On the Crystal Structure of Cinnabar

Karin Lundborg Aurivillius

Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm, Sweden

Previous Work on Mercury (II) Halides and Mercury (II) Chalcogenides

In connection with an X-ray investigation of mercury (II) oxyhalides it seemed of interest to review what is known about the type of bond between bivalent mercury and metalloids of group VII b (halogens) and VI b (chalcogens). As seen from the following retrospect much work has been done on the halogen compounds \( \text{HgX}_3 \) but relatively meagre data are available on the mercury compounds containing O, S, Se and Te.

From powder photographs of crystalline \( \text{HgF}_2 \) Ebert and Woitinek\(^1\) concluded that this compound is isomorphous with \( \text{CaF}_2 \). The F atoms, however, contribute very sparsely to the intensities, so their positions can not be regarded as proved. With the structure of Ebert and Woitinek every Hg atom is surrounded by 8 F atoms in a cubical arrangement and every F tetrahedically by 4 Hg atoms in the distance 2.4 kX and thus the structure probably is built up from \( \text{Hg}^{2+} \) and \( \text{F}^- \) ions. If this is so, \( \text{HgF}_2 \) forms an exception from the other mercury (II) halides, where mercury is coordinated with two and in one case with four X atoms.

By X-ray methods crystalline \( \text{HgCl}_2 \) and \( \text{HgBr}_2 \) have been found to be molecular compounds; each molecule \( \text{HgX}_2 \) can be regarded as linear (\( \text{HgCl}_2 \): Braekken and Harang\(^2\), Nieuwenkamp and Bijvoet\(^3\), Braekken and Scholten\(^4\), \( \text{HgBr}_2 \): Verweel and Bijvoet\(^5\)).

The distance \( \text{Hg} \rightarrow \text{Cl} \) is 2.25 kX (Braekken and Scholten\(^4\) and \( \text{Hg} \rightarrow \text{Br} \) 2.48 kX (\textit{Strukturbericht} 1928—1932, p. 19).

Yellow \( \text{HgI}_2 \), which is stable above 127° (Smits\(^6\)) is isomorphous with \( \text{HgBr}_2 \) (Verweel and Bijvoet\(^5\), Gorski\(^7\)). The distance \( \text{Hg} \rightarrow \text{I} \) has been calculated to be 2.62 kX (Gorski\(^7\)).
In the vapour state the compounds HgX₃ are also found to be linear or nearly linear. The following distances are found from electron interference studies on HgX₂ (gas):

\[
\begin{align*}
\text{Hg} & \to \text{Cl} 2.2_8 \text{ kX}, \quad \text{Hg} \to \text{Br} 2.3_8 \text{ kX}, \quad \text{Hg} \to \text{I} 2.5_5 \text{ kX} \text{ (Braune and Knoke)} \quad ^8 \\
\text{Hg} & \to \text{Cl} 2.3_4 \text{ kX}, \quad \text{Hg} \to \text{Br} 2.4_4 \text{ kX} \quad \text{Hg} \to \text{I} 2.6_1 \text{ kX} \text{ (Gregg et al.)} \quad ^9.
\end{align*}
\]

In red HgI₂, stable at ordinary temperature, a new type of coordination occurs. Thus every Hg atom is surrounded tetrahedrally by 4 I (Havighurst, Bijvoet, Classen and Karssen, Classen, Huggins and Magill). The distance Hg → I is 2.78 kX (Strukturbericht 1913—1928, p. 180).

According to Wells, p. 514 the colinear bonds (in HgCl₂ (s), HgBr₂ (s), yellow HgI₂ (s) and the gaseous molecules) are sp bonds, whereas the tetrahedral bonds in red HgI₂ are sp³ bonds.

The mercury (II) oxide can be prepared with two colours, yellow and red. It has been discussed by several authors if the yellow and the red oxides are identical or not (Gay-Lussac, Ostwald, Varet, Cohen, Hulett, Schick, Fuseya, Levi, Goldschmidt, Fricke, Zachariasen, Kolkmeijer, Kolkmeijer).

The conclusion is that the oxides are identical compounds; they give the same powder photographs and differ only in the grain size. The division of the yellow oxide is, however, finer than of the red one.

The structure of HgO is orthorhombic. Zachariasen has approximately fixed the positions of the Hg atoms (\(x_{\text{Hg}} \approx \frac{1}{2}\)) and discussed a few possibilities for the positions of the O atoms.

Of the mercury (II) sulphide two modifications are known; the red cinnabar and the black metacinnabar.

Metacinnabar is cubic. The structure is of the B 3 type, thus isomorphous with ZnS (blende) (Kolkmeijer, Bijvoet and Karssen, Lehmann, v. Olshausen, Buckley and Vernon, Hartwig, Goldschmidt).

The Hg atoms, therefore, are tetrahedrally surrounded by S atoms; the distance Hg → S is 2.52₅ kX (\(\frac{\sqrt{3}}{4}\)) since \(a = 5.83_2\) kX (Goldschmidt).

HgSe and HgTe are isomorphous with metacinnabar and have the cell edges \(a_{\text{HgSe}} = 6.06_8\) kX and \(a_{\text{HgTe}} = 6.44_0\) kX. The distance Hg → Se is 2.62₃ kX and Hg → Te 2.7₈₈ kX (Strukturbericht 1913—1928, p. 77) (Zachariasen, Hartwig, Goldschmidt, de Jong).

The four tetrahedral bonds the mercury atom forms in HgS (metacinnabar), HgSe and HgTe are probably sp³ bonds as in red HgI₂.
In the mercaptides Hg(SC₂H₅)₂, Hg(SC₄H₉)₂ and Hg(SC₆H₁₇)₂ the bonds S-Hg-S form straight or almost straight lines and are thus probably sp bonds. The distance Hg → S was calculated to be 2.5₀ kX from a Fourier projection, assuming the S-Hg-S bonds to be exactly colinear (Wells 38).

The other form of HgS, cinnabar, is hexagonal. By various authors, values for a have been reported from 4.12 to 4.16 kX and for c from 9.43 to 9.54 kX. A structure has been proposed which is denoted by Strukturbericht as B 9 (Mauguin 39, v. Olshausen 32).

The space groups proposed are D₃₄ or D₅₂, which give left handed or right handed spirals (Buckley and Vernon 33, de Jong and Willems 40).

With D₃₄ the point positions are:

3 Hg in 3 (a): x₁ 0 ½, 0 x₁ ½, x₁ x₁ 0 and
3 S in 3 (b): x₂ 0 ½, 0 x₂ ½, x₂ x₂ ½

For cinnabar no direct determination of the distances Hg → S has hitherto been made. The positions of the S atoms have been fixed by assuming the same distance Hg → S as found for metacinnabar. This distance is about the same as the sum of the atomic radii for covalent tetrahedral structures according to Pauling 41 (Hg = 1.48 kX, S = 1.04 kX).

From intensity calculations based on powder photographs Buckley and Vernon 33 found the value x₁ ≈ ½. With x₂ = 0.21 for the S parameter the same distance Hg → S was obtained as found in metacinnabar. This x₂ value also seemed to suit the intensities best.

From powder photographs de Jong and Willems 40 could conclude that x₁ is in one of the ranges 0.25—0.40 or 0.60—0.75 but could draw no conclusion as to the value of x₂. They found that with a coordination Hg → 6S or Hg → 4S, the Hg → S distances would be unbelievably long. They thus assumed that each Hg has 2 nearest S neighbours and that the distance Hg → S is 2.52 kX (the sum of the tetrahedral atomic radii!). They finally arrived at the values x₁ = 0.72₅ and x₂ = 0.55.

