The Crystal Structure of γ-Hg₃S₂Cl₂

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The order–disorder (OD) structure of γ-Hg₃S₂Cl₂ has been solved from its X-ray diffraction pattern, which contains both sharp spots and diffuse streaks with maxima. The structure consists of equivalent layers. For each layer there are two possible positions relative to the preceding layer, so that the pairs formed by the preceding layer and the given layer in either of these two positions are geometrically equivalent. Thus the symmetry of the structure may be described by an OD-groupoid family, namely

$$A(2) \ m \quad m$$
$$\{(b_{1/2}) \ 2_{1/2} \ 2\}$$
$$\{(b_{1/2}) \ 2_{1/2} \ 2\} \quad \text{(category III}a\text{)}$$

Although, as indicated by the diffuse streaks, the structure is disordered and thus no space group can be assigned to it, all the crystals investigated contained blocks of three-dimensionally periodic structures (polytypes), most frequently with the symmetry $A2/m$ and $F2/m$, which are special cases of the symmetry given above. The translation periods of the structure are $b = 16·82$ (1), $c = 9·081$ (6) Å with $α = 90°$, the 'width' of one layer is $a_0 = 4·664$ (3) Å and there are four formula units within the one-layer unit. The structure contains two-dimensional networks of Hg₃S pyramids with shared Hg-atoms, forming $[Hg_3S_2]_\infty^{2+}$ cations. The bonds Hg–S within these networks are covalent; Hg–Cl bonds are ionic. The model of the structure explains the distribution of intensities in reciprocal space as well as some chemical and mechanical properties.

Introduction

As a part of a general project dealing with crystal growth by means of gas transfer reactions, initiated and supervised by Dr A.J.Frueh Jr in this Laboratory, the crystal structure of γ-mercurydisulphonium chloride (γ-Hg₃S₂Cl₂) has been solved. The crystals were prepared by Carlson (1966, 1967) as a by-product of his successful attempts to simulate the conditions leading to the formation of mercury-ore deposits.

The compound Hg₃S₂Cl₂ was first described by Rose (1828) and its properties (*e.g.* photosensitivity) have since been studied (for references see Pascal, 1962), but only recently Puff & Küster (1962) investigated the crystallographic properties of mercury-dichalcogenium halides and determined the crystal structure of Hg₃S₂Cl₂. Carlson showed however that in addition to Puff & Küster's structure (α-modification) there exist two more modifications, β- and γ-Hg₃S₂Cl₂. Puff, Harpain & Hoop (1966) independently found the same modifications and, moreover, gave them the same names. The structure of the α-modification has been recently redetermined by Aurivillius (1967) and, independently, by Frueh & Gray (1968) in this Laboratory. Both these determinations confirmed Puff & Küster's results.

Experimental

γ-Hg₃S₂Cl₂ (Carlson, 1967) forms straw-yellow prismatic crystals elongated in the **c** direction, reaching maximum dimensions of $0·5 \times 0·5 \times 3$ mm. Morpho-

logically they exhibit orthorhombic symmetry (point group $2/mmm$) and possess an excellent (100) cleavage. All the crystals investigated were twinned or formed parallel intergrowths.

The diffraction pattern consists of sharp spots and diffuse streaks with maxima. The distribution of the intensities of the sharp spots is the same for all the crystals investigated; the distribution of the intensities along the diffuse streaks varies from crystal to crystal. The diffuse maxima can be divided into three mutually independent systems. One of them is present in all specimens and may be referred to a rectangular cell with

$$a = 9·328(5), \ b = 16·82(1), \ c = 9·081(6) \ Å \ ,$$

the diffuse streaks being parallel to **a***. The density $D_m = 6·83(5)$ proves that this unit cell contains 8 formula units; the X-ray density calculated on this basis is 6·814. Indices hkl in the following will refer to this cell. The entire diffraction pattern may be described as follows:

I. Sharp spots:

hkl present only for $h = \hat{h}$, $k = 2\hat{k}$, $l = 2\hat{l}$ ($\hat{h},\hat{k},\hat{l}$ integers)
$0\hat{k}\hat{l}$ present only for $\hat{k} = 2n$.

II. Diffuse streaks and maxima on them:

$ξkl$ present only for $k = 2n+1$, $l = 2n+1$ ($ξ$ is a continuous variable)

1st system of maxima (always present) for
$ξ = h$ (integer)

2nd system of maxima (in some specimens absent) for
$ξ = (2n+1)/2$

3rd system of maxima (in some specimens absent) for
$ξ = (2n+1)/4$

Diffractions with $k+l = 2n+1$ are absent .

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The sharp spots exhibit orthorhombic symmetry, but the maxima on the diffuse streaks show for some specimens orthorhombic, for other specimens only monoclinic symmetry with the c axis unique.

The crystals showing well developed diffuse maxima exhibit a slight deviation (about 0·5°) of the angle γ from 90°; this is the cause of the doubling of some lines on the X-ray powder diffraction pattern observed earlier by Carlson (1966).

For the measurement of the integrated intensities of the sharp spots a single-crystal diffractometer based on an equi-inclination Weissenberg geometry was used. The goniometer settings were calculated with a program written by Frueh (1966), and the calculation as well as the others mentioned below was carried out on an IBM 7044 computer. In order to reduce the difficulties caused by high absorption ($\mu = 670$ cm^{-1} for Mo radiation), a needle-shaped crystal with average diameter of about 60 μm was selected and its shape measured with an optical goniometer and microscope. The morphological data were then used for the absorption correction; this calculation was included in a general data reduction procedure, carried out using *DTRDA* and *DTRDB* programs written by Burnham (1961). Out of a total of 486 structure factors examined, 304 turned out to be detectable.

