prof. W. H. KEESOM).

§ 1. By the DEBYE-SCHERRER method black „*amorphous*" HgS was found to have ZnS-structure, with lattice parameter, 5.85 Å. [1]).

§ 2. By the BRAGG method the structure of the trigonal cinnaber was determined by MAUGUIN [2]): The dimensions of the cell are $a = b = 4.15$ Å, $c = 9.51$ Å; with only slight deviations the particles are arranged on a rhomboedric lattice. DEBYE-SCHERRER photograms of cinnaber made by us confirm completely the structure given by MAUGUIN.

§ 3. There appeared to be a striking agreement between the DEBYE films of the black and the red modifications (see the first photogram on the plate and columns 3 and 8 of the table). The lines of black HgS are found on the film of the red agreeing in place and for the greater part in intensity ratio, the total number of lines for the latter being larger. One would rather think the red to contain the black. This, however, is excluded by the fact that in the BRAGG method the measurements were made on a single homogeneous crystal. (In the powder method a transformation might occur by pulverising the sample [3]). *The agreement is caused by the complete equality of the dimensions in the octahedral- and basis plane of the regular resp. trigonal modification.* In these alternating Hg- and S-planes the particles are arranged in centered regular hexagons with sides $\frac{1}{2} \sqrt{2} \ a_{black} = 4.14$ Å $= a_{red}$.
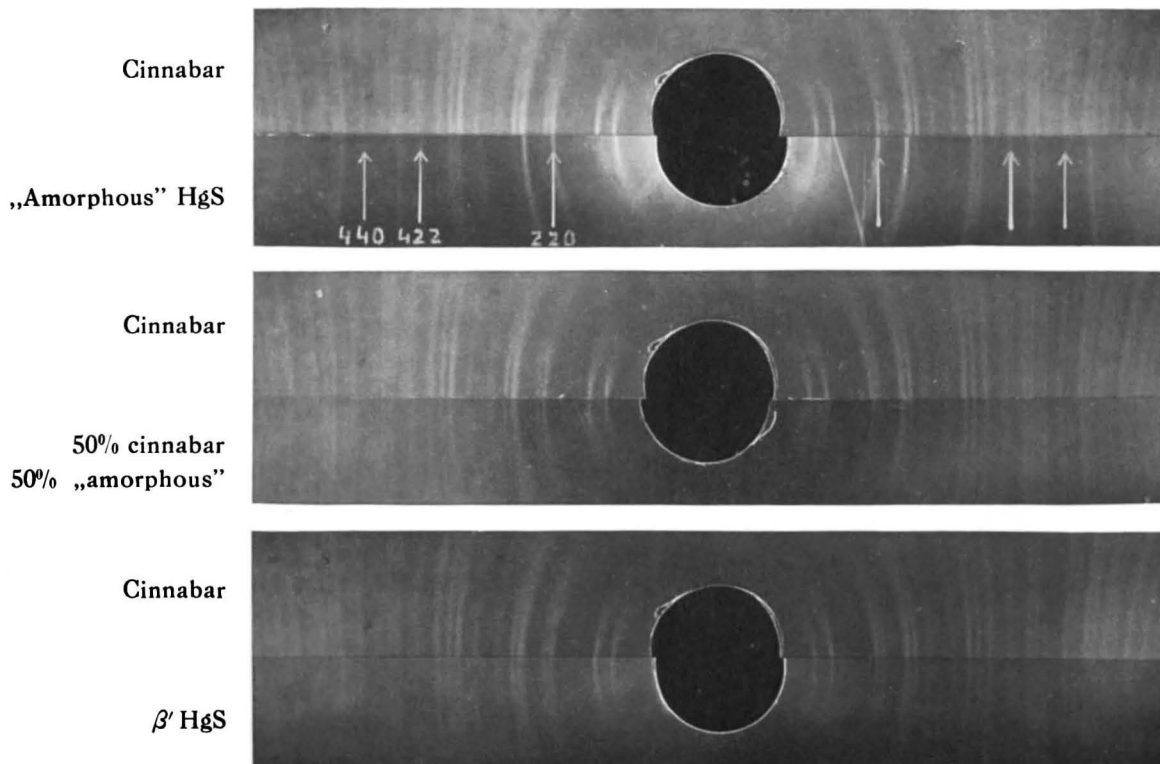
[1]) N. H. KOLKMEIJER, J. M. BIJVOET and A. KARSSEN. These Proceedings 27, p. 390 1924 Rec. trav. chim. 43, 677, 1924.

[2]) CH. MAUGUIN, Compt. rend. 176, 1483, 1923.

[3]) L. VEGARD. Z. Physik 5, 393, 1921.

