The crystal structure and one-dimensional disorder of the orange modification of HgI₂

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Auszug

Die schon mehrfach beschriebene metastabile orange Modifikation von HgJ₂ wurde durch Rekristallisation von HgJ₂ aus 2-Chloroäthanol dargestellt. Die Farbe der quadratischen blättchenförmigen Kristalle variierte von rot-orange bis gelb-orange. Die Röntgenaufnahmen der gelb-orangen Kristalle ließen auf eindimensionale Fehlordnung entlang c schließen; die Reflexe der rot-orangen waren scharf. Die Lauesymmetrie ist $4/mmm$, und die Gitter-konstanten sind doppelt so lang, wie diejenigen der roten Modifikation: $a = 8,776$, $c = 24,723$ Å, $c/a \simeq 2\sqrt{2}$. Die reziproken Netzebenen $hk0$ und hhl sind mit der Netzebene $hk0$ der roten Form identisch, und sehr viele Reflexe sind systematisch ausgelöscht. Die Struktur wurde auf Grund dieser Beobachtungen gelöst. Ihr Motiv ist eine Hg₄J₁₀-Gruppe, die durch vier eckenverknüpfte HgJ₄-Tetraeder in tetraedrischer Anordnung gebildet wird. Diese Gruppen sind wie die HgJ₄-Tetraeder der roten Modifikation zu HgJ₂-Schichten verknüpft, die mit J—J-Kontakten gestapelt sind. Im Unterschied zur roten Form gibt es aber zwei verschiedene Arten der Stapelung, die beide eine kubische dichteste Kugel-packung der Jodatome bedingen. Die eine führt zu einer Vierschicht- (rot-orange Kristalle), die andere zu einer Zweischicht-Struktur. Die Fehlordnung der gelb-orangen Kristalle ist durch diese beiden Stapelarten bedingt. Die Inten-sität der durch die Fehlordnung hervorgerufenen diffusen Streuung wurde berechnet und stimmt qualitativ mit den Beobachtungen überein.

Abstract

The metastable orange modification of HgI₂, described earlier by several authors, was obtained by recrystallization of HgI₂ from 2-chloroethanol in the form of square, platelike crystals ranging in color from red-orange to yellow-orange. The x-ray photographs of the yellow-orange crystals indicated one-dimensional disorder along c, whereas the reflections from the red-orange

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form were sharp. The Friedel symmetry is $4/mmm$ and the lattice constants are twice those of the red form, i.e., $a = 8.776$, $c = 24.723$ Å, $c/a \simeq 2\sqrt{2}$. Both the $hk0$ and hhl reciprocal-net planes are identical with the $hk0$ plane of the red form and there are many systematic extinctions. The structure was solved from these observations. The structural motif is a Hg_4I_{10} group, consisting of four corner-linked HgI_4 tetrahedra in a tetrahedral arrangement. These groups are connected into HgI_2 layers which are stacked with I—I contacts in the same way as the HgI_4 tetrahedra in the red form. In contrast to the red form, there exist two kinds of stacking, leading to a cubic close packing of the iodine atoms. One results in a four-layer structure (red-orange crystals), the other in a two-layer structure. The disorder of the yellow-orange crystals is caused by an irregular succession of the two kinds of stacking. The intensity of the diffuse scattering arising from the disorder was calculated, and is in qualitative agreement with the observations.

Introduction

Mercury (II) iodide, HgI_2, has an orange modification in addition to the well-known red and yellow forms (Bijvoet, Claassen and Karssen, 1926; Gorsky, 1934a; Jeffrey and Vlasse, 1967). It was first observed by Kohlschütter (1927) who obtained from HgI_2 vapor, orange tetragonal crystals with many faces. These crystals were more stable at room temperature than the yellow modification. Small orange plates were also obtained by precipitation from alcohol. Gorsky (1934b; 1935) prepared the orange modification by crystallizing HgI_2 from acetone at room temperature. The crystals were metastable at all temperatures between 15 and 140 °C. Laue and oscillation photographs showed that they were tetragonal, with space group* $I4_1/amd$ or $I4_1md$, and lattice constants almost exactly twice those of the red form, i.e., $a = 8.73$ Å and $c = 24.45$ Å. The systematic absences were not reported. Gorsky also described orange crystals with $a = 17.4$ Å and suspected them to be twins. Jeffrey and Vlasse (1967) prepared the orange modification by Gorsky's method. The Friedel symmetry was $4/mmm$ and the lattice constants $c = a = 24.85$ Å. Very unusual systematic extinctions were observed and the $hk0$ and $0kl$ reciprocal-net planes were found to be identical with the $hk0$ plane of the red modification. These crystals were described as twins. It is probable that they were *identical* with the crystals having $a = 17.4$ Å, reported by Gorsky (1935). The a axis used by Jeffrey and Vlasse corresponds to [110] in Gorsky's axial system.

* The space group is misprinted in the publication of 1934.

Crystal data

Crystals of the orange form were prepared by cooling a solution of HgI_2 in 2-chloroethanol saturated at the boiling point. Thin square plates with side lengths between 0.2 and 0.5 mm were obtained, together with crystals of the red and yellow forms. Their color ranged from red-orange to yellow-orange. The phase transformation into the red modification could be started simply by touching them. The red-orange crystals turned red slowly in the course of a day, whereas the yellow-orange crystals were more unstable and often took only minutes to transform. This sensitivity caused difficulty in mounting the crystals for photography and none remained orange for longer than about three days. They were examined by the precession and Weissenberg methods. The lattice constants were measured on a Picker 4-circle single-crystal diffractometer and refined by least squares. The x-ray data for the red-orange crystals are as follows:

Friedel symmetry: $4/mmm$

$a = 8.776$ ($\sigma = 0.001$) Å

$c = 24.723$ ($\sigma = 0.002$) Å

$c/a = 2.817 \simeq 2 \cdot \sqrt{2}$

The following reflections hkl are present:

$h,k = 2n$ and $h+k = 4n$: $l = 8n$

$h,k = 2n$ and $h+k = 4n+2$: $l = 2n$, but not $8n$

$h+k = 2n+1$: $l = 2n+1$

$h,k = 2n+1$:   no reflections.