The measurement of peak intensities of diffuse maxima (Dornberger-Schiff, 1966; Sedlacek & Dornberger-Schiff, 1965) was considerably more difficult since only a few of about 40 crystals investigated yielded Weissenberg photographs with reasonably well developed maxima. The best results were obtained with a larger crystal (about 0·1 × 0·2 mm in cross section) and Cu radiation. The peak intensities of stronger diffractions were determined using a recording microdensitometer and multiple-film technique; intensities of weak diffractions were estimated visually; the data reduction was carried out in a manner similar to that used for sharp diffractions. The majority of the specimens had the diffraction patterns exhibiting orthorhombic symmetry even for the diffuse maxima, but the relative values of the sums $|F(hkl)|^2 + |F(\bar{h}kl)|^2$ (A^2-values) of the first system of these maxima turned out to be the same for all specimens and were, as we shall see, more valuable for the structure analysis than the individual $|F(hkl)|^2$ values would have been. A total of 190 (178 non-zero) such A^2-values were obtained.

The observed distribution in reciprocal space corresponds to a structure lacking periodicity in the **a** direction, built of two-dimensionally periodic A-face centred layers with periods **b** and **c**. It was assumed that it is an OD-structure in Dornberger-Schiff's (1964, 1966) sense.

The superposition structure

The distribution of sharp diffractions ($k = 2\hat{k}$) in reciprocal space, taken by themselves, corresponds to a periodic structure, the so-called superposition structure (see *Appendix*). This has orthorhombic symmetry, lat-

tice constants $\hat{a} = a$, $\hat{b} = b/2$, $\hat{c} = c/2$ and space group *Pbmm*, *P2$_1$m* or *Pbm2*. Its electron density $\hat{\varrho}(xyz)$ is related to the electron density of the actual structure $\varrho(xyz)$ by the equation

$$\hat{\varrho}(xyz) = \tfrac{1}{2}[\varrho(xyz) + \varrho(x, y + \tfrac{1}{2}, z)]$$
$$= \tfrac{1}{2}[\varrho(xyz) + \varrho(x, y, z + \tfrac{1}{2})] . \tag{1}$$

Intensity statistics indicated the presence of a symmetry centre (at least for the heavy atoms); thus *Pbmm* was tentatively selected.

An attempt to solve the superposition structure by use of the minimum function failed because of heavy overlapping of the Hg–Hg vectors. However, a comparison of the intensities $I(\hat{h}\hat{k}0)$ with $\hat{h} + \hat{k} = 2n$ with the $I(hk0)$ values of the α modification (which, because of the space group $I2_13$, are present only for $h + k = 2n$), revealed their close similarity. Thus it was concluded that the projections of both structures may contain much the same atomic configuration, which in the case of the α modification is repeated by a vector $(\mathbf{a}_1 + \mathbf{a}_2)/2$. Two separate Patterson functions calculated with the $|F(\hat{h}\hat{k}0)|^2$ values with $\hat{h} + \hat{k} = 2n$ and with $\hat{h} + \hat{k} = 2n + 1$ respectively and the fact that *pgm* (the symmetry of the xy projection of *Pbmm*) is a subgroup of *cmm* (the symmetry of the xy projection of $I2_13$) made it possible to find the $\hat{x}$ and $\hat{y}$ coordinates of Hg atoms by eliminating the Hg–Hg vectors non-existent in the γ modification. Fig. 1 shows the projections of the structures of both the α and the γ modification (superposi-
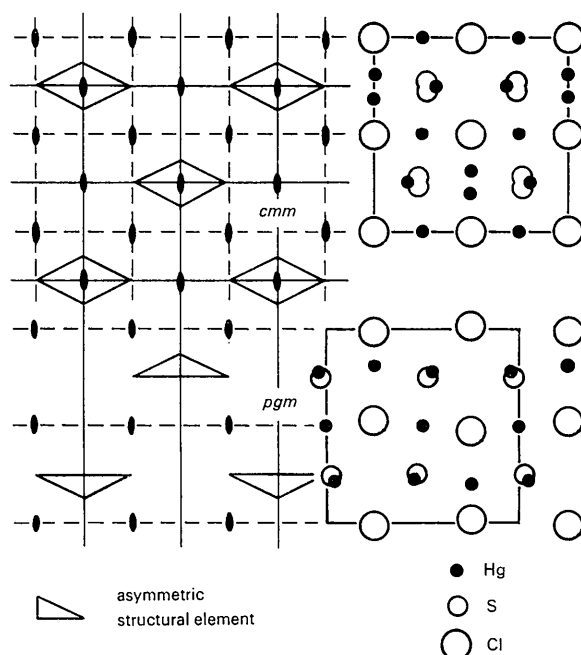

Fig. 1. xy projection of the crystal structure of α-Hg$_3$S$_2$Cl$_2$ (above, based on Frueh & Gray's (1968) data) and of the superposition structure of γ-Hg$_3$S$_2$Cl$_2$ (below) together with a coherently drawn diagram of the symmetry elements. Unit cells are outlined.

tion structure) alongside a coherently drawn diagram of the symmetry elements.

