**To be deposited in the IUCr electronic archives**

**Appendix** to "Neutron diffraction investigation of the temperature dependence of crystal structure and thermal motions of red $HgI_2$"
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## $HgI_2$, red modification: phonon model for wave vectors ($q_1$ $q_2$ 0)

### Atoms

Space group $P4_2/nmc$, origin at $\bar{1}$

Layer 1:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Hg1 | 1/4 3/4 1/4 | | | | | | |
| I1 | 1/4 1/4 0.39 | I1' | 1/4 5/4 0.39 | I1'' | 5/4 1/4 0.39 | | |
| I2 | 3/4 3/4 0.11 | I2' | –1/4 3/4 0.11 | I2'' | 3/4 –1/4 0.11 | I2''' | –14 –14 0.11 |

Layer 2:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Hg2 | 3/4 1/4 3/4 | | | | | | |
| I3 | 1/4 1/4 0.89 | I3' | 5/4 1/4 0.89 | I3'' | 1/4 5/4 0.89 | I3''' | 1/4 1/4 –0.11 |
| I4 | 3/4 3/4 0.61 | I4' | 3/4 –1/4 0.61 | I4'' | –1/4 3/4 0.61 | I4''' | –14 –14 0.61 |

### Force constant tensors

Interactions are assumed for nearest neighbors: 4 I around Hg on the corners of a tetrahedron; 12 I around I on the corners of a cuboctahedron. There are 1 type of Hg–I and 4 types of I–I vectors.

*Layer 1*

Hg1–I1, symmetry $m_x$, vector 0 –1/2 0.14 $-\begin{pmatrix} y_{11} & 0 & 0 \\ 0 & y_{22} & y_{23} \\ 0 & y_{32} & y_{33} \end{pmatrix}$

Symmetrically equivalent: Hg1–I1' with $m_y$, Hg1–I2 with $\bar{4}^{-1}$, Hg1–I2' with $\bar{4}$ .

I1–I1', symmetry $mm2$, vector 0 1 0, apical edge of $HgI_4$ tetrahedron $-\begin{pmatrix} j_{11} & 0 & 0 \\ 0 & j_{22} & 0 \\ 0 & 0 & j_{33} \end{pmatrix}$

I2–I2': interchange $\phi_{11}$ and $\phi_{22}$.

I1–I1'', symmetry *mm*2, vector 1 0 0, apical edge of empty tetrahedron $-\begin{pmatrix} e_{11} & 0 & 0 \\ 0 & e_{22} & 0 \\ 0 & 0 & e_{33} \end{pmatrix}$

I2–I2'': interchange $\varepsilon_{11}$ and $\varepsilon_{22}$.

I1–I2, symmetry $2_{-110}$, vector 1/2 1/2 –0.28, equatorial edge of $HgI_4$ $-\begin{pmatrix} \rho_{11} & \rho_{12} & \rho_{13} \\ \rho_{21} & \rho_{11} & \rho_{23} \\ \rho_{23} & \rho_{13} & \rho_{33} \end{pmatrix}$

Symmetry-equivalent neighbors of I1 by $m_x$, $m_y$, $2_{001}$.

*Layer 2*

Vectors are related to those of layer 1 by symmetry $\bar{1}$, thus we find the same tensors:
Hg2–I4 same as Hg1–I1
Hg2–I3 same as Hg1–I2
I4–I4' same as I1–I1'
I3–I3' same as I2–I2'
I4–I4'' same as I1–I1''
I3–I3'' same as I2–I2''
I4–I3 same as I1–I2

*Between layers, I–I contacts*

I1–I4, symmetry $\bar{1}$, vector 1/2 1/2 0.22 $-\begin{pmatrix} t_{11} & t_{12} & t_{13} \\ t_{12} & t_{22} & t_{23} \\ t_{13} & t_{23} & t_{33} \end{pmatrix}$

Symmetry-equivalent neighbors of I1 by $m_x$, $m_y$, $2_{001}$.

I2–I3''', equivalent to I1–I4 by $2_{-110}$ $-\begin{pmatrix} t_{22} & t_{12} & t_{23} \\ t_{12} & t_{11} & t_{13} \\ t_{23} & t_{13} & t_{33} \end{pmatrix}$

Symmetry-equivalent neighbors of I2 by $m_x$, $m_y$, $2_{001}$.

