Understanding Single-Crystal X-Ray Crystallography Exercises and Solutions

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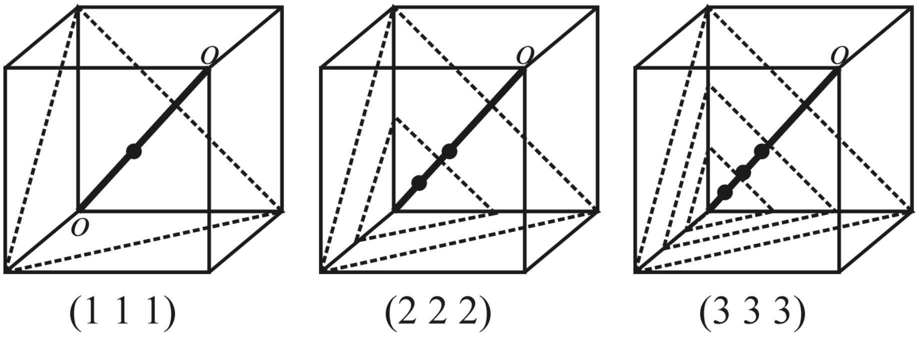
Chapter 1

Crystal Lattices

1. The copper atoms depicted in Fig. 1.1 are arranged in a cubic unit cell. Each edge of the cell has the same length: $a = b = c = 3.6147$ Å. Determine the distances between the planes with (a) (1 1 1), (b) (2 2 2), and (c) (3 3 3) indices.

Solution:



(a) The (1 1 1) plane (shown with dashed lines) is parallel to – and equidistant from – two other (1 1 1) planes that contain an origin, *o*. Thus the plane must pass through the center of the unit cell, dividing the diagonal of the unit cell in half:

$$d_{111} = \frac{(\sqrt{3})(3.6147 \text{ Å})}{2} = 3.1304 \text{ Å}.$$

(b) The (2 2 2) planes (which include the (1 1 1) planes) divide the diagonal into fourths:

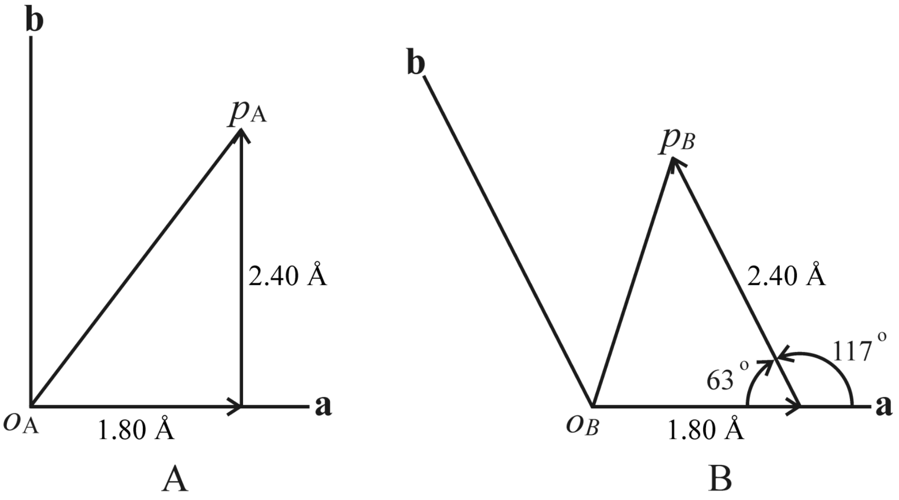
$$d_{222} = \frac{(\sqrt{3})(3.6147 \text{ Å})}{4} = 1.5652 \text{ Å} = \frac{d_{111}}{2}.$$

(c) The (3 3 3) planes (which also include the (1 1 1) planes) divide the diagonal into sixths:

$$d_{222} = \frac{(\sqrt{3})(3.6147\ \text{Å})}{6} = 1.0434\ \text{Å} = \frac{d_{111}}{3}.$$

2. Consider two 2-dimensional unit cells, each with the same axial lengths: $a =$ 2.40 Å and $b = 3.20$ Å. For unit cell A, $\gamma = 90^{\circ}$; for unit cell B, $\gamma = 117^{\circ}$. A point p is located in each unit cell at the end of the sum of a vector of magnitude 1.80 Å, parallel to the **a** axis and a vector of magnitude 2.40 Å, parallel to the **b** axis. (a) Determine the fractional coordinates of point p in each unit cell. (b) Determine the distance from the origin to point p in each unit cell.

Solution:



(a) The fractional coordinates are the same for both unit cells:

$$\begin{aligned} x_f &= \frac{1.80\ \text{Å}}{2.40\ \text{Å}} = 0.75 \\ y_f &= \frac{2.40\ \text{Å}}{3.20\ \text{Å}} = 0.75. \end{aligned}$$

(b) For unit cell A we use the Pythagorean theorem (or note that it is a 3:4:5 right triangle):

$$|\overrightarrow{o_A p_A}| = ((1.80\ \text{Å})^2 + (2.40\ \text{Å})^2)^{1/2} = 3.00\ \text{Å}.$$

For unit cell B we use the Law of Cosines (Fig. 1.24):

$$\begin{aligned} |\overrightarrow{o_B p_B}| &= ((1.80\ \text{Å})^2 + (2.40\ \text{Å})^2 - 2 \times 1.80\ \text{Å} \times 2.40\ \text{Å} \times \cos(63^{\circ}))^{1/2} \\ &= 2.25\ \text{Å}. \end{aligned}$$

3. (a) Derive a formula for the inverse of a 2×2 matrix and use matrix multiplication to demonstrate that your formula is correct ($\mathbf{D}\mathbf{D}^{-1} = \mathbf{I}$). (b) Compute the inverse of the following matrix:

$$\mathbf{D} = \begin{bmatrix} 1.000 & 2.000 & 3.000 \\ 2.000 & 1.000 & 3.000 \\ 3.000 & 2.000 & 1.000 \end{bmatrix}.$$

(c) Demonstrate that the matrix calculated in part (b) is $\mathbf{D}^{-1}$.

Solution:

(a)

$$\mathbf{D} = \begin{bmatrix} d_{11} & d_{12} \\ d_{21} & d_{22} \end{bmatrix} \qquad |\mathbf{D}| = d_{11}d_{22} - d_{12}d_{21}$$

$$\mathbf{D}_c = \begin{bmatrix} d_{22} & -d_{21} \\ -d_{12} & d_{11} \end{bmatrix} \qquad \mathbf{D}_c^T = \begin{bmatrix} d_{22} & -d_{12} \\ -d_{21} & d_{11} \end{bmatrix}$$

$$\mathbf{D}^{-1} = \frac{1}{d_{11}d_{22} - d_{12}d_{21}} \begin{bmatrix} d_{22} & -d_{12} \\ -d_{21} & d_{11} \end{bmatrix}$$

$$\mathbf{D}\mathbf{D}^{-1} = \frac{1}{d_{11}d_{22} - d_{12}d_{21}} \begin{bmatrix} d_{11} & d_{12} \\ d_{21} & d_{22} \end{bmatrix} \begin{bmatrix} d_{22} & -d_{12} \\ -d_{21} & d_{11} \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}.$$

(b) Using Eqn. 1.78,

$$\mathbf{D}^{-1} = \begin{bmatrix} -0.417 & 0.333 & 0.250 \\ 0.583 & -0.667 & 0.250 \\ 0.083 & 0.333 & -0.250 \end{bmatrix}.$$

(c) Using Eqn. 1.48,

$$\begin{bmatrix} 1.000 & 2.000 & 3.000 \\ 2.000 & 1.000 & 3.000 \\ 3.000 & 2.000 & 1.000 \end{bmatrix} \begin{bmatrix} -0.417 & 0.333 & 0.250 \\ 0.583 & -0.667 & 0.250 \\ 0.083 & 0.333 & -0.250 \end{bmatrix} = \begin{bmatrix} 0.998 & -0.002 & 0.000 \\ -0.002 & 0.998 & 0.000 \\ -0.002 & -0.002 & 1.000 \end{bmatrix}.$$

4. Show that (a) the inverse of a matrix for the rotation of angle φ about a coordinate axis (e.g., the x axis) is the rotation matrix for the $-\varphi$ rotation about the same axis, (b) the matrix for a reflection across a coordinate plane (e.g., the xz plane) is its own inverse, and (c) the inversion matrix is its own inverse.

Solution:

(a) Choosing a rotation about the y axis as an example,

$$\mathbf{R}_y(\varphi) = \begin{bmatrix} \cos\varphi & 0 & \sin\varphi \\ 0 & 1 & 0 \\ -\sin\varphi & 0 & \cos\varphi \end{bmatrix} \qquad \mathbf{R}_y(-\varphi) = \begin{bmatrix} \cos\varphi & 0 & -\sin\varphi \\ 0 & 1 & 0 \\ \sin\varphi & 0 & \cos\varphi \end{bmatrix}$$

$$
\begin{aligned}
\mathbf{R}_y(\varphi)\mathbf{R}_y(-\varphi) &= \begin{bmatrix} (\cos^2\varphi+\sin^2\varphi) & 0 & (-\cos\varphi\sin\varphi+\cos\varphi\sin\varphi) \\ 0 & 1 & 0 \\ (-\cos\varphi\sin\varphi+\cos\varphi\sin\varphi) & 0 & (\cos^2\varphi+\sin^2\varphi) \end{bmatrix} \\
&= \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \Longrightarrow (\mathbf{R}_y(\varphi))^{-1} = \mathbf{R}_y(-\varphi).
\end{aligned}
$$

(b)

$$
\mathbf{R}_{xy}\mathbf{R}_{xy} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}.
$$

(c)

$$
\mathbf{R}_i\mathbf{R}_i = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}.
$$

5. Using matrices, show that sequential rotations about a coordinate axis of φ_1 followed by φ_2 is equivalent to a single rotation of $(\varphi_1+\varphi_2)$ about the same axis.

Solution:

Choosing rotation about the x axis as an example,

$$
\mathbf{R}_x(\varphi_2)\mathbf{R}_x(\varphi_1) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\varphi_1 & -\sin\varphi_1 \\ 0 & \sin\varphi_1 & \cos\varphi_1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\varphi_2 & -\sin\varphi_2 \\ 0 & \sin\varphi_2 & \cos\varphi_2 \end{bmatrix}
$$

$$
= \begin{bmatrix} 1 & 0 & 0 \\ 0 & (\cos\varphi_1\cos\varphi_2-\sin\varphi_1\sin\varphi_2) & (-\sin\varphi_1\cos\varphi_2-\cos\varphi_1\sin\varphi_2) \\ 0 & (\cos\varphi_1\sin\varphi_2+\sin\varphi_1\cos\varphi_2) & (\cos\varphi_1\cos\varphi_2-\sin\varphi_1\sin\varphi_2) \end{bmatrix}
$$

From the trigonometric identities, $\cos(\varphi_1+\varphi_2)=\cos\varphi_1\cos\varphi_2-\sin\varphi_1\sin\varphi_2$ and $\sin(\varphi_1+\varphi_2)=\cos\varphi_1\sin\varphi_2+\sin\varphi_1\cos\varphi_2$,

$$
\begin{aligned}
\mathbf{R}_x(\varphi_2)\mathbf{R}_x(\varphi_1) &= \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos(\varphi_1+\varphi_2) & -\sin(\varphi_1+\varphi_2) \\ 0 & \sin(\varphi_1+\varphi_2) & \cos(\varphi_1+\varphi_2) \end{bmatrix} \\
&= \mathbf{R}_x(\varphi_1+\varphi_2).
\end{aligned}
$$

6. Show that (a) the rotation matrices for rotation about the coordinate axes are orthonormal matrices, (b) the inverses of these matrices are their transposes, and (c) the rotation of a general vector effected by any of these matrices does not alter the length of the vector.

Solution:

(a) Choosing rotation about the z axis as an example, the three column vectors of the rotation matrix are:

$$\mathbf{v_1} = \begin{bmatrix} \cos\varphi \\ -\sin\varphi \\ 0 \end{bmatrix} \qquad \mathbf{v_2} = \begin{bmatrix} \sin\varphi \\ \cos\varphi \\ 0 \end{bmatrix} \qquad \mathbf{v_3} = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$$

All column vectors are orthogonal and have unit lengths:

$$\begin{aligned}
\mathbf{v_1}\cdot\mathbf{v_2} &= \cos\varphi\sin\varphi - \sin\varphi\cos\varphi + 0 = 0 \\
\mathbf{v_1}\cdot\mathbf{v_3} &= 0+0+0 = 0 \\
\mathbf{v_2}\cdot\mathbf{v_3} &= 0+0+0 = 0 \\
v_1^2 &= \cos^2\varphi + \sin^2\varphi + 0^2 = 1 \\
v_2^2 &= \sin^2\varphi + \cos^2\varphi + 0^2 = 1 \\
v_3^2 &= 0^2 + 0^2 + 1^2 = 1
\end{aligned}$$

(b) Again, using rotation about z,

$$\begin{aligned}
\mathbf{R}_z\mathbf{R}_z^T &= \begin{bmatrix} \cos\varphi & \sin\varphi & 0 \\ -\sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \cos\varphi & -\sin\varphi & 0 \\ \sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{bmatrix} \\
&= \begin{bmatrix} (\cos^2\varphi + \sin^2\varphi) & (-\cos\varphi\sin\varphi + \cos\varphi\sin\varphi) & 0 \\ (-\cos\varphi\sin\varphi + \cos\varphi\sin\varphi) & (\cos^2\varphi + \sin^2\varphi) & 0 \\ 0 & 0 & 1 \end{bmatrix} \\
&= \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}.
\end{aligned}$$

(c) Using z rotation yet again,

$$\begin{bmatrix} \cos\varphi & \sin\varphi & 0 \\ -\sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \\ v_3 \end{bmatrix} = \begin{bmatrix} v_1\cos\varphi + v_2\sin\varphi \\ -v_1\sin\varphi + v_2\cos\varphi \\ v_3 \end{bmatrix}$$

$$\begin{aligned}
v^2 &= v_1^2 + v_2^2 + v_3^2 \\
v'^2 &= (v_1\cos\varphi + v_2\sin\varphi)^2 + (-v_1\sin\varphi + v_2\cos\varphi)^2 + v_3^2 \\
&= v_1^2\cos^2\varphi + 2v_1v_2\cos\varphi\sin\varphi + v_2^2\sin^2\varphi \\
&\quad + v_1^2\sin^2\varphi - 2v_1v_2\cos\varphi\sin\varphi + v_2^2\cos^2\varphi + v_3^2 \\
&= v_1^2(\cos^2\varphi + \sin^2\varphi) + v_2^2(\cos^2\varphi + \sin^2\varphi) + v_3^2 \\
&= v_1^2 + v_2^2 + v_3^2.
\end{aligned}$$

7. The monoclinic unit cell of CuO has the following parameters: $a = 4.6837(5)$Å, $b = 3.4226(6)$Å, $c = 5.1288(6)$Å, $\alpha = 90.00^o$, $\beta = 99.54^o(1)$ and $\gamma = 90.00^o$.[*]

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[*] Åsbrink, S. and Norrby, L.-J., *Acta. Cryst.*, B26, 8(1970).

The fractional coordinates of the contents of the unit cell are

atom	x_f	y_f	z_f	atom	x_f	y_f	z_f
Cu1	0.2500	0.2500	0.0000	O1	0.0000	0.4184	0.2500
Cu2	0.7500	0.7500	0.5000	O2	0.5000	0.9184	0.2500
Cu3	0.2500	0.7500	0.5000	O3	0.0000	0.5816	0.7500
Cu4	0.7500	0.2500	0.5000	O4	0.5000	0.0816	0.7500

(a) Determine the shortest (contact) distance between the copper(II) ions and the oxide ions in the unit cell. (b) Determine the volume of the unit cell. (c) Determine the mass of the unit cell in grams. (d) Determine the density of solid copper(II) oxide in g/cm^3.

Solution:

(a) Selecting the Cu1 atom, the oxygen atom with the nearest fractional coordinates appears to be O1 (in more complex crystal structures this will rarely be as obvious). The **B** matrix to convert fractional coordinates to Cartesian coordinates is determined from the cell parameters:

$$\mathbf{B} = \begin{bmatrix} 4.6837 & 0.0000 & -0.8500 \\ 0.0000 & 3.4226 & 0.0000 \\ 0.0000 & 0.0000 & 5.0579 \end{bmatrix}$$

$$\begin{aligned}
\mathbf{v}_{\text{Cu1}} &= \mathbf{B}\begin{bmatrix} 0.2500 \\ 0.2500 \\ 0.0000 \end{bmatrix} = \begin{bmatrix} 1.1709 \\ 0.8557 \\ 0.0000 \end{bmatrix} \\
\mathbf{v}_{\text{O1}} &= \mathbf{B}\begin{bmatrix} 0.0000 \\ 0.4184 \\ 0.2500 \end{bmatrix} = \begin{bmatrix} -0.2125 \\ 1.4320 \\ 1.2645 \end{bmatrix} \\
\mathbf{v}_{\text{CuO}} &= \mathbf{v}_{\text{Cu1}} - \mathbf{v}_{\text{O1}} = \begin{bmatrix} 1.3834 \\ -0.5763 \\ -1.2645 \end{bmatrix} \\
v_{\text{CuO}} &= ((1.3834\ \text{Å})^2 + (-0.5763\ \text{Å})^2 + (-1.2645\ \text{Å})^2)^{1/2} = 1.9608\ \text{Å}.
\end{aligned}$$

(b) From the unit cell parameters,

$$\begin{aligned}
V &= (4.6837\ \text{Å})(3.4226\ \text{Å})(5.1288\ \text{Å}) \times \\
&\quad (1 - 0 - \cos^2(99.54^{\text{o}}) - 0 + 2(0))^{1/2} = 81.08\ \text{Å}^3.
\end{aligned}$$

(c) Each unit cell contains four copper atoms and four oxygen atoms. The mass of 6.022×10^{23} atoms of Cu is 63.546 g. A single Cu atom has a mass of $63.546/(6.022 \times 10^{23})$ g $= 1.055 \times 10^{-22}$ g. The mass of a mole of O atoms is 15.9994 g. The mass of an oxygen atom is 2.657×10^{-23} g. The mass of a unit cell is therefore $4(1.055 \times 10^{-22}\ \text{g}) + 4(2.657 \times 10^{-23}\ \text{g}) = 5.283 \times 10^{-22}$ g.

(d) 1Å=10^{-8} cm. $\Longrightarrow 1\text{Å}^3 = 10^{-24}$ cm^3, and

$$D_{\text{CuO}} = \frac{5.283 \times 10^{-22}\ \text{g}}{81.08 \times 10^{-24}\ \text{cm}^3} = 6.515\ \text{g/cm}^3.$$

8. The orthorhombic unit cell of $CuSO_4$ has the following parameters:[*] $a = 8.39$Å, $b = 6.89$Å $c = 4.83$Å, $\alpha = 90.00^o$, $\beta = 90.00^o$ and $\gamma = 90.00^o$

The fractional coordinates of the unique atoms in the unit cell (repeated by symmetry in order to fill the cell) are

atom	x_f	y_f	z_f	atom	x_f	y_f	z_f
Cu1	0.000	0.000	0.000	O2	0.375	0.250	0.439
S1	0.185	0.250	0.445	O3	0.129	0.069	0.307
O1	0.141	0.250	0.755				

(a) Determine the average sulfur-oxygen distance and the average O-S-O angle in the sulfate ion. (b) The experimentally measured density of anhydrous copper sulfate is 3.6 g/cm^3. How many $CuSO_4$ units are in the unit cell? (c) The basic unit in the unit cell seems to be missing an oxygen atom. How can this be if the stoichiometry in the crystal is $CuSO_4$? Hint: The basic unit in the unit cell is called the *asymmetric* unit. You may have to read ahead in Chapter 2 to answer this question. The space group of the crystal is *Pnma*.