In the present work the author has tried to redetermine the positions of Hg and S in cinnabar with the aid of intensity calculations only, and without any previous assumption about distances and coordination. Work on HgO and Hg oxyhalides is in progress.

MATERIALS

For the X ray measurements of this investigation native cinnabar was used, which was kindly supplied by Professor S. Gavelin of the Mineralogical Institute, University of Stockholm.
For getting single crystals, suitable for X ray investigation, the native cinnabar crystal conglomerate was crushed. A number of fragments were picked out and examined by Laue photographs before two acceptable single crystals were found.

Reflexions, which should have the same intensities according to the Laue symmetry, showed different values because of the fact that the shape of the crystals (flat needles) did not show the same symmetry as the reciprocal lattice, and therefore the observed absorption shows a lower symmetry, too.

Of course the asymmetrical absorption effects might be diminished by grinding the crystal to cylindrical form, but it seemed that the single crystals available were too tiny for such a procedure.

Attempts to synthesize HgS crystals, suitable for X ray analysis, were not successful. Only microcrystalline cinnabar was obtained.

This synthetical cinnabar gave powder photographs identical with those of native cinnabar.

UNIT CELL AND SPACE GROUP

The dimensions of the unit cell were determined accurately from the powder photographs with CrKα radiation and focusing cameras of the Phragmén-Westgren type (Table 1).

The powder photographs could be interpreted with a hexagonal unit cell with:

\[ a = 4.137 \ \text{kX} = 4.146 \ \text{Å} \]
\[ c = 9.477 \ \text{kX} = 9.497 \ \text{Å} \]
\[ V = 140.4_6 \ \text{kX}^3 = 141.3_6 \ \text{Å}^3 \quad \text{Accuracy about 0.05 \%} \]

The cell dimensions according to de Jong and Willems (1926) are \( a = 4.12 \ \text{kX} \), \( c = 9.43 \ \text{kX} \).

The density according to Allen and Crenshaw⁴² is 8.176, thus allowing 3 formula units per unit cell (calculated density 8.19₆). Laue photographs, rotation and Weissenberg photographs around (001) (zero layer and first layer) and (010) (zero layer) were taken. From the Laue photographs, (incident beam parallel to the threefold axis) the Laue symmetry was found to be \( D_{3d}^{-3m} \). The only systematic extinction found was that \( 00l \) was absent for \( l \neq 3n \), which is characteristic of the space groups \( D_{3d}^{-6} \).

Because the unit cell contains 3 formula units and because cinnabar has a definite composition the only way to get an ordered structure was to assume the Hg atoms occupy one threefold point position. For each of the space
Table 1. Powder photographs of HgS (cinnabar). CrKa radiation.

<table>
<thead>
<tr>
<th>hkl</th>
<th>$10^4 \sin^2 \Theta_{\text{calc}}$</th>
<th>$10^4 \sin^2 \Theta_{\text{obs}}$</th>
<th>$I_{\text{obs}}$</th>
<th>hkl</th>
<th>$10^4 \sin^2 \Theta_{\text{calc}}$</th>
<th>$10^4 \sin^2 \Theta_{\text{obs}}$</th>
<th>$I_{\text{obs}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.1018</td>
<td>0.1007</td>
<td>w</td>
<td>006</td>
<td>0.5238</td>
<td>0.5247</td>
<td>w</td>
</tr>
<tr>
<td>101</td>
<td>.1163</td>
<td>.1150</td>
<td>vst</td>
<td>203</td>
<td>.5381</td>
<td>.5386</td>
<td>m</td>
</tr>
<tr>
<td>003</td>
<td>.1310</td>
<td>(.1301)</td>
<td>(st)</td>
<td>106</td>
<td>.6256</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>102</td>
<td>.1600</td>
<td>.1586</td>
<td>vst</td>
<td>204</td>
<td>.6399</td>
<td>.6400</td>
<td>st</td>
</tr>
<tr>
<td>103</td>
<td>.2237</td>
<td>.2230</td>
<td>vw</td>
<td>115</td>
<td>.6691</td>
<td>.6688</td>
<td>vvw</td>
</tr>
<tr>
<td>110</td>
<td>.3053</td>
<td>.3056</td>
<td>st</td>
<td>210</td>
<td>.7125</td>
<td>.7121</td>
<td>w</td>
</tr>
<tr>
<td>111</td>
<td>.3199</td>
<td>.3204</td>
<td>m</td>
<td>211</td>
<td>.7270</td>
<td>.7270</td>
<td>m</td>
</tr>
<tr>
<td>104</td>
<td>.3346</td>
<td>.3358</td>
<td>st</td>
<td>212</td>
<td>.7707</td>
<td>.7707</td>
<td>m</td>
</tr>
<tr>
<td>112</td>
<td>.3638</td>
<td>(.3624)</td>
<td>(m)</td>
<td>205</td>
<td>.7709</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>200</td>
<td>.4071</td>
<td>--</td>
<td>--</td>
<td>107</td>
<td>.8147</td>
<td>.8149</td>
<td>w</td>
</tr>
<tr>
<td>201</td>
<td>.4217</td>
<td>.4221</td>
<td>st</td>
<td>116</td>
<td>.8291</td>
<td>.8302</td>
<td>w</td>
</tr>
<tr>
<td>113</td>
<td>.4363</td>
<td>.4368</td>
<td>st</td>
<td>213</td>
<td>.8434</td>
<td>.8434</td>
<td>w</td>
</tr>
<tr>
<td>202</td>
<td>.4653</td>
<td>.4655</td>
<td>st</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the list of the powder photographs, the reflexions systematically absent and the $\beta$ reflexions have been omitted. If a tabulated reflexion coincides with a $\beta$ reflexion, the $\sin^2 \Theta_{\text{obs}}$ and the observed intensity of the resulting line are given in brackets. The observed intensities are indicated as follows: vst = very strong, st = strong, m = medium, w = weak, vw = very weak and vvw = very, very weak.

groups $D_3^{3-g}$ two different sets of threefold point positions 3 (a) and 3 (b) are possible. However, on displacing the origin of the unit cell by $c/2$ the positions 3 (a) could be made identical with the positions 3 (b). It was thus arbitrarily assumed that the Hg atoms are situated in 3 (a) with the coordinates:

$$
D_3^3: x_1 \bar{x}_1 0, \space x_1 2x_1 1/3, \space 2\bar{x}_1 \bar{x}_1 \bar{1}/3
$$
$$
D_3^2: x_1 \bar{x}_1 0, \space x_1 2x_1 2/3, \space 2\bar{x}_1 \bar{x}_1 \bar{1}/3
$$
$$
D_3^4: x_1 0 \bar{1}/3, \space 0 \space x_1 \bar{1}/3, \space \bar{x}_1 \bar{x}_1 0
$$
$$
D_3^5: x_1 0 \bar{1}/3, \space x_1 \bar{1}/3, \space \bar{x}_1 \bar{x}_1 0
$$

The space group $D_3^3$ or $D_3^2$ being assumed, maxima for the following $x$ values are expected, according to the interatomic distances Hg-Hg and Hg-S in the Patterson projections $P(xpz); z = 1/6, 1/4$ and $1/1$ (Table 2).