The $hk0$ and hhl reciprocal-net planes both were found to be *identical* with the $hk0$ plane of the red form. The estimated intensities are given in Table 1.

The space group which explains the largest fraction of the extinctions is $I4_1/amd$, in agreement with GORSKY (1935). Since the red form contains two formula units per cell, sixteen formula units can be expected per cell of the orange form. The calculated density is then 6.34 g · cm^{-3}, as compared to 6.38 g · cm^{-3} calculated for the red form (JEFFREY and VLASSE, 1967).

The yellow-orange crystals gave x-ray photographs indicating one-dimensional disorder along c. They had the same lattice constants as the red-orange crystals. No crystal was found to have an a-axis length of 17.4 Å, as reported by GORSKY. The reflections with $h,k = 2n$ were sharp with the same intensities as with the red-orange

Table 1. *Estimated intensities and calculated structure factors for the red-orange crystals (four-layer structure)*

h	k	l	I (estimated)	$|F_c|$
$4n$ $4n+2$	$4n$ $4n+2$	$16n$ $16n+8$	st +	$16(2f_I + f_{Hg})$
$4n$ $4n+2$	$4n$ $4n+2$	$16n+8$ $16n$	w	$16(2f_I - f_{Hg})$
$4n$ $4n+2$	$4n+2$ $4n$	$8n+4$ $8n+4$	st	$32 \cdot f_I$
$4n$ $4n+2$	$4n+2$ $4n$	$8n\pm2$ $8n\pm2$	m +	$8 \cdot \sqrt{2} \cdot f_{Hg} = 11.31 f_{Hg}$
$2n$ $2n+1$	$2n+1$ $2n$	$8n\pm1$ $8n\pm1$	w	$4\sqrt{2-\sqrt{2}}\, f_{Hg} = 3.06 f_{Hg}$
$2n$ $2n+1$	$2n+1$ $2n$	$8n\pm3$ $8n\pm3$	m —	$4\sqrt{2+\sqrt{2}}\, f_{Hg} = 7.39 f_{Hg}$

$$\left. \begin{array}{c} 4\sqrt{2-\sqrt{2}}\, f_{Hg} = 3.06 f_{Hg} \\ 4\sqrt{2+\sqrt{2}}\, f_{Hg} = 7.39 f_{Hg} \end{array} \right\} = \left[32\left(1-\cos\frac{\pi}{4}l\right)\right]^{\frac{1}{2}} \cdot f_{Hg}$$

crystals while those with $h,k = 2n+1$ were again absent. The reciprocal-lattice rows with $h+k = 2n+1$, however, consisted of diffuse reflections sitting on a streak, as shown in Fig. 1. In contrast to the
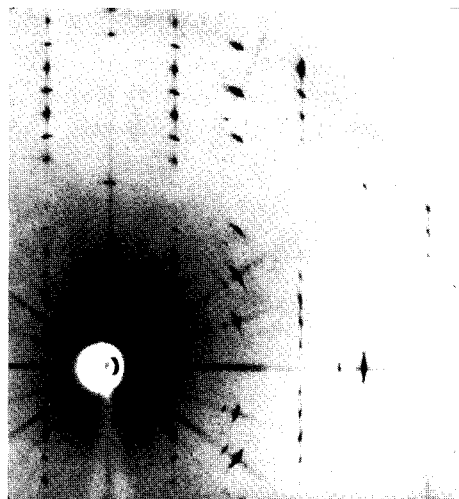

Fig. 1. Precession photograph showing the $h0l$ reciprocal-net plane of a yellow-orange disordered crystal. The intensities are strongly affected by absorption
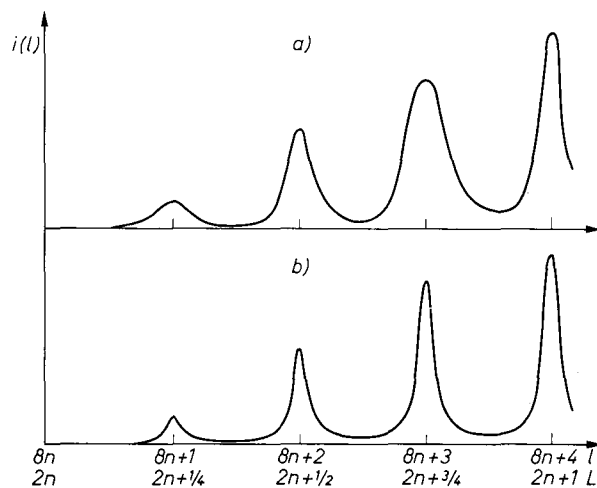

Fig. 2. (a) Mean curve for $i(l) = \dfrac{I(l)}{f_{Hg}^2}$ measured on a Weissenberg photograph of a very small disordered crystal along the streak $12l$. The curve is periodic with a period of eight in l and symmetrical at $l = 4n$. (b) The theoretical curve calculated with $s = 2$ and $\omega_1 = 1 - \omega_2 = 0.1$ is shown for comparison

red-orange crystals, the reflections with both l even and l odd were present, except the ones with $l = 8n$. The intensity along the streak was periodic with a periodicity of 8 in l, and the same for all rows, except for a general decrease towards larger angles due to the decrease in the magnitude of the atomic scattering factor. Measurements along the streak $12\,l$ were made over several periods on a Weissenberg film taken from a very small crystal with a flying-spot integrating micro-densitometer, using the smallest possible integrating area. Fifty measurements were made per period. Figure 2 shows the mean curve obtained for $i(l) = \dfrac{I}{f_{Hg}^2}$ (I = intensity, f_{Hg} = scattering factor for mercury). Its general characteristics are:

(a) It is symmetrical around $l = 4n$.

(b) The intensity is zero for $l = 8n$, and reaches its maximum for $l = 8n+4$.

(c) The reflections with l odd are more diffuse than the ones with l even.

(d) $i(l{=}1) : i(l{=}2) : i(l{=}3) : i(l{=}4) \sim 1 : 3.5 : 5.5 : 7$.

The measurements were not corrected for the Lorentz polarization factor or absorption since they could be explained only qualitatively.