Solution:

(a) The **B** matrix to convert fractional coordinates to Cartesian coordinates is straightforward, since all the angles are 90^o:

$$\mathbf{B} = \begin{bmatrix} 8.39 & 0.00 & 0.00 \\ 0.00 & 6.89 & 0.00 \\ 0.00 & 0.00 & 4.83 \end{bmatrix}$$

$$\begin{aligned}
\mathbf{v}_{\text{S1}} &= \mathbf{B}\begin{bmatrix} 0.185 \\ 0.250 \\ 0.445 \end{bmatrix} = \begin{bmatrix} 1.552 \\ 1.723 \\ 2.149 \end{bmatrix} \\
\mathbf{v}_{\text{O1}} &= \mathbf{B}\begin{bmatrix} 0.141 \\ 0.250 \\ 0.755 \end{bmatrix} = \begin{bmatrix} 1.183 \\ 1.723 \\ 3.647 \end{bmatrix} \\
\mathbf{v}_{\text{O2}} &= \mathbf{B}\begin{bmatrix} 0.375 \\ 0.250 \\ 0.439 \end{bmatrix} = \begin{bmatrix} 3.146 \\ 1.723 \\ 2.120 \end{bmatrix}
\end{aligned}$$

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[*] Rao, B.R., *Acta. Cryst.*, 14, 321(1961).

$$\begin{aligned}
\mathbf{v}_{\mathrm{SO1}} &= \mathbf{v}_{\mathrm{S1}} - \mathbf{v}_{\mathrm{O1}} = \begin{bmatrix} 0.369 \\ 0.000 \\ -1.498 \end{bmatrix} \\
\mathbf{v}_{\mathrm{SO2}} &= \mathbf{v}_{\mathrm{S1}} - \mathbf{v}_{\mathrm{O2}} = \begin{bmatrix} -1.594 \\ 0.000 \\ 0.029 \end{bmatrix} \\
v_{\mathrm{SO1}} &= ((0.369\ \text{Å})^2 + (0.000\ \text{Å})^2 + (-1.498\ \text{Å})^2)^{1/2} = 1.542\ \text{Å}. \\
v_{\mathrm{SO2}} &= ((-1.594\ \text{Å})^2 + (0.000\ \text{Å})^2 + (0.029\ \text{Å})^2)^{1/2} = 1.594\ \text{Å}.
\end{aligned}$$

Similarly, $v_{\mathrm{SO3}} = 1.490$ Å and $\langle v_{\mathrm{SO}} \rangle = 1.542$ Å.

$$\cos(\angle(\mathrm{O1} - \mathrm{S} - \mathrm{O2})) = \frac{\mathbf{v}_{\mathrm{SO1}} \cdot \mathbf{v}_{\mathrm{SO2}}}{v_{\mathrm{SO1}} v_{\mathrm{SO2}}}$$

$$= \frac{(0.369)(-1.594) + (0)(0) + (-1.498)(0.029)}{(1.542)(1.594)} = -0.257$$

$$\angle(\mathrm{O1} - \mathrm{S} - \mathrm{O2}) = 104.89^o.$$

Similarly, $\angle(\mathrm{O1} - \mathrm{S} - \mathrm{O3}) = 111.03^o$, $\angle(\mathrm{O2} - \mathrm{S} - \mathrm{O3}) = 107.89^o$ and $\langle \angle(\mathrm{O} - \mathrm{S} - \mathrm{O}) \rangle = 107.94^o$.

(b) Unit cell volume: $V = (8.39)(6.89)(4.83)\sqrt{(1 - 0 - 0 - 0 + 0)}\ \text{Å}^3 = 279\ \text{Å}^3 = 2.79 \times 10^{-22}\ \mathrm{cm}^3$. Unit cell mass: $3.6\ \mathrm{g/cm}^3 \times 2.79 \times 10^{-22}\ \mathrm{cm}^3 = 1.004 \times 10^{-21}$ g. Mass of a mole of $\mathrm{CuSO_4}$ formula units $= (63.546 + 32.066 + 4 \times 15.9994)$ g $= 159.61$ g. Mass of one formula unit: $159.61\ \mathrm{g}/6.022 \times 10^{23} = 2.65 \times 10^{-22}$ g. Number of formula units in the unit cell: (Unit cell mass)/(formula unit mass) $= 1.004 \times 10^{-21}\ \mathrm{g}/2.65 \times 10^{-22}\ \mathrm{g} = 3.8 \simeq 4$.

(c) The fourth oxygen atom bonded to the sulfur atom is generated by a *symmetry operation* that retains the values of x_f and z_f, but changes y_f by subtracting it from 1/2:

atom	x_f	y_f	z_f	atom	x_f	y_f	z_f
Cu1	0.000	0.000	0.000	O2	0.375	0.250	0.439
S1	0.185	0.250	0.445	O3	0.129	0.069	0.307
O1	0.141	0.250	0.755	O3′	0.129	0.431	0.307

$$\mathbf{v}_{\mathrm{O3'}} = \mathbf{B} \begin{bmatrix} 0.129 \\ 0.431 \\ 0.307 \end{bmatrix} = \begin{bmatrix} 1.083 \\ 2.970 \\ 1.483 \end{bmatrix}$$

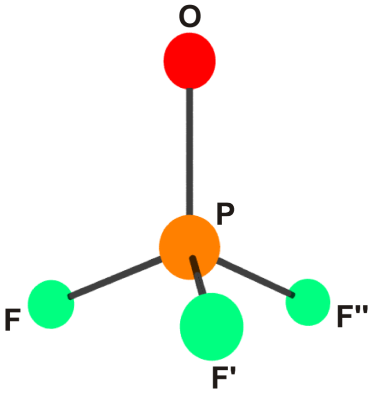
$$v_{\mathrm{SO3'}} = 1.490\ \text{Å} \quad (\text{the same as } v_{\mathrm{SO3}})$$

$$\angle(\mathrm{O1} - \mathrm{S} - \mathrm{O3}) = 111.03^o \quad (\text{the same as } v_{\mathrm{SO3}}).$$

Chapter 2

Crystal Symmetry

1. A ball and stick model of the POF_3 molecule is shown below:



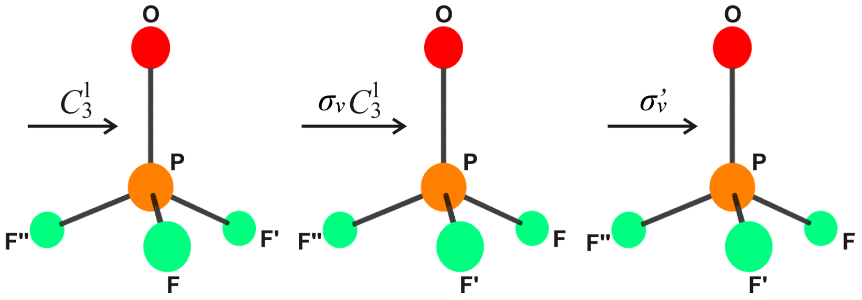
The fluorine atoms are all equivalent by symmetry. (a) Determine the symmetry elements and operations for the molecule. (b) Determine the point symmetry group of the molecule. (c) Create a multiplication table for the symmetry operations and show that the operations constitute a mathematical group (the point group in (b)) (d) Compare your multiplication table to Table 2.1. What can you conclude about the relationship between the point group of POF_3 and the point group of PF_5 from this comparison?.

Solution:

(a) Symmetry elements: C_3 rotation axis and three vertical mirror planes: P→O vector $\equiv C_3$ rotation axis, POF plane $\equiv \sigma_v$, POF$'$ plane $\equiv \sigma_v'$ and POF$''$ plane $\equiv \sigma_v''$. Set of symmetry operations: $\{E, C_3^1, C_3^2, \sigma_v, \sigma_v', \sigma_v''\}$.

(b) Beginning with Fig. 2.9, $n > 2$? Yes, $n = 3$. Multiple C_3 axes? No $\Rightarrow$ Fig. 2.10. $n > 1$? Yes, $N = 3$. S_6 coincident with C_3 only? No. $3C_2$ axes perpendicular to C_3? No. σ_h? No. $3\sigma_v$ mirror planes? Yes. $n = \infty$? No. The point group is C_{3v}.

(c) The table is generated by analyzing all of the products of the operations in the set. As an example, $\sigma_v C_3^1 = \sigma_v'$:



Multiplication table:

	E	C_3^1	C_3^2	σ_v	$\sigma_v^{'}$	$\sigma_v^{''}$
E	E	C_3^1	C_3^2	σ_v	$\sigma_v^{'}$	$\sigma_v^{''}$
C_3^1	C_3^1	C_3^2	E	$\sigma_v^{''}$	σ_v	$\sigma_v^{'}$
C_3^2	C_3^2	E	C_3^1	$\sigma_v^{'}$	$\sigma_v^{''}$	σ_v
σ_v	σ_v	$\sigma_v^{'}$	$\sigma_v^{''}$	E	C_3^1	C_3^2
$\sigma_v^{'}$	$\sigma_v^{'}$	$\sigma_v^{''}$	σ_v	C_3^2	E	C_3^1
$\sigma_v^{''}$	$\sigma_v^{''}$	σ_v	$\sigma_v^{'}$	C_3^1	C_3^2	E

Properties of the set $\{E, C_3^1, C_3^2, \sigma_v, \sigma_v', \sigma_v''\}$: The multiplication table demonstrates that the product of any two operations in the set produces another operation in the set. Focusing on the first row and column in the table, for the general operation, $\mathcal{O}$, $\mathcal{O}E = E\mathcal{O} = \mathcal{O}$, for every operation in the set. Thus the set has an identity element, E. All products of operations, e.g., $\mathcal{O}_i\mathcal{O}_j\mathcal{O}_k$, are associative: $\mathcal{O}_i(\mathcal{O}_j\mathcal{O}_k) = (\mathcal{O}_i\mathcal{O}_j)\mathcal{O}_k$. For every operation in the set, O_i, there is another operation, $\mathcal{O}_j$, such that $\mathcal{O}_i\mathcal{O}_j = \mathcal{O}_j\mathcal{O}_i = E$. Thus every element in the set has an inverse. The set of operations is a mathematical group.

(d) The D_{3h} ($6m2$) point group contains every element of the C_{3v} ($3m$) point group — thus the C_{3v} point group is a *subgroup* of the D_{3h} point group. Note that removal of the columns and rows for the C_2, S_3, and σ_h operations from the D_{3h} multiplication table results in the C_{3v} multiplication table.

2. Generate the matrix products for the (a)$C_2'S_3^2$ and (b) $S_3^2C_2'$ operation products for the D_{3h} point group. (c) Assess whether or not the matrix products produce the same results as the products of the operations given in Table 2.1. (d) Is the complete set of matrices for the D_{3h} point group a mathematical group? Explain your answer (why or why not?).

Solution:

(a) $C_2'S_3^2$:

$$\begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} (\frac{1}{4}+\frac{3}{4}) & (-\frac{\sqrt{3}}{4}+\frac{\sqrt{3}}{4}) & 0 \\ (\frac{\sqrt{3}}{4}-\frac{\sqrt{3}}{4}) & (-\frac{3}{4}-\frac{1}{4}) & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$= \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

(b) $S_3^2C_2'$:

$$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} (\frac{1}{4}-\frac{3}{4}) & (\frac{\sqrt{3}}{4}+\frac{\sqrt{3}}{4}) & 0 \\ (\frac{\sqrt{3}}{4}+\frac{\sqrt{3}}{4}) & (\frac{3}{4}-\frac{1}{4}) & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$= \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

(c) The matrix product in part (a) corresponds to the matrix for the σ_v operation; the matrix product in part (b) corresponds to the σ_v'' operation. The results are consistent with those derived from the products of the symmetry operations (Table 2.1).

(d) A multiplication table derived from the matrix products will correspond exactly to the products in Table 2.1. Since the matrix operations parallel the products of the operations, the matrix representation of a group is itself a mathematical group.

3. Using the scheme outlined in Figs. 2.9 and 2.10, verify the assignment of the Schönflies symbols for the point groups of lattices with a single rotoinversion axis.

Solution:

All of the point groups are lower symmetry point groups. The scheme in Fig. 2.9 leads to the one in Fig. 2.10 in each case.

(a) $\bar{1}$ only (Fig. 2.19(a)). Axis of highest symmetry: $C_1 \Rightarrow n = 1$. S_2 coincident with C_1 only? Yes. The point group is S_2.

(b) $\bar{2}$ only (Fig. 2.19(b)). Axis of highest symmetry: $C_1 \Rightarrow n = 1$. S_2 coincident with C_1 only? No. $n > 1$? No. σ_h? Yes. The point group is C_s.

(c) $\bar{3}$ only (Fig. 2.19(c)). Axis of highest symmetry: $C_3 \Rightarrow n = 3$. S_6 coincident with C_3 only? Yes. The point group is S_6.

(d) $\bar{4}$ only (Fig. 2.19(d)). Axis of highest symmetry: $C_2 \Rightarrow n = 2$. S_4 coincident with C_2 only? Yes. The point group is S_4.

(e) $\bar{6}$ only (Fig. 2.19(a)). Axis of highest symmetry: $C_3 \Rightarrow n = 3$. S_6 coincident with C_3 only? No. $n > 1$? Yes. $3C_2$s $\perp C_3$? No. σ_h? Yes. The point group is C_{3h}.

4. Using the scheme outlined in Figs. 2.9 and 2.10, determine Schönflies and Hermann-Mauguin notations for the point groups of the Bravais lattices for each crystal system. Figs. 2.11 and 2.42 may prove useful.

Solution:

(a) Triclinic → Fig. 2.9: Axis of highest symmetry: $C_1 \Rightarrow n = 1$. $n > 2$? No. → Fig. 2.10: S_2 coincident with C_1 only? No. $n > 1$? No. σ_h? No. i? Yes. The point group is $C_i \equiv \bar{1}$.

(b) Monoclinic → Fig. 2.9: Axis of highest symmetry: $C_2 \Rightarrow n = 2$. $n > 2$? No. → Fig. 2.10: S_4 coincident with C_2 only? No. $n > 1$? Yes. $2C_2$s $\perp C_2$? No. σ_h? Yes. The point group is $C_{2h} \equiv 2/m$.

(c) Orthorhombic → Fig. 2.9: Axis of highest symmetry: $C_2 \Rightarrow n = 2$. $n > 2$? No. → Fig. 2.10: S_4 coincident with C_2 only? No. $n > 1$? Yes. $2C_2$s $\perp C_2$? Yes. σ_h? Yes. $n = \infty$? No. The point group is $D_{2h} \equiv mmm$.

(d) Tetragonal → Fig. 2.9: Axis of highest symmetry: $C_4 \Rightarrow n = 4$. $n > 2$? Yes. Multiple C_4 axes? No. → Fig. 2.10: S_8 coincident with C_4 only? No. $n > 1$? Yes. $4C_2$s $\perp C_4$? Yes. σ_h? Yes. $n = \infty$? No. The point group is $D_{4h} \equiv 4/mmm$.

(e) Cubic → Fig. 2.9: Axis of highest symmetry: $C_4 \Rightarrow n = 4$. $n > 2$? Yes, $n = 4$. Multiple C_4 axes? Yes. $n = 5$? No. $n = 4$? Yes. σ? Yes. The point group is $O_h \equiv m3m$.

(f) Trigonal(H)/Hexagonal → Fig. 2.9: Axis of highest symmetry: $C_6 \Rightarrow n = 6$. $n > 2$? Yes. Multiple C_6 axes? No. → Fig. 2.10: S_12 coincident with C_6 only? No. $n > 1$? Yes. $6C_2$s $\perp C_6$? Yes. σ_h? Yes. $n = \infty$? No. The point group is $D_{6h} \equiv 6/mmm$.

(g) Rhombohedral → Fig. 2.9: Axis of highest symmetry: $C_3 \Rightarrow n = 3$. $n > 2$? Yes. Multiple C_3 axes? No. → Fig. 2.10: S_6 coincident with C_3 only? No. $n > 1$? Yes. $3C_2$s $\perp C_3$? Yes. σ_h? No. $3\sigma_d$s? Yes. The point group is $D_{3d} \equiv \bar{3}m$. Referring to Fig. 2.42, the dihedral mirror planes pass through the lattice points and the center of the cell. The diad axes bisect the dihedral angles between these planes.

5. The unit cell for the 2-mercaptopyridine crystal structure (Sec. 1.5.3) is described in a non-standard space group – $P2_1/n$. The standard setting is $P2_1/c$. (a) Determine the unit cell parameters for the $P2_1/c$ unit cell. (b) Determine the fractional coordinates of the S(1), C(1), and N(1) atoms in the $P2_1/c$ unit cell. (c) Verify the transformed coordinates in (b) by calculating the C(1)–S(1) and C(1)–N(2) interatomic distances and the N(1)–C(1)–S(1) interatomic angle in the $P2_1/c$ unit cell.