The fact that the relative intensities $I(\hat{h}k\hat{l})$ with the same $\hat{h},\hat{k}$ and with $\hat{l}=2n$ and $\hat{l}=2n+1$ respectively were very similar, showed that the $\hat{z}$ coordinates, at least for heavy atoms, must be very close to 0 or $\frac{1}{2}$. They were found using the generalized Patterson projection $P^{(1)}(uv)$. The coordinates of the light atoms were then found by means of a three-dimensional Fourier synthesis based on trial coordinates of Hg atoms. The superposition structure was refined by the Busing, Martin & Levy (1962) full-matrix least-squares program ORFLS, with the atomic scattering factors for neutral atoms published by Cromer & Waber (1965). During the refinement cycles each observation was assigned a weight inversely proportional to the square of its standard deviation as determined by the data reduction program from the counting statistics (Burnham, 1961). The observations below background level were replaced by values $|F_o|_{min}/\sqrt{3}$. For the last cycles of the refinement an anomalous dispersion correction was applied, as suggested by Patterson (1963). The correction values were taken from International Tables for X-ray Crystallography (1962). The final R value for all diffractions is 13·5%, for non-zero diffractions 8·9%. The difference synthesis after the last cycle proved the

correctness of the superposition structure and thus the space group Pbmm as well.

The final calculated structure factors together with the observed values are given in Table 1, the positional and anisotropic thermal parameters are given in Table 2. It should, however, be kept in mind that the temperature parameters in the expression for the temperature factor

$$\tau = \exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2 + 2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\}$$

reflect both thermal and positional displacements of atoms from their positions listed in Table 2 (see below).

The Hg(2) atoms in the superposition structure were found to contribute only with half weight to the structure factors, compared with other atoms. Going back to the equation (1) defining the superposition structure, this must mean that such half-weight atoms occur either at $x=\hat{x}$, $y=\hat{y}/2$, $z=\hat{z}$ and $(0\frac{1}{2}\frac{1}{2})$ plus these coordinates, or at $x=\hat{x}$, $y=(\hat{y}+1)/2$, $z=\hat{z}$ and $(0\frac{1}{2}\frac{1}{2})$ plus these coordinates; thus they repeat with periods $b=2\hat{b}$ and $c=2\hat{c}$. If, on the other hand, atoms occur at positions related by the translations $\hat{b}=b/2$ (and thus $\hat{c}=c/2$), they will show up in the superposition structure with weight 1 and will not contribute to the diffuse

Table 1. *Observed and calculated structure factors for the superposition structure*

In the columns from left to right the values of $\hat{h}$, F_o and F_c are listed. Undetectable diffractions are marked by n.

diffractions. Slight deviations from such positions, leading to their true repetition periods **b** and **c**, would cause changes in the apparent thermal vibrations. If significant, these deviations can be revealed in analyzing the diffuse maxima.

The symmetry of the real structure

As was shown above, the structure may be thought of as being built of A-centred layers with periods $b = 2\hat{b}$ and $c = 2\hat{c}$. Although arranged in a disordered manner, their superposition structure [see equation (1)] is periodic (space group $Pbmm$) irrespective of the disorder and does not depend on details of their arrangement, which varies from crystal to crystal.

An arrangement of structural elements, as shown in Fig. 2 left, has the following properties:

1. Its superposition structure has the space group and lattice constants demanded.

2. It may be thought of as being built of geometrically equivalent layers with plane space group $A2mm$.

3. Each layer is transformed into the next following layer, among others, by the partial symmetry operations $[..2]$, $[.2_{1/2}.]$ and either $[b_{+1/2}..]$ or $[b_{-1/2}..]$.*

4. Starting from any one layer, two symmetry operations $[b_{+1/2}..]$ and $[b_{-1/2}..]$ lead to two different

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* The indices on the symbols for the twofold axis and for the glide plane indicate the factor with which the conventional translation component of b/2 has to be multiplied in order to obtain the actual translation component. Partial operations transform only certain parts of the structure and not the entire structure into itself.

positions for the subsequent layer. The two pairs of layers formed in this way by the original and the subsequent layer are geometrically equivalent, one pair being transformed into the other, e.g. by the $[.m.]$ which transforms the original layer into itself and one possible position of the subsequent layer into the other possible position. Thus the symmetry of the structure is in keeping with the definition of OD structures (Dornberger-Schiff, 1964, pp. 11–16). This OD character is the cause of the disorder and of the differences in arrangement of the layers occuring in different crystals.

It is evident that partial symmetry operations are indispensable for the proper understanding of the structures of this kind. The set of the symmetry operations in such cases does not form a group because they are not all total. But the partial operations converting a layer into a layer form a groupoid in the sense of Brandt (Dornberger-Schiff, 1964, pp. 16–18). Thus it is convenient to characterize the symmetry of the whole family of these OD structures (as described by 1. to 4.) by an OD-groupoid family symbol, giving in the first line the plane space group of the individual layer (λ symmetry), and, within pairs of curly brackets, in the second and third line the operations transforming one layer into the subsequent one (σ symmetry). In our case the symbol reads

$$
\begin{array}{cc}
A(2) \; m & m \\
\{(b_{1/2}) \; 2_{1/2} \; 2\} \\
\{(b_{1/2}) \; 2_{1/2} \; 2\}
\end{array}
\tag{2}
$$

The parentheses indicate the direction of missing periodicity. The two separate lines for the σ symmetry

Table 2. *Structure parameters for the superposition structure* (*related to* $\hat{a}\hat{b}\hat{c}$)