**Simplified force constant model for illustrative purpose**

Results will be developed in terms of the complete $\boldsymbol{\psi}$, $\boldsymbol{\phi}$, $\boldsymbol{\varepsilon}$, $\boldsymbol{\rho}$ and $\boldsymbol{\tau}$ tensors, i.e. 23 force

constants. To give an intuitive meaning, the following simplified matrices are proposed. Assuming symmetry $mm2$ for all interactions, we approach idealized $HgI_4$ tetrahedra with $\bar{4}\,3m$ symmetry. Each tensor is reduced to 3 force constants (equivalent to a diagonal matrix), 1 longitudinal along the bond and 2 transverse perpendicular to the bond.

$\boldsymbol{\psi}$ tensor: $\psi_l$ longitudinal, $\psi_{t1}$ transverse perpendicular to $m$, $\psi_{t2}$ transverse in plane $m$.
$\psi_{11} = \psi_{t1}$; $\psi_{22} = (2\,\psi_l + \psi_{t2})/3$; $\psi_{33} = (\psi_l + 2\psi_{t2})/3$; $\psi_{23} = \psi_{32} = -2^{1/2}(\psi_l - \psi_{t2})/3$.

$\boldsymbol{\phi}$ tensor: $\phi_{22} = \phi_l$ longitudinal, $\phi_{11} = \phi_m$ transverse perpendicular $m_x$, $\phi_{33} = \phi_2$ transverse parallel to 2-axis.

$\boldsymbol{\varepsilon}$ tensor: $\varepsilon_{11} = \varepsilon_l$ longitudinal, $\varepsilon_{22} = \varepsilon_m$ transverse perpendicular $m_y$, $\varepsilon_{33} = \varepsilon_2$ transverse parallel to 2-axis.

$\boldsymbol{\rho}$ tensor: $\rho_l$ longitudinal, $\rho_m$ transverse perpendicular to pseudo-mirror, $\rho_2$ transverse along axis $2_{-110}$.
$\rho_{11} = \rho_{22} = (\rho_l + \rho_m + 2\rho_2)/4$; $\rho_{33} = (\rho_l + \rho_m)/2$; $\rho_{12} = \rho_{21} = (\rho_l + \rho_m - 2\rho_2)/4$;
$\rho_{13} = \rho_{23} = -(\rho_l - \rho_m)/8^{1/2}$.

$\boldsymbol{\tau}$ tensor: $\tau_l$ longitudinal, $\tau_m$ transverse perpendicular to pseudo-mirror, $\tau_2$ transverse along pseudo-axis $2_{-110}$.
$\tau_{11} = \tau_{22} = (\tau_l + \tau_m + 2\tau_2)/4$; $\tau_{33} = (\tau_l + \tau_m)/2$; $\tau_{12} = \tau_{21} = (\tau_l + \tau_m - 2\tau_2)/4$;
$\tau_{13} = \tau_{23} = +(\tau_l - \tau_m)/8^{1/2}$.

## Dynamical matrix

The dynamical matrix for wave vectors $2\pi(q_1\mathbf{a}_1^* + q_2\mathbf{a}_2^*)$ is a Hermitian 18×18 matrix composed of 3×3 matrices as follows:

$$\mathbf{D} = \begin{pmatrix} \mathrm{Hg_1\text{-}Hg_1} & \mathrm{Hg_1\text{-}I_1} & \mathrm{Hg_1\text{-}I_2} & \circ & \circ & \circ \\ \mathrm{I_1\text{-}Hg_1} & \mathrm{I_1\text{-}I_1} & \mathrm{I_1\text{-}I_2} & \circ & \circ & \mathrm{I_1\text{-}I_4} \\ \mathrm{I_2\text{-}Hg_1} & \mathrm{I_2\text{-}I_1} & \mathrm{I_2\text{-}I_2} & \circ & \mathrm{I_2\text{-}I_3} & \circ \\ \circ & \circ & \circ & \mathrm{Hg_2} \pm \mathrm{Hg_2} & \mathrm{Hg_2\text{-}I_3} & \mathrm{Hg_2\text{-}I_4} \\ \circ & \circ & \mathrm{I_3\text{-}I_2} & \mathrm{I_3\text{-}Hg_2} & \mathrm{I_3\text{-}I_3} & \mathrm{I_3\text{-}I_4} \\ \circ & \mathrm{I_4\text{-}I_1} & \circ & \mathrm{I_4\text{-}Hg_2} & \mathrm{I_4\text{-}I_3} & \mathrm{I_4\text{-}I_4} \end{pmatrix}$$

