

# The structure of orange $\text{HgI}_2$ . II. Diamond-type structure and twinning

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Received 15 July 2002

Accepted 5 September 2002

The metastable orange crystals of  $\text{HgI}_2$  comprise three different crystal structures all of which are built from corner-linked  $\text{Hg}_4\text{I}_{10}$  supertetrahedra. Two of the structures are end members with the maximum degree of order (MDO) of a polytypic layer structure. In this paper, the third structure ( $D$ ) determined from X-ray diffraction, a crystal chemical discussion of the four known tetrahedral  $\text{HgI}_2$  structures, and a twinning model are presented. All the various diffraction results published during the past 70 years are now explained. The  $\text{Hg}_4\text{I}_{10}$  supertetrahedra of the tetragonal structure  $D$  are corner-linked into two interpenetrating diamond-type networks. The stable red form and the three orange structures show the same cubic densest packing of I atoms and differ only in the distribution of Hg atoms in the tetrahedral voids. Transformations between the structures may involve only movements of Hg atoms, as implied by larger thermal displacement parameters of Hg than of I. A multiply twinned conglomerate of MDO1, MDO2 and  $D$ , each structure occurring in three orientations, results in metrically cubic crystals whose Bragg reflections are very close to reciprocal lattice points.

## 1. Introduction

In the preceding paper (Hostettler *et al.*, 2002), hereafter referred to as (I), we presented a quantitative determination of the polytypic layer structure of the orange metastable modification of  $\text{HgI}_2$ . However, different orange crystals present different types of diffraction patterns, and the polytypic structure is indeed only a partial solution of the problem of the orange phase. We now propose a complete solution.

Orange crystals of  $\text{HgI}_2$  are obtained together with the stable forms and a metastable yellow form, either by sublimation or from organic solvents. The orange crystals are mechanically unstable and must be handled carefully. For details, see (I). Table 1 shows the diverse symmetries and lattice constants published to date. Clearly, all lattice constants show a simple relation to the cubic closest packing of I atoms found in the red form (Jeffrey & Vlasse, 1967), which may be described by the average I—I distance  $d_0$  or the average edge length  $a_0 = (2)^{1/2}d_0 = 6.2 \text{ \AA}$  of the corresponding face-centered cube. The first careful investigation with Laue diffraction methods and optical goniometry (Gorskii, 1934, 1935) found tetragonal and trigonal crystals. Gorskii suspected the latter to be twins. Jeffrey & Vlasse (1967) used the Weissenberg method and polarized light microscopy. They observed a metrically cubic cell with tetragonal symmetry and twin domains. The observations of Gorskii were in part reproduced by Schwarzenbach (1969), who found tetragonal crystals with symmetry  $I4_1/amd$  and polytypically disordered crystals with the same apparent unit cell. His idealized quali-

**Table 1**Structural information on the orange form of HgI<sub>2</sub> published to date.

Either the space group or the Laue symmetry is reported;  $s = a/d_0$ ,  $t = c/d_0$ , where  $d_0 = 4.38 \text{ \AA} \simeq a_{\text{red}} \simeq c_{\text{red}}/[2(2)^{1/2}]$  is the average I—I distance in the red form. The conventional  $c$  axis of the primitive cell in space group  $P4_2/nmc$  is  $c/2$ . (1) and (2) do not propose a structure; (3) proposes an idealized structure whose general features are confirmed by (1). Crystals were grown from solution, (1) and (2) from acetone, (3) from 2-chloroethanol. References: (1) Gorskii (1934, 1935); (2) Jeffrey & Vlasse (1967); (3) Schwarzenbach (1969).

Reference	Morphology	Symmetry	$Z$	$a$ (Å)	$c$ (Å)	$s$	$t$
(1)	Truncated bipyramid	$I4_1/amd$ or $I41md$	16	8.73 (3)	24.45 (4)	2	4(2) <sup>1/2</sup>
(1)	Hexagonal plate	$3m$		17.4	—	4	
(2)	Pyramid	$4/mmm$	128	24.85 (5)	24.85 (5)	4(2) <sup>1/2</sup>	4(2) <sup>1/2</sup>
(3)	Square plates	$I4_1/amd$ , $P4_2/nmc$	16	8.776 (1)	24.732 (2)	2	4(2) <sup>1/2</sup>

tative structure was confirmed and refined quantitatively by (1). The structural units are Hg<sub>4</sub>I<sub>10</sub> supertetrahedra, corner-linked into layers with symmetry  $p4m2$ . As in the red stable modification of HgI<sub>2</sub>, the I atoms form a cubic closest packing and the Hg atoms occupy one-quarter of the tetrahedral interstices. To a good approximation, the investigated crystal consisted of domains whose structures are those of the two stacking variants with a maximum degree of order: MDO1 with symmetry  $I4_1/amd$  and MDO2 with symmetry  $P4_2/nmc$ . A disordered conglomerate of these two structures fully explains one type of diffraction pattern obtained in the present work (see I). In this publication, we propose a third type of structure for another orange crystal. We designate this new type of structure by  $D$  because it consists of diamond-type networks of supertetrahedra. A conglomerate of the three structures MDO1, MDO2 and  $D$ , each in three twin orientations, yields an explanation of all the diffraction results published during the past 70 years.