	Black HgS			By reducing in the direction of c splitted up into	$10^3 sin^2 \frac{\vartheta}{2}$ (calculated)	Red HgS	
Nr.	Indices	$10^3 sin^2 \frac{\vartheta}{2}$ (observed)	Intensities			Intensities	$10^3 sin^2 \frac{\vartheta}{2}$ (observed)
1	2	3	4	5	6	7	8
1	111	52	vs	$10\bar{1}1$	53	vs	54
				0003	60	vf	59
2	200	69	f	$10\bar{1}2$	72	vs	72
3	220	139	vs⁻	$11\bar{2}0$	139	s	141
				$\bar{1}014$	152	ms	155
4	311	191	vs	$20\bar{2}1$	192	vs	196
				$11\bar{2}3$	199		
				$10\bar{1}5$	212	s	212
5	222	208˙	vf	$20\bar{2}2$	211	,,	,,
				0006	238	f	241
6	400	278	vf	$20\bar{2}4$	291	fm	289
7	331	330	m	$\bar{2}3\bar{1}1$	324	s	327
				$20\bar{2}5$	351	ms	350
				$10\bar{1}7$	370		
8	420	347	m	$12\bar{3}2$	350	,,	,,
				$11\bar{2}6$	377	ms⁻	377
9	422	416 .	m	$30\bar{3}0$	416	f	420
				$21\bar{3}4$	430		
				$10\bar{1}8$	470	m+	466
10	333	468	m	$30\bar{3}3$	476	m	479
	511			$12\bar{3}5$	490		
				$20\bar{2}7$	509	vf	504
				0009	536		
11	440	555	f⁻	$22\bar{4}0$	555	fm	555
				$20\bar{2}8$	609		

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For the face-centered cubic modification the expression for $sin^2 \frac{\vartheta}{2}$ reads after transformation to trigonal axes: $\frac{8}{3} A (h_1^2 + h_2^2 + h_1 h_2) + \frac{1}{3} A h_4^2$: for the black HgS $A = 17.35$, [1]) hence

$$sin^2 \frac{\vartheta}{2}_{black} = 46.27 (h_1^2 + h_2^2 + h_1 h_2) + 5.78 h_4^2. \quad . \quad . \quad (1)$$

Now we assume A_{red} to be *exactly* equal to the corresponding value of the black modification (for justification see below), the first constant in the expression $sin^2 \frac{\vartheta}{2}_{red}$ thus obtaining the same value 46.27. Then the value 6.62 for the second constant gives the diffraction angles of column 6, c-value = 9.46 Å, and density 8,24; these values closely correspond with the observed diffraction angles of column 8, Mauguin's c-value 9.51 Å and the values of the density given in the literature (about 8,1 [2]). Hence:

$$sin^2 \frac{\vartheta}{2}_{red} = 46.27 (h_1^2 + h_2^2 + h_1 h_2) + 6.62 h_4^2. \quad . \quad . \quad (2)$$

According to equations (1) and (2) the shortening of the trigonal axis will give a clear difference in diffraction angle only for the planes $h_4 > 2$, as appears from column 3 and 6. Column 5 gives the planes in which those of column 2 are split up by the trigonal transformation.

To decide to which degree the dimensions in basis or octahedral plane are equal, we compared as exactly as possible the diffraction angles of the planes for which the trigonal axis is zone-axis. Measuring separate films of both modifications the exactness is diminished by differences in thickness and excentricity of the rod and in the change of length of the films by their treatment. This was avoided by exposing a mixture of 50 °/₀ black and 50 °/₀ red; *no widening of the lines was observed for the mentioned zone* (see second photogram of the plate: the planes of this zone are marked on the first photogram. *So the angles of these reflections appear to differ less than some tenth m.m. for both modifications, the dimensions in the basis plane thus agreeing within some tenth percents.*

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[1]) N. H. Kolkmeijer, J. M. Bijvoet and A. Karssen l.c.

[2]) Landolt-Börnstein, Physik. Chem. Tabelle. 4e Aufl. p. 182.

§ 4. *Comparison of the Structure of the Trigonal and Cubic Modifications.*

We found the same arrangement and exactly the same dimension in octahedra or basis plane. Thus the difference beween the regular and hexagonal modifications consists only in the manner in which these planes are piled up, at least as regards the arrangement of the centres of the particles. A similar behaviour is found, inter alia, in some allotropic forms which crystallize cubically and hexagonally close packed (Co, Ce), and in the cubic zincblende and hexagonal Wurtzite. But in these cases in both modifications the relative position of neighbour planes is the same, the tetrahedral grouping of the particles being preserved. In the case of HgS on the contrary in the trigonal modification, the piling up of· the basis planes differs much more and the tetrahedral arrangement is lost (the distance of the basis planes too being changed). So in this case the equality of the dimensions in the octahedral or basis plane is still more remarkable.

§ 5. By *X*-ray analysis none of the different HgS modifications described by ALLEN and CRENSHAW were found to contain crystals different from those of the ordinary black and red forms. The third diagram of the plate gives the comparison of the films of red and β'-HgS, the latter being mentioned by these investigators as a doubtless new modification.

§ 6. We intend to examine whether the natural black HgS — the regular metacinnaberiet — is identical in crystalstructure with black „amorphous" HgS, as soon as this material will be at our disposal.

§ 7. *Summary.* The cubical (black) and trigonal (red) mercury-sulphide have exactly the same dimensions in the octahedral or basis plane. This explains the striking agreement between their DEBYE-SCHERRER photograms.

β'-HgS nor any other of the modifications mentioned by ALLEN and CRENSHAW form a new modification.

For the preparation of the several HgS forms we wish to express here our hearty thanks to Mr. J. RINSE, chem. docts. Amsterdam, who is occupied with a thermodynamical study of the system HgS.

Utrecht, } 27 October 1924.
Amsterdam, }