Standard deviations σ are in parentheses

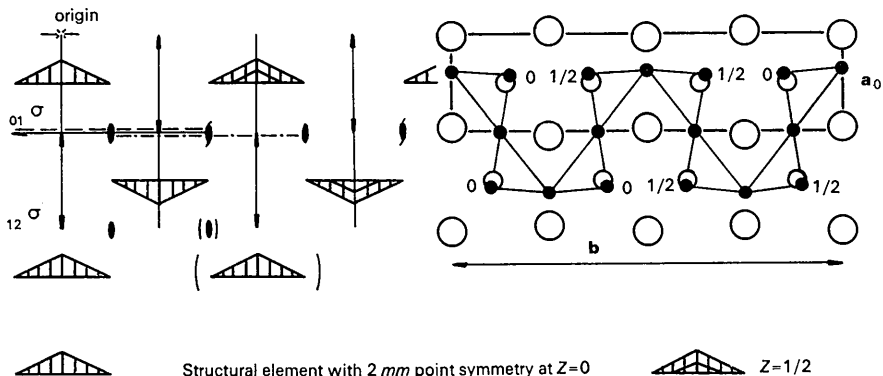|	Mult.	$\hat{x}$	$\hat{y}$	$\hat{z}$	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Hg(1)	2	$\frac{1}{4}$	0	0	0·0063 (3)	0·0081 (4)	0·0311 (15)	0·0009 (4)	0	0
Hg(2)	$\frac{4}{2}$	0·2218 (4)	−0·0528 (5)	$\frac{1}{4}$	0·0083 (5)	0·0106 (7)	0·0057 (18)	−0·0023 (5)	0	0
Hg(3)	2	0·1987 (3)	$\frac{1}{4}$	0	0·0069 (4)	0·0083 (5)	0·0631 (24)	0	0	0
S	4	0·2471 (13)	−0·0345 (16)	0	0·0046 (13)	0·0099 (22)	0·0215 (60)	−0·0019 (15)	0	0
Cl(1)	2	0·4708 (31)	$\frac{1}{4}$	$\frac{1}{4}$	0·0217 (48)	0·0089 (31)	0·0173 (92)	0	0	0
Cl(2)	2	0·0162 (22)	$\frac{1}{4}$	$\frac{1}{4}$	0·0060 (22)	0·0145 (34)	0·0128 (74)	0	0	0

Fig. 2. The structure scheme of γ-Hg$_3$S$_2$Cl$_2$ (right), showing two layers (one-layer unit outlined and the $z_{Hg(2)}$ coordinates given) together with a coherently drawn diagram of the symmetry elements in the OD-groupoid family $A(2)mm/\{(b_{1/2})2_{1/2}2\}/\{(b_{1/2})2_{1/2}2\}$.

indicate that there are two different kinds of pairs of adjacent layers in the structure (Fig. 2).

Within this OD-groupoid family there are two periodic structures with maximum degree of order (MDO structures). Both are monoclinic (c axis unique) and consist of equivalent triples of layers. The first, MDO_1, is periodic after two layers and possesses symmetry $A2/m$. The second, MDO_2, is periodic after four layers, possesses symmetry $F2/m$ and lattice constants $2\mathbf{a},\mathbf{b},\mathbf{c}$ (Fig. 3). It is obvious that the first system of diffuse maxima corresponds to MDO_1 and the second system to MDO_2. General experience shows that the MDO structures occur most frequently among the members of the family of OD structures. Thus the fact that the first and the second systems of diffuse maxima correspond exactly to those positions in reciprocal space where the diffractions of the MDO_1 and MDO_2 structures should be, is a further indication that the considerations concerning the symmetry of γ-$Hg_3S_2Cl_2$ are correct.

The third system of diffuse maxima does not correspond to any MDO structure but may be caused by regions of an ordered structure with 8-layer period.
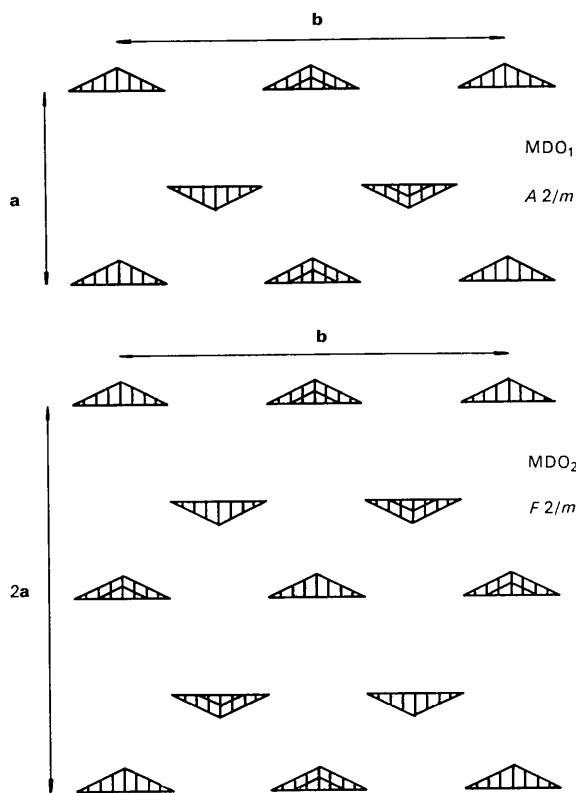

Fig. 3. The sequence of layers in the structures of the maximum degree of order (MDO_1 and MDO_2) belonging to the OD-groupoid family $A(2)mm/\{(b_{1/2})2_{1/2}2\}/\{(b_{1/2})2_{1/2}2\}$. The meaning of the symbolic structural elements is the same as in Fig. 2.

A C 24B – 7

Determination of the structure of a single layer

To solve an OD structure consisting of equivalent layers means to determine the structure of the individual layer and its repetition (OD-groupoid family) scheme. This enables us to obtain all the necessary crystallochemical information about such a structure.