## 2. Experimental

### 2.1. The samples

The preparation of the orange crystals and the tetragonal diffraction patterns obtained with the polytypic samples (1) and (2) have been described in (I). We denote the corresponding tetragonal lattice constants (line 4 in Table 1) by  $a_{\text{poly}}$  and  $c_{\text{poly}}$ . Sample (3) was studied with a Stoe image-plate detector and Mo  $K\alpha$  radiation. The metric derived from reconstructed images of reciprocal lattice planes such as the one shown in Fig. 1 is cubic, in agreement with Jeffrey & Vlasse (1967). The precision of the orientation matrix and lattice constants of this crystal is mediocre since the reflection spots are multi-peaked and difficult to localize. It proved to be impossible to derive reflection intensities of acceptable quality. As evidenced by Fig. 1, there are many systematic absences and rods of diffuse scattering along three perpendicular directions. In addition, the reciprocal lattice planes  $2kl$  and  $h2l$ , which are equivalent under cubic symmetry, look very similar. This feature strongly suggests that (3) is a multiple twin of the polytypic tetragonal crystals reported by (I). A superposition of domains of this structure in three different orientations results in a cubic metric and also in cubic symmetry if the three orientations occur with the same frequency. Sample (3) indeed produces the reflections implied

by this model. However, it also produces additional unexplained reflections, showing that the above model is not complete.

Sample (4) right after its preparation showed the same diffraction pattern as the polytypic (1) presented in (I). However, when it was reexamined a month later, its color had changed to a more yellowish hue, and the diffraction pattern was rather different. The symmetry was still tetragonal, but the space group from systematic absences was now  $I4_1/acd$  with lattice constants  $a_D = 12.4 \text{ \AA} \simeq 2^{1/2}a_{\text{poly}}$  and  $c_D = 24.7 \text{ \AA} \simeq c_{\text{poly}}$  (the code  $D$  refers to the diamond-type network to be described below). No prominent diffuse scattering was observed, and in particular there were no diffuse rods. The reflections were of reasonably good quality (Fig. 2). An intensity data set was collected at room temperature on a Stoe IPDS diffractometer using graphite-monochromated Mo  $K\alpha$  radiation. Details of measurement and structure determination are shown in Table 2.