The matrices in the lower triangle are the complex-conjugate-transposed matrices in the upper triangle. Abbreviating $c_1 = \cos\pi q_1$; $c_2 = \cos\pi q_2$; $s_1 = \sin\pi q_1$; $s_2 = \sin\pi q_2$:

$$\text{Hg1–Hg1} = 2\mathrm{m}_{Hg}^{-1}\begin{pmatrix} y_{11}+y_{22} & 0 & 0 \\ 0 & y_{11}+y_{22} & 0 \\ 0 & 0 & 2\mathrm{y}_{33} \end{pmatrix}$$

$$\text{I1–I1} = 4\mathrm{m}_{I}^{-1}\begin{pmatrix} \frac{y_{11}}{2}+\rho_{11}+j_{11}s_2^2+e_{11}s_1^2+t_{11} & 0 & 0 \\ 0 & \frac{y_{22}}{2}+\rho_{11}+j_{22}s_2^2+e_{22}s_1^2+t_{22} & 0 \\ 0 & 0 & \frac{y_{33}}{2}+\rho_{33}+j_{33}s_2^2+e_{33}s_1^2+t_{33} \end{pmatrix}$$

$$\text{I2–I2} = 4\mathrm{m}_{I}^{-1}\begin{pmatrix} \frac{y_{22}}{2}+\rho_{11}+j_{22}s_1^2+e_{22}s_2^2+t_{22} & 0 & 0 \\ 0 & \frac{y_{11}}{2}+\rho_{11}+j_{11}s_1^2+e_{11}s_2^2+t_{11} & 0 \\ 0 & 0 & \frac{y_{33}}{2}+\rho_{33}+j_{33}s_1^2+e_{33}s_2^2+t_{33} \end{pmatrix}$$

$$\text{Hg1–I1} = 2\left(m_{Hg}m_I\right)^{-1/2}\begin{pmatrix} -y_{11}c_2 & 0 & 0 \\ 0 & -y_{22}c_2 & +iy_{23}s_2 \\ 0 & +iy_{32}s_2 & -y_{33}c_2 \end{pmatrix}$$

$$\text{Hg1–I2} = 2\left(m_{Hg}m_I\right)^{-1/2}\begin{pmatrix} -y_{22}c_1 & 0 & +iy_{23}s_1 \\ 0 & -y_{11}c_1 & 0 \\ +iy_{32}s_1 & 0 & -y_{33}c_1 \end{pmatrix}$$

$$\text{I1–I2} = 4\mathrm{m}_{I}^{\pm 1}\begin{pmatrix} -\rho_{11}c_1c_2 & +\rho_{12}s_1s_2 & -i\rho_{13}s_1c_2 \\ +\rho_{21}s_1s_2 & -\rho_{11}c_1c_2 & -i\rho_{23}c_1s_2 \\ -i\rho_{23}s_1c_2 & -i\rho_{13}c_1s_2 & -\rho_{33}c_1c_2 \end{pmatrix}$$

$$\text{I1–I4} = 4\mathrm{m}_{I}^{\pm 1}\begin{pmatrix} -t_{11}c_1c_2 & +t_{12}s_1s_2 & -it_{13}s_1c_2 \\ +t_{12}s_1s_2 & -t_{22}c_1c_2 & -it_{23}c_1s_2 \\ -it_{13}s_1c_2 & -it_{23}c_1s_2 & -t_{33}c_1c_2 \end{pmatrix}$$

$$\text{I2–I3} = 4\mathrm{m}_I^{\pm 1}\begin{pmatrix} -t_{22}c_1c_2 & +t_{12}s_1s_2 & -it_{23}s_1c_2 \\ +t_{12}s_1s_2 & -t_{11}c_1c_2 & -it_{13}c_1s_2 \\ -it_{23}s_1c_2 & -it_{13}c_1s_2 & -t_{33}c_1c_2 \end{pmatrix}$$

Hg2–Hg2 = Hg1–Hg1
I3–I3 = I2–I2
I4–I4 = I1–I1
Hg2–I3 = Hg1–I2
Hg2–I4 = Hg1–I1
I3–I4 = I2–I1 = (I1–I2)transposed

*Isolated layer:*
The dynamical matrix is given by the upper 9×9 submatrix of **D**, consisting of the Hg1, I1 and I2 matrices, but *without the* $\tau_{ij}$ *contributions*. The lower 9×9 submatrix of **D**, consisting of the Hg2, I3 and I4 matrices, represents the same layer rotated by 90°.

**Eigenvectors at point *M*, $q_1 = q_2 = 1/2$**

$s_1 = s_2 = 1$; $c_1 = c_2 = 0$.