The coordinates of all atoms except the atoms Hg(2) within one layer follow directly from the coordinates of these atoms in the superposition structure (see above). From the Hg(2) positions of the superposition structure two essentially different sets of positions within a layer, complying with the $A2mm$ symmetry, would be in keeping (Fig. 4). It should be easy to choose the correct one from a first generalized Patterson projection $P^{(1)}(uv)$. In such a projection a peak at about $(0, 0·2)$ should appear, corresponding to an interatomic vector 2–3 and 4–5. This peak will be positive in case (c), negative in case (b) (Fig. 4). For such a Patterson function the peak-intensities of the 1st system of diffuse maxima were used, because the others were poorly developed. Sums $|F(hk1)|^2 + |F(\bar{h}k1)|^2 = |A(hk1)|^2$ were used as coefficients for this generalized Patterson function, which therefore corresponds to a periodic structure (lattice constants $\mathbf{a},\mathbf{b},\mathbf{c}$) containing only the even-numbered layers (see Appendix). The only prominent peak is indeed the one expected (and those related to it by symmetry and antisymmetry) and it is negative. Thus the case shown in Fig. 4(b) is realized.

In order to find the possible deviations of other atoms from their averaged positions (Table 2), the first generalized electron-density projection was calculated with the $|A(hk1)|$ values and phases based on the Hg(2) coordinates. This projection revealed a small minimum in the Hg(3) position indicating that the z component of the Hg(2)–Hg(3) vectors exceeded $c/4$. After adjusting the virtual individual isotropic temperature coefficients, the R value dropped from 29·5% to 21·3%. The final difference synthesis showed only general background without any significant features in the atomic positions. Thus the structure of the single layer may be considered as being essentially correct.

A rather high value of R for the A-values has to be expected for the following reason. In order to obtain intensities above the background, a relatively big crystal, Cu radiation and film methods had to be used for the diffuse maxima. The absorption was therefore enormous ($\mu = 1331$ cm^{-1}) and could not be fully allowed for by the absorption correction.* For the sharp diffractions a far smaller crystal and counter methods yielded far more reliable data.

The observed and calculated A-values are shown in Table 3; the corresponding atomic coordinates are in Table 4. The individual isotropic temperature coeffi-

* Another reason might be a possible deviation from the true OD-character; this question cannot be discussed within this paper.

cients here have no simple physical meaning, since peak intensities have been used.

In order to confirm the structure for MDO$_1$ as deduced from the structure of the single layer and from the sequence of layers in the MDO$_1$, a crystal with the smallest possible twinning effect on its diffraction pattern was chosen. The sequence of strong and weak diffuse maxima agreed very well with the calculated values for pure MDO$_1$.

The accuracy of coordinates

Except for the Hg(2) atoms, the superposition structure yields only average atomic positions for the structure of the single layer, their possible deviations being concealed in the coefficients of the thermal vibrations. It would seem to be logical to determine the true values and their standard deviations by the least-squares technique from the Λ-values. This would imply that the entire structure is only as good as the Λ-values are, regardless of the superposition structure. This is, however, not so. A discussion of the corresponding equipoints in both *Pbmm* and *A2mm* groups, with respect to the σ-symmetry of the OD-groupoid family (2), shows that only $z_{Hg(3)}$, zs and the x coordinates of Cl atoms need to be determined from the Λ-values, because only those may be affected by overlapping in the superposition structure. All other coordinates can be derived from the superposition structure with far greater precision. The x_{Cl} coordinates however, showed strong interactions during the least-squares cycles and it was impossible to refine them using the data presently available. Thus, the values derived from the superposition structure were used. For the Cl(1) atoms the larger β_{11} coefficient suggested a possible overlapping and accordingly a larger σ-value was chosen.

Description of the structure

In Fig. 2 a portion of the structure is shown, containing two layers (zero and first) together with the symmetry

scheme of the OD-groupoid family (2). The coordinates in Table 4 refer to the zero layer. The partial operations transforming the zero layer into the first layer ($_{01}\sigma$, or,
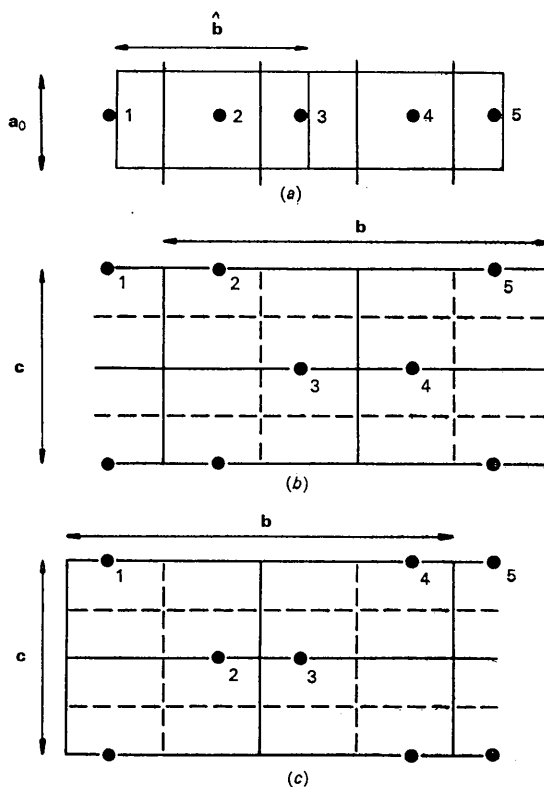
Fig. 4. Positions of the Hg(2) atoms within one layer as deduced from the superposition structure. Corresponding atoms are numbered in the same way. (a) xy projection. The z coordinates may be either 0 or $\frac{1}{2}$. Out of the planes marked one must be a mirror plane, the other is a c-glide plane. (b) and (c) The two possible arrangements of the atoms in yz projection.

Table 3. *Observed and calculated Λ-values*

In the columns from left to right the values of h, F_o, F_c and α are listed. Undetectable diffractions are marked by n.