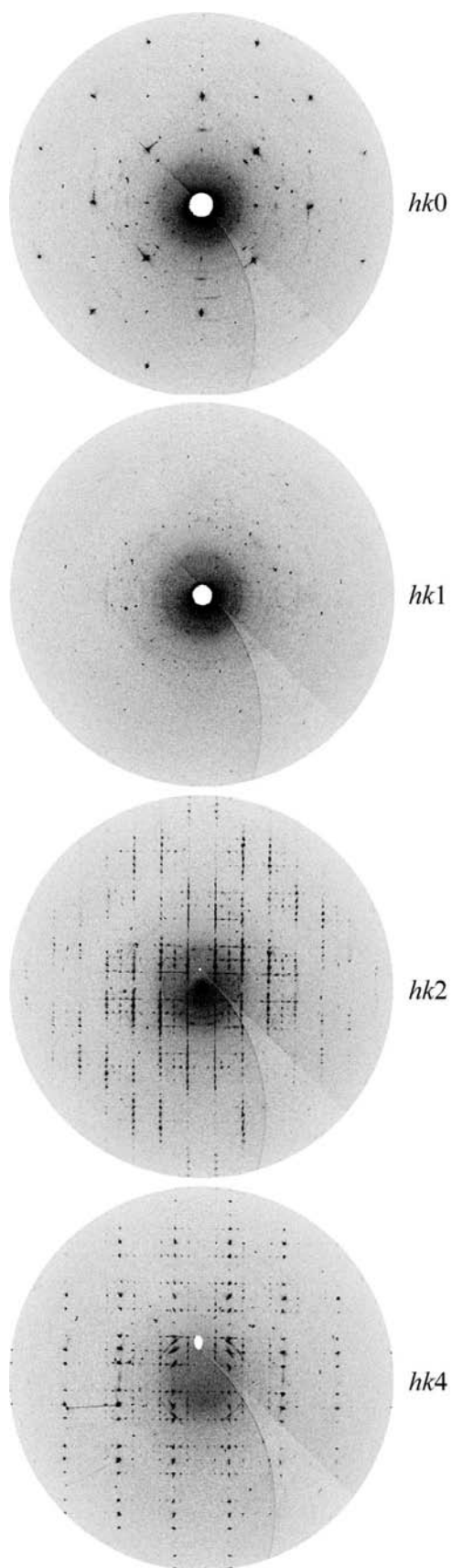
### 2.2. Data reduction

The Bragg intensities of (4) were extracted from the IP images using the software of the Stoe image-plate diffractometer (Stoe & Cie GmbH, 1997). The intensities were then corrected for Lorentz and polarization effects. Absorption was corrected analytically using the shape of the crystal measured with a high-resolution telescope. From the image-plate exposures of (3) and (4) at room temperature, undistorted layers of the reciprocal lattices (Figs. 1 and 2) were reconstructed using the *SPACE* software (Stoe & Cie GmbH, 1997).

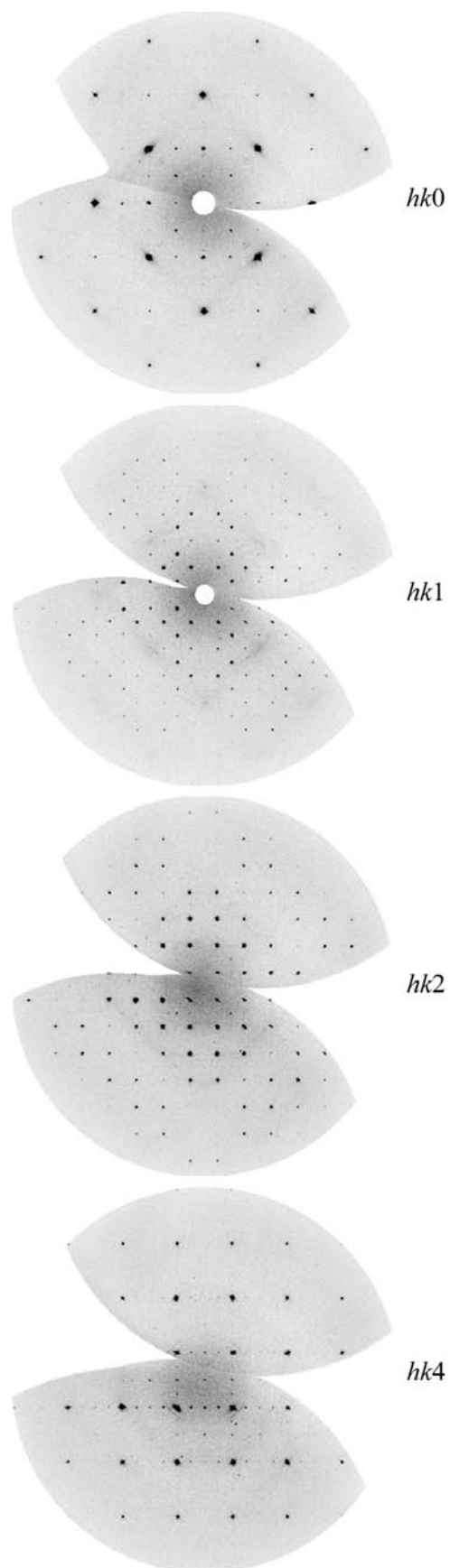
### 2.3. Structure determination for (4)

The structure was solved by direct methods (*SHELXS97*; Sheldrick, 1997b). The three independent I atoms which form a cubic closest-sphere packing were identified by maxima in the E map. The Hg atoms were found in tetrahedral interstices that cluster into supertetrahedra. This structural model was then refined by least squares including anisotropic displacement parameters. Final parameters are given in Tables 3 and 4.<sup>1</sup>

<sup>1</sup>Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK0120). Services for accessing these data are described at the back of the journal.



**Figure 1**  
Sample (3), reciprocal layers reconstructed from the image-plate data. The indices refer to a cubic cell with lattice constant  $a = 24.63$  (3) Å.  $hk3$ ,  $hk5$  and  $hk7$  layers are similar to  $hk1$ ;  $hk6$  to  $hk2$ ; and  $hk8$  to  $hk0$ .



**Figure 2**  
Sample (4), reciprocal layers reconstructed from the image-plate data. The indices refer to the tetragonal cell given in Table 2.