Thus if the Hg atoms are arranged according to space groups $D_3^3$ or $D_3^2$, the Patterson projections $P(xpz)$ (Table 2) would be symmetrical curves. However, such symmetrical projections can only be expected if $I_{\text{Hg}} = I_{\text{Hg}}$
Table 2. Expected maxima, due to interatomic distances Hg → Hg and Hg → S in P (xµz), space groups $D_3^h$ and $D_3^6$ being assumed. $x_1$ is the Hg parameter and $x_2$ is the S parameter.

<table>
<thead>
<tr>
<th>Projection</th>
<th>Expected $x$ value for the maxima</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hg → Hg</td>
</tr>
<tr>
<td>$P (x p \frac{1}{6})$</td>
<td>$\pm (x_1 - x_2)$</td>
</tr>
<tr>
<td></td>
<td>$\pm (2x_1 + x_2)$</td>
</tr>
<tr>
<td>$P (x p \frac{1}{4})$</td>
<td>$\pm 3x_1$</td>
</tr>
<tr>
<td></td>
<td>$0$</td>
</tr>
</tbody>
</table>

and $I_{h0l} = I_{l0h}$. Actually, $I_{h0l} \neq I_{l0h}$, as seen from the reflexions $h0l$. Therefore $D_3^h$ and $D_3^6$ can be excluded.

The point positions in $D_3^6$ are mirror images of those in $D_3^6$ (Fig. 1). On calculating the intensities from the structure factors A and B (International tables 43), $D_3^4$ and $D_3^6$ give the same result if the signs of the parameters are reverted ($x y z$ in $D_3^4$ correspond to $-x' y' z'$ in $D_3^6$).

As seen from Fig. 1, with the threefold point positions of $D_3^4$ the atoms will be coiled into lefthanded spirals and with those of $D_3^6$ into right handed spirals, if the $xyz$ axes form a right coordinate system (as in the International tables).

![Figure 1. Spiral chains of the mercury atoms of HgS (cinnabar). The Hg atoms are arranged according to space groups $D_3^4$ (left) and $D_3^6$ (right). The arrows point in the direction of the x and y axes.](image-url)
CRYSTAL STRUCTURE OF CINNABAR

The optical rotating power of cinnabar crystals has been investigated by several authors (des Cloizeaux 44, Wyrouboff 45, Tschemar 46, Melville and Lindgren 47, Becquerel 48, Rose 49).

According to these authors both dextrorotary and laevorotary cinnabar crystals exist. By the X ray methods it is not possible to distinguish between $D_3^4$ and $D_3^6$, nor to decide which of the dextrorotary crystal and the laevorotary crystal crystallizes with the symmetry $D_3^4$ and which with $D_3^6$.

As mentioned above the same structure factors are obtained for $D_3^6$ as for $D_3^4$. Therefore only the space group $D_3^4$ is considered in the following.

METHOD OF ATTACK

An attempt was first made to determine the parameters by the method of trial and error. This proved to be very laborious, due to the complicated form of the structure factors A and B. Moreover, on account of the asymmetrical absorption it was difficult to compare the calculated values of $I$ with those observed. It seemed that the best way of attacking the structure problem was to use Patterson and Fourier analysis.

If several different projections are used for the determination of the parameters, the intensities of quite a large number of reflexions will be considered. Errors in visually estimated intensities will cause a spread of the values of the parameters obtained from these different projections. In the average value of the parameters, it may be hoped that the errors, caused by the intensities, have partially cancelled out.

The following Patterson projections were computed: $P(xpz)$ with $z = \frac{1}{4}$, $\frac{1}{4}$ and $\frac{1}{2}$, based on the reflexions $h0l$ and $P(x0p)$ and $P(2x0p)$, based on the reflexions $hk0$.

The Patterson projections were calculated using both values of $I$ and $^{\text{\text{\text{\text{F}}}^\text{\text{}^2}}}$ (see p. 1420). From the Patterson projection $P(xp\frac{1}{2})$ (Table 5) a preliminary value of the Hg parameter was obtained and, with the aid of this value, the signs of the amplitudes of the reflexions could be calculated.

Then Fourier analyses were computed, based on $^{\text{\text{\text{\text{F}}}^\text{\text{}^2}}}$ ($V^{\text{\text{}^2}}$) values for the reflexions equivalent to $h00$, $hk0$ etc. and for $h0,3L$ ($l = 3L$, $L$ = whole number) and on the obtained signs of the amplitudes. If only these reflexions are considered, the Fourier analysis will give a density function $q_3$ which can be referred to a hypothetical unit cell with a centre of symmetry in the projection $q_3(xz\bar{Z})$ (p. 1421—24).

The zero level is unknown in the curves obtained from the Patterson and Fourier projections, and false maxima may be introduced because of the limited number of reflexions used. However, the highest maxima in the curves
will probably give rather accurate values for the positions of the Hg atoms and it seems that the minor peaks might give information on the positions of the S atoms. If the maxima of different projections give the same values for the parameters of Hg and S, this will add to the probability of these values.

With the aid of mean values of $x_1$ and $x_2$, calculated from all these projections the value of the phase angle $a_{mol}$ for every reflexion $h0l$ was computed. Then it was possible to calculate a Fourier synthesis based on all reflexions $h0l$ and to obtain more accurate values for the parameters of Hg and S (p. 1426—28).

INTENSITIES

The values of $I_{h0l}$ and $I_{hk0}$ were estimated visually from the Weissenberg photographs.

In order to reduce the errors introduced by the absorption effects, average values of $I$ were used for reflexions which should have the same intensities because of the Laue symmetry $D_{3d}$-3m (Table 3).

"$F^2$" for each reflexion was calculated from "$F^2 = I/f$, where $I$ is the estimated value of the intensity, $f = 1 + \cos^2 2\Theta/\sin 2\Theta$ and $\Theta$ is the glancing angle. For each reflexion, $f$ was taken from a curve where $1 + \cos^2 2\Theta/\sin 2\Theta$ had been plotted against $\sin^2 \Theta$. $\sin^2 \Theta$ was calculated from $\sin^2 \Theta = k_1 (h^2 + k^2 + hk) + k_2 l^2$, where $k_1 = \lambda^2/3a^2$ and $k_2 = \lambda^2/4c^2$. $a$ and $c$ were obtained from the powder photographs.

Table 3. Estimated intensities and mean values of $I$ for some reflexions $h0l$ and $hk0$ from Weissenberg photographs of HgS. CuKα radiation.

<table>
<thead>
<tr>
<th>hkl</th>
<th>$I_{estimated}$</th>
<th>$I_{mean\ value}$</th>
<th>hkl</th>
<th>$I_{estimated}$</th>
<th>$I_{mean\ value}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>208</td>
<td>30</td>
<td>45</td>
<td>210</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>202</td>
<td>83</td>
<td>45</td>
<td>120</td>
<td>40</td>
<td>36</td>
</tr>
<tr>
<td>204</td>
<td>35</td>
<td>30</td>
<td>230</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>20  10</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>303</td>
<td>80</td>
<td>79</td>
<td>310</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>303</td>
<td>75</td>
<td>79</td>
<td>130</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>303</td>
<td>80</td>
<td></td>
<td>140</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>309</td>
<td>80</td>
<td></td>
<td>340</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>402</td>
<td>15</td>
<td>11</td>
<td>110</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>404</td>
<td>7</td>
<td></td>
<td>120</td>
<td>65</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>210</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>101</td>
<td>15</td>
<td>9</td>
<td>220</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>107</td>
<td>3</td>
<td></td>
<td>240</td>
<td>20</td>
<td>28</td>
</tr>
</tbody>
</table>
CRYSTAL STRUCTURE OF CINNABAR

In these "\( F^2 \)" values no correction was thus made for thermal movement, nor for absorption.