Table 4. *Structure parameters for the one-layer structure (related to* **abc**)

Standard deviations σ are in parentheses

	Mult.	Derived from superposition structure			Derived from one-layer coefficients				Used for interatomic functions		
		x	y	z	x	y	z	B	x	y	z
Hg(1)	8/4	½	⅛	¼					½	⅛	¼
Hg(2)	4	0·2218 (4)	0·1514 (3)	0	0·2218	0·1499 (4)	0	5·8	0·2218 (4)	0·1514 (3)	0
Hg(3)	8	0·1987 (3)	0	0·2500	0·1944 (26)	0	0·2738 (15)	5·1	0·1897 (3)	0	0·2738 (15)
S	2	0·2471 (13)	0·1423 (8)	0·2500	0·2661 (202)	0·1330 (93)	0·2596 (51)	3·4	0·2471 (13)	0·1423 (8)	0·2596 (51)
Cl(1a)	2	0·4708 (31)	0	0					0·4708 (100)	0	0
Cl(1b)	2	0·4708 (31)	0	½					0·4708 (100)	0	½
Cl(2a)	2	0·0162 (22)	0	0					0·0162 (22)	0	0
Cl(2b)	2	0·0162 (22)	0	¾					0·0162 (22)	0	¾

generally $_{2p,2p+1}\sigma)^*$ are the operations listed in the second line of the symbol (2). The axonometric picture of these two layers is shown in Fig. 5(a). Fig. 5(b) shows the other alternative. It is clear that both alternatives are geometrically equivalent. A similar situation exists between the first and the second layer. The corresponding symmetry operations ($_{12}\sigma$, or, generally $_{2p-1,2p}\sigma$) are listed in the third line of the OD-groupoid family symbol (2).

The interesting role of the Hg(1) atoms is worthwhile mentioning. They occupy all inversion centres on $_{2p,2p+1}[..2_1]$, all the positions half way between them on $_{2p,2p+1}[..2]$ and have to be considered as equally divided between two neighbouring layers. Such a division is as justified as, e.g. the division of an atom at $(0yz)$ between two neighbouring unit cells. With respect to the plane space group of the single layer $A2mm$, however, these halves occupy a general eight-fold position (Table 4).

If the interatomic forces between two adjacent layers only were responsible for building up the structure, then we should have to expect continuous diffuse streaks for $l=2n+1$ with uniformly distributed intensity, resulting from a random distribution of layers over their possible positions. The presence of maxima on these streaks shows that some forces, although small, between a given layer and the next-but-one layer do exist, preferring obviously the formation of the MDO$_1$ structure. The crystallization process is, however, extremely sensitive to small changes in the crystallization conditions, giving thus a chance for the MDO$_2$ structure and perhaps another ordered 8-layered structure to appear in any individual crystal. The tendency of the γ-Hg$_3$S$_2$Cl$_2$ to form twins and parallel intergrowths is obvious from the above considerations.

Discussion

The interatomic distances and bond angles, calculated with Busing, Martin & Levy's (1964) *ORFFE* function-and-error program, together with those of the α modification (Frueh & Gray, 1968) are given in Table 5.

The structures of both α and γ modifications have in common that they consist of trigonal pyramids Hg$_3$S with shared Hg atoms, forming thus [Hg$_3$S$_2$]$_\infty^{2+}$ cations (Puff & Küster, 1962; Aurivillius, 1967). The chloride ions are distributed in both modifications in a very similar way so that each Hg atom has six neighbours: two S atoms (linear sp bond) and four Cl ions in the corners of a distorted octahedron. The weaker Hg–Cl bonds can be broken very easily in alkaline solutions (for references see Pascal, 1962) and the Cl ions completely removed from the structures.†

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* The indices preceding the symbol of a symmetry operation indicate the layers, transformed and resulting respectively (see Dornberger-Schiff, 1964 or 1966).

† In contradiction to the claim of Bacanov & Abaulina (1961), the brownish-black residue of such a decomposition is not an individual compound Hg$_3$OS$_2$, but consists of HgO and HgS (both modifications of each). A report about this will be published elsewhere.

The network of Hg$_3$S pyramids in both structures is, however, quite different. In the structure of the α modification these pyramids possess $3mm$ symmetry; the network of their covalent Hg-S bonds extends in three dimensions through the entire structure (Fig. 6). In the structure of the γ modification the pyramids are distorted and the network of their covalent Hg-S

(a)

(b)

Fig. 5. The structure scheme of γ-Hg$_3$S$_2$Cl$_2$. The shared corners of the pyramids are occupied by the Hg atoms; unshared corners are occupied by the S atoms. A pair of layers: one even and one odd layer (in this sequence), but only the Cl atoms at their common boundary are shown. (a) An arrangement of layers corresponding to Fig. 2. (b) the other, geometrically equivalent arrangement.
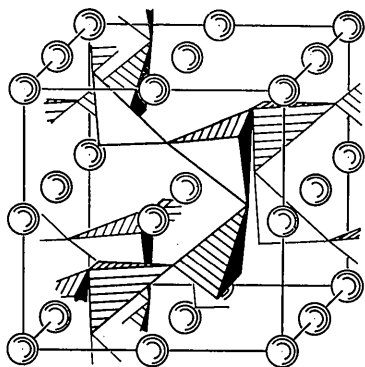
Fig. 6. The structure scheme of α-Hg$_3$S$_2$Cl$_2$ (based on Frueh & Gray's (1968) data). The meaning of the structural units is the same as in Fig. 5

bonds extends only in two dimensions. Each pair of adjacent layers consisting of one even and one odd layer (in this sequence) contains one such network with a system of Hg-S bonds penetrating their common boundary. None of these bonds penetrates the boundary between odd and even layers (in this sequence) and the entire structure is held together across these boundaries only by much weaker Hg-Cl bonds. This explains the excellent (100) cleavage of γ-Hg$_3$S$_2$Cl$_2$.