**Table 2**  
Crystal data and experimental details of (4) after the change of its color.

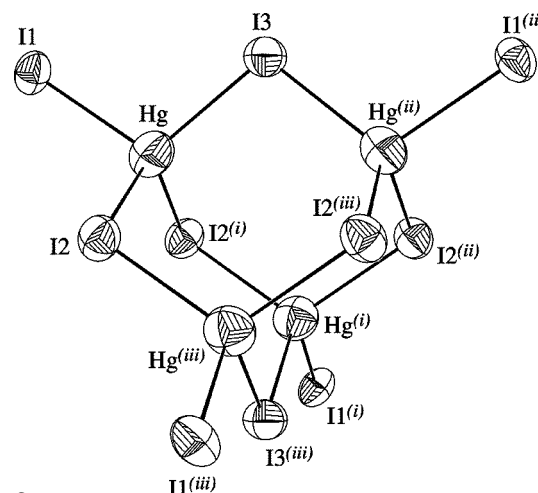
Crystal data	
Chemical formula	HgI <sub>2</sub>
Chemical formula weight	454.39
Cell setting, space group	Tetragonal, <i>I</i> <sub>4</sub> /acd
<i>a</i> , <i>c</i> (Å)	12.3930 (18), 24.889 (5)
<i>V</i> (Å <sup>3</sup> )	3822.6 (11)
<i>Z</i>	32
<i>D</i> <sub>x</sub> (Mg m <sup>-3</sup> )	6.316
Radiation type	Mo <i>K</i> α
No. of reflections for cell parameters	978
$\theta$ range (°)	0.99–23.23
$\mu$ (mm <sup>-1</sup> )	44.920
Temperature (K)	293 (1)
Crystal form, colour	Parallelepiped, yellow-orange
Crystal size (mm)	0.18 × 0.08 × 0.06
Data collection	
Diffraction	Stoe IPDS
Data collection method	$\varphi$ scans
Absorption correction	Analytical
<i>T</i> <sub>min</sub>	0.012
<i>T</i> <sub>max</sub>	0.217
No. of measured, independent and observed reflections	22930, 685, 455
Criterion for observed reflections	<i>I</i> > 2σ( <i>I</i> )
<i>R</i> <sub>int</sub> before, after absorption correction	0.379, 0.112
$\theta$ <sub>max</sub> (°)	23.23
Range of <i>h</i> , <i>k</i> , <i>l</i>	0 → <i>h</i> → 9 0 → <i>k</i> → 13 0 → <i>l</i> → 27
Refinement	
Refinement on	<i>F</i> <sup>2</sup>
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.045, 0.0977, 1.783
No. of reflections and parameters used in refinement	685, 29
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.028P)^2 + 5.8P]$ where $P = (F_o^2 + 2F_c^2)/3$
( $\Delta/\sigma$ ) <sub>max</sub>	0.000
$\Delta\rho_{max}$ , $\Delta\rho_{min}$ (e Å <sup>-3</sup> )	1.147, -1.325

Computer programs used: IPDS (Stoe & Cie GmbH, 1997), SHELXS97 (Sheldrick, 1997b), SHELXL97 (Sheldrick, 1997a).

### 3. Description of the diamond-type structure

With the present structure determination, we now know four tetrahedral structures of HgI<sub>2</sub>: the stable red form and three orange structures. Since the different orange structures occur together, even in a single specimen (see below), and since their relative stabilities can hardly be assessed, we prefer to refer to a single metastable orange phase comprising the three structures MDO1, MDO2 and *D*. The new orange structure *D* has key features in common with the polytypic structures MDO1 and MDO2 described in (I): it is composed of corner-linked Hg<sub>4</sub>I<sub>10</sub> supertetrahedra, the I-atom substructure forms a cubic closest packing, all HgI<sub>4</sub> tetrahedra are symmetrically equivalent, and the Hg–I–Hg angles of 103° to 104° are approximately, but somewhat smaller than, tetrahedral (Fig. 3). However, the supertetrahedra are not linked into layers but rather into two interpenetrating three-dimensional networks (Fig. 4). The new structure differs

from MDO1, MDO2 and the red structure only by the distribution of Hg atoms in tetrahedral voids of the closest-packed I-atom substructure. All tetrahedral HgI<sub>2</sub> structures have similar nearest-neighbor distances Hg–I and I–I, and angles I–Hg–I and Hg–I–Hg close to tetrahedral. Interatomic distances of *D* are given in Table 5. There are four different Hg–I bonds, which average to 2.790 (2) Å, a value at 1 s.u. of those observed in red HgI<sub>2</sub>, MDO1 or MDO2. The edge of the supertetrahedron perpendicular to the *c* axis is more bent, as in the MDO structures, I1–I3–I1<sup>(ii)</sup> = 175.52 (4)°, while the other edges show an angle I1–I2–I1<sup>(iii)</sup> = 177.37 (6)° (for the codes, see Table 5). These angles show that the Hg<sub>4</sub>I<sub>10</sub> supertetrahedra (symmetry  $\bar{4}$ ) are slightly more distorted than those of the MDO structures (symmetry  $\bar{4}2m$ ). The lengths of the I1–I2 and I1–I2<sup>(i)</sup> edges differ by 0.14 Å; they would be equal for an idealized structure with *x*(I2) = *y*(I2) = *y*(I1) = 0.5 and *z*(I2) = 0.125. As in the MDO structures, the I–I distances inside the supertetrahedra



**Figure 3**  
Hg<sub>4</sub>I<sub>10</sub> supertetrahedron of the diamantoid structure of HgI<sub>2</sub>. I3–I3<sup>(iii)</sup> direction is along the *c* axis, while I1–I1<sup>(ii)</sup> is along the *a*–*b* diagonal. The atomic displacement parameters are drawn at the 80% probability level. Symmetry symbols as in Table 5.