Solution:

(a) The transformation is identical to the $Pn \rightarrow Pc$ transformation described in Sec. 2.4.4:

$$\mathbf{B} = \begin{bmatrix} 6.112 & 0 & -2.861 \\ 0 & 6.326 & 0 \\ 0 & 0 & 14.025 \end{bmatrix} = \begin{bmatrix} \mathbf{a}_c & \mathbf{b}_c & \mathbf{c}_c \end{bmatrix},$$

where $\mathbf{a}_c$, $\mathbf{b}_c$, and $\mathbf{c}_c$ are the $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ axes for the $P2_1/n$ unit cell in crystal Cartesian coordinates. Denoting the $P2_1/c$ axes as $\mathbf{a}'_c$, $\mathbf{b}'_c$, and $\mathbf{c}'_c$,

$$\mathbf{a}'_c = \mathbf{c}_c = \begin{bmatrix} -2.861 \\ 0 \\ 14.025 \end{bmatrix} \qquad \mathbf{b}'_c = \mathbf{b}_c = \begin{bmatrix} 0 \\ 6.326 \\ 0 \end{bmatrix}$$

$$\mathbf{c}'_c = -(\mathbf{a}_c + \mathbf{c}_c) = \begin{bmatrix} -3.251 \\ 0 \\ -14.025 \end{bmatrix}$$

$$a' = c = 14.314 \text{ Å}$$

$$b' = b = 6.326\text{Å}$$

$$c' = ((-3.251)^2 + (-14.025)^2)^{1/2} = 14.392\text{Å}$$

$$\cos\beta' = \frac{\mathbf{a}'_c \cdot \mathbf{c}'_c}{a'c'} = \frac{(-2.861)(-3.251) + (14.025)(-14.025)}{14.318 \cdot 14.392} = -0.90987$$

$$\beta' = 155.43^{\circ}.$$

(b)

$$\text{S(1)}: \begin{bmatrix} \bar{1} & 0 & 1 \\ 0 & 1 & 0 \\ \bar{1} & 0 & 0 \end{bmatrix} \begin{bmatrix} 0.7403 \\ 0.0629 \\ 0.4073 \end{bmatrix} = \begin{bmatrix} -0.3330 \\ 0.0629 \\ -0.7403 \end{bmatrix}$$

$$\text{C(1)}: \begin{bmatrix} \bar{1} & 0 & 1 \\ 0 & 1 & 0 \\ \bar{1} & 0 & 0 \end{bmatrix} \begin{bmatrix} 0.5501 \\ 0.2608 \\ 0.3860 \end{bmatrix} = \begin{bmatrix} -0.1641 \\ 0.2608 \\ -0.5501 \end{bmatrix}$$

$$\text{N(1)}: \begin{bmatrix} \bar{1} & 0 & 1 \\ 0 & 1 & 0 \\ \bar{1} & 0 & 0 \end{bmatrix} \begin{bmatrix} 0.3705 \\ 0.2616 \\ 0.4294 \end{bmatrix} = \begin{bmatrix} 0.0589 \\ 0.2616 \\ -0.3705 \end{bmatrix}$$

(c)

$$\mathbf{B} = \begin{bmatrix} 14.314 & 0 & -13.089 \\ 0 & 6.326 & 0 \\ 0 & 0 & 5.984 \end{bmatrix}$$

$$\text{S(1)}: \mathbf{B} \begin{bmatrix} -0.3330 \\ 0.0629 \\ -0.7403 \end{bmatrix} = \begin{bmatrix} 4.294 \\ 0.398 \\ -4.430 \end{bmatrix} \qquad \text{C(1)}: \mathbf{B} \begin{bmatrix} -0.1641 \\ 0.2608 \\ -0.5501 \end{bmatrix} = \begin{bmatrix} 4.851 \\ 1.650 \\ -3.292 \end{bmatrix}$$

$$\text{N(1)}: \mathbf{B} \begin{bmatrix} 0.0589 \\ 0.2616 \\ -0.3705 \end{bmatrix} = \begin{bmatrix} 5.693 \\ 1.650 \\ -2.217 \end{bmatrix}.$$

$$\begin{aligned}
\overrightarrow{\mathrm{C(1)S(1)}} &= [(4.923)\ (0.398)(-4.430)] - [(4.851)\ (1.650)\ (-3.292)] \\
&= [(0.072)\ (-1.252)\ (-1.138)] \\
\overrightarrow{\mathrm{C(1)N(1)}} &= [(5.693)\ (1.655)(-2.217)] - [(4.851)\ (1.650)\ (-3.292)] \\
&= [(0.842)\ (0.005)\ (1.0758)] \\
|\overrightarrow{\mathrm{C(1)S(1)}}| &= ((0.072)^2 + (-1.252)^2 + (-1.138)^2)^{1/2} = 1.693\text{Å} \\
|\overrightarrow{\mathrm{C(1)N(1)}}| &= ((0.842)^2 + (0.005)^2 + (1.075)^2)^{1/2} = 1.365\text{Å} \\
\overrightarrow{\mathrm{C(1)S(1)}} &\cdot \overrightarrow{\mathrm{C(1)N(1)}} = -1.169 \\
\cos\nu &= \frac{-1.169}{(1.693)(1.365)} = -0.506. \\
\nu &= 120.4^{\mathrm{o}}.
\end{aligned}$$

6. Recall that the product of local operations of a space group must generate another local operation if the translations generated by the product are negated (or ignored!). (a) For the $P2/c$ space group, diad rotation axes are postulated to result from a combination of c-glide operations, inversion operations, and translation group operations: $\mathbf{S}(2) = \mathbf{S}(t_j)\mathbf{S}(\bar{1})\mathbf{S}(c)$. Determine the locations of the diad axes in the $P2/c$ unit cell. (b) Verify that the $\mathbf{S}(2)$ operator in the $P2/c$ space group is given by Eqn. 2.36. (c) For the $P2_1/c$ space group, c-glide planes are postulated to result from a combination of diad screw operations (about axes at the locations determined in part (a)), inversion operations, and translation group operations: $\mathbf{S}(c) = \mathbf{S}(\mathbf{t}_j)\mathbf{S}(\bar{1})\mathbf{S}(2_1)$. Determine the locations of the glide planes in the $P2_1/c$ unit cell. (d) Verify that the $\mathbf{S}(c)$ operator in the $P2_1/c$ space group is given by Eqn. 2.37.

Solution:

(a)

$$\begin{aligned}
\mathbf{S}(c)\begin{bmatrix} x_f \\ y_f \\ z_f \end{bmatrix} &= \begin{bmatrix} x_f \\ \bar{y}_f \\ z_f + \frac{1}{2} \end{bmatrix} \\
\mathbf{S}(\bar{1})\mathbf{S}(c)\begin{bmatrix} x_f \\ y_f \\ z_f \end{bmatrix} &= \begin{bmatrix} \bar{x}_f \\ y_f \\ \bar{z}_f + \frac{1}{2} \end{bmatrix} \\
\mathbf{S}(\mathbf{t}_j)\mathbf{S}(\bar{1})\mathbf{S}(c)\begin{bmatrix} x_f \\ y_f \\ z_f \end{bmatrix} &= \begin{bmatrix} m_1 - x_f \\ m_2 + y_f \\ m_3 - z_f + \frac{1}{2} \end{bmatrix}.
\end{aligned}$$

The $\mathbf{S}(2)$ operation on an atom at the point of intersection of the diad axis with the ac plane, $[x_f^*\ 0 z_f^*]$, leaves the atom position unchanged, and

$$\begin{bmatrix} x_f^* \\ 0 \\ z_f^* \end{bmatrix} = \begin{bmatrix} m_1 - x_f^* \\ m_2 + 0 \\ m_3 - z_f^* + \frac{1}{2} \end{bmatrix}, \quad \text{resulting in}$$

$$x_f^* = \frac{m_1}{2} \qquad y_f^* = 0 \qquad z_f^* = \frac{m_3}{2} + \frac{1}{4}.$$

Thus, for m_1 and m_3 zero or one, $x_f^* = 0$ or $x_f^* = \frac{1}{2}$; $z_f^* = \frac{1}{4}$ or $z_f^* = \frac{3}{4}$. Diad axes intersect the ac plane at $[\frac{1}{2}\ 0\ \frac{1}{4}]$, $[\frac{1}{2}\ 0\ \frac{3}{4}]$, $[0\ 0\ \frac{1}{4}]$, and $[0\ 0\ \frac{3}{4}]$.

(b) Rotation of a point at $[x_f\ y_f\ z_f]$ about the diad axis at $[\frac{1}{2}\ 0\ \frac{1}{4}]$: Translate to origin $\rightarrow [(x_f - \frac{1}{2})\ y_f\ (z_f - \frac{1}{4})]$. Diad rotation about $b \rightarrow [-(x_f - \frac{1}{2})\ y_f\ \ -(z_f - \frac{1}{4})]$. Translate to original location $\rightarrow [(-(x_f - \frac{1}{2}) + \frac{1}{2})\ y_f\ (-(z_f - \frac{1}{4}) + \frac{1}{4})] = [\bar{x}_f\ y_f\ (\bar{z} + \frac{1}{2})]$ This is effectively the same as rotating $[x_f\ y_f\ z_f]$ about the b axis, followed by a translation of $\frac{1}{2}c$ along $\mathbf{c}$; $\mathbf{S}(2) = \mathbf{R}(2) + [0\ 0\ \frac{1}{2}]$:

$$\mathbf{S}(2) \begin{bmatrix} x_f \\ y_f \\ z_f \end{bmatrix} = \begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{bmatrix} \begin{bmatrix} x_f \\ y_f \\ z_f \end{bmatrix} + \begin{bmatrix} 0 \\ 0 \\ \frac{1}{2} \end{bmatrix} = \begin{bmatrix} \bar{x}_f \\ y_f \\ \bar{z}_f + \frac{1}{2} \end{bmatrix}.$$

(c) The $\mathbf{S}(2_1)$ operation is the $\mathbf{S}(2)$ operation in the $P2/c$ space group from part (b), followed by a translation of $\frac{1}{2}b$ along the $\mathbf{b}$ axis: $\mathbf{S}(2_1) = \mathbf{R}(2) + [0\ 0\ \frac{1}{2}] + [0\ \frac{1}{2}\ 0] = R(2) + [0\ \frac{1}{2}\ \frac{1}{2}]$, and

$$\begin{aligned} \mathbf{S}(2_1) \begin{bmatrix} x_f \\ y_f \\ z_f \end{bmatrix} &= \begin{bmatrix} \bar{x}_f \\ y_f + \frac{1}{2} \\ \bar{z}_f + \frac{1}{2} \end{bmatrix} \\ \mathbf{S}(\bar{1})\mathbf{S}(2_1) \begin{bmatrix} x_f \\ y_f \\ z_f \end{bmatrix} &= \begin{bmatrix} x_f \\ \bar{y}_f + \frac{1}{2} \\ z_f + \frac{1}{2} \end{bmatrix} \\ \mathbf{S}(\mathbf{t}_j)\mathbf{S}(\bar{1})\mathbf{S}(2_1) \begin{bmatrix} x_f \\ y_f \\ z_f \end{bmatrix} &= \begin{bmatrix} m_1 + x_f \\ m_2 - y_f + \frac{1}{2} \\ m_3 + z_f + \frac{1}{2} \end{bmatrix}. \end{aligned}$$

The reflection portion of the $\mathbf{S}(c)$ operation on an atom $[0\ y_f^*\ 0]$ at the point of intersection of the glide plane with the b axis, leaves the atom position unchanged, but the c translation places a symmetry-equivalent atom at $[0\ y_f^*\ \frac{1}{2}]$, and

$$\begin{bmatrix} 0 \\ y_f^* \\ \frac{1}{2} \end{bmatrix} = \begin{bmatrix} m_1 + 0 \\ m_2 - y_f^* + \frac{1}{2} \\ m_3 + 0 + \frac{1}{2} \end{bmatrix}, \quad \text{resulting in}$$

$$x_f^* = 0 \qquad y_f^* = \frac{m_2}{2} \qquad z_f^* = 0.$$

For m_2 zero or one, $y_f^* = \frac{1}{4}$ or $y_f^* = \frac{3}{4}$. The glide planes intersect the b axis at $[0\ \frac{1}{4}\ 0]$ and $[0\ \frac{3}{4}\ 0]$.

(d) Reflection of a point at $[x_f\ y_f\ z_f]$ across the plane at $[0\ \frac{1}{4}\ 0]]$ changes y_f to $\frac{1}{2} - y_f$ (Fig. 2.60). This is effectively a reflection across the ac plane ($\mathbf{R}(m)$), followed by a translation of $\frac{1}{2}b$ along $\mathbf{b}$. The c-glide operation adds $\frac{1}{2}$ to z_f: $[x_f\ y_f\ z_f] \rightarrow [x_f\ (\bar{y}_f + \frac{1}{2})\ z_f + \frac{1}{2}] \Rightarrow \mathbf{S}(c) = \mathbf{R}(m) + [0\ \frac{1}{2}\ 0] + [0\ 0\ \frac{1}{2}] = \mathbf{R}(m) + [0\ \frac{1}{2}\ \frac{1}{2}]$:

$$\mathbf{S}(c) \begin{bmatrix} x_f \\ y_f \\ z_f \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x_f \\ y_f \\ y_f \end{bmatrix} + \begin{bmatrix} 0 \\ \frac{1}{2} \\ \frac{1}{2} \end{bmatrix} = \begin{bmatrix} x_f \\ \bar{y}_f + \frac{1}{2} \\ z_f + \frac{1}{2} \end{bmatrix}.$$

7. The transformation of unit cells from one setting to another does not affect the locations of the atoms, and therefore does not affect the locations of the symmetry elements in the lattice. (a)Use the locations of the points of intersection of the screw axes with the *ac* plane and the glide planes with the *b* axis in the $P2_1/c$ unit cell to determine the location of these symmetry elements in the $P2_1/n$ unit cell.* (b) Determine the symmetry operators, $\mathbf{S}(n)$ and $\mathbf{S}(2_1)$, for the *n*-glide and diad screw operations in the $P2_1/n$ unit cell. (c) Given the general position, $[x_f\ y_f\ z_f]$, in the $P2_1/n$ unit cell, determine the symmetry-equivalent general positions within the unit cell. (d) Determine the location of all the S(1)-C(1) bonded pairs in the 2-mercaptopyridine crystal structure (Sec. 1.5.3). Verify that all of the transformed pairs have the same internuclear distance.

Solution:

(a) Since the *b* axis and *ac* plane in the lattice do not change when the $P2_1/c$ unit cell is transformed into the $P2_1/n$ unit cell the points of intersection of the glide planes and screw axes will remain in the same positions in the lattice. Only their coordinates will be affected by the change of basis – we can transform the points as if they were atoms in the unit cell. Denoting $\mathbf{v}_n$ as a vector in the $P2_1/n$ unit cell and $\mathbf{v}_c$ as the same vector in the $P2_1/c$ unit cell, the transformation of coordinates in $P2_1/n$ to coordinates in $P2_1/c$ is given by Eqn. 2.17:

$$\begin{bmatrix} -1 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{bmatrix} \mathbf{v}_n = \mathbf{v}_c.$$

To transform the intersection points from $P2_1/c$ to $P2_1/n$ we have

$$\mathbf{v}_n = \begin{bmatrix} \bar{1} & 0 & 1 \\ 0 & 1 & 0 \\ \bar{1} & 0 & 0 \end{bmatrix}^{-1} \mathbf{v}_c = \begin{bmatrix} 0 & 0 & \bar{1} \\ 0 & 1 & 0 \\ 1 & 0 & \bar{1} \end{bmatrix} \mathbf{v}_c.$$

The diad screw axes intersect the *ac* plane in the $P2_1/c$ unit cell at $[0\ 0\ \frac{1}{4}]$, $[\frac{1}{2}\ 0\ \frac{1}{4}]$, $[0\ 0\ \frac{3}{4}]$, and $[\frac{1}{2}\ 0\ \frac{3}{4}]$. In the $P2_1/n$ unit cell,

$$\begin{bmatrix} 0 & 0 & \bar{1} \\ 0 & 1 & 0 \\ 1 & 0 & \bar{1} \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ \frac{1}{4} \end{bmatrix} = \begin{bmatrix} -\frac{1}{4} \\ 0 \\ -\frac{1}{4} \end{bmatrix} = \begin{bmatrix} \frac{3}{4} \\ 0 \\ \frac{3}{4} \end{bmatrix}$$

$$\begin{bmatrix} 0 & 0 & \bar{1} \\ 0 & 1 & 0 \\ 1 & 0 & \bar{1} \end{bmatrix} \begin{bmatrix} \frac{1}{2} \\ 0 \\ \frac{1}{4} \end{bmatrix} = \begin{bmatrix} -\frac{1}{4} \\ 0 \\ \frac{1}{4} \end{bmatrix} = \begin{bmatrix} \frac{3}{4} \\ 0 \\ \frac{1}{4} \end{bmatrix}$$

$$\begin{bmatrix} 0 & 0 & \bar{1} \\ 0 & 1 & 0 \\ 1 & 0 & \bar{1} \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ \frac{3}{4} \end{bmatrix} = \begin{bmatrix} -\frac{3}{4} \\ 0 \\ -\frac{3}{4} \end{bmatrix} = \begin{bmatrix} \frac{1}{4} \\ 0 \\ \frac{1}{4} \end{bmatrix}$$

$$\begin{bmatrix} 0 & 0 & \bar{1} \\ 0 & 1 & 0 \\ 1 & 0 & \bar{1} \end{bmatrix} \begin{bmatrix} \frac{1}{2} \\ 0 \\ \frac{3}{4} \end{bmatrix} = \begin{bmatrix} -\frac{3}{4} \\ 0 \\ -\frac{1}{4} \end{bmatrix} = \begin{bmatrix} \frac{1}{4} \\ 0 \\ \frac{3}{4} \end{bmatrix}$$

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*You can also locate these points using the "group theory" approach. You might wish to do it both ways!

The glide plane intersects the b axis at $[0\ \frac{1}{4}\ 0]$ in the $P2_1/c$ unit cell. Since the b axis is the same axis in both unit cells, we would not expect a change in the coordinates of the intersection point:

$$\begin{bmatrix} 0 & 0 & \bar{1} \\ 0 & 1 & 0 \\ 1 & 0 & \bar{1} \end{bmatrix} \begin{bmatrix} 0 \\ \frac{1}{4} \\ 0 \end{bmatrix} = \begin{bmatrix} 0 \\ \frac{1}{4} \\ 0 \end{bmatrix}.$$

The same holds for the glide plane intersecting the b axis at $[0\ \frac{3}{4}\ 0]$.

(b) The glide operation involves a reflection across a plane at $[0\ \frac{1}{4}\ 0] \Rightarrow \mathbf{S}(m) = \mathbf{R}(m) + [0\ \frac{1}{2}\ 0]$, followed by a translation of $[\frac{1}{2}\ 0\ \frac{1}{2}]$ along the diagonal. Thus $\mathbf{S}(n) = \mathbf{R}(m) + [0\ \frac{1}{2}\ 0] + [\frac{1}{2}\ 0\ \frac{1}{2}] = \mathbf{S}(m) + [\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}]$.

The diad screw operator at $[\frac{1}{4}\ 0\ \frac{3}{4}]$ is generated by considering the transformation of a general point at $[x_f\ y_f\ z_f]$: Translate to origin $\rightarrow [(x_f - \frac{1}{4})\ y_f\ (z_f - \frac{3}{4})]$. Diad rotation about $b \rightarrow [(-(x_f - \frac{1}{4}))\ y_f\ (-(z_f - \frac{3}{4}))]$. Translate to original location $\rightarrow [(-(x_f - \frac{1}{4}) + \frac{1}{4})\ y_f\ (-(z_f - \frac{3}{4}) + \frac{3}{4})] = [(\bar{x}_f + \frac{1}{2})\ y_f\ (\bar{z} + \frac{3}{2})] \equiv [(\bar{x}_f + \frac{1}{2})\ y_f\ (\bar{z} + \frac{1}{2})]$. The screw operation is completed by translating $\frac{1}{2}b$ along $\mathbf{b} \rightarrow [(\bar{x}_f + \frac{1}{2})\ (y_f + \frac{1}{2})\ (\bar{z} + \frac{1}{2})]$. This is effectively the same as rotating $[x_f\ y_f\ z_f]$ about the b axis, followed by a translation of $\frac{1}{2}$ along each of the axes. Thus $\mathbf{S}(2_1) = \mathbf{R}(2) + [\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}]$.