The mean values of \( I \) and "\( F^2 \)" for \( hkl \) are given in Table 4 a, for \( h0l \) in Table 4 b. Values of "\( F \)" for the reflexions \( h00 \) are given in Table 4 c and values of "\( F \)" for the reflexions \( h0,3L \) in Table 4 d.

Since the values for \( I \), "\( F^2 \)" and "\( F \)" are given in an arbitrary scale, the Patterson function and the electron density \( \varrho \) obtained in the following are also expressed on a relative scale.

ON THE FUNCTION \( \varphi_3 \)

The complex structure factor of \( hkl \) can be expressed by

\[
F_{hkl} = \int \int \int e^{-2\pi i (hx + ky + lx)} \varrho(xyz) \, dx\,dy\,dz
\]

where \( \varrho \) is the electron density, thus \( \varrho(xyz) \, dx\,dy\,dz \) is the average number of electrons in the volume element \( dx\,dy\,dz \).

Table 4 a. Mean values of \( I \) and "\( F^2 \)" from \( hkl \) from Weissenberg photograph of HgS. CuKa radiation.

<table>
<thead>
<tr>
<th>( k )</th>
<th>( 0k0 )</th>
<th>( 1k0 )</th>
<th>( 2k0 )</th>
<th>( 3k0 )</th>
<th>( 4k0 )</th>
<th>( 5k0 )</th>
<th>( 0k0 )</th>
<th>( 1k0 )</th>
<th>( 2k0 )</th>
<th>( 3k0 )</th>
<th>( 4k0 )</th>
<th>( 5k0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>34</td>
<td>46</td>
<td>46</td>
<td>34</td>
<td>7</td>
<td>20</td>
<td>20</td>
<td>7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>62</td>
<td>10</td>
<td>28</td>
<td>10</td>
<td>62</td>
<td>34</td>
<td>44</td>
<td>10</td>
<td>28</td>
<td>10</td>
<td>44</td>
<td>7</td>
</tr>
<tr>
<td>3</td>
<td>35</td>
<td>32</td>
<td>32</td>
<td>35</td>
<td>10</td>
<td>46</td>
<td>35</td>
<td>27</td>
<td>27</td>
<td>35</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>62</td>
<td>4</td>
<td>32</td>
<td>28</td>
<td>46</td>
<td>2</td>
<td>28</td>
<td>2</td>
<td>27</td>
<td>28</td>
<td>20</td>
</tr>
<tr>
<td>1</td>
<td>13</td>
<td>13</td>
<td>62</td>
<td>32</td>
<td>10</td>
<td>34</td>
<td>3</td>
<td>3</td>
<td>28</td>
<td>27</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td>0</td>
<td>13</td>
<td>4</td>
<td>35</td>
<td>62</td>
<td>3</td>
<td>2</td>
<td>35</td>
<td>44</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>13</td>
<td>62</td>
<td>32</td>
<td>10</td>
<td>34</td>
<td>3</td>
<td>28</td>
<td>27</td>
<td>10</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>32</td>
<td>28</td>
<td>46</td>
<td>2</td>
<td>27</td>
<td>28</td>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>35</td>
<td>10</td>
<td>46</td>
<td>35</td>
<td>10</td>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>62</td>
<td>34</td>
<td>44</td>
<td>7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 4b. Mean values of $I$ and $\langle F^2 \rangle$ from $h0l$ from Weissenberg photograph of HgS.
CuKa radiation.

<table>
<thead>
<tr>
<th>$l$</th>
<th>$00l$</th>
<th>$10l$</th>
<th>$20l$</th>
<th>$30l$</th>
<th>$40l$</th>
<th>$00l$</th>
<th>$10l$</th>
<th>$20l$</th>
<th>$30l$</th>
<th>$40l$</th>
</tr>
</thead>
<tbody>
<tr>
<td>± 12</td>
<td>60</td>
<td>10</td>
<td>3</td>
<td>47</td>
<td>78</td>
<td>41</td>
<td>3</td>
<td>2</td>
<td>45</td>
<td>28</td>
</tr>
<tr>
<td>± 6</td>
<td>9</td>
<td>116</td>
<td>36</td>
<td>12</td>
<td>4</td>
<td>72</td>
<td>34</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>60</td>
<td>23</td>
<td>5</td>
<td>31</td>
<td>27</td>
<td>15</td>
<td>5</td>
<td>19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>± 3</td>
<td>47</td>
<td>6</td>
<td>12</td>
<td>79</td>
<td>38</td>
<td>16</td>
<td>2</td>
<td>8</td>
<td>48</td>
<td>23</td>
</tr>
<tr>
<td>± 9</td>
<td>0</td>
<td>45</td>
<td>75</td>
<td>11</td>
<td>0</td>
<td>31</td>
<td>64</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>50</td>
<td>27</td>
<td>25</td>
<td>28</td>
<td>20</td>
<td>17</td>
<td>23</td>
<td>14</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4c. Values for $\langle F \rangle$ of the reflexions $h00$, calculated from the average $\langle F^2 \rangle$ of $h00$, $0h0$ and $h0h$ in the Weissenberg photograph $hk0$.

$hkl$ | 100 | 200 | 300 | 400 |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$hkl$</td>
<td>1.7</td>
<td>1.4</td>
<td>5.9</td>
<td>6.6</td>
</tr>
</tbody>
</table>

Table 4d. Values of $\langle F \rangle$ of the reflexions $h0,3L$, calculated from $\langle F^2 \rangle$ in the Weissenberg photograph $h0L$.

<table>
<thead>
<tr>
<th>$l$</th>
<th>$00l$</th>
<th>$10l$</th>
<th>$20l$</th>
<th>$30l$</th>
<th>$40l$</th>
</tr>
</thead>
<tbody>
<tr>
<td>± 12</td>
<td>6.4</td>
<td>1.6</td>
<td>1.4</td>
<td>6.7</td>
<td>5.3</td>
</tr>
<tr>
<td>± 6</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>± 9</td>
<td>3.9</td>
<td>1.4</td>
<td>2.9</td>
<td>7.0</td>
<td>4.7</td>
</tr>
<tr>
<td>± 3</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>
CRYSTAL STRUCTURE OF CINNABAR

\[ F_{h0l} = \int_0^1 \int_0^1 e^{-2\pi i (hx+iy)} dxdz \int_0^1 \int_0^1 e^{-2\pi i (hx+iz)} \varrho(xyz) dydz \]

where \( \varrho(xyz) \) is the projection of the electron density \( \varrho(xyz) \) on the \( xz \) plane.

For the reflexions \( h0,3L \)

\[ F_{h0,3L} = \int_0^1 \int_0^1 e^{-2\pi i (hx+3Lz)} \varrho(xpz) dxdz \]  \hspace{1cm} (1)

The electron density \( \varrho(xpz) \) is the same for \( z, z + \frac{1}{2}, z + \frac{3}{2} \) but the term \( e^{-2\pi i (hx+3Lz)} \) has the same value for \( z, z + \frac{1}{2}, z + \frac{3}{2} \). Thus the \( z \) period is 1 for \( \varrho(xpz) \) and \( \frac{1}{3} \) for \( e^{-2\pi i (hx+3Lz)} \). The \( xz \) plane can therefore be divided into 3 parts, corresponding points of which give the same value for the complex term \( e^{-2\pi i (hx+3Lz)} \).