APPENDIX

If $\Phi(\xi\eta\zeta)$ is the Fourier transform of the structural element with symmetry $2mm$ with respect to the origin at the intersection of its own mirror plane $[.m.]$ and partial glide plane $[b_{1/2}..]$ (Fig. 3) then $F_0(\xi kl) = \Phi(\xi kl)[1 + (-1)^{k+l}]$ is the Fourier transform of the zero layer, referred to the periods $\mathbf{b}$ and $\mathbf{c}$. The Fourier transform of the first layer is then

$$F_1(\xi kl) = F_0(\xi kl) \exp\left\{2\pi i(2\xi + \frac{\alpha_1}{4} k)\right\}, \qquad (3)$$

where the two values of the parameter $\alpha_1 = \pm 1$ correspond to the two possible positions of the first layer. All even layers L_{2p} and all odd layers L_{2p+1} are translationally equivalent to the zero layer L_0 and the first layer L_1 respectively, the translation vectors being

$$\mathbf{T}_{2p} = 2p\mathbf{a}_0 + \frac{\alpha_{2p}}{2} \mathbf{b} \qquad \mathbf{T}_{2p+1} = 2p\mathbf{a}_0 + \frac{\alpha_{2p+1}}{2} \mathbf{b},$$

where $\mathbf{a}_0$ is a vector perpendicular to the layer plane with an absolute value equal to the width of the individual layer.

The Fourier transform of the entire structure containing $2M$ layers can now be expressed as a sum of the contributions of both even and odd layers (referred to the unit $\mathbf{a}_0$)

$$F(\xi kl) = F_0(\xi kl) \frac{1}{2M} \sum_{p=0}^{M-1} \exp\left\{2\pi i \left(2p\xi\right.\right.$$

$$\left. + \frac{\alpha_{2p}}{2} k \right)\right\} + F_1(\xi kl) \frac{1}{2M} \sum_{p=0}^{M-1}$$

$$\exp\left\{2\pi i \left(2p\xi + \frac{\alpha_{2p+1}}{2} k \right)\right\}$$

$$= F_0 S_0 + F_1 S_1 . \qquad (4)$$

If $k=2\hat{k}$ then (4) is independent of the parameters α_{2p} and α_{2p+1} ($=\pm1$) (and thus of the disorder) and

$$S_0=S_1=\frac{1}{2M}\sum_{p=0}^{M-1}\exp\{2\pi i(2p\xi+n\hat{k})\}.$$

For large values of M, $S_0=S_1=0$ unless 2ξ is equal to an integer number $\hat{h}$, and $S_0=S_1=\frac{1}{2}$ for $\xi=\hat{h}/2$. In this case, using (3)

$$F(\hat{h}\hat{k}l)=\frac{1}{2}[\Phi(\hat{h}\hat{k}l)+\Phi(\bar{\hat{h}}\hat{k}l)$$

$$\exp\{2\pi i(\hat{h}+\frac{\alpha_1}{2}\hat{k})\}][1+(-1)^{2\hat{k}+l}].$$

α_1 is irrelevant and $F(\hat{h}\hat{k}l)\neq0$ only for $l=2\hat{l}$; thus

$$F(\hat{h}\hat{k}\hat{l})=\Phi(\hat{h}\hat{k}\hat{l})+(-1)^{\hat{k}}\Phi(\bar{\hat{h}}\hat{k}\hat{l}).\qquad(5)$$

Equation (5) represents the Fourier transform of the superposition structure.

For the points in reciprocal space corresponding to the first system of diffuse maxima we have $h=2\xi$, $k=2n+1$ and $l=2m+1$. Substituting into (3) and (4) we have

$$F_1(hkl)=F_0(\bar{h}kl)i^{\alpha_1k}\qquad(6)$$

$$S_0=\frac{1}{2M}\sum_{p=0}^{M-1}\exp\left\{2\pi i\left(ph+\frac{\alpha_{2p}}{2}k\right)\right\}$$

$$=\frac{1}{2M}\sum_{p=0}^{M-1}(-1)^{\alpha_{2p}k}=s$$

$$S_1=\frac{1}{2M}\sum_{p=0}^{M-1}(-1)^{\alpha_{2p+1}k}=d.$$

Table 5. *Interatomic distances and bond angles in γ-$Hg_3S_2Cl_2$ and their comparison with those in α-$Hg_3S_2Cl_2$*