(c) Given $[x_f\ y_f\ z_f]$ (1),

$$\mathbf{S}(2_1) \begin{bmatrix} x_f \\ y_f \\ z_f \end{bmatrix} = \begin{bmatrix} \bar{x}_f + \frac{1}{2} \\ y_f + \frac{1}{2} \\ \bar{z}_f + \frac{1}{2} \end{bmatrix} \quad (2) \qquad \mathbf{S}(\bar{1}) \begin{bmatrix} x_f \\ y_f \\ z_f \end{bmatrix} = \begin{bmatrix} \bar{x}_f \\ \bar{y}_f \\ \bar{z}_f \end{bmatrix} \quad (3)$$

$$\mathbf{S}(\bar{1}) \begin{bmatrix} \bar{x}_f + \frac{1}{2} \\ y_f + \frac{1}{2} \\ \bar{z}_f + \frac{1}{2} \end{bmatrix} = \begin{bmatrix} x_f + \frac{1}{2} \\ \bar{y}_f + \frac{1}{2} \\ z_f + \frac{1}{2} \end{bmatrix} \quad (4).$$

(d)

$$\begin{aligned}
&\mathrm{S}(1) : (0.7403, 0.0629, 0.4073) \quad (1) \\
&\mathrm{S}(1)' : (-0.7403, -0.0629, -0.4073) = (1 - 0.7403, 1 - 0.0629, 1 - 0.4073) \\
&\qquad = (0.2597, 0.9371, 0.5927) \quad (2) \\
&\mathrm{S}(1)'' : (-0.7403 + 0.5, 0.0629 + 0.5, -0.4073 + 0.5) \\
&\qquad = (0.7597, 0.5629, 0.0927) \quad (3) \\
&\mathrm{S}(1)''' : (-0.7597, -0.5629, -0.0927) \\
&\qquad = (0.2403, 0.4371, 0.9073) \quad (4) \\
&\mathrm{C}(1) : (0.5501, 0.2608, 0.3860) \quad (1) \\
&\mathrm{C}(1)' : (0.4499, 0.7392, 0.6140) \quad (2) \\
&\mathrm{C}(1)'' : (0.9499, 0.7608, 0.1140) \quad (3) \\
&\mathrm{C}(1)''' : (0.0501, 0.2392, 0.8860) \quad (4).
\end{aligned}$$

Cartesian coordinates for S(1)′ and C(1)′:

$$\text{S}(1):\mathbf{B}\begin{bmatrix}0.2597\\0.9371\\0.5927\end{bmatrix}=\begin{bmatrix}-0.1080\\5.9281\\8.3126\end{bmatrix}$$

$$\text{C}(1):\mathbf{B}\begin{bmatrix}0.4499\\0.7392\\0.6140\end{bmatrix}=\begin{bmatrix}0.9931\\4.6762\\8.6114\end{bmatrix}$$

$$\overrightarrow{\text{C}(1)'\text{S}(1)'}=\begin{bmatrix}-1.1011\\1.2519\\-0.2988\end{bmatrix}$$

$$|\overrightarrow{\text{C}(1)'\text{S}(1)'}|=1.694\text{ Å},\quad\text{etc.}$$

8. Referring to Fig. 2.47, it was postulated that the symmetry element located at the $2'$ location was a diad rotational axis, but this assertion was not proved (any symmetry element that would transform an atom onto itself would have worked). (a) Show that an axis located at the position in the figure is a two-fold rotational axis. (b) Prove that any axis with a location resulting from a general product of a diad rotational operation about an axis at the origin followed by a translation from a vector in the translation group, $\mathbf{S}(\mathbf{t}_j)\mathbf{S}(2)$, $\mathbf{t}_j = [m_1\ m_2\ m_3]$, is a diad rotational axis. m_1, m_2, and m_3 are arbitrary integers.

Solution:

(a) To prove this we transfer the origin to the point of intersection of the axis where it crosses the *ac* plane at $[-\frac{1}{2}\ 0\ 1]$. This is accomplished by subtracting $[-\frac{1}{2}\ 0\ 1]$ from the coordinates of the original point at $[x_f\ y_f\ z_f]$ and a symmetry-equivalent point generated from the initial rotation and translation at $[(\bar{x}_f-1)\ y_f\ (\bar{z}_f+2)]$. The coordinates of these points with respect to the new origin are $[(x_f+\frac{1}{2})\ y_f\ (z_f-1)]$ and $[(\bar{x}_f-\frac{1}{2})\ y_f\ (\bar{z}_f+1)]$, respectively. Diad rotation of the original point about the axis generates the symmetry-equivalent point:

$$\begin{bmatrix}\bar{1}&0&0\\0&1&0\\0&0&\bar{1}\end{bmatrix}\begin{bmatrix}x_f+\frac{1}{2}\\y_f\\z_f-1\end{bmatrix}=\begin{bmatrix}-(x_f+\frac{1}{2})\\y_f\\-(z_f-1)\end{bmatrix}=\begin{bmatrix}\bar{x}_f-\frac{1}{2}\\y_f\\\bar{z}_f+1\end{bmatrix}.$$

(b) The general symmetry element (putative diad axis) intersects the *ac* plane at $\left[\frac{m_1}{2}\ 0\ \frac{m_3}{2}\right]$. The original point is at $[x_f\ y_f\ z_f]$. The rotation of this point (a vector to this point) about a diad axis intersecting the *ac* plane at $[0\ 0\ 0]$, followed by a $[m_1\ 0\ m_3]$ translation, generates a symmetry-equivalent point at $[(\bar{x}_f+m_1)\ y_f\ (\bar{z}_f+m_3)]$. Re-establishing the origin at $\left[\frac{m_1}{2}\ 0\ \frac{m_3}{2}\right]$ transforms the original vector to $\left[\left(x_f-\frac{m_1}{2}\right)\ y_f\ \left(z_f-\frac{m_3}{2}\right)\right]$, and the vector to the symmetry equivalent point to $\left[\left(\bar{x}_f+\frac{m_1}{2}\right)\ y_f\ \left(\bar{z}+\frac{m_3}{2}\right)\right]$. Diad rotation of a point at

$\left[\left(x_f - \dfrac{m_1}{2}\right)\ y_f\ \left(z_f - \dfrac{m_3}{2}\right)\right]$ about an axis located on the translated origin results in

$$\begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{bmatrix} \begin{bmatrix} x_f - \dfrac{m_1}{2} \\ y_f \\ z_f - \dfrac{m_3}{2} \end{bmatrix} = \begin{bmatrix} -(x_f - \dfrac{m_1}{2}) \\ y_f \\ -(z_f - \dfrac{m_3}{2}) \end{bmatrix} = \begin{bmatrix} \bar{x}_f + \dfrac{m_1}{2} \\ y_f \\ \bar{z}_f + \dfrac{m_3}{2} \end{bmatrix}.$$

The original point is related to the symmetry-equivalent point through a diad rotation about the axis.

9. The general positions for the $P2_12_12_1$ space group are listed in the *International Tables for Crystallography* as: (1) $x,\ y,\ z$ (2) $\bar{x} + \frac{1}{2},\ \bar{y},\ z + \frac{1}{2}$ (3) $\bar{x},\ y + \frac{1}{2},\ \bar{z} + \frac{1}{2}$ (4) $x + \frac{1}{2},\ \bar{y} + \frac{1}{2},\ \bar{z}$. (a) Determine the matrix operators for the local operators in $P2_12_12_1$ from these general positions. (b) Demonstrate that the set of local operations resulting from the application of these operators to a general vector *behaves like* a mathematical group if symmetry-equivalent positions due to translations from vectors in the translation group are transformed to equivalent positions without the translations.

Solution:

(a)

$$\mathbf{S}(1) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} + \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix} \qquad \mathbf{S}(2) = \begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{bmatrix} + \begin{bmatrix} \frac{1}{2} \\ 0 \\ \frac{1}{2} \end{bmatrix}$$

$$\mathbf{S}(3) = \begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{bmatrix} + \begin{bmatrix} 0 \\ \frac{1}{2} \\ \frac{1}{2} \end{bmatrix} \qquad \mathbf{S}(4) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{bmatrix} + \begin{bmatrix} \frac{1}{2} \\ \frac{1}{2} \\ 0 \end{bmatrix}.$$

(b) The simplest approach is to generate all of the possible products (i.e., a multiplication table). We begin with the effects of each operator on a general vector:

$$\mathbf{S}(1) \begin{bmatrix} x_f \\ y_f \\ z_f \end{bmatrix} = \begin{bmatrix} x_f \\ y_f \\ z_f \end{bmatrix} \qquad \mathbf{S}(2) \begin{bmatrix} x_f \\ y_f \\ z_f \end{bmatrix} = \begin{bmatrix} \bar{x}_f + \frac{1}{2} \\ \bar{y}_f \\ z_f + \frac{1}{2} \end{bmatrix}$$

$$\mathbf{S}(3) \begin{bmatrix} x_f \\ y_f \\ z_f \end{bmatrix} = \begin{bmatrix} \bar{x}_f \\ y_f + \frac{1}{2} \\ \bar{z}_f + \frac{1}{2} \end{bmatrix} \qquad \mathbf{S}(4) \begin{bmatrix} x_f \\ y_f \\ z_f \end{bmatrix} = \begin{bmatrix} x_f + \frac{1}{2} \\ \bar{y}_f + \frac{1}{2} \\ z_f \end{bmatrix}$$

i. Identity Rule:

$$\mathbf{S}(1)\mathbf{S}(2) \begin{bmatrix} x_f \\ y_f \\ z_f \end{bmatrix} = \mathbf{S}(1) \begin{bmatrix} \bar{x}_f + \frac{1}{2} \\ \bar{y}_f \\ z_f + \frac{1}{2} \end{bmatrix} = \begin{bmatrix} \bar{x}_f + \frac{1}{2} \\ \bar{y}_f \\ z_f + \frac{1}{2} \end{bmatrix}$$

$$\Longrightarrow \mathbf{S}(1)\mathbf{S}(2) = \mathbf{S}(2).$$

Clearly, $\mathbf{S}(1)\mathbf{S}(1) = \mathbf{S}(1)$, $\mathbf{S}(1)\mathbf{S}(2) = \mathbf{S}(2)\mathbf{S}(1) = \mathbf{S}(2)$, $\mathbf{S}(1)\mathbf{S}(3) = \mathbf{S}(3)\mathbf{S}(1) = \mathbf{S}(3)$, and $\mathbf{S}(1)\mathbf{S}(4) = \mathbf{S}(4)\mathbf{S}(1) = \mathbf{S}(4)$. Thus $\mathbf{S}(1) \equiv \mathbf{S}(E) \equiv E$.

ii. Inverse Rule:

$$\mathbf{S}(2)\mathbf{S}(2)\begin{bmatrix} x_f \\ y_f \\ z_f \end{bmatrix} = \mathbf{S}(2)\begin{bmatrix} \bar{x}_f + \frac{1}{2} \\ \bar{y}_f \\ z_f + \frac{1}{2} \end{bmatrix} = \begin{bmatrix} x_f - \frac{1}{2} + \frac{1}{2} \\ y_f \\ z_f + \frac{1}{2} + \frac{1}{2} \end{bmatrix} = \begin{bmatrix} x_f \\ y_f \\ z_f \end{bmatrix} + \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}.$$

Similarly,

$$\mathbf{S}(3)\mathbf{S}(3)\begin{bmatrix} x_f \\ y_f \\ z_f \end{bmatrix} = \begin{bmatrix} x_f \\ y_f \\ z_f \end{bmatrix} + \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} \quad \text{and} \quad \mathbf{S}(4)\mathbf{S}(4)\begin{bmatrix} x_f \\ y_f \\ z_f \end{bmatrix} = \begin{bmatrix} x_f \\ y_f \\ z_f \end{bmatrix} + \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}.$$

Translating each of these positions back to the original positions from their symmetry-equivalent locations in an adjacent unit cell renders each of the products effectively equal to the identity: $\mathbf{S}(1)\mathbf{S}(1) \equiv E$, $\mathbf{S}(2)\mathbf{S}(2) \equiv E$, $\mathbf{S}(3)\mathbf{S}(3) \equiv E$, and $\mathbf{S}(4)\mathbf{S}(4) \equiv E$. Ignoring symmetry-equivalent translations, every operation is its own inverse.

iii. Closure Rule:
In addition to the products above,

$$\begin{aligned} \mathbf{S}(3)\mathbf{S}(2)\begin{bmatrix} x_f \\ y_f \\ z_f \end{bmatrix} &= \mathbf{S}(3)\begin{bmatrix} \bar{x}_f + \frac{1}{2} \\ \bar{y}_f \\ z_f + \frac{1}{2} \end{bmatrix} = \begin{bmatrix} x_f - \frac{1}{2} \\ \bar{y}_f + \frac{1}{2} \\ \bar{z}_f - \frac{1}{2} + \frac{1}{2} \end{bmatrix} = \begin{bmatrix} x_f + \frac{1}{2} \\ \bar{y}_f + \frac{1}{2} \\ \bar{z}_f \end{bmatrix} \\ \mathbf{S}(2)\mathbf{S}(3)\begin{bmatrix} x_f \\ y_f \\ z_f \end{bmatrix} &= \mathbf{S}(2)\begin{bmatrix} \bar{x}_f \\ y_f + \frac{1}{2} \\ \bar{z}_f + \frac{1}{2} \end{bmatrix} = \begin{bmatrix} x_f + \frac{1}{2} \\ \bar{y}_f - \frac{1}{2} \\ \bar{z}_f + \frac{1}{2} + \frac{1}{2} \end{bmatrix} = \begin{bmatrix} x_f + \frac{1}{2} \\ \bar{y}_f + \frac{1}{2} \\ \bar{z}_f + 1 \end{bmatrix}. \end{aligned}$$

Translating the second product back to the originating unit cell by $[0\ 0\ \bar{1}\,]$ renders $\mathbf{S}(3)\mathbf{S}(2) \equiv \mathbf{S}(2)\mathbf{S}(3) \equiv \mathbf{S}(4)$. Similarly, $\mathbf{S}(2)\mathbf{S}(4) \equiv \mathbf{S}(4)\mathbf{S}(2) \equiv \mathbf{S}(3)$ and $\mathbf{S}(3)\mathbf{S}(4) \equiv \mathbf{S}(4)\mathbf{S}(3) \equiv \mathbf{S}(2)$. Provided that symmetry-equivalent translations are negated, every product of operations results in another operation.

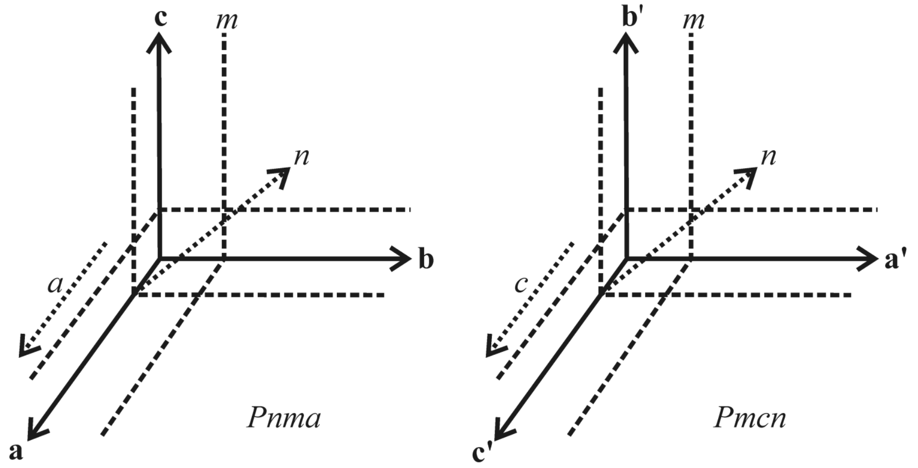
iv. Associativity:
$\mathbf{S}(3)\Big(\mathbf{S}(2)\mathbf{S}(4)\Big) \equiv \mathbf{S}(2)\mathbf{S}(2) \equiv E$ and $\Big(\mathbf{S}(3)\mathbf{S}(2)\Big)\mathbf{S}(4) \equiv \mathbf{S}(4)\mathbf{S}(4) \equiv E$, etc.
Note that every product in this particular "group" is commutative. A commutative group is known as an *Abelian group.*

10. Referring to Exercise 8 at the end of Chapter 1, the $CuSO_4$ crystal structure was reported to pack in the *Pnma* space group. This is space group No. 62 in the *International Tables for Crystallography.* Although it is more common to transform a unit cell in a non-standard setting into one in the standard setting (in this case *Pnma*), consider transforming the unit cell and its contents into the non-standard *Pmcn* unit cell. (a) Determine the cell parameters of the transformed unit cell and develop a matrix that will transform the fractional coordinates of the Cu, S, and O atoms from the *Pnma* unit cell to the *Pmcn* unit cell. (b) Look up the general and special positions in the *Pnma* unit cell and determine their locations in the *Pmcn* unit cell. (c) Determine the coordinates of the atoms in the asymmetric unit of the *Pmcn* unit cell. Are the contents of the cell consistent with $CuSO_4$ stoichiometry? (e) When the unit cell is transformed from *Pnma* to *Pmcn*, what happens to the indices

of reflections from each set of lattice planes in the crystal? (You may have to read ahead in Chapter 3 to answer this question).

Solution:

(a) Unit cell axes and glide/mirror planes for *Pnma* and *Pmcn*:



Thus $\mathbf{a}' = \mathbf{b}$, $\mathbf{b}' = \mathbf{c}$, and $\mathbf{c}' = \mathbf{a}$. Both unit cells are right-handed (no need to change signs of coordinates): $\mathbf{a} \times \mathbf{b} = \mathbf{c}$ and $\mathbf{a}' \times \mathbf{b}' = \mathbf{c}'$.
$a' = 6.89$Å, $b' = 4.83$Å $c' = 8.39$Å, $\alpha = 90.00^{\rm o}$, $\beta = 90.00^{\rm o}$ and $\gamma = 90.00^{\rm o}$.