We replace \( z \) in (1) by a parameter

\[ Z = 3z \]  \hspace{1cm} (2)

and find

\[ F_{h0,3L} = \int_0^1 \int_0^1 e^{-2\pi i (hx+LZ)} \varrho_3(xpZ) dxdZ \]  \hspace{1cm} (3)

where \( \varrho_3 \) is defined by

\[ \varrho(x, y, z) + \varrho(x, y, z + \frac{1}{2}) + \varrho(x, y, z + \frac{3}{2}) = 3 \varrho_3(x, y, z) \]  \hspace{1cm} (4)

The \( Z \) period of \( \varrho_3(xpZ) \) and its projection \( \varrho_3(xpZ) \) is 1.

By reversal of (3) we find

\[ \varrho_3(xpZ) = \sum_h \sum_L F_{h0,3L} e^{-2\pi i (hx+LZ)} = \sum_h \sum_L F_{h0,3L} \cos 2\pi (hx + LZ) \]  \hspace{1cm} (5)

The general point position \( xyz \) \((6 (c)) \) of \( D_4^1 \), if transferred to the projection \( \varrho_3(xpZ) \) will give points at \( \pm (xpZ, ypZ, (y-x) pZ) \). Since the projection has thus a centre of symmetry, \( F_{h0,3L} = F_{h0,3L} \) and the sine terms cancel out in (5).

In a hypothetical cell with the electron density \( \varrho_3(xyZ) \) each atomic position 3 (a) in the ordinary cell (p. 1415) will correspond to 3 maxima of electron density at \( x00,0x0 \) and \( \bar{x}00 \). The projection \( \varrho_3(xpZ) \) from the reflexions \( h0,3L \) has maxima in \( xp0,0p0 \) and \( \bar{x}00 \) and the cut \( \varrho_3(xp0) \) has maxima at \( x, 0 \) and \( \bar{x} \).

In the same manner an atomic position 3 (b) (p. 1415) gives in the projection \( \varrho_3(xpZ) \) maxima of electron density at \( xp\frac{1}{2}, 0p\frac{1}{2} \) and \( \bar{x}p\frac{1}{2} \). The cut \( \varrho_3(xp\frac{1}{2}) \) gives maxima at \( x, 0 \) and \( \bar{x} \).
For the two cuts desired, equation (5) gives:

\[ q_a(xp0) = \sum_h \sum_L F_{h0,3L} \cos 2\pi hx = \sum_h \cos 2\pi hx \left[ \sum_{L_{\text{even}}} F_{h0,3L} + \sum_{L_{\text{odd}}} F_{h0,3L} \right] \]  

\[ (6) \]

\[ q_a(xp_{1/2}) = \sum_h \sum_L F_{h0,3L} \cos 2\pi (hx + \frac{1}{2}) = \sum_h \cos 2\pi hx \left[ \sum_{L_{\text{even}}} F_{h0,3L} - \sum_{L_{\text{odd}}} F_{h0,3L} \right] \]  

\[ (7) \]

These functions will be used in the calculations which follow.

PRELIMINARY DETERMINATION OF THE PARAMETERS

The highest maximum of the Patterson projections is found in \( P(xp_{1/2}) \) at \( x = 0.29 \) (Fig. 2). This must be due to the distance Hg \( \rightarrow \) Hg, which should give a maximum of weight 2 at \( x_1 \) (Table 5). From this follows \( x_1 = 0.71 \).

In order to secure more information on the positions of the Hg atoms and especially on the positions of the S atoms the Fourier sums \( q_a(xp0) \) and \( q_a(xp_{1/2}) \) were calculated from (6) and (7), using solely the reflexions \( h0,3L \). The signs of the amplitudes (Table 4 d) were determined using the approximate parameter \( x_1 = 0.71 \) and neglecting the influence of the S atoms.

Atoms in the point position 3 (a) (levels 0, \( \frac{1}{4} \) and \( \frac{3}{4} \)) should give maxima at 0, \( x \) and \( \bar{x} \) in the function \( q_a(xp0) \). In the same way atoms in the point position 3 (b) (levels \( \frac{1}{4}, \frac{1}{2} \) and \( \frac{3}{4} \)) should give maxima at 0, \( x \) and \( \bar{x} \) in \( q_a(xp_{1/2}) \). Now in each of the two cuts there is one such group of maxima (Fig. 3). The high maxima in \( q_a(xp0) \) are due to Hg atoms, which occupy 3 (a) according to our arbitrary assumption in calculating the signs. From the much lower maximum in \( q_a(xp_{1/2}) \) it was concluded that the S atoms occupy the point position 3 (b).
The cut \( q_3(xp0) \) gives the value \( x_1 = 0.71 \) for the Hg parameter and
\( q_3(xp\frac{1}{2}) \) the value \( x_2 \approx 0.50 \) for the S parameter (Fig. 3, Table 6).

If we consider separately the sums \( \sum_h \sum_{L \text{ even}} "F"_{\lambda,0,2L} \cos 2\pi hx \) and
\( \sum_h \sum_{L \text{ odd}} "F"_{\lambda,0,2L} \cos 2\pi hx \), which were used for calculating \( q_3(xp0) \) and \( q_3(xp\frac{1}{2}) \),
we find the values \( x_1 = 0.72 \) and \( x_1 = 0.71 \) (Fig. 4).

Since it seemed definite that Hg occupies 3 (a) and S 3 (b), Tables 5 and 6 were made giving the expected positions of maxima in various Patterson and
Fourier cuts, the positions observed, and the derived values for \( x_1 \) and \( x_2 \).

The Fourier sum \( q(xp0) \) was computed, using the reflexions \( h00 \) and equivalents from the photograph \( hh0 \).

From this projection a value \( x_1 = 0.73 \) was obtained for the Hg parameter
(Fig. 5, Table 6). Since the cut \( q(xp0) \) is based on only a few reflexions, less
weight should be ascribed to this value \( x_1 = 0.73 \) than to the other values for
\( x_1 \), which seem to be of greater accuracy.

From the Fourier projections (Table 6) and the Patterson projection
\( P(xp\frac{1}{2}) \) (Fig. 2, Table 5) the average value \( 0.72 \pm 0.01 \) was assumed for the
Hg parameter on calculating the S parameter \( x_2 \).

As seen from Table 5 the projections based on values of \( I \) and those based
on values of \( "F^2" \) gave somewhat different values for \( x_2 \).

The value \( x_2 = 0.50 \) from the cut \( q_3(xp\frac{1}{2}) \) (Table 6) is not very accurate
since the maximum at 0.50 (Fig. 3) may also consist of two overlapping maxima.

The average value of the S parameter was assumed to be \( 0.48 \pm 0.02 \).
Table 5. Patterson projections

\( x_1 \) is the Hg parameter and \( x_2 \) the S parameter.