The eigenvectors have the form
$x_{\mathrm{Hg1}}\ y_{\mathrm{Hg1}}\ z_{\mathrm{Hg1}}$ / $x_{\mathrm{I1}}\ y_{\mathrm{I1}}\ z_{\mathrm{I1}}$ / $x_{\mathrm{I2}}\ y_{\mathrm{I2}}\ z_{\mathrm{I2}}$ / $x_{\mathrm{Hg2}}\ y_{\mathrm{Hg2}}\ z_{\mathrm{Hg2}}$ / $x_{\mathrm{I3}}\ y_{\mathrm{I3}}\ z_{\mathrm{I3}}$ / $x_{\mathrm{I4}}\ y_{\mathrm{I4}}\ z_{\mathrm{I4}}$ /

*Single isolated layer*

Mode 1: $\mathbf{v}_1 = 0\ 0\ 0\ /\ 1\ 0\ 0\ /\ 0\ 1\ 0$; eigenvalue $\omega_1^2 = 4m_{\mathrm{I}}^{-1}(\psi_{11}/2 + \rho_{11} + \rho_{12} + \phi_{11} + \varepsilon_{11}) \approx 2m_{\mathrm{I}}^{-1}(\psi_{t1} + \rho_l + \rho_m + 2\phi_m + 2\varepsilon_l)$. Libration. Deformation obeys $\bar{4}$ axis. $\varepsilon_l$ is across the empty tetrahedron.

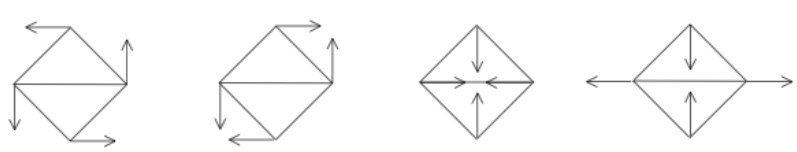
Mode 2: $\mathbf{v}_2 = 0\ 0\ 0\ /\ 1\ 0\ 0\ /\ 0\ {-1}\ 0$; eigenvalue $\omega_2^2 = 4m_{\mathrm{I}}^{-1}(\psi_{11}/2 + \rho_{11} - \rho_{12} + \phi_{11} + \varepsilon_{11}) \approx 2m_{\mathrm{I}}^{-1}(\psi_{t1} + 2\rho_2 + 2\phi_m + 2\varepsilon_l)$. Deformation obeys $2_{-110}$ symmetry.

Mode 3: $\mathbf{v}_3 = 0\ 0\ 0\ /\ 0\ 1\ 0\ /\ {-1}\ 0\ 0$; eigenvalue $\omega_3^2 = 4m_{\mathrm{I}}^{-1}(\psi_{22}/2 + \rho_{11} - \rho_{12} + \phi_{22} + \varepsilon_{22}) \approx 2m_{\mathrm{I}}^{-1}(2\psi_l/3 + \psi_{t2}/3 + 2\rho_2 + 2\phi_l + 2\varepsilon_m)$. Breathing mode.

Modes 4, 5: $\mathbf{v}_{4,5} = 0\ 0\ ia\ /\ 0\ b\ 0\ /\ b\ 0\ 0$; two eigenvalues. If $\psi_{32} = 0$, then one mode moves only I with $\omega_4^2 = 2m_{\mathrm{I}}^{-1}(2\psi_l/3 + \psi_{t2}/3 + \rho_l + \rho_m + 2\phi_l + 2\varepsilon_m)$, the other moves only Hg with $\omega_5^2 = 4m_{\mathrm{Hg}}^{-1}\psi_{33}$.

Modes 6, 7: $\mathbf{v}_{6,7} = a\ 0\ 0\ /\ 0\ 0\ 0\ /\ 0\ 0\ ib$; again, if $\psi_{23} = 0$, I and Hg are decoupled.