To determine the transformation matrix write a general vector in both coordinate bases:

$$\begin{aligned}
\mathbf{v}_f &= x_f\,\mathbf{a} + y_f\,\mathbf{b} + z_f\,\mathbf{c} \\
&= x'_f\,\mathbf{a}' + y'_f\,\mathbf{b}' + z'_f\,\mathbf{c}' \\
&= x'_f\,\mathbf{b} + y'_f\,\mathbf{c} + z'_f\,\mathbf{a} \\
&= z'_f\,\mathbf{a} + x'_f\,\mathbf{b} + y'_f\,\mathbf{c}.
\end{aligned}$$

Thus $x'_f = y_f$, $y'_f = z_f$, $z'_f = x_f$, and

$$\begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} x_f \\ y_f \\ z_f \end{bmatrix} = \begin{bmatrix} y_f \\ z_f \\ x_f \end{bmatrix} = \begin{bmatrix} x'_f \\ y'_f \\ z'_f \end{bmatrix}.$$

(b) The matrix in (a) will transform any coordinates in the *Pnma* unit cell into coordinates in the *Pmcn* unit cell. This includes those of the general and special positions:

$$\begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} \bar{x}_f + \frac{1}{2} \\ \bar{y}_f \\ z_f + \frac{1}{2} \end{bmatrix} = \begin{bmatrix} \bar{y}_f \\ z_f + \frac{1}{2} \\ \bar{x}_f + \frac{1}{2} \end{bmatrix} = \begin{bmatrix} x'_f \\ y'_f + \frac{1}{2} \\ \bar{z}'_f + \frac{1}{2} \end{bmatrix}$$

$$\begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} \bar{x}_f \\ y_f + \frac{1}{2} \\ \bar{z}_f \end{bmatrix} = \begin{bmatrix} y_f + \frac{1}{2} \\ \bar{z}_f \\ \bar{x}_f \end{bmatrix} = \begin{bmatrix} x'_f + \frac{1}{2} \\ \bar{y}'_f \\ \bar{z}'_f \end{bmatrix}$$

$$\begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} x_f + \frac{1}{2} \\ \bar{y}_f + \frac{1}{2} \\ \bar{z}_f \end{bmatrix} = \begin{bmatrix} \bar{y}_f + \frac{1}{2} \\ \bar{z}_f + \frac{1}{2} \\ x_f + \frac{1}{2} \end{bmatrix} = \begin{bmatrix} \bar{x}'_f + \frac{1}{2} \\ \bar{y}'_f + \frac{1}{2} \\ z'_f + \frac{1}{2} \end{bmatrix}.$$

These three general positions, along with $[x'_f \ y'_f \ z'_f]$ are related to the other four general positions by inversion operations (the inversion centers remain in their same positions), and are obtained simply by negating the coordinates. The multiplicity of the general position is 8. The special positions each have a multiplicity of 4, and include two positions on each mirror plane – and the inversion centers characteristic of a centrosymmetric unit cell. In the *Pnma* unit cell the mirror planes are parallel to the *ac* plane and intersect the *b* axis at $[0 \ \frac{1}{4} \ 0]$ and $[0 \ \frac{3}{4} \ 0]$. The special positions are denoted by $x \ \frac{1}{4} \ z$, etc. These positions transform to

$$\begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} x_f \\ \frac{1}{4} \\ z_f \end{bmatrix} = \begin{bmatrix} \frac{1}{4} \\ z_f \\ x_f \end{bmatrix} = \begin{bmatrix} \frac{1}{4} \\ y'_f \\ z'_f \end{bmatrix}.$$

The special position in the *Pmcn* unit cell is on a mirror plane that intersects the *a* axis at $[0 \ \frac{1}{4} \ 0]$ and is parallel to the *bc* plane, as expected. The inversion centers transform as

$$\begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ \frac{1}{2} \end{bmatrix} = \begin{bmatrix} 0 \\ \frac{1}{2} \\ 0 \end{bmatrix}, \quad \text{etc.}$$

An inversion center bisecting **c** in *Pnma* is now bisecting $\mathbf{b}'$ in *Pmcn*, again as expected.

(c) Location of the asymmetric unit in the *Pmcn* unit cell:

atom	x_f	y_f	z_f	atom	x_f	y_f	z_f
Cu1	0.000	0.000	0.000	O2	0.250	0.439	0.375
S1	0.250	0.445	0.185	O3	0.069	0.307	0.129
O1	0.250	0.755	0.141				

Cu1 is on a special position – an inversion center at the origin with a multiplicity of 4. S1, O1, and O2 are all on special positions, located on the mirror planes, each with a multiplicity of 4. O3 is in a general position with a multiplicity of 8. There are therefore 4 Cu atoms, 4 S atoms, and 16 O atoms in the unit cell – four formula units of $CuSO_4$ in the unit cell.

(d) The indices of the reflections are the indices of the *hkl* planes from which the reflections are observed when diffraction occurs. With this knowledge it is possible to solve the problem here, although a knowledge of diffraction and the reciprocal lattice will make the solution here more obvious. Recall that the indices of the planes, h, k, l, were the integer number of equal segments that each set of planes divide the *a*, *b* and *c* axes into. The first of these sets of parallel planes intersects the origin, and the second intersects a, b and c at $[1/h\ 0\ 0]$, $[0\ 1/k\ 0]$, and $[0\ 0\ 1/l]$, respectively. These fractional coordinates will transform just as any fractional coordinates do. This is made simpler if we create the vector $[1/h\ 1/k\ 1/l]$ and transform it:

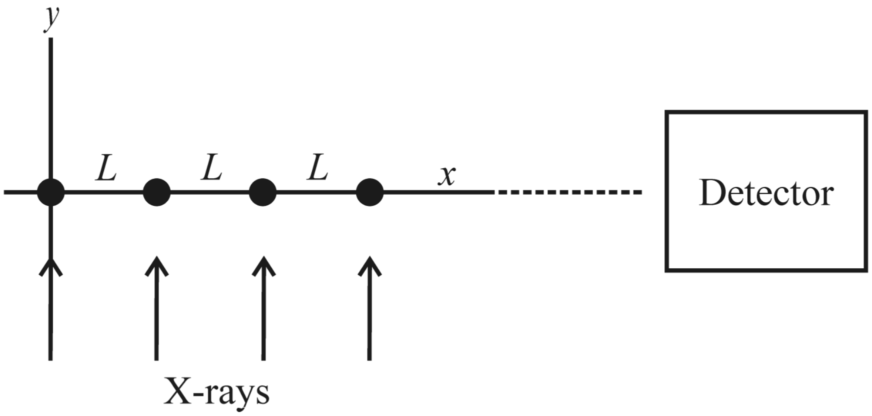
$$\begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} 1/h \\ 1/k \\ 1/l \end{bmatrix} = \begin{bmatrix} 1/k \\ 1/l \\ 1/h \end{bmatrix} = \begin{bmatrix} 1/h' \\ 1/k' \\ 1/l' \end{bmatrix}.$$

Thus $1/h' = 1/k$, etc. and $h' = k$, $k' = l$ and $l' = h$; the vector $[h\ k\ l]$ transforms just like $[x_f\ y_f\ z_f]$. Vectors with components that are indices will take on special significance in Chapter 3.

Chapter 3

Crystal Diffraction: Theory

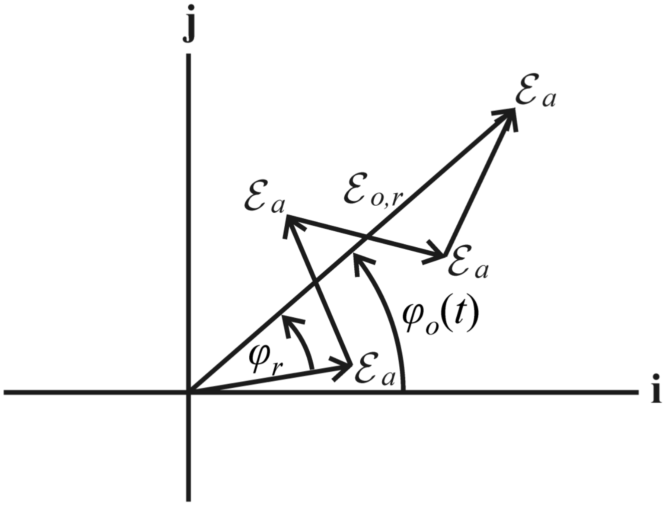
1. Consider four equally spaced hydrogen atoms, arranged in a line along the x axis of a Cartesian coordinate system:



A monochromatic, in-phase X-ray beam with $\lambda = 1.500\text{Å}$ is directed parallel to the y axis; the atom at the origin is selected as the scattering (phase) reference. A wave detector is placed at a distance of one meter from the origin. The maximum electric field due to each atom observed at the detector (measured in the absence of the other atoms) is $\mathcal{E}_a$. (a) Determine general formulae for the maximum amplitude of the resultant wave observed at the detector, $\mathcal{E}_{o,r}$, and its relative phase, φ_r, with respect to a wave scattered from the origin. (b) Determine $\mathcal{E}_{o,r}$ when $L = 1.125\text{Å}$, $L = 2.250\text{Å}$, and $L = 4.500\text{Å}$. Note that since the frequencies of all of the waves and the resultant wave are the same, all of the wave vectors rotate together in time. Thus $\mathcal{E}_{o,r}$ and φ_r remain constant, and are conveniently evaluated at $t = 0$.

Solution:

(a) The general case ($\nu = c/\lambda$):



$$\mathcal{E}_i(t) = \mathcal{E}_a \cos(2\pi\nu\, t) + \mathcal{E}_a \cos\left(2\pi\nu\, \left(t + \frac{L}{c}\right)\right) + \mathcal{E}_a \cos\left(2\pi\nu\, \left(t + \frac{2L}{c}\right)\right)$$

$$+ \mathcal{E}_a \cos\left(2\pi\nu\, \left(t + \frac{3L}{c}\right)\right) = \mathcal{E}_a \sum_{k=0}^{3} \cos\left(2\pi\left(t + \frac{kL}{\lambda}\right)\right)$$

$$\mathcal{E}_j(t) = \mathcal{E}_a \sum_{k=0}^{3} \sin\left(2\pi\left(t + \frac{kL}{\lambda}\right)\right)$$

$$\mathcal{E}_{o,r} = (\mathcal{E}_i(t)^2 + \mathcal{E}_j(t)^2)^{1/2} \qquad \varphi_o(t) = \arctan\frac{\mathcal{E}_j(t)}{\mathcal{E}_i(t)}.$$

At $t = 0$ the scattering from the atom at the origin has $\cos(2\pi\nu\, t) = 1$ and $\sin(2\pi\nu\, t) = 0$; its wave vector is coincident with the x axis. Thus $\varphi_r = \varphi_o(0)$, and

$$\mathcal{E}_i(0) = \mathcal{E}_a \sum_{k=0}^{3} \cos\left(2\pi\left(\frac{kL}{\lambda}\right)\right) \qquad \mathcal{E}_j(0) = \mathcal{E}_a \sum_{k=0}^{3} \sin\left(2\pi\left(\frac{kL}{\lambda}\right)\right)$$

$$\mathcal{E}_{o,r} = (\mathcal{E}_i(0)^2 + \mathcal{E}_j(0)^2)^{1/2} \qquad \varphi_r = \arctan\frac{\mathcal{E}_j(0)}{\mathcal{E}_i(0)}.$$

(b) $L = 1.125\text{Å} = 3\lambda/4$:

$$\mathcal{E}_i(0) = \mathcal{E}_a \sum_{k=0}^{3} \cos\left(\pi\left(\frac{3k}{2}\right)\right) = (1+0-1+0)\mathcal{E}_a = 0$$

$$\mathcal{E}_j(0) = \mathcal{E}_a \sum_{k=0}^{3} \sin\left(\pi\left(\frac{3k}{2}\right)\right) = (0-1+0+1)\mathcal{E}_a = 0$$

$$\mathcal{E}_{o,r} = 0.$$

$L = 2.250\text{Å} = 3\lambda/2$:

$$\mathcal{E}_i(0) = \mathcal{E}_a \sum_{k=0}^{3} \cos(\pi 3k) = (1-1+1-1)\mathcal{E}_a = 0$$

$$\mathcal{E}_i(0) = \mathcal{E}_a \sum_{k=0}^{3} \sin(\pi 3k) = (0+0+0+0)\mathcal{E}_a = 0$$

$$\mathcal{E}_{o,r} = 0.$$

$L = 4.500\text{Å} = 3\lambda$:

$$\mathcal{E}_i(0) = \mathcal{E}_a \sum_{k=0}^{3} \cos(\pi 6k) = (1+1+1+1)\mathcal{E}_a = 4\mathcal{E}_a$$

$$\mathcal{E}_i(0) = \mathcal{E}_a \sum_{k=0}^{3} \sin(\pi 6k) = (0+0+0+0)\mathcal{E}_a = 0$$

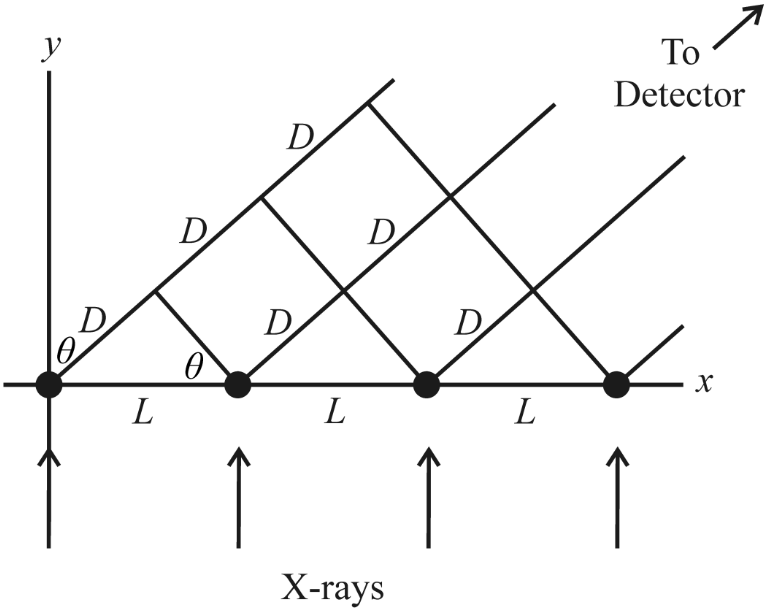
$$\mathcal{E}_{o,r} = 4\mathcal{E}_a;$$

the atoms are separated by an integral number of wavelengths and the waves scattered from all four atoms are in phase.

2. The detector in Exercise 1 can be rotated in the xy plane so that its distance from the origin remains constant. Because the distances between the atoms are orders of magnitude different from the distance to the detector, the waves emanating from each atom can be considered to be traveling along parallel vectors toward a point on the detector in any direction (See Fig. 3.8). (a) Determine general formulae for the maximum amplitude of the resultant wave observed at the detector, $\mathcal{E}_{o,r}$, and its relative phase, φ_r. These formulae will be similar to those derived in Exercise 1, but will contain the detector angle, θ, between a vector to the center of the detector and the y axis. (b) Determine the smallest non-zero angle through which the detector must be rotated to observe a maximum intensity at the detector (a diffraction maximum) and $\mathcal{E}_{o,r}$ and φ_r for this angle for $L = 1.125\text{Å}$, $L = 2.250\text{Å}$, and $L = 4.500\text{Å}$. (c) Determine the smallest angle through which the detector must be rotated to observe a minimum intensity at the detector (a diffraction minimum) and $\mathcal{E}_{o,r}$ and φ_r for this angle for $L = 1.125\text{Å}$, $L = 2.250\text{Å}$, and $L = 4.500\text{Å}$.

Solution:

(a) Equal vectors of length L between atoms result in equal projections on the parallel wave vectors, each of length D. The differences in distances to the detector for waves scattered from each atom now depends on $D = L\cos(90^{\circ} - \theta) = L\sin\theta$.



Referring to the solution for Exercise 1,

$$\mathcal{E}_i(t) = \mathcal{E}_a \sum_{k=0}^{3} \cos\left(2\pi\left(t + \frac{kD}{\lambda}\right)\right) \equiv \mathcal{E}_a \sum_{k=0}^{3} \cos\left(2\pi\left(t + \frac{kL\sin\theta}{\lambda}\right)\right)$$

$$\mathcal{E}_j(t) = \mathcal{E}_a \sum_{k=0}^{3} \sin\left(2\pi\left(t + \frac{kD}{\lambda}\right)\right) \equiv \mathcal{E}_a \sum_{k=0}^{3} \sin\left(2\pi\left(t + \frac{kL\sin\theta}{\lambda}\right)\right)$$

$$\mathcal{E}_{o,r} = (\mathcal{E}_i(t)^2 + \mathcal{E}_j(t)^2)^{1/2} \qquad \varphi_o(t) = \arctan\frac{\mathcal{E}_j(t)}{\mathcal{E}_i(t)}.$$

(b) An intensity maximum will be observed at the detector when the angle is set so that the waves emanating from each atom *in the direction of the path to the detector* are all in phase, separated by an integer number of wavelengths, i.e., $D = n\lambda$. The first maximum will be observed at

$D = \lambda$. Evaluating the superposition of waves at $t = 0$ gives

$$\mathcal{E}_i(0) = \mathcal{E}_a \sum_{k=0}^{3} \cos\left(2\pi\left(\frac{k\lambda}{\lambda}\right)\right) = \mathcal{E}_a \sum_{k=0}^{3} \cos 2k\pi = 4\,\mathcal{E}_a$$

$$\mathcal{E}_j(0) = \mathcal{E}_a \sum_{k=0}^{3} \sin\left(2\pi\left(\frac{k\lambda}{\lambda}\right)\right) = \mathcal{E}_a \sum_{k=0}^{3} \sin 2k\pi = 0$$

$$\mathcal{E}_{o,r} = 4\,\mathcal{E}_a \qquad\qquad \varphi_r = \arctan\frac{\mathcal{E}_j(0)}{\mathcal{E}_i(0)} = 0.$$

The phase of the resultant wave is the same as the phases (all identical) of the waves scattering from each atom.

For $D = \lambda$, $\sin\theta = D/L = \lambda/L$. For $L = 1.125\text{Å} = 3\lambda/4$, $\sin\theta = 4/3$, which is impossible. There are no diffraction maxima for $L < \lambda$. For $L = 2.250\text{Å} = 3\lambda/2$, $\sin\theta = 2/3$ and $\theta = 41.8^{\circ}$. For $L = 4.450\text{Å} = 3\lambda$, $\sin\theta = 1/3$ and $\theta = 19.5^{\circ}$.

(c) An intensity minimum will be observed at the detector when the angle is set so that the waves emanating from each atom *in the direction of the path to the detector* are 180° out of phase with those emanating from an adjacent atom (we can consider superpositioning the waves in pairs, then superpositioning the resultant from each pair). This will occur when the waves differ by a half integral number of wavelengths. The first minimum will be observed at $D = \lambda/2$. Evaluating the superposition of waves at $t = 0$ gives

$$\mathcal{E}_i(0) = \mathcal{E}_a \sum_{k=0}^{3} \cos\left(2\pi\left(\frac{k\lambda}{2\lambda}\right)\right) = \mathcal{E}_a \sum_{k=0}^{3} \cos k\pi = 0$$

$$\mathcal{E}_j(0) = \mathcal{E}_a \sum_{k=0}^{3} \sin\left(2\pi\left(\frac{k\lambda}{2\lambda}\right)\right) = \mathcal{E}_a \sum_{k=0}^{3} \sin k\pi = 0$$

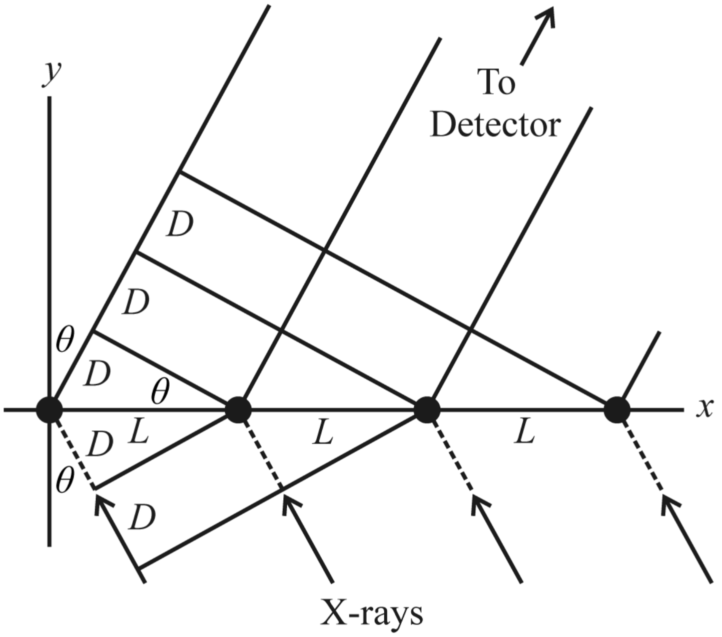
$$\mathcal{E}_{o,r} = 0.$$

For $D = \lambda/2$, $\sin\theta = D/L = \lambda/(2L)$. For $L = 1.125\text{Å} = 3\lambda/4$, $\sin\theta = 2/3$, and $\theta = 41.8^{\circ}$. For $L = 2.250\text{Å} = 3\lambda/2$, $\sin\theta = 1/3$ and $\theta = 19.5^{\circ}$. For $L = 4.450\text{Å} = 3\lambda$, $\sin\theta = 1/6$ and $\theta = 9.6^{\circ}$.