<table>
<thead>
<tr>
<th>Projection</th>
<th>( x ) value expected distance</th>
<th>( x ) value observed distance</th>
<th>( x ) value calc.</th>
<th>rel. weight in units</th>
<th>rel. weight observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P (xp \frac{1}{2}) )</td>
<td>( \pm (x_1-x_2) )</td>
<td>( \pm 0.23 \pm 0.23 )</td>
<td>0.49</td>
<td>2</td>
<td>high</td>
</tr>
<tr>
<td>Fig. 6</td>
<td>( \bar{x}_1 ) ( 2x_1 )</td>
<td>0.29 ( 0.29 )</td>
<td>0.71</td>
<td>2</td>
<td>high</td>
</tr>
<tr>
<td>( P (xp \frac{1}{2}) )</td>
<td>( x_1 )</td>
<td>0.81 ( 0.80 )</td>
<td>2</td>
<td>high, broad</td>
<td></td>
</tr>
<tr>
<td>Fig. 7</td>
<td>( -(x_1+x_2) ) ( x_2 )</td>
<td>0.45 ( 0.47 )</td>
<td>0.45 ( 0.47 )</td>
<td>2</td>
<td>high</td>
</tr>
<tr>
<td>( P (x0p) )</td>
<td>( x_1-x_2 )</td>
<td>0.26 ( 0.23 )</td>
<td>0.46</td>
<td>small</td>
<td></td>
</tr>
<tr>
<td>Fig. 8</td>
<td>( x_1-x_2 )</td>
<td>0.26</td>
<td>0.49</td>
<td>small</td>
<td></td>
</tr>
</tbody>
</table>

**FINAL FOURIER CUTS**

Finally the Fourier sums \( \varphi (xp0) \) and \( \varphi (xp\frac{1}{2}) \) were computed using all reflexions \( h0l \).

\[
\varphi(xp) = \sum_{h} \sum_{l} e^{-2\pi i(hx+lx)} F_{h0l} = \sum_{h} \sum_{l} e^{-2\pi i(hx+lx)} (A_{h0l} + iB_{h0l}) = \\
= \sum_{h} \sum_{l} \left[A_{h0l} \cos2\pi(hx + lx) - B_{h0l} \sin2\pi(hx + lx) \right]
\]

since the imaginary terms cancel out.

Table 6. Fourier sums.

\( x_1 \) is the Hg parameter and \( x_2 \) the S parameter.

<table>
<thead>
<tr>
<th>cut</th>
<th>( x ) value expected</th>
<th>( x ) value observed</th>
<th>( x ) calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \varphi (xp0) )</td>
<td>0, ( \pm x_1 )</td>
<td>0.29, 0.71</td>
<td>0.71</td>
</tr>
<tr>
<td>( \varphi (xp\frac{1}{2}) )</td>
<td>0, ( \pm x_2 )</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>( \varphi (xp0) ) (prel.)</td>
<td>0, ( \pm x_1 )</td>
<td>0.27, 0.73</td>
<td>0.73</td>
</tr>
<tr>
<td>( \varphi (xp0) ) (final)</td>
<td>( x_1 )</td>
<td>0.720</td>
<td>0.720</td>
</tr>
<tr>
<td>( \varphi (xp\frac{1}{2}) ) (final)</td>
<td>( x_2 )</td>
<td>0.48( \frac{1}{4} )</td>
<td></td>
</tr>
</tbody>
</table>
The cut $q(xp0)$ was calculated to study the Hg parameter and the cut $q(xp\frac{1}{4})$ to study the S parameter.

$$q(xp0) = \sum_h \sum_i A_{h0i} \cos 2\pi hx - \sum_h \sum_i B_{h0i} \sin 2\pi hx$$

$$q(xp\frac{1}{4}) = \left[ \sum_h \sum_i A_{h0i} \cos 2\pi hx - \sum_h \sum_i B_{h0i} \sin 2\pi hx \right]_{l \text{ even}} - \left[ \sum_h \sum_i A_{h0i} \cos 2\pi hx - \sum_h \sum_i B_{h0i} \sin 2\pi hx \right]_{l \text{ odd}}$$

The values of $A_{h0i}$ and $B_{h0i}$ that were used for these projections were calculated from $A_{h0i} = \left| F''_{h0i} \right| \cos \alpha_{h0i}$, $B_{h0i} = \left| F''_{h0i} \right| \sin \alpha_{h0i}$, $\alpha_{h0i} = \text{phase angle}$.

For each reflexion $h0l$, $A_{h0i}$ and $B_{h0i}$ were also computed according to the appropriate terms of the structure factors in the *International tables* and with the aid of the values $x_1 = 0.72$, $x_2 = 0.48$ and $\alpha_{h0i}$ calculated from

$$\alpha_{h0i} = \text{arctg} \frac{B_{h0i}}{A_{h0i}}.$$

$F''$ was calculated from the visually estimated values of $I$ of the reflexions $h0l$ (p. 1420).

In Table 7 are given the values for $\left| F''_{h0i} \right| \sin \alpha_{h0i}$ and in 8 the values for $\left| F''_{h0i} \right| \cos \alpha_{h0i}$.

The projections $q(xp0)$ and $q(xp\frac{1}{4})$ are given in Fig. 11. The cut $q(xp0)$ has a very high and well defined maximum at 0.720, from which the Hg para-

### Table 7.

| $\left| F''_{h0i} \right| \sin \alpha_{h0i}$ | $B_{h0i}$ |
|---------------------------------|----------|
| $h \rightarrow 0$ | 1 | 2 | 3 | 4 | 5 |
| 0 | 0 | 1.625 | 4.500 | 0 | 0 | 3.900 |
| 1 | 0 | 7.358 | 3.270 | 0 | 4.855 | 3.510 |
| 2 | 0 | 5.045 | 1.928 | 0 | 6.327 | 4.100 |
| 3 | 0 | 1.923 | 3.717 | 0 | 2.288 | 3.286 |
| 4 | 0 | 1.530 | 1.148 | 0 | 2.121 | 4.743 |

### Table 8.

| $\left| F''_{h0i} \right| \cos \alpha_{h0i}$ | $A_{h0i}$ |
|---------------------------------|----------|
| $h \rightarrow 0$ | 1 | 2 | 3 | 4 | 5 |
| 0 | 6.463 | 0.926 | 2.686 | 3.947 | 0 |
| 1 | 1.581 | 0.926 | 2.686 | 1.444 | 2.256 |
| 2 | 1.414 | 2.185 | 1.982 | 2.881 | 2.786 |
| 3 | 6.636 | 2.930 | 1.139 | 6.950 | 4.001 |
| 4 | 5.320 | 1.148 | 2.121 | 4.743 | 1.337 | 1.824 |
meter was fixed at $0.720 \pm 0.003$. The sulphur parameter was fixed at $0.485 \pm 0.01$ from $q(xp\tfrac{1}{2})$.

There seemed to be no point in trying to obtain greater accuracy with the experimental data available.

**DETAILED DISCUSSION OF THE PATTERNSON PROJECTIONS**

$P(xp\tfrac{1}{2})$: (Fig. 2)

The projection has its highest maximum at $x = 0.29$ due to the distance Hg → Hg of weight 2 at $x = 0.29$. A Hg → Hg maximum of weight 1 would be expected at $x \approx 0.40$. However, it seems probable that the maximum at $x \approx 0.40$ is concealed by the maximum at 0.29. Maxima are also expected from interatomic distances S → S in this projection. However, they are too small to stand out among the false maxima.

$P(xp\tfrac{1}{2})$: (Fig. 6)

The cut based on the values of $I$ has a small maximum at $x = 0.50$ which could not be found in the cut "$F^2$". The projection of "$F^2$" sums probably gives more accurate values than that of $I$ sums. The Hg → S maximum of weight 1 expected at $0$ is not observed.

**Figure 11. Fourier sums of HgS (cinnabar).**

Full curve: $q(xp0)$
Dotted $\circ q(xp\tfrac{1}{2})$

**Figure 6. Patterson function $P(xp\tfrac{1}{2})$ of HgS (cinnabar).**

Full curve: $\sum_{h} F_{h0}\cos2\pi(hx + \tfrac{1}{2})$
Dotted $\circ \sum_{h} I_{h0}\cos2\pi(hx + \tfrac{1}{2})$
Figure 7. Patterson function $P(xp_{1/2})$ of HgS (cinnabar).