Modes 8, 9: $\mathbf{v}_{8,9} = 0\ a\ 0\ /\ 0\ 0\ ib\ /\ 0\ 0\ 0$; degenerate with modes 6, 7; again, if $\psi_{23} = 0$, I and Hg are decoupled.



| mode 1 | mode 2 | mode 3 | mode 4 |
|---|---|---|---|
| acoustical | acoustical | optical | optical |

transverse longitudinal transverse longitudinal

*Complete structure with two layers per cell*

Modes 1, 2, 3: $\mathbf{V}_{1,2,3}$ = 0 0 0 / $a$ 0 0 / 0 $a$ 0 / 0 0 $-ic$ / $b$ 0 0 / 0 $b$ 0; this is mode $\mathbf{v}_1$ for layer 1 and modes $\mathbf{v}_{4,5}$ for layer 2. In layer 1 the empty tetrahedra, and in layer 2 the filled tetrahedra are deformed into lozenges. $\mathbf{v}_1$ dominates in $\mathbf{V}_1$, $\mathbf{v}_4$ in $\mathbf{V}_2$ and $\mathbf{v}_5$ in $\mathbf{V}_3$. The smaller the elements of $\boldsymbol{\tau}$, the more independent are the layers. If $\tau_{12} = 0$, then 0 0 0 / 1 0 0 / 0 1 0 / 0 0 0 / 0 0 0 is an eigenvector, layer 1 vibrates with the libration mode $\mathbf{v}_1$ and layer 2 is not affected. The eigenvalue is then as above with an additional term $\tau_{11}$ which represents a "friction" between layers: $\Omega_1^2 = 4m_1^{-1}(\psi_{11}/2 + \rho_{11} + \rho_{12} + \phi_{11} + \varepsilon_{11} + \tau_{11})$. Similarly, $\mathbf{v}_{4,5}$ are also eigenmodes of an isolated layer for $\tau_{12} = 0$.

Modes 4, 5, 6: $\mathbf{V}_{4,5,6}$ = 0 0 $-ic$ / 0 $b$ 0 / $b$ 0 0 / 0 0 / 0 $a$ 0 / $a$ 0 0; this is modes $\mathbf{v}_{4,5}$ for layer 1 and mode $\mathbf{v}_1$ for layer 2. Degenerate with $\mathbf{V}_{1,2,3}$.

Modes 7, 8: $\mathbf{V}_{7,8}$ = 0 0 0 / $a$ 0 0 / 0 $-a$ 0 / 0 0 0 / $b$ 0 0 / 0 $-b$ 0; mode $\mathbf{v}_2$ for layer 1 and mode $\mathbf{v}_3$ for layer 2. Breathing mode of the filled tetrahedra in layer 1, and of the empty tetrahedra in layer 2; similar arguments as for $\mathbf{V}_{1,2.3}$.

Modes 9, 10: $\mathbf{V}_{9,10}$ = 0 0 0 / 0 $b$ 0 / $-b$ 0 0 / 0 0 0 / 0 $a$ 0 / $-a$ 0 0; mode $\mathbf{v}_3$ for layer 1 and mode $\mathbf{v}_2$ for layer 2. Degenerate with $\mathbf{V}_{7,8}$.

Modes 11, 12: $\mathbf{V}_{11,12}$ = $a$ 0 0 / 0 0 0 / 0 0 $ib$ / 0 0 0 / 0 0 0 / 0 0 0; modes $\mathbf{v}_{6,7}$ for layer 1, layer 2 at rest.

Modes 13, 14: $\mathbf{V}_{13,14}$ = 0 0 0 / 0 0 0 / 0 0 0/ 0 $a$ 0 / 0 0 0 / 0 0 $ib$; modes $\mathbf{v}_{6,7}$ for layer 2, layer 1 at rest. Degenerate with $\mathbf{V}_{11,12}$.

Modes 15, 16: $\mathbf{V}_{13,14}$ = 0 $a$ 0 / 0 0 $ib$ / 0 0 0 /0 0 0 / 0 0 0 / 0 0 0; modes $\mathbf{v}_{8,9}$ for layer 1, layer 2 at rest. Degenerate with $\mathbf{V}_{11,12}$ and with $\mathbf{V}_{13,14}$.

Modes 17, 18: $\mathbf{V}_{17,18}$ = 0 0 0 / 0 0 0 / 0 0 0/ $a$ 0 0 / 0 0 $ib$ / 0 0 0; modes $\mathbf{v}_{8,9}$ for layer 2, layer 1 at rest. Degenerate with $\mathbf{V}_{11,12}$, $\mathbf{V}_{13,14}$ and $\mathbf{V}_{15,16}$.

## Conclusion

The mode $\mathbf{V}_1$ is a low-frequency libration mode, but not as low-frequency as $\mathbf{v}_1$ in the isolated layer and in the chess board since it is coupled with layer mode $\mathbf{v}_4$ and there is friction between adjacent layers. The linear combination $a\mathbf{V}_1 + b\mathbf{V}_4$ is a mode of libration of slightly deformed tetrahedra. This coupling probably prevents a soft-mode phase

transition.