3. The detector and the X-ray source in Exercise 2 are modified so that vectors in the direction of the X-ray beam and vectors toward the detector both make equal angles with the y axis (Fig. 3.11). (a) Determine general formulae for the maximum amplitude of the resultant wave observed at the detector, $\mathcal{E}_{o,r}$, and its relative phase, φ_r. (b) Determine the smallest angle through which the detector must be rotated to observe a maximum intensity at the detector (a diffraction maximum) and $\mathcal{E}_{o,r}$ and φ_r for this angle for $L = 1.125\text{Å}$, $L = 2.250\text{Å}$, and $L = 4.500\text{Å}$. (c) Determine the smallest angle through which the detector must be rotated to observe a minimum intensity at the detector (a diffraction minimum) and $\mathcal{E}_{o,r}$ and φ_r for this angle for $L = 1.125\text{Å}$, $L = 2.250\text{Å}$, and $L = 4.500\text{Å}$.

Solution:

(a) As in Exercise 2, equal vectors of length L between atoms results in equal projections on the parallel wave vectors, each of length D. The wave scattered from each atom travels an additional distance of $2D$ in comparison with an atom to its right, where $D = L\sin\theta$:



Referring to the solution for Exercise 2,

$$\mathcal{E}_i(t) = \mathcal{E}_a \sum_{k=0}^{3} \cos\left(2\pi\left(t + \frac{k(2D)}{\lambda}\right)\right) \equiv \mathcal{E}_a \sum_{k=0}^{3} \cos\left(2\pi\left(t + \frac{kL2\sin\theta}{\lambda}\right)\right)$$

$$\mathcal{E}_j(t) = \mathcal{E}_a \sum_{k=0}^{3} \sin\left(2\pi\left(t + \frac{k(2D)}{\lambda}\right)\right) \equiv \mathcal{E}_a \sum_{k=0}^{3} \sin\left(2\pi\left(t + \frac{kL2\sin\theta}{\lambda}\right)\right)$$

$$\mathcal{E}_{o,r} = (\mathcal{E}_i(t)^2 + \mathcal{E}_j(t)^2)^{1/2} \qquad \varphi_o(t) = \arctan\frac{\mathcal{E}_j(t)}{\mathcal{E}_i(t)}.$$

(b) The first maximum will be observed at $D = \lambda/2$, since $2D = \lambda$. Evaluating the superposition of waves at $t = 0$ gives

$$\mathcal{E}_i(0) = \mathcal{E}_a \sum_{k=0}^{3} \cos\left(2\pi\left(\frac{k2\lambda}{2\lambda}\right)\right) = \mathcal{E}_a \sum_{k=0}^{3} \cos 2k\pi = 4\,\mathcal{E}_a$$

$$\mathcal{E}_j(0) = \mathcal{E}_a \sum_{k=0}^{3} \sin\left(2\pi\left(\frac{k2\lambda}{2\lambda}\right)\right) = \mathcal{E}_a \sum_{k=0}^{3} \sin 2k\pi = 0$$

$$\mathcal{E}_{o,r} = 4\,\mathcal{E}_a \qquad \varphi_r = \arctan\frac{\mathcal{E}_j(0)}{\mathcal{E}_i(0)} = 0.$$

Just as in Exercise 2, the phase of the resultant wave is the same as the phases (all identical) of the waves scattering from each atom.

For $D = \lambda/2$, $\sin\theta = D/L = \lambda/2L$. For $L = 1.125\text{Å} = 3\lambda/4$, $\sin\theta = 2/3$, and $\theta = 41.8^{\circ}$. For $L = 2.250\text{Å} = 3\lambda/2$, $\sin\theta = 1/3$ and $\theta = 19.5^{\circ}$. For $L = 4.450\text{Å} = 3\lambda$, $\sin\theta = 1/6$ and $\theta = 9.6^{\circ}$.

The first minimum will be observed at $D = \lambda/4$, since $2D = \lambda/2$. Evaluating the superposition of waves at $t = 0$ gives

$$\begin{aligned}
\mathcal{E}_i(0) &= \mathcal{E}_a \sum_{k=0}^{3} \cos\left(2\pi\left(\frac{k2\lambda}{4\lambda}\right)\right) = \mathcal{E}_a \sum_{k=0}^{3} \cos k\pi = 0 \\
\mathcal{E}_j(0) &= \mathcal{E}_a \sum_{k=0}^{3} \sin\left(2\pi\left(\frac{k2\lambda}{4\lambda}\right)\right) = \mathcal{E}_a \sum_{k=0}^{3} \sin k\pi = 0 \\
\mathcal{E}_{o,r} &= 0.
\end{aligned}$$

For $D = \lambda/4$, $\sin\theta = D/L = \lambda/(4L)$. For $L = 1.125\text{Å} = 3\lambda/4$, $\sin\theta = 1/3$, and $\theta = 19.5^{\circ}$. For $L = 2.250\text{Å} = 3\lambda/2$, $\sin\theta = 1/6$ and $\theta = 9.6^{\circ}$. For $L = 4.450\text{Å} = 3\lambda$, $\sin\theta = 1/12$ and $\theta = 4.8^{\circ}$.

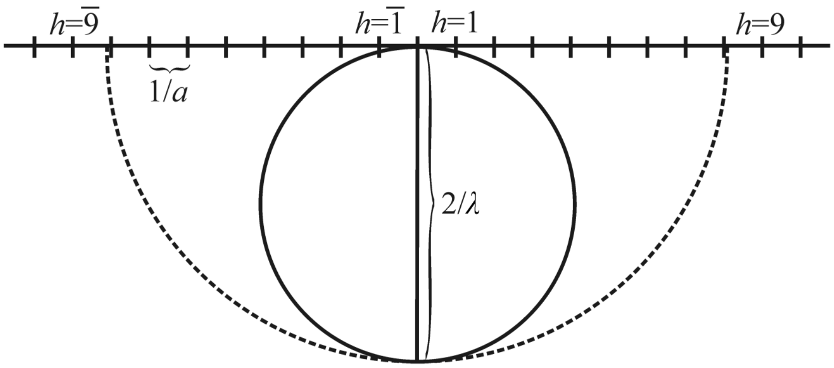
4. X-rays for crystal structure determination are commonly generated by bombarding specific metals with high-energy electrons. The metals most often used are copper and molybdenum, which emit average wavelengths of 1.5418 Å and 0.7107 Å, respectively, after passing through a monochromator. Referring to Fig. 3.15, with the area detector (screen) at a distance of 0.1 meters from the crystal, consider a one-dimensional crystal lattice with $a = 10$ Å – typical of a small-molecule crystal structure. The spots on the screen are finite in size – with widths on the order of a millimeter. To measure the intensity of a single spot, it must not overlap with adjacent spots. (a) Determine the number of diffraction maxima (spots on the screen) that it is possible to observe for each wavelength. (b) Determine the distance between the spots on the screen for $h = 1$ and $h = 2$. (c) Repeat (a) for a unit cell with $a = 100$ Å, typical of a macromolecular crystal structure. (d) Repeat (b) for the 100 Å unit cell.

Solution:

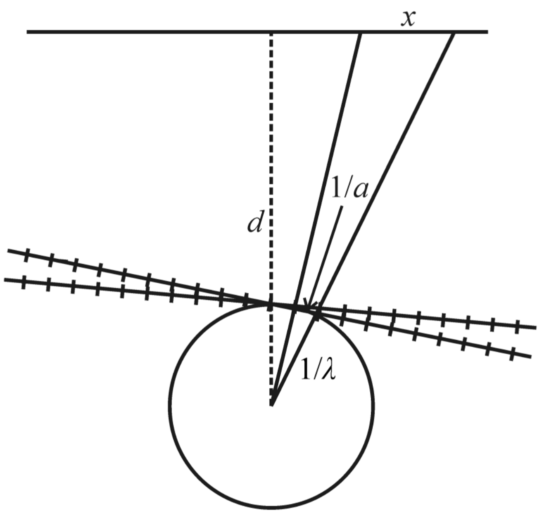
(a) As the crystal is rotated, a reciprocal lattice vector with index h and length h= $|h|/a$ will fail to cross the circle of reflection if h is greater than $2/\lambda$. For a reflection to be observed, $|h| \leq 2a/\lambda$:

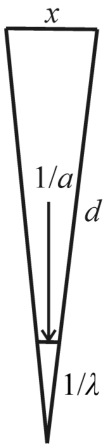
$$\begin{aligned}
&\text{Cu}: \quad |h| \leq \frac{20\text{Å}}{1.5418\text{Å}} \leq 12.97 \Longrightarrow -12 \leq h \leq 12. \qquad \text{24 reflections.} \\
&\text{Mo}: \quad |h| \leq \frac{20\text{Å}}{0.7107\text{Å}} \leq 28.14 \Longrightarrow -28 \leq h \leq 28. \qquad \text{56 reflections.}
\end{aligned}$$

(b) The distance from the crystal to the screen, d, is orders of magnitude greater than the distances between lattice points, and can be considered essentially constant as the reciprocal lattice is rotated through the circle of reflection. Thus the relationship between adjacent points in the



reciprocal lattice and the images on the screen can be approximated by two similar isosceles triangles:





$$\frac{x}{d} = \frac{1/a}{1/\lambda} = \frac{\lambda}{a}$$

$$\text{Cu}: \quad \frac{x}{0.1\text{m}} = \frac{1.5418\text{Å}}{10\text{Å}} \Longrightarrow x = 0.015\text{m} = 15\text{mm}$$

$$\text{Mo}: \quad \frac{x}{0.1\text{m}} = \frac{0.7107\text{Å}}{10\text{Å}} \Longrightarrow x = 0.007\text{m} = 7\text{mm}.$$

(c)

$$\text{Cu}: \quad |h| \leq \frac{200\text{Å}}{1.5418\text{Å}} \leq 129.71 \Longrightarrow -129 \leq h \leq 129. \qquad \text{258 reflections.}$$

$$\text{Mo}: \quad |h| \leq \frac{200\text{Å}}{0.7107\text{Å}} \leq 281.41 \Longrightarrow -281 \leq h \leq 281. \qquad \text{562 reflections.}$$

(d)

$$\begin{aligned}
\text{Cu}: &\quad \frac{x}{0.1\text{m}} = \frac{1.5418\text{Å}}{100\text{Å}} \Longrightarrow x = 0.0015\text{m} = 1.5\text{mm} \\
\text{Mo}: &\quad \frac{x}{0.1\text{m}} = \frac{0.7107\text{Å}}{100\text{Å}} \Longrightarrow x = 0.0007\text{m} = 0.7\text{mm}.
\end{aligned}$$

5. In Chapter 1 an expression for the unit cell volume in terms of the unit cell parameters was derived for a general (triclinic) unit cell. In Chapter 3 relationships between the direct and reciprocal unit cell parameters were derived for the general case. (a) Derive explicit expressions for the unit cell volumes of monoclinic, orthorhombic, tetragonal, cubic, trigonal/hexagonal, and rhombohedral unit cells. (b) Derive expressions for the direct↔reciprocal unit cell relationships for each of the unit cell types in part (a).

Solution:

(a) The volume expressions are all derived from the triclinic formula:

$$\begin{aligned}
&\text{Triclinic}: \quad V = abc(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)^{1/2} \\
&\text{Monoclinic}: \quad V = abc(1 - 0 - \cos^2\beta - 0 + 2(0))^{1/2} = abc(1 - \cos^2\beta)^{1/2} \\
&\qquad\qquad\qquad = abc\sin\beta \\
&\text{Orthorhombic}: \quad V = abc(1 - 0 - 0 - 0 + 2(0))^{1/2} = abc \\
&\text{Tetragonal}: \quad V = aac(1 - 0 - 0 - 0 + 2(0))^{1/2} = a^2c \\
&\text{Cubic}: \quad V = aaa(1 - 0 - 0 - 0 + 2(0))^{1/2} = a^3 \\
&\text{Trigonal/Hexagonal}: \quad V = aac(1 - \cos^2\gamma)^{1/2} = a^2c\sin\gamma = a^2c\frac{\sqrt{3}}{2} \\
&\text{Rhombohedral}: \quad V = aaa(1 - \cos^2\alpha - \cos^2\alpha - \cos^2\alpha + 2\cos\alpha\cos\alpha\cos\alpha)^{1/2} \\
&\qquad\qquad\qquad = a^3(2\cos^3\alpha - 3\cos^2\alpha + 1)^{1/2}.
\end{aligned}$$

(b) The direct lattice formulas are obtained from the reciprocal lattice formulas below by adding asterisks to the parameters without an asterisk, and removing it from those that do:

Monoclinic :

$$a^* = \frac{bc\sin\alpha}{abc\sin\beta} = \frac{1}{a\sin\beta} \qquad b^* = \frac{ac\sin\beta}{abc\sin\beta} = \frac{1}{b} \qquad c^* = \frac{ab\sin\gamma}{abc\sin\beta} = \frac{1}{c\sin\beta}$$

$$\cos\alpha^* = \frac{0-0}{1} = 0 \qquad \cos\beta^* = \frac{0-\cos\beta}{\sin\alpha\sin\gamma} = -\cos\beta \qquad \cos\gamma^* = \frac{0-0}{1} = 0$$

Orthorhombic :

$$a^* = \frac{bc}{abc} = \frac{1}{a} \qquad b^* = \frac{ac}{abc} = \frac{1}{b} \qquad c^* = \frac{ab}{abc} = \frac{1}{c}$$

$$\cos\alpha^* = \frac{0-0}{1} = 0 \qquad \cos\beta^* = \frac{0-0}{1} = 0 \qquad \cos\gamma^* = \frac{0-0}{1} = 0$$

Tetragonal :

$$a^* = \frac{bc}{abc} = \frac{1}{a} \qquad c^* = \frac{ab}{abc} = \frac{1}{c} \qquad \cos\alpha^* = \cos\beta^* = \cos\gamma^* = 0$$

Cubic :

$$a^* = \frac{bc}{abc} = \frac{1}{a} \qquad \cos\alpha^* = \cos\beta^* = \cos\gamma^* = 0$$

Trigonal/Hexagonal ($\alpha = \beta = 90^o,\ \gamma = 120^o$) :

$$a^* = \frac{ac\sin\alpha}{a^2 c\sin\gamma} = \frac{2}{a\sqrt{3}} \qquad c^* = \frac{a^2\sin\gamma}{a^2 c\sin\gamma} = \frac{1}{c}$$

$$\cos\alpha^* = \cos\beta^* = 0 \qquad \cos\gamma^* = \frac{0 - \cos\gamma}{\sin\alpha\sin\beta} = -\cos\gamma = -\frac{1}{2}$$

Rhombohedral (a = b = c, $\alpha = \beta = \gamma$) :

$$a^* = \frac{aa\sin\alpha}{a^3(2\cos^3\alpha - 3\cos^2\alpha + 1)^{1/2}} = \frac{\sin\alpha}{a(2\cos^3\alpha - 3\cos^2\alpha + 1)^{1/2}}$$

$$\cos\alpha^* = \frac{\cos^2\alpha - \cos\alpha}{\sin^2\alpha}.$$

6. In Chapter 1 the **B** matrix was derived to transform a direct lattice vector, $[x_f\ y_f\ z_f]$, into Cartesian coordinates, $[x_c\ y_c\ z_c]$. Using identical arguments (see Fig. 4.14), a vector in reciprocal fractional coordinates, $[x^*_f\ y^*_f\ z^*_f]$, can be transformed into a vector in reciprocal Cartesian coordinates, $[x^*_c\ y^*_c\ z^*_c]$ by the $\mathbf{B}^*$ matrix for the structure. (a) Using the cell parameters for the mercaptopyridine unit cell in Sec. 1.5.3, determine the reciprocal cell parameters and the $\mathbf{B}^*$ matrix for the structure. (b) Determine the distance between the planes with $(h\ k\ l) = (1\ 2\ 3)$ in the mercaptopyridine lattice. (c) Determine the distance between the planes with $(h\ k\ l) = (4\ 5\ 6)$. (d) Calculate the Bragg diffraction angles for the reflections from both sets of planes for copper and molybdenum radiation (the wavelengths are given in Exercise 4).