Full curve: $\sum_h^\infty F_{h00}^2 \cos 2\pi (hx + \frac{1}{2})$
Dotted: $\sum_h I_{h00} \cos 2\pi (hx + \frac{1}{2})$

$P(xp_{1/2})$: (Fig. 7)

The maximum at $x = 0.80 - 0.81$ is not of the same height but much broader than the Hg → S maximum found at 0.45 ("$F^2$" sum) and 0.47 (I sum). This maximum (0.80–0.81) is probably due to overlapping of a Hg → S maximum expected at 0.72 and a Hg → S maximum, expected at 0.80.

Figure 8. Patterson function $P(x0p)$ of HgS (cinnabar).

Full curve: $\sum_h^\infty F_{h00}^2 \cos 2\pi hx$
Dotted: $\sum_h I_{h00} \cos 2\pi hx$

$P(x0p)$: (Fig. 8)

In the cut $P(x0p)$ maxima depending on the distance Hg → S are expected. The cut I gives its highest maximum at $x = 0.23$ and a smaller one at $x = 0.42$. In the cut "$F^2$" there is only one maximum at $x = 0.26$. No significance could be ascribed to the maximum at $x = 0.42$ (cut I).

Figure 9. Patterson function $P(2xp) = \sum_h^\infty F_{h00}^2 \cos 2\pi (2h + k)x$ of HgS (cinnabar).

$P(2xp)$: (Fig. 9)

In the cut $P(2xp)$ are expected maxima, resulting from the interaction between maxima depending on the distance Hg → Hg and maxima depending on the distance Hg → S (Fig. 10). The projection has a much too complicated appearance to give a clear understanding about the parameters of Hg and S.
FINAL STRUCTURE PROPOSITION

Now that the positions of the sulphur and the mercury atoms have been determined, the intensities of the reflexions \(hk0\) and \(h0l\) of the Weissenberg photographs were calculated, considering the scattering power of both the Hg and the S atoms.

In Tables 9 and 10 the calculated values of \(I\) are compared with the observed intensities of the reflexions in the Weissenberg photographs \(hk0\) and \(h0l\). They agree as closely as can be expected, bearing in mind that the “observed intensities” are mean values of the estimated intensities, which sometimes differ considerably because of asymmetrical absorption (see again Table 3).

Thus the following structure is proposed for HgS (cinnabar):
Hexagonal, \(a = 4.146\ \text{Å},\ c = 9.497\ \text{Å},\ 3\ \text{HgS per unit cell.}\)
Table 9. Calculated and observed intensities of $hk0$ from Weissenberg photograph of HgS. CuKa radiation. The calculated intensity is given on the left of each column and the intensity estimated on the right.

$$I_{\text{calc.}} = \frac{2}{3} \left( \frac{F}{f_{\text{Hg}}} \right)^2 \times 10^3$$

<table>
<thead>
<tr>
<th>$k$</th>
<th>5</th>
<th>4</th>
<th>3</th>
<th>2</th>
<th>1</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>0k0</td>
<td>55</td>
<td>44</td>
<td>23</td>
<td>35</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>3</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>1k0</td>
<td>10</td>
<td>7</td>
<td>8</td>
<td>10</td>
<td>18</td>
<td>27</td>
<td>45</td>
<td>28</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>2k0</td>
<td>30</td>
<td>20</td>
<td>15</td>
<td>28</td>
<td>18</td>
<td>27</td>
<td>1</td>
<td>2</td>
<td>45</td>
<td>28</td>
</tr>
<tr>
<td>3k0</td>
<td>30</td>
<td>20</td>
<td>8</td>
<td>10</td>
<td>23</td>
<td>35</td>
<td>18</td>
<td>27</td>
<td>18</td>
<td>27</td>
</tr>
<tr>
<td>4k0</td>
<td>10</td>
<td>7</td>
<td>55</td>
<td>44</td>
<td>8</td>
<td>10</td>
<td>15</td>
<td>28</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>5k0</td>
<td>10</td>
<td>7</td>
<td>48</td>
<td>20</td>
<td>48</td>
<td>20</td>
<td>10</td>
<td>7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 10. Calculated and observed intensities of $h0l$ from Weissenberg photograph of HgS. CuKa radiation. The calculated intensity is given on the left of each column and the intensity estimated on the right.

$$I_{\text{calc.}} = \frac{2}{3} \left( \frac{F}{f_{\text{Hg}}} \right)^2 \times 10^3$$

<table>
<thead>
<tr>
<th>$l$</th>
<th>00$l$</th>
<th>10$\bar{l}$</th>
<th>20$\bar{l}$</th>
<th>30$\bar{l}$</th>
<th>40$\bar{l}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>69</td>
<td>41</td>
<td>1</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>$\pm 12, \pm 6$</td>
<td> </td>
<td> </td>
<td> </td>
<td> </td>
<td> </td>
</tr>
<tr>
<td>1, 7</td>
<td>4</td>
<td>4</td>
<td>39</td>
<td>72</td>
<td>12</td>
</tr>
<tr>
<td>$5, \bar{11}$</td>
<td> </td>
<td> </td>
<td> </td>
<td> </td>
<td> </td>
</tr>
<tr>
<td>2, 8</td>
<td>57</td>
<td>27</td>
<td>11</td>
<td>15</td>
<td>3</td>
</tr>
<tr>
<td>$4, \bar{10}$</td>
<td> </td>
<td> </td>
<td> </td>
<td> </td>
<td> </td>
</tr>
<tr>
<td>$\pm 3$</td>
<td>34</td>
<td>16</td>
<td>3</td>
<td>2</td>
<td>11</td>
</tr>
<tr>
<td>$\pm 9$</td>
<td> </td>
<td> </td>
<td> </td>
<td> </td>
<td> </td>
</tr>
<tr>
<td>4, 10</td>
<td>0</td>
<td>0</td>
<td>35</td>
<td>31</td>
<td>32</td>
</tr>
<tr>
<td>$2, \bar{8}$</td>
<td> </td>
<td> </td>
<td> </td>
<td> </td>
<td> </td>
</tr>
<tr>
<td>5, 11</td>
<td>37</td>
<td>20</td>
<td>8</td>
<td>17</td>
<td>8</td>
</tr>
<tr>
<td>$1, \bar{7}$</td>
<td> </td>
<td> </td>
<td> </td>
<td> </td>
<td> </td>
</tr>
</tbody>
</table>
Space group \( D_4 \) \(-\) C\(3\_2 \)

3 Hg in 3 (a): \( x 0 \frac{1}{4}, 0 x \frac{1}{6}, \bar{x} \bar{x} 0 \) \( x = 0.720 \pm 0.003 \)
3 S in 3 (b): \( x 0 \frac{1}{8}, 0 x \frac{1}{4}, \bar{x} \bar{x} \frac{1}{4} \) \( x = 0.485 \pm 0.01 \)

DISCUSSION OF THE STRUCTURE

If S — Hg — S are to lie on a straight line, \( x_1 \) and \( x_2 \) must satisfy the equation: \( x_1 = 1 - \frac{1}{2} x_2 \). The Hg parameter \( x_1 = 0.720 \pm 0.003 \) is determined with greater accuracy than the S parameter \( x_2 = 0.485 \pm 0.01 \). If the value 0.720 for \( x_1 \) is inserted in the above equation the value \( x_2 = 0.56 \) is obtained and differs too greatly from the experimental value \( x_2 = 0.485 \). Thus S — Hg — S do not lie on a straight line.