Determination of the ordered structure

The structure of the red-orange form was determined from the relationship of its diffraction pattern to that of the red modification, and from the many systematic extinctions. In the red modification, the iodine atoms are cubic close packed. The mercury atoms occupy one quarter of the tetrahedral holes in such a way that sheets of corner-linked HgI_4 tetrahedra are formed perpendicular to c which are stacked upon each other with I—I contacts. Since the $hk0$, hhl and $h\bar{h}l$ reciprocal-net planes of the orange form all are *identical* with the $hk0$ plane of the red form, the projections of the structure of the orange form along [001], [110] and [1$\bar{1}$0] must be the *same* and *equal* to the projection of the red form along [001]. The two structures are therefore closely related. The iodine atoms are also cubic close packed in the orange form, with the square nets parallel to (001), (110) and (1$\bar{1}$0), and the mercury atoms necessarily occupy one quarter of the tetrahedral holes. This is also suggested by the relationship between the cell parameters of the two forms.

The coordinates of the iodine atoms are $(000, \frac{1}{4}\frac{1}{4}\frac{1}{8}) + 00z, \frac{1}{2}0z, 0\frac{1}{2}z,$ $\frac{1}{2}\frac{1}{2}z$; $z = 0, \frac{1}{4}, \frac{1}{2}, \frac{3}{4}$. Any deviation of z from these values produces reflections not consistent with the extinction rules found. The iodine atoms contribute only to the reflections with h, k even, $h + k + \frac{1}{2}l = 4n$. The mercury atoms occupy the following positions:

$$0\tfrac{1}{4}z_{11}, \quad 0\tfrac{1}{4}z_{12}, \quad 0\tfrac{3}{4}z_{21}, \quad 0\tfrac{3}{4}z_{22}, \quad \tfrac{1}{4}0z_{31}, \quad \tfrac{1}{4}0z_{32}, \quad \tfrac{3}{4}0z_{41}, \quad \tfrac{3}{4}0z_{42},$$

$$\tfrac{1}{2}\tfrac{1}{4}z_{51}, \quad \tfrac{1}{2}\tfrac{1}{4}z_{52}, \quad \tfrac{1}{2}\tfrac{3}{4}z_{61}, \quad \tfrac{1}{2}\tfrac{3}{4}z_{62}, \quad \tfrac{1}{4}\tfrac{1}{2}z_{71}, \quad \tfrac{1}{4}\tfrac{1}{2}z_{72}, \quad \tfrac{3}{4}\tfrac{1}{2}z_{81}, \quad \tfrac{3}{4}\tfrac{1}{2}z_{82}.$$

The following relations for the z_{ij} are obtained by calculating the coordinates of the mercury atoms in the three projections on (001), (110) and ($1\bar{1}0$) and equating them:

(a) $z_{ij} = \dfrac{2n_{ij} - 1}{16}$, n_{ij} being an integer.

(b) $z_{1i} \neq z_{4i} \neq z_{6i} \neq z_{7i}$; $z_{2i} \neq z_{3i} \neq z_{5i} \neq z_{8i}$;

     $z_{1i} \neq z_{3i} \neq z_{6i} \neq z_{8i}$; $z_{2i} \neq z_{4i} \neq z_{5i} \neq z_{7i}$ $(i = 1, 2)$

i.e., the z_{ij} fall into four different groups:

$$g_1: z_{11}, z_{12}, z_{61}, z_{62} \qquad\qquad g_2: z_{21}, z_{22}, z_{51}, z_{52}$$

$$g_3: z_{31}, z_{32}, z_{81}, z_{82} \qquad\qquad g_4: z_{41}, z_{42}, z_{71}, z_{72}$$

The z_{ij} belonging to one group are all different. g_2 is a permutation of g_1, i.e., holds the same elements. The same applies for g_3 and g_4. However, g_1 and g_2 have no elements in common with g_3 and g_4. The evaluation of the structure-factor expression for the mercury atoms, taking into account these conditions, shows that $F_{Hg}(h,k,l) = 0$ if h and k are both odd, or if $h + k = 4n$ and $l \neq 8n$, or if $h + k = 4n + 2$ and $l = 8n$. The majority of the extinctions are therefore due to the identity of the three projections. However, there exist a large number of structures satisfying the conditions mentioned. Further relations between the z_{ij} can be obtained by satisfying the remaining extinctions and imposing tetragonal symmetry on the structure. The reflections hkl with $h + k = 4n + 2$ should be absent if l is odd, but present if $l = 8n \pm 2$. Evaluation of the structure-factor formula shows that this is the case if z_{ij} and $z_{ij} + \frac{1}{2}$ belong to the same, z_{ij} and $z_{ij} \pm \frac{1}{4}$ belong to different groups, i.e., $z_{i1} \neq z_{i2} \pm \frac{1}{4}$. Since the observed Friedel symmetry is $4/mmm$, at least some of the rows of iodine atoms parallel to c must coincide with 4, $\bar{4}$, 4_1, 4_2 or 4_3 axes. It is easy to show that a 4 or 4_2 axis along $00z$ would lead to $z_{1i} = z_{3i}$ or $z_{1i} = z_{3i} + \frac{1}{2}$.

Both 4 and 4_2 are thus incompatible with the relations already established between the z_{ij}. Assuming a $\bar{4}$ axis along $00z$ gives $z_{1i} = z_{2i} = = -z_{3i} = -z_{4i}$; $z_{5i} = z_{6i} = -z_{7i} = -z_{8i}$. Only three different structures satisfy these conditions, one of which can be excluded because its translation period along $\mathfrak{c}$ is half the one measured. The other two structures have the following z_{ij}:

(a) $z_{11} = z_{21} = \frac{1}{16}$ $z_{31} = z_{41} = \frac{13}{16}$ $z_{51} = z_{61} = \frac{9}{16}$

       $z_{71} = z_{81} = \frac{5}{16}$ $z_{i2} = z_{i1} + \frac{1}{8}$

(b) $z_{11} = z_{21} = \frac{1}{16}$ $z_{31} = z_{41} = \frac{5}{16}$ $z_{51} = z_{61} = \frac{9}{16}$

       $z_{71} = z_{81} = \frac{13}{16}$ $z_{i2} = z_{i1} - \frac{3}{8}$.