Solution:

(a) Monoclinic unit cell with $a = 6.112$ Å, $b = 6.326$ Å, $c = 14.314$ Å, $\beta = 101.53^o$, $V = 542.3$ Å^3. From the monoclinic formula in the solution for Exercise 5, $a^* = 0.1670$ Å^{-1}, $b^* = 0.1581$ Å^{-1}, $c^* = 0.0713$ Å^{-1}, $\alpha^* = 90.00^o$, $\beta^* = 78.47^o$, $\gamma^* = 90.00^o$, and $V^* = 1.844 \times 10^{-3}$ Å^{-3}.

$$\mathbf{B}^* = \begin{bmatrix} a^* & b^*\cos\gamma^* & c^*\cos\beta^* \\ 0 & b^*\sin\gamma^* & \frac{c^*(\cos\alpha^* - \cos\beta^*\cos\gamma^*)}{\sin\gamma^*} \\ 0 & 0 & \frac{V^*}{a^* b^* sin\gamma^*} \end{bmatrix} = \begin{bmatrix} 0.1670 & 0.0000 & 0.0143 \\ 0.0000 & 0.1581 & 0.0000 \\ 0.0000 & 0.0000 & 0.0699 \end{bmatrix}.$$

(b) $\mathbf{h}_{123} = [x^*_f\ y^*_f\ z^*_f] = [1\ 2\ 3]$:

$$\mathbf{B}^* \begin{bmatrix} 1 \\ 2 \\ 3 \end{bmatrix} = \begin{bmatrix} 0.2099 \\ 0.3162 \\ 0.2907 \end{bmatrix} = \begin{bmatrix} x^*_c \\ y^*_c \\ z^*_c \end{bmatrix}$$

$$\mathrm{h}_{123} = (x_c^2 + y_c^2 + z_c^2)^{1/2} = 0.4336\ \text{Å}^{-1}$$

$$d_{123} = \frac{1}{\mathrm{h}_{123}} = 2.306\ \text{Å}.$$

(c) $\mathbf{h}_{456} = [x_f^* \; y_f^* \; z_f^*] = [4\ 5\ 6]$:

$$\mathbf{B}^* \begin{bmatrix} 4 \\ 5 \\ 6 \end{bmatrix} = \begin{bmatrix} 0.7358 \\ 0.7905 \\ 0.4194 \end{bmatrix} = \begin{bmatrix} x_c^* \\ y_c^* \\ z_c^* \end{bmatrix}$$

$$\mathrm{h}_{456} = (x_c^2 + y_c^2 + z_c^2)^{1/2} = 1.1585\ \text{Å}^{-1}$$

$$d_{456} = \frac{1}{\mathrm{h}_{456}} = 0.8631\ \text{Å}.$$

(d) $\sin\theta_{hkl} = \lambda/(2d_{hkl}) = \lambda\,\mathrm{h}_{hkl}/2$:

$$\sin\theta_{123}(\mathrm{Cu}) = \frac{1.5418\ \text{Å} \times 0.4336\text{Å}^{-1}}{2} = 0.334 \qquad \theta_{123} = 19.51^{\mathrm{o}}$$

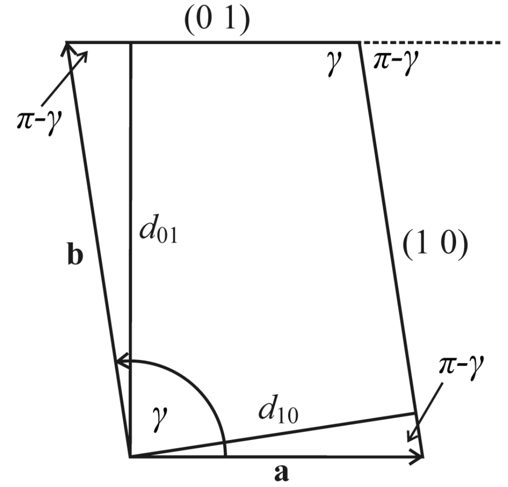
$$\sin\theta_{123}(\mathrm{Mo}) = \frac{0.7107\ \text{Å} \times 0.4336\text{Å}^{-1}}{2} = 0.154 \qquad \theta_{123} = 8.86^{\mathrm{o}}$$

$$\sin\theta_{456}(\mathrm{Cu}) = \frac{1.5418\ \text{Å} \times 0.8631\text{Å}^{-1}}{2} = 0.665 \qquad \theta_{456} = 41.71^{\mathrm{o}}$$

$$\sin\theta_{456}(\mathrm{Mo}) = \frac{0.7107\ \text{Å} \times 0.8631\text{Å}^{-1}}{2} = 0.307 \qquad \theta_{456} = 17.86^{\mathrm{o}}.$$

7. The hypothetical two-dimensional carbon monoxide structure modeled in Fig. 3.33 has $a = 4.855$ Å, $b = 6.953$ Å, and $\gamma = 98.8^{\mathrm{o}}$. (a) Referring to Fig. 3.20, determine expressions for the two-dimensional reciprocal cell parameters — a^*, b^*, and γ^*. (b) Adopting the convention that the a and a^* axes are coincident with the the unit vector $\mathbf{i}$ in their respective orthonormal coordinate systems, derive the $\mathbf{B}$ and $\mathbf{B}^*$ matrices that convert vectors in direct and reciprocal fractional coordinates to Cartesian coordinates. (c) Determine a^*, b^*, and γ^* for the CO unit cell. (d) Determine the distances between the (1 2) and (2 3) lines in the two-dimensional lattice.

Solution:



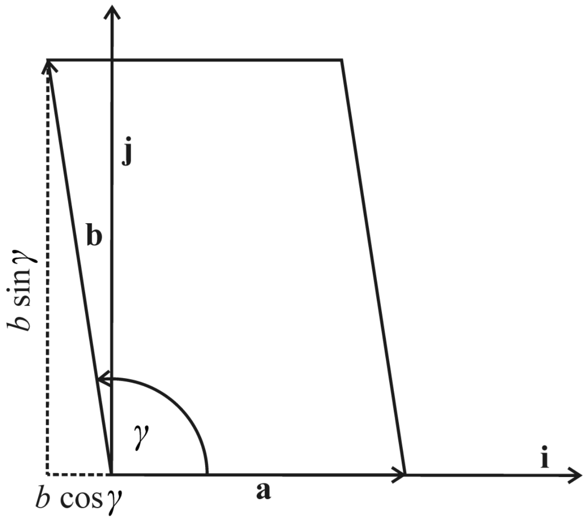
(a) $\mathbf{a}^* = \mathbf{h}_{10} \Rightarrow a^* = \mathrm{h}_{10} = 1/d_{10}$, $\mathbf{b}^* = \mathbf{h}_{01} \Rightarrow b^* = \mathrm{h}_{01} = 1/d_{01}$, and $\sin\gamma^* = (1/a)/a^* = 1/(aa^*)$.

$$\begin{aligned}
\sin(\pi-\gamma) &= \sin\gamma = \frac{d_{10}}{a} = \frac{1}{\mathrm{h}_{10}a} = \frac{1}{a^*a}\\
a^* &= \frac{1}{a\sin\gamma}.\\
\sin(\pi-\gamma) &= \sin\gamma = \frac{d_{01}}{b} = \frac{1}{\mathrm{h}_{01}b} = \frac{1}{b^*b}\\
b^* &= \frac{1}{b\sin\gamma}.\\
\sin\gamma^* &= \frac{1}{a^*a} = \sin\gamma.
\end{aligned}$$

Since γ^* is an acute angle, $\gamma^* = \pi - \gamma$.

(b) The Cartesian components of the direct lattice vectors are

$$\begin{aligned}
\mathbf{a_c} &= a_x\mathbf{i} + a_y\mathbf{j} = a\mathbf{i} + 0\mathbf{j}\\
\mathbf{b_c} &= b_x\mathbf{i} + b_y\mathbf{j} = b\cos\gamma\,\mathbf{i} + b\sin\gamma\,\mathbf{j}.
\end{aligned}$$



$$\begin{aligned}
\mathbf{C} &= \begin{bmatrix} a & 0 \\ b\cos\gamma & b\sin\gamma \end{bmatrix}\\
\mathbf{B} &= \mathbf{C}^T = \begin{bmatrix} a & b\cos\gamma \\ 0 & b\sin\gamma \end{bmatrix}.
\end{aligned}$$

Substituting $\mathbf{a}^*$, $\mathbf{b}^*$, and γ^* in the figure above:

$$\mathbf{B}^* = \begin{bmatrix} a^* & b^*\cos\gamma^* \\ 0 & b^*\sin\gamma^* \end{bmatrix}.$$

(c)

$$\begin{aligned} a^* &= \frac{1}{4.855\text{Å}\sin(98.8^{\mathrm{o}})} = 0.208\ \text{Å}^{-1} \\ b^* &= \frac{1}{6.953\text{Å}\sin(98.8^{\mathrm{o}})} = 0.146\ \text{Å}^{-1} \\ \gamma^* &= \pi - \gamma = 81.2^{\mathrm{o}}. \end{aligned}$$

(d)

$$\mathbf{B}^* = \begin{bmatrix} 0.208 & 0.022 \\ 0 & 0.144 \end{bmatrix}$$

$$\mathbf{h}_{12}: \quad \mathbf{B}^* \begin{bmatrix} 1 \\ 2 \end{bmatrix} = \begin{bmatrix} 0.252 \\ 0.288 \end{bmatrix} \quad \mathrm{h}_{12} = (0.252^2 + 0.288^2)^{1/2} = 0.383\ \text{Å}^{-1}$$

$$d_{12} = \frac{1}{\mathrm{h}_{12}} = \frac{1}{0.362\text{Å}^{-1}} = 2.613\text{Å}$$

$$\mathbf{h}_{23}: \quad \mathbf{B}^* \begin{bmatrix} 2 \\ 3 \end{bmatrix} = \begin{bmatrix} 0.482 \\ 0.432 \end{bmatrix} \quad \mathrm{h}_{23} = (0.482^2 + 0.432^2)^{1/2} = 0.647\ \text{Å}^{-1}$$

$$d_{23} = \frac{1}{\mathrm{h}_{23}} = \frac{1}{0.647\text{Å}^{-1}} = 1.545\text{Å}.$$

8. The hypothetical carbon monoxide unit cell in Exercise 7 has the following contents:

atom	x	y
C1	0.567	0.278
O1	0.377	0.262
C2	0.433	0.722
O2	0.623	0.738

The parameters for Eqn. 3.100 for the scattering factors of carbon and oxygen are:

	a_1	b_1	a_2	b_2	a_3	b_3	a_4	b_4	c
C	2.3100	20.8439	1.0200	10.2075	1.5886	0.5687	0.8650	51.6512	0.2156
O	3.0485	13.2771	2.2868	5.7011	1.5463	0.3239	0.8670	32.9089	0.2508

Determine the amplitudes and phase angles of the structure factors for the (1 2) and (2 3) reflections (Hint: Do Exercise 7 first).

Solution:

Scattering factors for the (1 2) reflection ($s_{12} = \mathrm{h}_{12}/2 = 0.192$):

$$\begin{aligned}
\mathrm{C}: f_{\mathrm{C}}(1,2) &= 2.3100\, e^{-20.8439\, s_{12}^2} + 1.0200\, e^{-10.2075\, s_{12}^2} \\
&\quad +1.5886\, e^{-0.5687\, s_{12}^2} + 0.8650\, e^{-51.6512\, s_{12}^2} + 0.2156 \\
&= 3.678 \\
\mathrm{O}: f_{\mathrm{O}}(1,2) &= 5.767.
\end{aligned}$$

$$\begin{aligned}
A_{12} &= \quad 3.678\cos(-2\pi((1)(0.567) + (2)(0.278))) \\
&\quad + 5.767\cos(-2\pi((1)(0.377) + (2)(0.262))) \\
&\quad + 3.678\cos(-2\pi((1)(0.433) + (2)(0.722))) \\
&\quad + 5.767\cos(-2\pi((1)(0.623) + (2)(0.738))) \\
&= 14.640 \\
B_{12} &= \quad 3.678\sin(-2\pi((1)(0.567) + (2)(0.278)) \\
&\quad + 5.767\sin(-2\pi((1)(0.377) + (2)(0.262))) \\
&\quad + 3.678\sin(-2\pi((1)(0.433) + (2)(0.722))) \\
&\quad + 5.767\sin(-2\pi((1)(0.623) + (2)(0.738))) \\
&= 0 \\
F_{12} &= (14.640^2 + (0)^2)^{1/2} = 14.640 \\
\sin\varphi_{12} &= \frac{B_{12}}{F_{12}} = 0; \quad \cos\varphi_{12} = \frac{A_{12}}{F_{12}} = 1 \\
\varphi_{12} &= 0.
\end{aligned}$$

Similarly, $s_{23} = \mathrm{h}_{23}/2 = 0.324$, $f_{\mathrm{C}}(2,3) = 2.323$, $f_{\mathrm{O}}(2,3) = 3.785$, $A_{23} = -2.779$, $B_{23} = 0$ and $F_{23} = 2.779$; $\sin\varphi_{23} = 0$, $\cos\varphi_{23} = -1$, and $\varphi_{23} = \pi$.

9. Given the following "experimental" structure factor amplitudes and phases for the hypothetical carbon monoxide crystal in Exercises 7 and 8, calculate the electron density at (a) the origin of the unit cell, (b) the center of O1, and (c) the midpoint between C1 and O1.

h	k	F_{hk}	φ_{hk}	h	k	F_{hk}	φ_{hk}	h	k	F_{hk}	φ_{hk}
0	0	28.000	0	1	0	19.496	π	2	0	4.865	0
0	1	3.065	π	1	1	3.510	π	2	1	4.782	0
0	2	21.171	π	1	2	14.640	0	2	2	3.580	π
0	3	5.727	0	1	3	0.210	0	2	3	2.779	π
0	4	11.950	0	1	4	8.757	π	2	4	2.128	0
0	5	5.699	π	1	5	1.439	0	2	5	1.317	0

h	k	F_{hk}	φ_{hk}	h	k	F_{hk}	φ_{hk}	h	k	F_{hk}	φ_{hk}
3	0	3.884	0	4	0	6.155	π	5	0	5.034	0
3	1	1.270	π	4	1	2.836	π	5	1	5.075	0
3	2	3.937	π	4	2	6.581	0	5	2	5.940	π
3	3	1.353	0	4	3	1.427	0	5	3	3.372	π
3	4	3.587	0	4	4	6.370	π	5	4	6.210	0
3	5	1.432	π	4	5	0.060	π	5	5	1.640	0

Solution:

The two-dimensional analog of Eqn. 3.111 is

$$\rho(x,y) = \frac{1}{A_c}\sum_h\sum_k F_{hk}\cos(2\pi(hx+ky)-\varphi_{hk}),$$

where $A_c = ab\sin\gamma$. The two-dimensional version of Eqn. 3.114 can also be used here, since the structure is centrosymmetric.

(a) Substituting $x = 0$ and $y = 0$ along with the amplitudes and phases from the table gives

$$\rho(0,0) = 0.31\,\mathrm{e}/\text{Å}^2.$$

(b) O1 is at $x = 0.377$ and $y = 0.262$, giving

$$\rho(0.377, 0.262) = 4.71\,\mathrm{e}/\text{Å}^2.$$

(c) The midpoint between C1 and O1 is at $x = (0.567 + 0.377)/2$ and $y = (0.278 + 0.262)/2$:

$$\rho(0.472, 0.270) = 2.10\,\mathrm{e}/\text{Å}^2.$$

Chapter 4

Crystal Diffraction: Experiment

1. A crystal of mercaptopyridine (Sec. 1.5.3) is aligned so that its a axis is perpendicular to the direction of the incident X-ray beam ($\lambda = 0.7107$ Å) along the z axis of the laboratory reference frame. An area detector is positioned so that its plane is perpendicular to the incident beam at a distance of 9 cm from the crystal. (a) Predict the distance between the horizontal rows of diffraction maxima (spots) on the detector surface. (b) Predict the location of the spots on the detector surface from the (0 1 0) and (0 0 1) reflections.

Solution:

(a) The $\mathbf{b}^*\mathbf{c}^*$ plane is perpendicular to the $\mathbf{a}$ (rotation) axis; The xy plane contains the $(0\ k\ l)$ reciprocal lattice points. The $(0\ k\ l)$ and $(1\ k\ l)$ reciprocal lattice planes generate spots on the detector surface as they pass through the sphere of reflection, resulting in triangles similar to those in Fig. 4.5. In this case d^* is the projection of $\mathbf{a}^*$ onto $\mathbf{a}$, and $a = \lambda/\sin\eta$.

$$\begin{aligned}
\sin\eta &= \frac{\lambda}{a} = \frac{0.7107\ \text{Å}}{6.112\ \text{Å}} = 0.116 \\
\eta &= 6.677^{\text{o}} \\
\tan\eta &= \frac{L}{D} = \frac{L}{9\ \text{cm}} = 0.117 \\
L &= 1.05\ \text{cm.}
\end{aligned}$$

(b) The (0 1 0) reciprocal lattice point is at the end of the $\mathbf{b}^* = [0\ 1\ 0]$ vector. Referring to Fig. 4.1, the point lies in the xy plane, intersecting the sphere when $\mathbf{h} = \mathbf{b}^*$. The diffraction vector, $\mathbf{d}$, will be at angle $2\theta_{010}$

with respect to the incident beam, with $\sin\theta_{010} = \lambda\, b^*/2$. Thus,

$$\begin{aligned}
b^* = \frac{1}{b} &= 0.1581\ \text{Å}^{-1} \\
\sin\theta_{010} &= \frac{0.7107\ \text{Å}0.1581\ \text{Å}^{-1}}{2} = 0.056. \\
\theta_{010} &= 3.22^{\circ} \\
x_d &= D\tan 2\theta_{010} = 1.02\ \text{cm} \\
y_d &= 0.
\end{aligned}$$

Similarly, $c^* = 1/(c\sin\beta) = 0.0713\ \text{Å}^{-1}$ and $\sin\theta_{001} = \lambda\, c^*/2$, resulting in $x_d = 0.46$ cm and $y_d = 0$.

2. The orientation matrix for the mercaptopyridine crystal used to determine the structure discussed in Sec 1.5.3, employing Mo $K\alpha$ radiation (0.71073 Å), was

$$\mathbf{A}^* = \begin{bmatrix} 0.02650 & -0.04430 & 0.06840 \\ -0.04094 & -0.14859 & -0.02004 \\ 0.15986 & -0.03066 & -0.00154 \end{bmatrix}.$$

(a) Determine the Eulerian angles and detector angle for the $(2\,\bar{4}\,11)$ reflection for the rotation of the crystal and the observation of a diffraction maximum in the bisecting position. (b) A reflection is located with the following Eulerian and detector angles: $2\theta = 21.673^{\circ}$, $\omega = 0.114^{\circ}$, $\varphi = 119.921^{\circ}$, $\chi = 60.878^{\circ}$, $2\theta = 21.673^{\circ}$. What are its indices?

Solution:

(a)

$$\begin{aligned}
\tan\varphi &= -\frac{(0.02650)(2) + (-0.04430)(-4) + (0.06840)(11)}{(-0.04094)(2) + (-0.14859)(-4) + (-0.02004)(11)} \\
&= -3.3646 \\
\varphi &= -73.45^{\circ} = 286.55^{\circ} \\
\tan\chi &= \frac{(0.15986)(2) + (-0.03066)(-4) + (-0.00154)(11)}{(-0.04094)(2) + (-0.14859)(-4) + (-0.02004)(11)} \cos 73.45^{\circ} \\
&= 0.4149 \\
\chi &= 22.54^{\circ} \\
\sin\omega &= -\frac{(0.15986)(2) + (-0.03066)(-4) + (-0.00154)(11)}{2\sin 22.54^{\circ}} 0.71073 \\
&= 0.3944 \\
\omega &= \theta = 23.23^{\circ} \\
2\theta &= 46.46^{\circ}.
\end{aligned}$$

(b) $\theta = 10.837^{\circ}$, $\omega - \theta = -10.723^{\circ}$ and

$$\frac{2\sin 10.37^{\circ}}{0.71073\ \text{Å}} = 0.529\ \text{Å}^{-1}$$

$$\begin{aligned}
\mathbf{h_l} &= 0.529\ \text{Å}^{-1}\begin{bmatrix}(-0.488)(-0.186)-(0.873)(0.487)(0.983)\\(0.873)(-0.186)+(-0.488)(0.487)(0.983)\\(0.874)(0.983)\end{bmatrix}\\
&= \begin{bmatrix}-0.172\\-0.209\\0.454\end{bmatrix}\\
\mathbf{A}^{*-1} &= \begin{bmatrix}-0.2090 & -1.1736 & 5.9896\\-1.7704 & -5.9483 & -1.2299\\13.5542 & -3.3978 & -3.1171\end{bmatrix}\\
\mathbf{A}^{*-1}\mathbf{h_l} &= \begin{bmatrix}k\\k\\l\end{bmatrix} = \begin{bmatrix}3.00\\0.98\\-3.04\end{bmatrix} \equiv \begin{bmatrix}3\\1\\\bar{3}\end{bmatrix}.
\end{aligned}$$

3. In part (a) of the previous exercise the reflection vector, $\mathbf{h_r}$, was oriented with the angles ω, χ, and φ into the diffraction condition in the bisecting position with specific Eulerian angles for each reflection. When an area detector is employed, χ, φ, and the detector angle, τ, are fixed; $\mathbf{h_r}$ is oriented with ω alone. From Eqn. 4.26, for a given reflection, $\mathbf{X\Phi A^*h}$ is a specified vector, $\mathbf{v}$, oriented by ω: $\mathbf{\Omega v} = \mathbf{h_r}$. (a) Derive an expression for ω in terms of $\mathbf{h_r} = [h_x\ h_y\ h_z]$ and $\mathbf{v} = [v_x\ v_y\ v_z]$. (b) For $\chi = 54.73^{\circ}$ and $\phi = 270^{\circ}$, determine the ω angle that will orient the $(2\ \bar{4}\ 11)$ reflection vector of the mercaptopyridine crystal in the previous exercise into the diffraction condition. (c) Determine the location of the $(2\ \bar{4}\ 11)$ "spot" on an area detector surface for the settings of χ and φ in (b), a crystal-to-detector distance of 6 cm, and a detector angle of 26°.