**Table 3**  
Atomic coordinates for the diamantoid structure of orange HgI<sub>2</sub>.

Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>	
Hg	32 <i>g</i> 1	0.37417 (6)	0.37379 (7)	0.06244 (3)	0.0490 (3)
I1	32 <i>g</i> 1	0.49952 (8)	0.51362 (11)	0.12489 (16)	0.0390 (6)
I2	16 <i>d</i> 2..	1/2	1/4	-0.00709 (6)	0.0396 (6)
I3	16 <i>e</i> . 2.	1/4	0.51427 (15)	0.0	0.0378 (6)

**Table 4**  
Atomic displacement parameters for the diamantoid structure of orange HgI<sub>2</sub>.

The displacement factor expression is  $\exp(-2\pi^2 \sum U^{ij} a_i^* a_j^* h_i h_j)$ .

	<i>U</i> <sup>11</sup>	<i>U</i> <sup>22</sup>	<i>U</i> <sup>33</sup>	<i>U</i> <sup>12</sup>	<i>U</i> <sup>13</sup>	<i>U</i> <sup>23</sup>
Hg	0.0501 (6)	0.0492 (6)	0.0488 (5)	0.0031 (4)	-0.0064 (4)	0.0053 (4)
I1	0.0428 (10)	0.0325 (8)	0.0416 (7)	-0.0011 (5)	-0.0075 (5)	-0.0008 (17)
I2	0.039 (2)	0.045 (2)	0.0349 (9)	0.0032 (7)	0.0	0.0
I3	0.0416 (16)	0.0294 (11)	0.0425 (10)	0.0	-0.0131 (6)	0.0

**Table 5**

Interatomic distances (Å) for the diamantoid structure of orange HgI<sub>2</sub>.

Codes for supertetrahedron as in (I): *c* corner; *m* mid-edge; *E* aligned on edge; *e* oblique to edge; *l* contact between supertetrahedra of the same network. Codes for contacts between the two networks: *v*<sub>1</sub> perpendicular to *c* axis; *v*<sub>2</sub> oblique to *c* axis.

Intranetwork		Internetwork			
Hg–I1	2.795 (1)	<i>c</i>	I2–I2 <sup>(v)</sup>	4.134 (3)	<i>v</i> <sub>1</sub>
Hg–I2	2.799 (2)	<i>m</i>	I2–I2 <sup>(viii)</sup>	4.151 (2)	<i>v</i> <sub>1</sub>
Hg–I2 <sup>(i)</sup>	2.779 (3)	<i>m</i>	I3–I1 <sup>(vi)</sup>	4.263 (1)	<i>v</i> <sub>1</sub>
Hg–I3	2.789 (1)	<i>m</i>	I2–I1 <sup>(vi)</sup>	4.406 (3)	<i>v</i> <sub>2</sub>
I1–I2	4.385 (3)	<i>E</i>	I2–I1 <sup>(vii)</sup>	4.270 (3)	<i>v</i> <sub>2</sub>
I1–I2 <sup>(i)</sup>	4.526 (3)	<i>E</i>	I2–I3 <sup>(vi)</sup>	4.144 (3)	<i>v</i> <sub>2</sub>
I1–I3	4.511 (2)	<i>E</i>			
I2–I2 <sup>(i)</sup>	4.621 (2)	<i>e</i>			
I2–I3	4.633 (3)	<i>e</i>			
I2 <sup>(i)</sup> –I3	4.637 (3)	<i>e</i>			
I2–I3 <sup>(iv)</sup>	4.148 (3)	<i>l</i>			

are 0.2–0.5 Å longer than the I–I contacts between supertetrahedra. Thus, the presence of the Hg atoms in the interstitial sites tends to increase the volume of the supertetrahedra. Surprisingly, the atomic displacement parameters of the Hg atoms are on average larger than those of the I atoms,  $U_{\text{eq(Hg)}} = 0.0490$  (3),  $\langle U_{\text{eq(I)}} \rangle = 0.0388$  (6) Å<sup>2</sup>. This observation appears to agree with the transformation of the polytypic to the diamond-type structure, which presumably is due to a diffusion of Hg atoms between tetrahedral voids of an otherwise unchanged densest packing of I atoms.