The same two structures are obtained with a different origin by assuming a 4_1 or 4_3 axis along $00z$. They both have the space group symmetry $I4_1/amd$. (a) is characterized by edge-sharing, (b) by corner-sharing HgI_4 tetrahedra. They can be distinguished by their structure factors for the reflections hkl with $h+k$ odd, having the same extinctions and structure factors for all the other reflections:

(a) $|F_{Hg}| = \begin{cases} 7.39 f_{Hg} & l = 8n \pm 1 \\ 3.06 f_{Hg} & l = 8n \pm 3 \end{cases}$ (b) $|F_{Hg}| = \begin{cases} 3.06 f_{Hg} & l = 8n \pm 1 \\ 7.39 f_{Hg} & l = 8n \pm 3. \end{cases}$

The experimental data are compatible only with (b). The structure is therefore unambiguously determined and is, after a shift of the origin, described as follows (International tables for x-ray crystallography, Vol. I, 1952):

Space group $I4_1/amd$, origin at $\bar{4}m2$

     8 I(1) in e (mm) with $z = \frac{1}{8}$

     8 I(2) in e (mm) with $z = \frac{3}{8}$

   16 I(3) in g (2) with $x = \frac{1}{4}$

   16 Hg   in h (m) with $x = \frac{1}{4}$, $z = \frac{5}{16}$.

The calculated structure factors are listed in Table 1. They are in good agreement with the estimated intensities. No attempt has been made to measure quantitative intensities, since the five parameters which are not fixed by the space-group symmetry are very accurately determined by the non-space-group extinctions.

Description of the structure and of the one-dimensional disorder

The structure of the orange modification of HgI_2 consists, as does the structure of the red modification, of corner-linked HgI_4 tetrahedra which form layers perpendicular to c. In contrast to the red modification, the motif of the layers is not a single HgI_4 tetrahedron, but consists of a tetrahedral configuration of four corner-linked HgI_4 tetrahedra forming the Hg_4I_{10} group shown in Fig. 3. It has the form of a large tetrahedron, with iodine atoms in the corners and the middle of the edges and an octahedral hole around
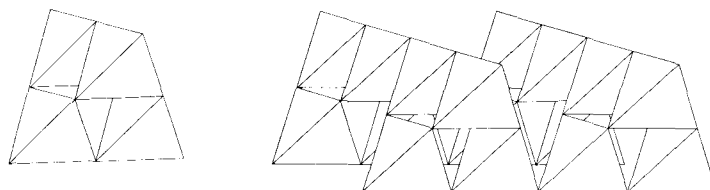

Fig. 3. Hg_4I_{10} group and HgI_2 layer. The iodine atoms occupy the corners and the mercury atoms the centers of the tetrahedra

the center. Its symmetry is required to be $\bar{4}m2$ by the space-group symmetry. The Hg_4I_{10} group is isotypic with the contents of the unit cell in the zincblende structure and with the individual molecules in the P_4O_{10} structure. As shown in Fig. 3, the Hg_4I_{10} groups are connected into HgI_2 layers by sharing corners in exactly the same way as the single tetrahedra form layers in the red modification. The stacking of the layers is also analogous in the two forms. Two adjacent layers are turned relative to each other by $90°$ and stacked in such a way that the lower edges of the tetrahedra of the upper layer lie midway between the upper edges of the tetrahedra of the lower layer. In the red form, the centers of the tetrahedra in the two layers are displaced by $\frac{1}{2}$ (a + b), and this is the only stacking which leads to a close packing of the iodine atoms. In the orange modification, however, there exist two possible stacking positions which lead to the same packing of the iodine atoms, but different arrangements of the mercury atoms. The centers of the Hg_4I_{10} groups in adjacent layers can be displaced either by $\frac{1}{2}$ a (or $\frac{1}{2}$ b), or by $\frac{1}{2}$ (a + b) as in the red form. The first kind of stacking leads to a four-layer structure, as shown in Fig. 4, which is the structure of the red-orange crystals deduced above. The second kind produces the two-layer structure shown in Fig. 5. Its space group is $P4_2/nmc$. The structure factors of the two structures are the same except for the reflections hkl with
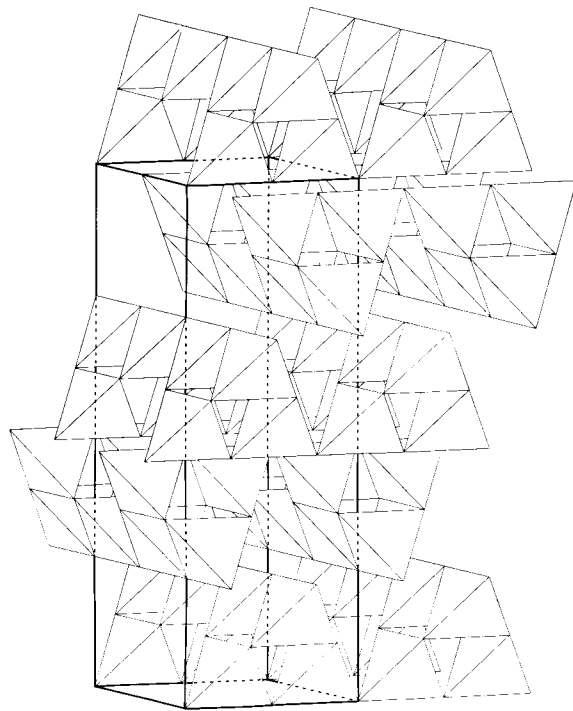
Fig. 4. View of the four-layer structure. The centers of the Hg_4I_{10} groups in neighboring layers are displaced by $\frac{1}{2}$ **a** or $\frac{1}{2}$ **b**
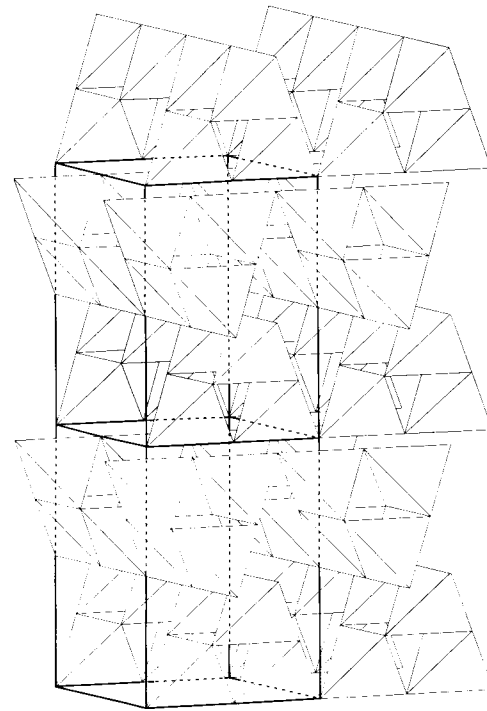
Fig. 5. View of the two-layer structure. The centers of the Hg_4I_{10} groups in neighboring layers are displaced by $\frac{1}{2}$ (**a** + **b**)