The bonding angle \( S_1 — Hg^* — S_1 (\theta_1) \) (Fig. 12) was calculated from the formula:

\[
\tan \frac{\theta_1}{2} = \frac{\sqrt{0.75x_2^2 + \left(\frac{c}{a}\right)^2 \frac{1}{36}}}{1 - x_1 - 0.50x_2}
\]

and the angle \( Hg_1 — S_1 — Hg^* (\theta_2) \) (Fig. 12) was evaluated from:

\[
\tan \frac{\theta_2}{2} = \frac{\sqrt{0.75 (1 - x_1)^2 + \left(\frac{c}{a}\right)^2 \frac{1}{36}}}{x_2 - 0.50 (1 - x_1)}
\]

With \( x_1 = 0.720 \pm 0.003 \) and \( x_2 = 0.485 \pm 0.01 \) the value of \( \theta_1 \) and \( \theta_2 \) are: \( \theta_1 = 172^\circ.4 \pm 1^\circ.7, \theta_2 = 105^\circ.2 \pm 2^\circ.0 \).

As seen \( \theta_1 \), the angle between the mercury bonds is not far from \( 180^\circ \), which is the angle between the mercury bonds of the halogen compounds HgCl\(_2\) (s), HgBr\(_2\) (s), yellow HgJ\(_2\) (s), the gaseous molecules HgX\(_2\) and HgSR \((R = n\text{-}alkyl\text{ group})\) (p. 1413). \( \theta_2 \), the angle between the bonds from a sulphur atom, lies close to the values found for molecules containing 2-covalent S \([\text{SCL}_2 103^\circ, \text{S}_2\text{Cl}_2 105^\circ \pm 5^\circ \text{ (Wells 14, p. 305)}] \).

By assuming \( x_1 = 0.720 \) and \( x_2 = 0.485 \) the following distances and coordination were obtained:

The neighbourhood of one mercury atom \((\bar{x}_1 x_1 0)\) Hg * in Fig. 12:

2 S at \( 2.3_6 \text{ Å } S_1 \) 6 Hg at \( 4.1_5 \text{ Å } Hg_0 \)
2 S \( 3.1_0 \text{ Å } S_2 \) 2 Hg \( 3.7_5 \text{ Å } Hg_1 \)
2 S \( 3.3_0 \text{ Å } S_3 \) 4 Hg \( 4.1_0 \text{ Å } Hg_2, Hg_3 \)
Figure 12. *xy* projection of the structure of cinnabar. The diagram shows the coordination of the atoms. The small circles 1, 2, 3 show the S atoms and the larger ones ○₁, ○₂, ○₃ the Hg atoms. The distances Hg→Hg, Hg→S and S→S are listed in the text. The dotted line unites the atoms of one spiral chain.

The neighbourhood of one sulphur atom \( (\bar{x}, \bar{x}, \frac{1}{2}) \) S* in figure 12:

<table>
<thead>
<tr>
<th>Hg</th>
<th>2.3 Å Hg₂</th>
<th>6 S at 4.1 Å S₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg</td>
<td>3.1 Å Hg₃</td>
<td>2 S 4.8 Å S₃</td>
</tr>
<tr>
<td>Hg</td>
<td>3.3 Å Hg₄</td>
<td>4 S 3.7 Å S₁, S₂</td>
</tr>
</tbody>
</table>

(The distance Hg* → S* is 4.8 Å.)
If HgS were built up from Hg²⁺ and S²⁻ ions, the distance Hg → S would be 2.94 kX. (Hg²⁺: \( r = 1.10 \text{ kX} \), S²⁻: \( r = 1.84 \text{ kX} \), according to Pauling ⁴¹). This value is much longer than that found, 2.3₆ Å. Also, the distance calculated from covalent tetrahedral radii, 2.52 Å, seems to differ too much from the obtained value.

From the distances Hg → X in HgX₂ (gas) (Braune and Knoke ⁸, Gregg et al⁹, see page 1414) and the normal covalent radii (Wells ¹⁰, p. ⁸¹) the 2-covalent Hg radius was calculated to be \( \approx 1.2₇ \text{ Å} \). If the 2-covalent S radius is 1.04 Å (Wells ¹⁴, p. ⁸¹), the distance Hg → S should be 2.3₂ Å, if the forces between the Hg and S atoms are exclusively homopolar.

The distance Hg → S actually found is 2.3₆ Å.

From this distance Hg → S 2.3₆ Å (2.3₆ kX) and the values of \( \Theta_1 \) and \( \Theta_2 \) the conclusion can be drawn that the bond between Hg and S is mainly homo-
polar (sp type) in spite of the deviation of the angle from the normal value, 180°, for sp bonds.

Thus the structure of HgS can be described as consisting of a series of infinite spiral chains \(-S-Hg-S-\), running parallel to the c-axis of the hexagonal unit cell (Figs. 13 and 14).

Within the chain each atom is strongly bound, chiefly by homopolar forces, to its two immediate neighbours, but between the chains the forces are far less strong, and the interatomic distances are correspondingly considerably greater than within the chain. The chains probably support each other by means of the longer Hg → S contacts. It can be noted that the Hg atoms approximate a close-packed lattice.

**SUMMARY**

The crystal structure of native cinnabar has been investigated. The positions of the Hg and S atoms have been determined by means of Fourier synthesis. The cell edges are: \(a = 4.14_8\) Å, \(c = 9.49_7\) Å (accuracy 0.05%). The following structure is proposed:

Space group: \(D_3^4 \rightarrow C.\ 3_1\ 2\)

3 Hg in the point position 3 (a): \(x\ 0\ \frac{1}{3},\ 0\ x\ \frac{2}{3},\ \bar{x}\ \bar{x}\ 0,\)

\(x = 0.720 \pm 0.003\)

3 S in the point position 3 (b): \(x\ \frac{5}{6},\ 0\ x\ \frac{1}{6},\ \bar{x}\ \bar{x}\ \frac{1}{2}\)

\(x = 0.48_6 \pm 0.01\)

The structure is built up of infinite spiral chains, \((-S-Hg-)\), running parallel to the c axis of the hexagonal unit cell.

The angle S-Hg-S is 172°.4 ± 1°.7 and the angle Hg-S-Hg 105°.2 ± 2°.0.

The distances Hg → S within the chain are 2.3_8 Å.

From the angles and distances the bonds seem to be mainly covalent sp bonds.

A 2-covalent Hg radius \(\approx 1.2_7\) Å may be probable.

I wish to thank the Head of the Department Professor A. Ölander for his kind interest. I am much indebted to Professor L. G. Sillén for suggesting the subject of this investigation and for helpful advice and continued interest during my work.

**REFERENCES**

17. Ostwald, W. Z. physik. Chem. 34 (1900) 495.
18. Varet, R. Compt. rend. 120 (1895) 622.
35. Goldschmidt, V. M. G. V. VIII (1927).
41. Pauling, L. Z. Krist. 87 (1934) 205.
42. Allen, E. T., and Crenshaw, J. L. Z. anorg. Chem. 79 (1913) 158.
44. Des Cloizeaux, A. Compt. rend. 44 (1857) 876.
49. Rose, H. N. Jahrb. Mineralog. 29 (1910) 94.

Received June 22, 1950.