	Octahedron around Hg(1) Distance (Å)	Mult.	Octahedron around Hg(2) Distance (Å)	Mult.	Octahedron around Hg(3) Distance (Å)	Mult.	Octahedron in α-$Hg_3S_2Cl_2$ Distance (Å)	Mult.
Hg–S	2·38 (1)	2	2·37 (5)	2	2·44 (2)	2	2·45 (2)	2
Hg–Cl	3·11 (1)	4	3·45 (6) / 3·31 (8) / 3·19 (1) / 2·77 (2)	1 / 1 / 1 / 1	3·55 (7) / 3·27 (7) / 3·01 (2) / 2·67 (2)	1 / 1 / 1 / 1	2·87 (1) / 3·38 (2)	2 / 2
S–Cl	3·97 (7) / 3·95 (6) / 3·87 (7) / 3·85 (6)	2 / 2 / 2 / 2	3·99 (3) / 3·97 (7) / 3·95 (6) / 3·86 (3)	2 / 2 / 2 / 2	3·99 (3) / 3·95 (6) / 3·89 (3) / 3·85 (6)	2 / 2 / 2 / 2	>4 / 3·94 (3) / 3·83 (2)	2 / 4 / 2
Cl–Cl	>4	2×2	>4	4×1	>4	2×2	>4	2×2
	Angle (°)		Angle (°)		Angle (°)		Angle (°)	
S–Hg–S	176 (2) (180·0)	1	166·4 (7)	1	157·8 (8)	1	166 (1)	1
Cl–Hg–Cl	93·9 (2) / 86·1 (3)	2 / 2	113·2 (9) / 89·8 (1) / 79 (1) / 77·7 (3)	1 / 1 / 1 / 1	106·0 (4) / 91 (1) / 83 (1) / 80 (1)	1 / 1 / 1 / 1	109 (1) / 86·2 (7) / 78·7 (1)	1 / 2 / 1
S–Hg–Cl	92 (2) / 91 (2) / 89 (2) / 88 (2)	2 / 2 / 2 / 2	96·8 (4) / 90·5 (4) / 86·9 (3) / 83·4 (4)	2 / 2 / 2 / 2	99·1 (9) / 93·5 (9) / 83·6 (8) / 80·3 (8)	2 / 2 / 2 / 2	95·6 (6) / 92 (1) / 86 (1) / 83·6 (5)	2 / 2 / 2 / 2

	Pyramid Hg$_3$S γ-$Hg_3S_2Cl_2$ Distance (Å)	Mult.	Pyramid Hg$_3$S α-$Hg_3S_2Cl_2$ Distance (Å)	Mult.
Hg–S	2·38 (1) / 2·37 (5) / 2·44 (2)	1 / 1 / 1	2·45 (2)	3
Hg–Hg	3·56 (1) / 3·516 (3) / 3·476 (2)	1 / 1 / 1	3·546 (1)	3
	Angle (°)		Angle (°)	
Hg–Hg–Hg	61·3 (2) / 59·9 (1) / 58·8 (1)	1 / 1 / 1	60·0	3
Hg–S–Hg	96 (1) / 94 (1) / 95·8 (5)	1 / 1 / 1	92 (1)	3

Both S_0 and S_1 are real numbers varying for different members of the OD-groupoid family (2). The square of $|F(hkl)|$ is

$$|F(hkl)|^2 = s^2|F_0|^2 + d^2|F_1|^2 + sd(F_0\tilde{F}_1 + \tilde{F}_0 F_1) .$$

From this and from (6) follows that

$$|F(hkl)|^2 + |F(\bar{h}kl)|^2 = (s^2 + d^2) [|F_0(hkl)|^2 + |F_0(\bar{h}kl)|^2] ,$$

and taking the symmetry of individual layers into account,

$$|F_0(hkl)|^2 = |F_1(hkl)|^2$$
$$= \frac{1}{2(s^2+d^2)} [|F(hkl)|^2 + |F(\bar{h}kl)|^2] .$$

Here $1/2(s^2+d^2)$ is a common weighting factor for all diffuse maxima of the first system. The values $|A(hkl)|^2 = |F(hkl)|^2 + |F(\bar{h}kl)|^2$ are thus proportional to the values $|F_0(hkl)|^2$ and may thus be used as if they were the $|F|^2$ values of a structure (lattice constants a, b, c) containing only the even-numbered layers of the MDO$_1$ structure.

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Cation Distribution in Y$_3$Al$_{5-c}$Ga$_c$O$_{12}$ Garnet

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A direct determination of the cation distribution in the garnet system Y$_3$Al$_{5-c}$Ga$_c$O$_{12}$ (with $c \simeq 1,2,3,4$) from single-crystal X-ray diffraction data has been made. The lattice constants range from 12·002 Å for Y$_3$Al$_5$O$_{12}$ to 12·275 Å for Y$_3$Ga$_5$O$_{12}$. The results show that even at higher values of c the gallium ions prefer the tetrahedral sites in the garnet structure more than the aluminum ions. Although the gallium ions are reported to have a larger ionic radius than the aluminum ions (the Shannon-Prewitt radii are Ga^{3+} = 0·47, Al^{3+} = 0·39 Å), the fractions of the total Ga^{3+} in the tetrahedral sites are 84%, 77%, 68% and 63% for $c \simeq 1$, 2, 3 and 4 respectively. The value 60% represents a random distribution.

Introduction

Magnetic studies of the systems Y$_3$Fe$_{5-c}$Al$_c$O$_{12}$ and Y$_3$Fe$_{5-c}$Ga$_c$O$_{12}$* have shown that in the garnet structure for $c \leq 3$ the Ga^{3+}, Al^{3+} and Fe^{3+} ions have different preferences for the tetrahedral sites. This preference increases on going from Fe^{3+} to Al^{3+} to Ga^{3+}. The studies of the effect of pressure and temperature on the

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* For an extensive bibliography see Geller, Cape, Espinosa & Leslie (1966).

synthetic garnets, Y$_3$Fe$_5$O$_{12}$, Y$_3$Al$_5$O$_{12}$ and Y$_3$Ga$_5$O$_{12}$ (Marezio, Remeika & Jayaraman, 1966; Marezio, Remeika & Dernier, 1966) have corroborated this sequence of site preference, which cannot be explained in terms of a size effect. The Shannon & Prewitt (1968) ionic radii are Fe^{3+} = 0·50, Al^{3+} = 0·39 and Ga^{3+} = 0·47 Å.

In oxide compounds the greater preference of Ga^{3+} ions, over both Fe^{3+} and Al^{3+}, for the tetrahedral sites seems to be the reason for the differences between the gallium oxide compounds and the iron or aluminum