$h+k = 2n+1$ and $l \neq 8n$. If the two-layer structure is described in the same axial system as the four-layer structure ($c = 24.732$ Å), then it produces only the reflections with $l = 2n$ ($l \neq 8n$), whereas the four-layer structure gives only the reflections with $l = 2n+1$. The structure factors of the two-layer structure are $|F| = 4 \cdot \sqrt{2} \, f_{Hg}$ ($l = 8n \pm 2$) and $8 \cdot f_{Hg}$ ($l = 8n+4$), i.e., $|F| = \left[32\left(1 - \cos\frac{\pi}{4}l\right)\right]^{1/2} \cdot f_{Hg}$, as in the four-layer structure.
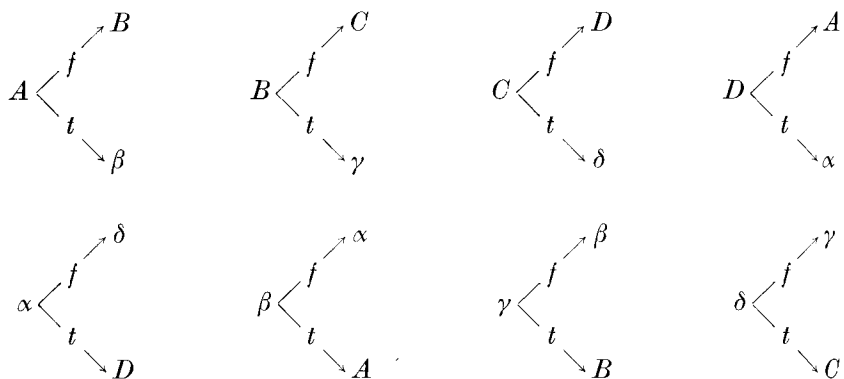
The one-dimensional disorder of the yellow-orange crystals is caused by an irregular succession of the two kinds of stacking. These crystals gave both the reflections hkl with $l = 2n$ and $l = 2n+1$ for $h+k = 2n+1$, besides the continuous streaks. Since there does not exist an ordered structure with both kinds of reflections, the disordered structure seems to be qualitatively a mixture of the four-layer and the two-layer structures.

The environment of the atoms in the four-layer and two-layer structures differ only at long range, since the relative positions of three consecutive levels of HgI_4 tetrahedra are the same in both structures. The distributions of the mercury atoms around a mercury atom differ only for distances greater than 9 Å, the distributions of the mercury atoms around an iodine atom differ for distances greater than 6.5 Å. The distributions of the iodine atoms around an iodine or a mercury atom are the same in both structures. The energies of formation of the two structures should therefore be nearly the same. The HgI_4 tetrahedra are slightly distorted, due to the small deviation of the axial ratio c/a from $2\sqrt{2}$. They have the same dimensions in the four-layer and the two-layer structure. The Hg—I distance is 2.683 Å, which is 0.1 Å shorter than the distance found in the red form (JEFFREY and VLASSE, 1967). The I—I distances are 4.388 Å and 4.379 Å. They are in good agreement with the corresponding distances in the red form. The I—Hg—I angles, as well as the Hg—I—Hg angles, are 109.68 and 109.36 °.

Calculation of the diffuse intensities

The stacking of the HgI_2 layers can be described in a manner similar to the stacking of close-packed nets of spheres. Two consecutive layers have relative positions either as in the four-layer or as in the two-layer structure. These two kinds of stacking are symbolized by the letters f and t. Every succession of layers can be described by a succession of the letters f and t in the same way as the letters c and h are used for the close packing of the spheres.

If the layers are denoted by letters, then the four-layer structure is given by $ABCD$. The layers which are t-stacked on A, B, C and D are denoted by β, γ, δ and α. A, B, C, D, α, β, γ, δ are the eight different positions a HgI_2 layer can occupy. C, α and γ are shifted relative to A by $\frac{1}{2}$ ($\mathbf{a}+\mathbf{b}$), $\frac{1}{2}$ $\mathbf{a}$ and $\frac{1}{2}$ $\mathbf{b}$. B, D, β and δ are mirrored on (001) relative to A (or turned by $90°$) and shifted by $\frac{1}{2}$ $\mathbf{a}$, $\frac{1}{2}$ $\mathbf{b}$, $\frac{1}{2}$ ($\mathbf{a}+\mathbf{b}$) and 0. The following stackings are possible:

$$
A \Big\langle \begin{array}{l} {}^{\nearrow B} \\ {}^f \\ {}_t \\ {}_{\searrow \beta} \end{array}
\qquad
B \Big\langle \begin{array}{l} {}^{\nearrow C} \\ {}^f \\ {}_t \\ {}_{\searrow \gamma} \end{array}
\qquad
C \Big\langle \begin{array}{l} {}^{\nearrow D} \\ {}^f \\ {}_t \\ {}_{\searrow \delta} \end{array}
\qquad
D \Big\langle \begin{array}{l} {}^{\nearrow A} \\ {}^f \\ {}_t \\ {}_{\searrow \alpha} \end{array}
$$

$$
\alpha \Big\langle \begin{array}{l} {}^{\nearrow \delta} \\ {}^f \\ {}_t \\ {}_{\searrow D} \end{array}
\qquad
\beta \Big\langle \begin{array}{l} {}^{\nearrow \alpha} \\ {}^f \\ {}_t \\ {}_{\searrow A} \end{array}
\qquad
\gamma \Big\langle \begin{array}{l} {}^{\nearrow \beta} \\ {}^f \\ {}_t \\ {}_{\searrow B} \end{array}
\qquad
\delta \Big\langle \begin{array}{l} {}^{\nearrow \gamma} \\ {}^f \\ {}_t \\ {}_{\searrow C.} \end{array}
$$