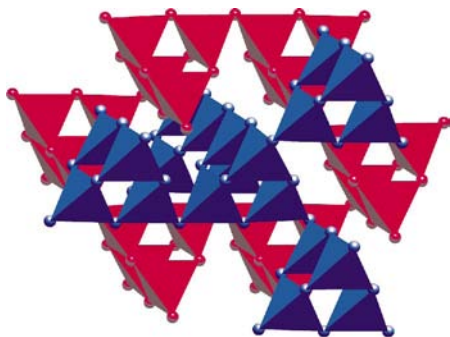
Structure *D* can be decomposed into two identical interpenetrating substructures. One such substructure comprises all the supertetrahedra that can be reached by a path starting at one tetrahedron and passing through linking corners. It has the geometry of a four-connected diamond-type network, the centers of the supertetrahedra being arranged in a tetragonally distorted diamond structure (Fig. 5). The substructures are independent in the sense that supertetrahedra in different networks have at most van der Waals contacts and there is no path leading from one network to the other *via* a corner common to two tetrahedra. The structure is thus a geometrical analog of the well known double-diamond networks such as Cu<sub>2</sub>O (*e.g.* Restori & Schwarzenbach, 1986) or Zn(CN)<sub>2</sub> and Cd(CN)<sub>2</sub> (Hoskins & Robson, 1990). The *D* structure of HgI<sub>2</sub> is also adopted by other compounds; a search in the Inorganic Crystal Structure Database (ICSD; Bergerhoff & Brown, 1987) for binary compounds having space-group symmetry *I4*<sub>1</sub>/*acd* gives four references for this structure type: ZnI<sub>2</sub>, ZnBr<sub>2</sub>, GeS<sub>2</sub> and BeCl<sub>2</sub>. ZnI<sub>2</sub> has been reported by Fourcroy *et al.* (1978) but was not described as two interpenetrating networks. The structure of ZnBr<sub>2</sub> is isotopic with ZnI<sub>2</sub> but has been reported with another choice of origin (Chieh & White, 1984). The structure of BeCl<sub>2</sub> presents considerably distorted networks, while GeS<sub>2</sub> adopts this structure under a moderate pressure at high temperature (MacLachlan *et al.*, 1998).

We now discuss the simplest corner-linked networks of tetrahedral voids in closest-sphere packings. The number of tetrahedral voids in a closest sphere packing is twice the number of spheres. These voids can be subdivided into two

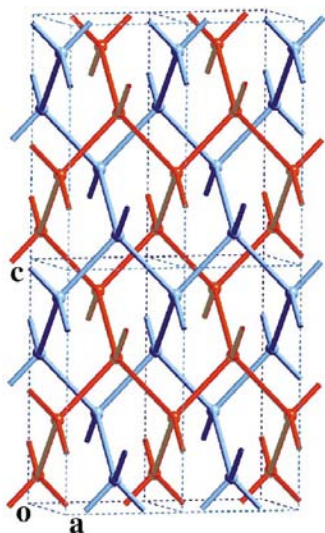
equivalent interpenetrating frameworks. In each framework, the tetrahedra are connected only by shared corners, and not by edges or (in the hexagonal case) faces, and four tetrahedra meet in each corner. In a cubic packing these have the same orientation, whereas in a hexagonal packing three have the same and the fourth has the inverse orientation. Filling all tetrahedra in a corner-linked network with cations results in the cubic Zinkblende or the hexagonal Wurtzite structure. In order to obtain a structure with the stoichiometry *AX*<sub>2</sub> where each anion *X* connects only two tetrahedra, only one-third of the corner-linked neighbors of any given tetrahedron are to be occupied with cations. In the two simplest out of the large number of such possible structures, all I atoms and all Hg atoms are symmetrically equivalent, and the symmetry of Hg is at least  $\bar{4}$  (Fig. 6). The two structures both derive from the cubic closest packing where all corner-linked tetrahedra have the same orientation. One of them is the layer structure of the red modification of HgI<sub>2</sub> with space group *P4*<sub>2</sub>/*nmc*, containing tetrahedra with symmetry  $\bar{4}2m$ ;  $\gamma$ -ZnCl<sub>2</sub> also adopts this structure (Brehler, 1961). The other simple structure has space group *I4*<sub>2</sub>*d*. It consists of a diamond-type network of single tetrahedra with symmetry  $\bar{4}$ . It is realized by zinc chloride,  $\alpha$ -ZnCl<sub>2</sub> (Oswald & Jaggi, 1960; Brehler, 1961), GeS<sub>2</sub> (Prewitt & Young, 1965) and by a modification of SiO<sub>2</sub> (Boisen *et al.*, 1994) but has not been found for HgI<sub>2</sub>. If in these structures the single tetrahedra are replaced by their fractal complications, the supertetrahedra, the site symmetries  $\bar{4}2m$  and  $\bar{4}$  ensure that all single tetrahedra, *i.e.* all Hg atoms, remain symmetrically equivalent. Three structures with cubic-closest-packed I atoms are thereby obtained. From the red form of HgI<sub>2</sub> result two structures of orange HgI<sub>2</sub>: MDO1 and MDO2 [see Figs. 1 and 5 in (I)]. Note that the contacts between layers of supertetrahedra are not equivalent to the contacts between layers of single tetrahedra. From the ZnCl<sub>2</sub> structure formed by a single diamond-type network the orange structure *D* is obtained, which contains two interpenetrating such networks (Figs. 4 and 5). We conclude that there exist five tetrahedral closest-packed structures with stoichiometry *AX*<sub>2</sub> possessing coordination number 2 for the anions and symmetrically equivalent cations. It is interesting to note that HgI<sub>2</sub> realizes four of them. It is easy to imagine structures built from super-supertetrahedra, the next fractal complication. They present interesting polytypic and diamond-type variants. However, such structures present large clusters with I atoms not linked to any Hg atoms, as well as symmetrically inequivalent sets of single tetrahedra.