For the calculation of the diffuse intensities, the length of the c axis is taken to be the thickness of one layer, i.e., $C = \dfrac{c}{4}$. The index relative to C is $L = \dfrac{l}{4}$. The intensity $I(L)$ along a reciprocal-lattice row is given by (Wilson, 1942)

$$
I(L) = N_1{}^2 N_2{}^2 \sum_{m=-(N_3-1)}^{N_3-1} (N_3 - |m|) J_m \exp\left(-2\pi i L m\right), \qquad (1)
$$

where (Jagodzinski, 1954)

$$
J_m = \sum_r \sum_s p_r P_{rs}^{(m)} F_r F_s^*, \qquad (2)
$$

N_1, N_2 = numbers of unit cells in the crystal in the direction of the $\mathbf{a}$ and $\mathbf{b}$ axes. They are assumed to be large.

N_3 = number of layers.

p_r = "a priori" probability of finding a layer with position r.

$P_{rs}^{(m)}$ = "a posteriori" probability of finding a layer with position s, m layers from one with position r.

F_r = structure factor of the layer with position r.

Only the mercury atoms need to be considered in the calculation. F_r is therefore

$$F_r(\mathbf{H}) = f_{Hg} \sum_j \exp(2\pi i \mathbf{x}_{rj}\mathbf{H}), \tag{3}$$

$\mathbf{x}_{rj}$ being the fractional coordinates of the mercury atoms of the layer with position r. For layer A they are $\frac{1}{4}0 - \frac{1}{4}$; $\frac{3}{4}0 - \frac{1}{4}$; $0\frac{1}{4}\frac{1}{4}$; $0\frac{3}{4}\frac{1}{4}$. $\mathbf{H}$ is a reciprocal vector. The structure factors for the different positions are:

$$F_B = \exp(\pi i h) \cdot F_A^* \qquad\qquad F_\alpha = \exp(\pi i h) \cdot F_A$$

$$F_C = \exp(\pi i h + \pi i k) \cdot F_A \qquad F_\beta = \exp(\pi i h + \pi i k) \cdot F_A^*$$

$$F_D = \exp(\pi i k) \cdot F_A^* \qquad\qquad F_\gamma = \exp(\pi i k) \cdot F_A$$

$$F_\delta = F_A^*.$$

If all the layers in a crystal are in the mean equivalent, the following relations hold between the probabilities:

(a) $P_{AB}^{(m)} = P_{BC}^{(m)} = P_{CD}^{(m)} = P_{DA}^{(m)} = P_{\alpha\delta}^{(m)} = P_{\beta\alpha}^{(m)} = P_{\gamma\beta}^{(m)} = P_{\delta\gamma}^{(m)}$

$P_{AC}^{(m)} = P_{BD}^{(m)} = \cdots\cdots\cdots$ etc.

Therefore, only the probabilities $P_{Ak}^{(m)}$ have to be determined. It is evident that

$$P_{AB}^{(m)} = P_{AD}^{(m)} = P_{A\beta}^{(m)} = P_{A\delta}^{(m)} = 0 \text{ for } m \text{ even}$$

and

$$P_{AA}^{(m)} = P_{AC}^{(m)} = P_{A\alpha}^{(m)} = P_{A\gamma}^{(m)} = 0 \text{ for } m \text{ odd.}$$

(b) The "a priori" probabilities are the same for all the positions occurring in a crystal, since $p_k = \lim\limits_{m\to\infty} P_{ik}^{(m)}$.

(c) $P_{A\alpha}^{(m)} = P_{A\gamma}^{(-m)}$, since the crystal is tetragonal. Because $P_{ik}^{(m)} = P_{ki}^{(-m)}$ for all probabilities, it follows that $P_{A\alpha}^{(m)} = P_{A\gamma}^{(m)}$.

(d) Since the positions B and β are always stacked on the positions A and γ, it follows that

$$P_{AB}^{(m)} + P_{A\beta}^{(m)} = P_{AA}^{(m-1)} + P_{A\gamma}^{(m-1)}.$$

The following relations are proved in a similar way:

$$P_{AD}^{(m)} + P_{A\delta}^{(m)} = P_{AC}^{(m-1)} + P_{A\alpha}^{(m-1)}$$

$$P_{AA}^{(m)} + P_{A\alpha}^{(m)} = P_{AD}^{(m-1)} + P_{A\beta}^{(m-1)}$$

$$P_{AC}^{(m)} + P_{A\gamma}^{(m)} = P_{AB}^{(m-1)} + P_{A\delta}^{(m-1)}.$$

Evaluation of (2) and (3) for h, k both even gives

$$J_m = \begin{cases} 16 f_{\mathrm{Hg}}^2 \cdot \cos^2 \dfrac{\pi}{2} L, & h + k = 4n \\[2ex] (-1)^m 16 f_{\mathrm{Hg}}^2 \cdot \sin^2 \dfrac{\pi}{2} L, & h + k = 4n + 2. \end{cases}$$

The reflections are therefore sharp on these lattice rows. If $h + k = 4n$, the mercury atoms contribute to the reflections with $L = 2n$ $(l = 8n)$; if $h + k = 4n + 2$, the mercury atoms contribute to the reflections with $L = \dfrac{2n + 1}{2}$ $(l = 8n \pm 2)$. $J_m = 0$ for h, k both odd, since $F_A = 0$. For $h + k = 2n + 1$, J_m is

$$J_m = \begin{cases} 4 (P_{AA}^{(m)} - P_{AC}^{(m)}) f_{\mathrm{Hg}}^2; & m = 2n \\[2ex] - 2 \, [(P_{AA}^{(m+1)} - P_{AC}^{(m+1)}) \exp (- i \pi L) + \\[1ex] \qquad + (P_{AA}^{(m-1)} - P_{AC}^{(m-1)}) \cdot \exp (i \pi L)] f_{\mathrm{Hg}}^2, & m = 2n + 1. \end{cases}$$