#### 4. Multi-domain twinning

The cubic metric and peculiar intensity distribution of the diffraction patterns of (3) (Fig. 1) suggest a multiple twin. The various domains possessing the structures MDO1, MDO2 and *D* have the same closest-packed substructure of I atoms and differ only in the distribution of the Hg atoms. If this substructure is supposed to extend uninterruptedly across all domain boundaries throughout the crystal (apart from the fact that tetrahedra filled with Hg atoms are somewhat larger than



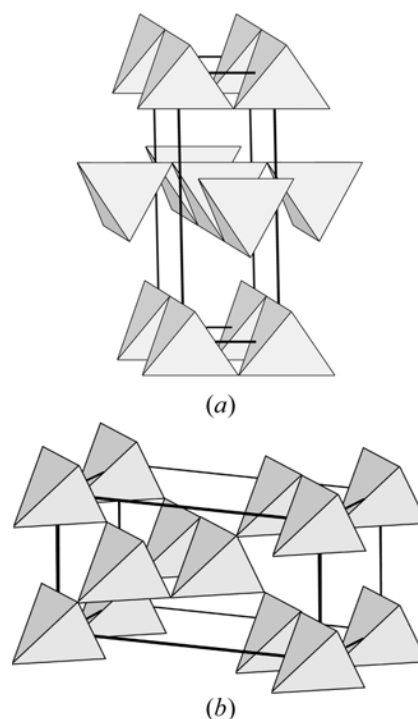
**Figure 4**  
Interpenetrating diamond-type frameworks of supertetrahedra in structure *D*. The red part shows a six-membered ring, and the blue part shows the coordination of a supertetrahedron with symmetry 4. [0 1 0] vertical, [2 0 1] horizontal.



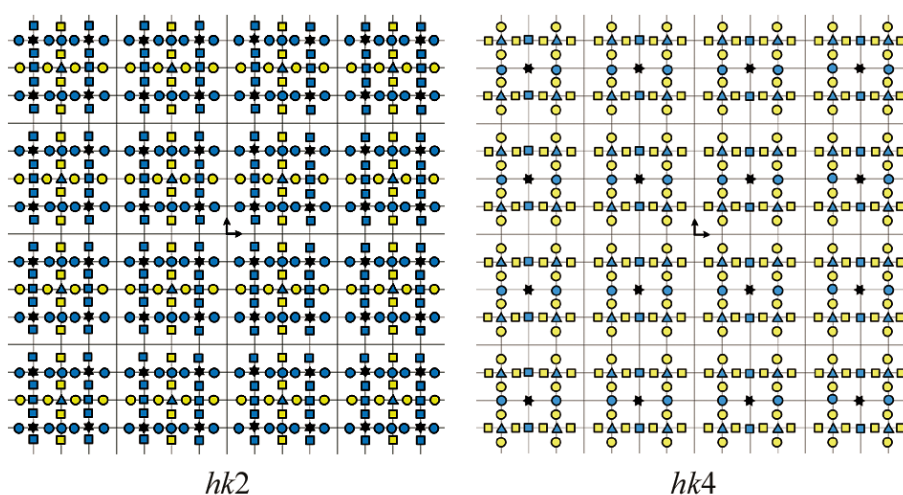
**Figure 5**  
Interpenetration of the two networks of the diamondoid structure of orange  $\text{HgI}_2$ . Each supertetrahedron is represented by its center of gravity. Both networks are identical, symmetry  $I4_1/amd$ .

empty ones), the mutual orientations of the individual structures are easily derived. We refer MDO1 and MDO2 to the same lattice constants  $a_{\text{poly}}$ ,  $b_{\text{poly}}$  and  $c_{\text{poly}}$  and structure *D* to  $a_D$ ,  $b_D$  and  $c_D$  of Table 2. One orientation of the MDO structures is then  $a_{\text{poly}}$  along  $[\bar{1}10]_{\text{cubic}}$ ,  $b_{\text{poly}}$  along  $[110]_{\text{cubic}}$  and  $c_{\text{poly}}$  along  $[001]_{\text{cubic}}$ . The other two orientations result from cyclic permutations of the cubic indices. One *D* structure has the orientation  $a_D$  along  $[100]_{\text{cubic}}$ ,  $b_D$  along  $[010]_{\text{cubic}}$  and  $c_D$  along  $[001]_{\text{cubic}}$ . The other orientations result again from cyclic permutations of the indices. Since the ratio  $c_{\text{poly}}/a_{\text{poly}} = 2.8119$  (11) is somewhat smaller than the ideal value  $2(2)^{1/2} = 2.8284$ , and  $c_D/a_D = 2.0083$  (7) is somewhat larger than 2.0, the reflections from different domains

do not overlap exactly and the reflection spots should indeed be multi-peaked. Fig. 7 shows the decomposition of the diffraction pattern of Fig. 1 into contributions from the  $3 \times 3$  domain types. The observed reflections in all of the reciprocal space recorded by our experiments are well explained by the multi-domain twin model involving all three supertetrahedral structures.



**Figure 6**  
The two simplest tetrahedral structures  $AX_2$  with close-packed anions and all *X* and all *A* atoms symmetrically equivalent. (a)  $P4_2/nmc$  realized e.g. by red  $\text{HgI}_2$ , (b)  $I4_2d$ , e.g.  $\alpha\text{-ZnCl}_2$ , in the same orientation as one of the diamondoid networks in Fig. 4.



**Figure 7**  
Identification of the reflections in Fig. 1 with the twin domains. Blue indicates the MDO structures; yellow, structure *D*; black, the superimposed reflections  $\text{MDO} + D$ . Circles, squares and triangles indicate  $c_{\text{poly}}$  or  $c_D$  of the twin domain parallel to  $a_{\text{cubic}}$ ,  $b_{\text{cubic}}$ ,  $c_{\text{cubic}}$ , respectively. The stars designate locations where reflections of all domains overlap.

## 5. Conclusions

Our results explain the previously observed lattice constants (Table 1) for the orange form of  $\text{HgI}_2$ , at least as far as the descriptions of the early experiments can be interpreted. Jeffrey & Vlasse (1967) probably observed a twinned crystal where domains in different orientations occur in different volume ratios, hence the cubic metric and tetragonal symmetry. The trigonal crystal of Gorskii (1934) most probably is a plate of a twinned crystal with cubic metric and orientation  $(111)_{\text{cubic}}$ . The length of the shortest apparent translation  $[1\bar{1}0]_{\text{cubic}}$  perpendicular to  $[111]_{\text{cubic}}$  is  $8d_0 \simeq 35 \text{ \AA}$ , *i.e.* twice the reported value. The details of the Laue experiment were not described, but it might be imagined that only relatively strong reflections were observed leading to an apparent lattice constant of  $4d_0$ . The other values reported in Table 1 correspond to the polytypic MDO structures.

The tetrahedral modifications of  $\text{HgI}_2$  form closely related structures, all of which show the same first coordinations of Hg by I and of I by Hg atoms. The structures show the simplest distributions of Hg atoms in corner-linked tetrahedral voids of closest-packed I atoms with roughly tetrahedral bond angles I–Hg–I and Hg–I–Hg, and domains of these distributions may form a composite crystal. The energies of these structures are probably very similar. The structures of the domain boundaries are not known. However, model building shows that contacts of layers of supertetrahedra of the MDO structures with different twin orientations create arrangements of supertetrahedra typical for the *D* structure, and analogous contacts of the *D* structure domains create arrangements typical for the layers. The only crystal with pure *D* structure at our disposal had transformed from an MDO structure, possibly aided by irradiation with X-rays. Also, the orange crystals transform spontaneously to the red form and nuclei of the red form are easily created by touching the crystal. This suggests that the Hg atoms are mobile inside the I-atom substructure and diffuse between tetrahedral voids.

The halides of Zn form the same or analogous structures. They realize the single-tetrahedral *D* structure ( $\alpha\text{-ZnCl}_2$ ) and the supertetrahedral *D* structure ( $\text{ZnI}_2$ ,  $\text{ZnBr}_2$ ), whereas the

layer structures have been observed only with  $\text{ZnCl}_2$  ( $\gamma$ -phase) and  $\text{HgI}_2$ . We cannot imagine why supertetrahedra should be the most stable geometry in  $\text{ZnI}_2$  and  $\text{ZnBr}_2$ . Possibly, one or several of the other structures might also be realized by these compounds. Note that the halides of the group IIB element Cd do not realize any of these structures but form octahedral structures.

We are grateful to Dr Henrik Birkedal for fruitful discussions. We thank the Swiss National Science Foundation for financial support.

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