If N_3 is assumed to be large, equation (1) gives:

$$I(L) = 8 N_1^2 N_2^2 f_{\mathrm{Hg}}^2 (1 - \cos \pi L) \sum_{m = -\left(\frac{N_3}{2} - 1\right)}^{\frac{N_3}{2} - 1} \left(\frac{N_3}{2} - |m|\right) \Delta P^{(2m)} \exp (- 4 \pi i L m)$$

$$\Delta P^{(2m)} = P_{AA}^{(2m)} - P_{AC}^{(2m)}. \tag{5}$$

$\Delta P^{(2m)}$ equals $+ 1$ for the ordered two-layer structure and $(- 1)^m$ for the four-layer structure. Equation (4) gives the results discussed earlier for these structures. $\Delta P^{(2m)}$ tends to zero with increasing m, if the structure is disordered and the intensity is then

$$I(L) = 4 N_1^2 N_2^2 N_3 f_{\mathrm{Hg}}^2 (1 - \cos \pi L) \left[1 + 2 \sum_{m = 1}^{\infty} \Delta P^{(2m)} \cos 4 \pi L m\right],$$

$$h + k = 2n + 1. \tag{6}$$

$i(L) = \dfrac{I(L)}{f_{\mathrm{Hg}}^2}$ is thus given by a periodic function with period $\frac{1}{2}$ in L, which is modulated by $(1 - \cos \pi L)$. Its general properties agree well with the observed intensity distribution.

$\Delta P^{(2m)}$ depends on the range of interaction s of the layers (Jagodzinski, 1949 I). The case $s = 2$ is treated in this paper, i.e., the position of the mth layer is assumed to depend on the positions of the $(m-1)$st and $(m-2)$nd layers. The disorder is given by the probabilities

ω_1 that an f stacking is followed by a t stacking, and ω_2 that a t stacking is followed by a t stacking:

The derivation of the intensity is similar in many respects to the one for close-packed spheres and $s = 3$ (JAGODZINSKI, 1949 II).

If $a_1^{(n)}$ is the probability that the nth layer has the position A and is f stacked, $a_2^{(n)}$ that it is t stacked, then $a_1^{(n)} + a_2^{(n)} = P_{AA}^{(n)}$. Similarly, $c_1^{(n)} + c_2^{(n)} = P_{AC}^{(n)}$; $\alpha_1^{(n)} + \alpha_2^{(n)} = P_{A\alpha}^{(n)}$; $\gamma_1^{(n)} + \gamma_2^{(n)} = P_{A\gamma}^{(n)}$. Since an f-stacked layer of position A can be obtained through the stacking sequences $CDA(ff)$ and $\alpha DA(tf)$, a t-stacked layer through the sequences $\gamma \beta A(ft)$ and $A \beta A(tt)$:

$$a_1^{(n+2)} = (1 - \omega_1)^2 c_1^{(n)} + (1 - \omega_1)(1 - \omega_2) c_2^{(n)}$$
$$+ \omega_1(1 - \omega_2)\alpha_1^{(n)} + \omega_2(1 - \omega_2)\alpha_2^{(n)}$$

$$a_2^{(n+2)} = \omega_1(1 - \omega_1)\gamma_1^{(n)} + \omega_1(1 - \omega_2)\gamma_2^{(n)} + \omega_1 \omega_2 a_1^{(n)} + \omega_2^2 a_2^{(n)}$$

Analogous relations hold for $c_i^{(n+2)}$, $\alpha_i^{(n+2)}$ and $\gamma_i^{(n+2)}$. Denoting the sums $a_1^{(n)} - c_1^{(n)} + \alpha_1^{(n)} - \gamma_1^{(n)}$ and $a_2^{(n)} - c_2^{(n)} + \alpha_2^{(n)} - \gamma_2^{(n)}$ by $d_1^{(n)}$ and $d_2^{(n)}$, it follows that

$$d_1^{(n)} = [\omega_1(1 - \omega_2) - (1 - \omega_1)^2] d_1^{(n-2)} + [\omega_1(1 - \omega_2) - (1 - \omega_2)^2] d_2^{(n-2)}$$

$$d_2^{(n)} = [\omega_1^2 - \omega_1(1 - \omega_2)] d_1^{(n-2)} + [\omega_2^2 - \omega_1(1 - \omega_2)] d_2^{(n-2)}$$

$$d_1^{(n)} + d_2^{(n)} = P_{AA}^{(n)} - P_{AC}^{(n)} + P_{A\alpha}^{(n)} - P_{A\gamma}^{(n)} = \Delta P^{(n)},$$

i.e., $\begin{pmatrix} d_1^{(n)} \\ d_2^{(n)} \end{pmatrix} = (\mathbf{M}[\omega_1 \omega_2]) \begin{pmatrix} d_1^{(n-2)} \\ d_2^{(n-2)} \end{pmatrix}.$

In order to calculate $\Delta P^{(n)} = \Delta P^{(2m)}$ as a function of ω_1 and ω_2, it is necessary to determine the mth power of the matrix $\mathbf{M}$. This can be done by diagonalizing $\mathbf{M}$:

$$(\mathbf{M})^m = (\mathbf{V})[(\mathbf{V})^{-1}(\mathbf{M})(\mathbf{V})]^m(\mathbf{V})^{-1}.$$

The quantities $d_1^{(0)} = a_1^{(0)}$ and $d_2^{(0)} = a_2^{(0)}$ are equal to the probabilities of finding in the crystal an f stacking and a t stacking respectively. They are determined by the two equations $a_1^{(0)} + a_2^{(0)} = 1$ and $a_2^{(0)} = \omega_1 a_1^{(0)} + \omega_2 a_2^{(0)}$.

Thus

$$a_1^{(0)} = \frac{1 - \omega_2}{1 - \omega_2 + \omega_1}, \qquad a_2^{(0)} = \frac{\omega_1}{1 - \omega_2 + \omega_1}.$$

The result for $\Delta P^{(2m)}$ is

$$\Delta P^{(2m)} = \frac{1 + K_1}{2} \cdot \left[\frac{K_2 + S}{2}\right]^m + (-1)^m \cdot \frac{1 - K_1}{2} \left[\frac{K_2 - S}{2}\right]^m \tag{7}$$

$$K_1 = \frac{S}{K_2} \cdot \frac{1 + (\omega_1 - \omega_2)^2}{1 - (\omega_1 - \omega_2)^2}$$

$$K_2 = [4(\omega_1 - \omega_2)^2 + S^2]^{1/2}$$

$$S = Sp\,(\mathbf{M}) = \omega_2^2 - (1 - \omega_1)^2.$$

If the range of interaction is $s = 1$, then $\omega_1 = \omega_2 = \omega$, and (7) reduces to

$$\Delta P^{(2m)} = (2\omega - 1)^m, \tag{8}$$

ω being the probability that a layer is t stacked.

The intensity distribution for $s = 1$ is therefore

$$I(L) = 4 N_1^2 N_2^2 N_3 f_{Hg}^2 (1 - \cos \pi L) [1 + 2 \sum_{m=1}^{\infty} (2\omega - 1)^m \cos 4\,\pi L m]$$

$$= 4 N_1^2 N_2^2 N_3 f_{Hg}^2 (1 - \cos \pi L) \frac{2\omega\,(1 - \omega)}{1 - 2\omega + 2\omega^2 - (2\omega - 1)\cos 4\pi L},$$

$$h + k = 2n + 1. \tag{9}$$

The second part of this function has its maxima at $L = \frac{1}{4}, \frac{3}{4}, \cdots$, if $\omega < \frac{1}{2}$ and at $L = 0, \frac{1}{2}, 1, \cdots$, if $\omega > \frac{1}{2}$. The modulating part $(1 - \cos \pi L)$ eliminates the peaks at $L = 0, 2, \cdots$ and slightly shifts the other maxima. The intensity distribution is approximately that of the two-layer structure with broadened reflections if $\omega > \frac{1}{2}$, and that of the four-layer structure if $\omega < \frac{1}{2}$.

The intensity for $s = 2$ is

$$I(L) =$$

$$2 N_1^2 N_2^2 N_3 f_{Hg}^2 (1 + K_1)(1 - \cos \pi L) \left[1 + 2 \sum_{m=1}^{\infty} \left(\frac{K_2 + S}{2}\right)^m \cdot \cos 4\pi L m\right]$$

$$+ 2 N_1^2 N_2^2 N_3 f_{Hg}^2 (1 - K_1)(1 - \cos \pi L)$$

$$\times \left[1 + 2 \sum_{m=1}^{\infty} (-1)^m \left(\frac{K_2 - S}{2}\right)^m \cdot \cos 4\pi L m\right], \tag{10}$$

$$0 \le \frac{K_2 \pm S}{2} \le 1, \qquad -1 \le K_1 \le +1, \qquad h + k = 2n + 1.$$

The first part of this function gives the intensity distribution of the disordered two-layer structure with broadened maxima near $L = \frac{1}{2}$, $1, \cdots$; the second part gives the intensities of the disordered four-layer structure with broadened maxima near $L = \frac{1}{4}, \frac{3}{4}, \cdots$. The intensity distribution is therefore that of a "mixture" of the two structures in amounts proportional to $(1 + K_1)$ and $(1 - K_1)$. If $\omega_1 + \omega_2 = 1$, then $S = 0$ and $K_1 = 0$. The apparent amounts of two- and four-layer structure are then equal and the intensities of the maxima are $i\,(\frac{1}{4})$:

$$i\left(\tfrac{1}{2}\right): i\left(\tfrac{3}{4}\right): i(1) = \left(1 - \tfrac{\sqrt{2}}{2}\right): 1 : \left(1 + \tfrac{\sqrt{2}}{2}\right): 2 = 1 : 3.414 : 5.828 : 6.828,$$

$i = \dfrac{I(L)}{f^2_{\mathrm{Hg}}}$. The breadth of the peaks is given by $\frac{1}{2}\,K_2 = |2\omega_1 - 1|$
$= |2\omega_2 - 1|$.

If $S > 0$, then $K_1 > 0$, and the maxima at $L = \frac{1}{2}, 1, \cdots$ are higher and sharper than the ones at $L = \frac{1}{4}, \frac{3}{4}, \cdots$. If $S < 0$, then $K_1 < 0$, and the situation is reversed. Thus, the larger the proportional amount of one structure in the apparent "mixture", the sharper and higher the corresponding maxima.

Equation (10) qualitatively explains the observed diffuse intensities as shown in Fig. 2. The intensities at the maxima point to $\omega_1 + \omega_2 \sim 1$. The curve with $\omega_1 = 1 - \omega_2 = 0.1$ is included in Fig. 2. Equation (10), however, cannot explain the fact that the reflections with l odd $(L = \frac{1}{4}, \frac{3}{4}, \cdots)$ are more diffuse than the ones with l even $(L = \frac{1}{2}, 1, \cdots)$. Numerical calculations assuming $s = 3$ showed that an increase in the range of interaction cannot explain the observed intensities either. In general, additional peaks are produced due to the occurrence of a six-layer (fft), an eight-layer $(fftt)$ and a twelve-layer structure (ftt).

The observations point rather to a real mixture of domains with four- and two-layer structure. The four-layer structure is more abundant, yet more disordered than the two-layer structure. The domains scatter the x-rays independently of each other. Possibly, these domains are the product of a phase transformation. Since the pure two-layer structure has not been found, it is probable that it transforms into the four-layer structure. In analogy to the theory forwarded by JAGODZINSKI (1949 III) for wurtzite, it can be concluded that many nuclei of the four-layer structure are formed at places where the two-layer structure is most disordered. The remaining domains of the two-layer structure will therefore be more ideal and give sharper reflections.

Since the observations can be explained only qualitatively, no accurate measurements of the diffuse intensities were made, and the

corrections for absorption, and the polarization and two-dimensional Lorentz factors (Zachariasen, 1967) were neglected.

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