Solution:

(a) Using $\mathbf{\Omega v} = \mathbf{h_r}$,

$$\begin{bmatrix}\cos\omega & -\sin\omega & 0\\ \sin\omega & \cos\omega & 0\\ 0 & 0 & 1\end{bmatrix}\begin{bmatrix}v_x\\v_y\\v_z\end{bmatrix} = \begin{bmatrix}h_x\\h_y\\h_z\end{bmatrix}$$

$$v_x\cos\omega - v_y\sin\omega = h_x$$

$$v_y\cos\omega + v_x\sin\omega = h_y$$

$$\frac{v_x}{v_y}\cos\omega - \sin\omega = \frac{h_x}{v_y}$$

$$\frac{v_y}{v_x}\cos\omega + \sin\omega = \frac{h_y}{v_x}$$

Adding the last two equations results in

$$\begin{aligned}
\cos\omega &= \frac{h_x v_x + h_y v_y}{v_x^2 + v_y^2}\\
\omega &= \arccos\left(\frac{h_x v_x + h_y v_y}{v_x^2 + v_y^2}\right).
\end{aligned}$$

(b) In the diffraction condition $h_x = -2\sin^2\theta/\lambda$, $h_z = v_z$, and we need to determine only θ and h_y in order to obtain ω; both θ and h_y can be derived from the magnitude of the reflection vector, h= $|\mathbf{h}| = |\mathbf{h_r}| = |\mathbf{h_l}|$:

$$\begin{aligned}
\mathbf{A}^*\mathbf{h} &= \mathbf{A}^* \begin{bmatrix} 2 \\ \bar{4} \\ 11 \end{bmatrix} = \begin{bmatrix} 0.9826 \\ 0.2920 \\ 0.4254 \end{bmatrix} = \mathbf{h_l}; \\
\text{h} &= (0.9826^2 + 0.2920^2 + 0.4254^2)^{1/2} = 1.110\ \text{Å}^{-1} \\
\theta &= \arcsin\left(\frac{1.110\ \text{Å}^{-1} 0.71073\ \text{Å}}{2}\right) = 23.23^{\text{o}}
\end{aligned}$$

The vector, $\mathbf{v}$, is now determined from $\mathbf{v} = \mathbf{X\Phi A^*h} = \mathbf{X\Phi h_l}$:

$$\begin{aligned}
\mathbf{v} &= \begin{bmatrix} v_x \\ v_y \\ v_z \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0.5774 & 0.8164 \\ 0 & -0.8164 & 0.5744 \end{bmatrix} \begin{bmatrix} 1 & \bar{1} & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0.9826 \\ 0.2920 \\ 0.4254 \end{bmatrix} \\
&= \begin{bmatrix} -0.2920 \\ 0.9147 \\ -0.5566 \end{bmatrix} \\
h_x &= \frac{-2\sin^2 23.23^{\text{o}}}{0.71073} = -0.4377 \\
h_z &= -0.5566 \\
h_y &= (1.110^2 - 0.4377^2 - 0.5566^2)^{1/2} = 0.8546 \\
\cos\omega &= 0.9865 \\
\omega &= 9.41^{\text{o}}.
\end{aligned}$$

(c) The detector is at $\tau = 26^{\text{o}}$, and

$$\begin{bmatrix} 0.8988 & 0.4384 & 0 \\ -0.4384 & 0.8988 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} (0.71073)(-0.4377) + 1 \\ (0.71073)(0.8546) \\ (0.71073)(-0.5566) \end{bmatrix} = \begin{bmatrix} 0.8854 \\ 0.2439 \\ -0.3956 \end{bmatrix} = \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix}$$

$$x_d = -6.00 \left(\frac{0.2439}{0.8854}\right) \text{ cm} = -1.65 \text{ cm}$$

$$y_d = 6.00 \left(\frac{-0.3956}{0.8854}\right) \text{ cm} = -2.68 \text{ cm}.$$

4. The mercaptopyridine crystal in Exercise 2 provided 14 reflections with the following refined diffractometer angles:

Reflection #	2θ	ω	ϕ	χ
1	7.951	−0.633	229.286	54.806
2	9.389	0.113	318.467	56.348
3	10.222	0.174	294.654	49.341
4	13.746	−0.272	89.943	75.436
5	14.861	0.069	310.896	77.474

Reflection #	2θ	ω	ϕ	χ
6	15.929	0.315	269.490	3.521
7	16.010	0.327	215.404	18.527
8	17.496	0.286	245.219	358.839
9	18.831	−0.213	309.305	57.254
10	19.954	0.257	70.621	43.299
11	21.673	0.114	119.921	60.878
12	22.477	0.079	19.438	73.882
13	23.399	−0.208	239.967	65.376
14	24.324	0.132	285.315	69.025

In the search for axial solutions using integer triples ranging from $(n_1,\ n_2,\ n_3) = (-5,-5,-5)$ to $(5,5,5)$, 57 potential unit cell axes, $\mathbf{v} = [v_x\ v_y\ v_z]$, with lengths of 25 Å or less were determined using Eqn. 4.40 — based on $\mathbf{Z}^{-1}$ created from the first three reflections in the list:

$$\begin{aligned} v_x &= n_1 z^i_{11} + n_2 z^i_{21} + n_3 z^i_{31} \\ v_y &= n_1 z^i_{12} + n_2 z^i_{22} + n_3 z^i_{32} \\ v_z &= n_1 z^i_{13} + n_2 z^i_{23} + n_3 z^i_{33}. \end{aligned}$$

These trial solutions were tested using Eqn. 4.41, which must provide an integer (in practice, a number close to an integer) for $\mathbf{h_l} \equiv \mathbf{z}$ for each reflection:

$$v_x z_x + v_y z_y + v_z z_z = m.$$

The candidates that meet this test are the Cartesian components of each potential unit cell axis; the selection of the "best" unit cell is facilitated by computing their lengths and angles with respect to one another, looking for short axes with angles approaching 90°. Although the solutions for this crystal provided the monoclinic unit cell described in the text, we consider another possible solution from the 57 candidates (the "$\mathbf{u}$" subscript indicates that the unit cell is not the reduced unit cell for the lattice — see Exercise 5):

axis	n_1	n_2	n_3	v_x	v_y	v_z
$\mathbf{a_u}$	1	1	1	−0.1980	−1.1664	5.9618
$\mathbf{b_u}$	−1	−2	−2	−1.5685	−4.7848	−7.1966
$\mathbf{c_u}$	2	2	3	15.1534	1.4349	4.0624

(a) Determine the parameters for the unit cell. (b) Determine the indices of the reflections in the list based on the unit cell.

Solution:

(a) Axial lengths and angles are determined from the vector components:

$$\begin{aligned}
a &= ((-0.1980)^2 + (-1.1664)^2 + (5.9618)^2)^{1/2} = 6.078 \text{ Å} \\
b &= ((-1.5685)^2 + (-4.7848)^2 + (-7.1966)^2)^{1/2} = 8.783 \text{ Å} \\
c &= ((15.1534)^2 + (1.4349)^2 + (4.0624)^2)^{1/2} = 15.754 \text{ Å} \\
\cos\alpha &= \frac{(-1.5685)(15.1534) + (-4.7848)(1.4349) + (-7.1966)(4.0624)}{(8.783)(15.754)} \\
\alpha &= 115.64^{\mathrm{o}} \\
\beta &= 78.22^{\mathrm{o}} \\
\gamma &= 133.89^{\mathrm{o}}.
\end{aligned}$$

(b) The **A** matrix consists of the Cartesian components of the axial vectors:

$$\mathbf{A} = \begin{bmatrix} -0.1980 & -1.1664 & 5.9618 \\ -1.5685 & -4.7848 & -7.1966 \\ 15.1534 & 1.4349 & 4.0624 \end{bmatrix}$$

The indices of the reflections are given by $\mathbf{h}_i = \mathbf{A}\mathbf{z}_i$. For example, for reflection #10, using Eqn. 4.37,

$$\omega_{10} - \theta_{10} = 0.257^{\mathrm{o}} - 9.997^{\mathrm{o}} = -9.74^{\mathrm{o}}$$

$$\mathbf{z}_{10} = \frac{2\sin 9.997^{\mathrm{o}}}{0.71073} \times$$

$$\begin{bmatrix} \cos 70.621^{\mathrm{o}} \sin -9.74^{\mathrm{o}} - \sin 70.621^{\mathrm{o}} \cos 43.299^{\mathrm{o}} \cos -9.74^{\mathrm{o}} \\ \sin 70.621^{\mathrm{o}} \sin -9.74^{\mathrm{o}} + \cos 70.621^{\mathrm{o}} \cos 43.299^{\mathrm{o}} \cos -9.74^{\mathrm{o}} \\ \sin 43.299^{\mathrm{o}} \cos -9.74^{\mathrm{o}} \end{bmatrix}$$

$$= \begin{bmatrix} -0.3572 \\ 0.0384 \\ 0.3296 \end{bmatrix}$$

$$\mathbf{h}_{10} = \mathbf{A}\mathbf{z}_{10} = \begin{bmatrix} 1.99 \\ -2.00 \\ -4.02 \end{bmatrix} \equiv \begin{bmatrix} 2 \\ \bar{2} \\ \bar{4} \end{bmatrix}.$$

Indices for all 14 reflections:

Reflection #	h	k	l	Reflection #	h	k	l
1	1	$\bar{1}$	2	8	0	0	6
2	1	$\bar{2}$	2	9	2	$\bar{4}$	4
3	1	$\bar{2}$	3	10	2	$\bar{2}$	$\bar{4}$
4	2	$\bar{2}$	0	11	3	$\bar{2}$	$\bar{1}$
5	2	$\bar{3}$	2	12	3	$\bar{4}$	0
6	0	$\bar{1}$	6	13	3	$\bar{4}$	6
7	1	0	4	14	3	$\bar{5}$	5

5. When refined by the method of least squares, the unreduced cell in the previous problem results in the following orientation matrix:

$$\mathbf{A}^* = \begin{bmatrix} -0.01781 & 0.02410 & 0.06840 \\ -0.18953 & -0.16863 & -0.02004 \\ 0.12920 & -0.03220 & -0.00154 \end{bmatrix}.$$

Eqns. 4.68 can be utilized to produce linear combinations of the Cartesian components of the refined unit cell axes in order to produce a "Buerger" reduced cell. For the unreduced unit cell defined by the orientation matrix above, the integers (p, q, r) ranging from $(-2, -2, -2)$ to $(2, 2, 2)$ produce 124 lattice vectors, 62 of which are unique (for every vector created from (p, q, r), its negative will be created with $(-p, -q, -r)$). The shortest 20 of these are tabulated below:

axis	p	q	r	length	axis	p	q	r	length
$\mathbf{v}_1$	1	0	0	6.1071	$\mathbf{v}_{11}$	1	0	−1	15.6495
$\mathbf{v}_2$	1	1	0	6.3268	$\mathbf{v}_{12}$	1	2	1	15.6555
$\mathbf{v}_3$	2	1	0	8.7917	$\mathbf{v}_{13}$	0	0	1	15.7231
$\mathbf{v}_4$	0	1	0	8.7952	$\mathbf{v}_{14}$	2	2	1	15.7272
$\mathbf{v}_5$	2	0	0	12.2141	$\mathbf{v}_{15}$	1	−1	−1	16.6519
$\mathbf{v}_6$	2	2	0	12.6537	$\mathbf{v}_{16}$	2	1	1	16.8559
$\mathbf{v}_7$	1	−1	0	13.7577	$\mathbf{v}_{17}$	0	2	0	17.5904
$\mathbf{v}_8$	1	2	0	14.0525	$\mathbf{v}_{18}$	2	0	−1	17.8098
$\mathbf{v}_9$	0	1	1	14.3168	$\mathbf{v}_{19}$	0	2	1	17.8168
$\mathbf{v}_{10}$	1	1	1	14.3962	$\mathbf{v}_{20}$	1	0	1	18.0033

(a) Determine the Cartesian components of the refined unit cell axes. (b) Determine "Buerger" cell parameters for the lattice. (c) Use the Buerger unit cell to determine the "Niggli" reduced cell for the lattice. (c) Determine the indices for the reflections listed in Exercise 4 based on the reduced cell.

Solution:

(a) The row vectors of the direct lattice matrix, $\mathbf{A} = \mathbf{A}^{*-1}$, are the Cartesian components of the unit cell axes:

$$\begin{aligned}
\mathbf{A} &= \mathbf{A}^{*-1} = \begin{bmatrix} -0.20899 & -1.17358 & 5.98960 \\ -1.56146 & -4.77470 & -7.21943 \\ 15.11567 & 1.37692 & 4.10327 \end{bmatrix} \\
\mathbf{a_u} &= a_x\mathbf{i} + a_y\mathbf{j} + a_z\mathbf{k} = (-0.20899)\mathbf{i} + (-1.17358)\mathbf{j} + (5.98960)\mathbf{k} \\
\mathbf{b_u} &= b_x\mathbf{i} + b_y\mathbf{j} + b_z\mathbf{k} = (-1.56146)\mathbf{i} + (-4.77470)\mathbf{j} + (-7.21943)\mathbf{k} \\
\mathbf{c_u} &= c_x\mathbf{i} + c_y\mathbf{j} + c_z\mathbf{k} = (15.11567)\mathbf{i} + (1.37692)\mathbf{j} + (4.10327)\mathbf{k}.
\end{aligned}$$

(b) Cartesian components for potential reduced cell axes:

$$\begin{aligned}\mathbf{v_r} &= p\,\mathbf{a_u} + q\,\mathbf{b_u} + r\,\mathbf{c_u} = v_x\mathbf{i} + v_y\mathbf{j} + v_z\mathbf{k} \\ &= (pa_x + qb_x + rc_x)\mathbf{i} + (pa_y + qb_y + rc_y)\mathbf{j} + (pa_y + qb_y + rc_y)\mathbf{k}.\end{aligned}$$

$\mathbf{v}_1 = 1\,\mathbf{a_u}$ and $\mathbf{v}_2 = 1\,\mathbf{a_u} + 1\,\mathbf{b_u}$ are the two shortest vectors. $\mathbf{v}_3$ is the vector sum of $\mathbf{v}_1$ and $\mathbf{v}_2$:

$$\mathbf{v}_3 = 2\,\mathbf{a_u} + 1\,\mathbf{b_u} = 1\,\mathbf{a_u} + (1\,\mathbf{a_u} + 1\,\mathbf{b_u}) = \mathbf{v}_1 + \mathbf{v}_2.$$

Similarly, $\mathbf{v}_4 = \mathbf{v}_2 - \mathbf{v}_1$, $\mathbf{v}_5 = 2\,\mathbf{v}_1$, $\mathbf{v}_6 = 2\,\mathbf{v}_2$, $\mathbf{v}_7 = 2\,\mathbf{v}_1 - \mathbf{v}_2$, and $\mathbf{v}_8 = 2\,\mathbf{v}_2 - \mathbf{v}_1$. All of these vectors lie in the same plane as $\mathbf{v}_1$ and $\mathbf{v}_2$. $\mathbf{v}_9$ is the first vector in the sequence with a component for $\mathbf{c_u}$, and therefore not coplanar with $\mathbf{v}_1$ and $\mathbf{v}_2$; the three shortest non-coplanar vectors are $\mathbf{v}_1$, $\mathbf{v}_2$, and $\mathbf{v}_9$. Assigning $\mathbf{a_r}$, $\mathbf{b_r}$, and $\mathbf{c_r}$ in order of increasing length gives:

axis	p	q	r	v_x	v_y	v_z	length
$\mathbf{a_r}$	1	0	0	−0.2090	−1.1736	5.9896	6.107
$\mathbf{b_r}$	1	1	0	−1.7704	−5.9483	−1.2298	6.327
$\mathbf{c_r}$	0	1	1	13.5542	−3.3978	−3.1162	14.317

(c) The Niggli matrix,

$$\begin{bmatrix} 37.30 & 40.03 & 204.97 \\ 0.04 & -17.51 & 0.00 \end{bmatrix},$$

is consistent with the criteria in Table 4.1. The Buerger reduced unit cell is a Type I Niggli reduced cell.

(d) $\mathbf{h}_i = \mathbf{A}\mathbf{z}_i$, where the $\mathbf{A}$ matrix consists of the Cartesian components of the axial vectors:

$$\mathbf{h}_i = \begin{bmatrix} -0.2090 & -1.1736 & 5.9896 \\ -1.7704 & -5.9483 & -1.2298 \\ 13.5542 & -3.3978 & -3.1162 \end{bmatrix} \mathbf{z}_i.$$

See the solution to the previous exercise for the computation of the $\mathbf{h_l} \equiv \mathbf{z}$ vectors. The resulting indices:

h	k	l	2θ	ω	ϕ	χ
1	0	1	7.951	−0.633	229.286	54.806
1	$\bar{1}$	0	9.389	0.113	318.467	56.348
1	$\bar{1}$	1	10.222	0.174	294.654	49.341
2	0	$\bar{2}$	13.746	−0.272	89.943	75.436
2	$\bar{1}$	$\bar{1}$	14.861	0.069	310.896	77.474
0	$\bar{1}$	5	15.929	0.315	269.490	3.521

h	k	l	2θ	ω	ϕ	χ
1	1	4	16.010	0.327	215.404	18.527
0	0	6	17.496	0.286	245.219	358.839
2	$\bar{2}$	0	18.831	−0.213	309.305	57.254
2	0	$\bar{6}$	19.954	0.257	70.621	43.299
3	1	$\bar{3}$	21.673	0.114	119.921	60.878
3	$\bar{1}$	$\bar{4}$	22.477	0.079	19.438	73.882
3	$\bar{1}$	2	23.399	−0.208	239.967	65.376
3	$\bar{2}$	0	24.324	0.132	285.315	69.025

6. According to Eqn, 4.37, any three indexed reflections that are linearly independent (so that $\mathbf{H}^{-1}$ has an inverse) are sufficient to define the orientation matrix and unit cell parameters. Reflections 11, 13, and 7 in the array in Exercise 2 have indices of ($2\ 0\ \bar{6}$), ($3\ \bar{1}\ 2$), and ($1\ 1\ 4$), respectively. (a) Demonstrate that the reciprocal lattice vectors for the reflections are linearly independent. (b) Determine the orientation matrix based solely on the three reflections. (c) Calculate the metric tensor and determine the unit cell parameters based solely on the three reflections.

Solution:

(a) Linear independence is illustrated by showing that the matrix of reciprocal lattice vector components is invertible, i.e., that it has a non-zero determinant:

$$\mathbf{H} = \begin{bmatrix} 2 & 3 & 1 \\ 0 & \bar{1} & 1 \\ \bar{6} & 2 & 4 \end{bmatrix} ; \quad \begin{vmatrix} 2 & 3 & 1 \\ 0 & \bar{1} & 1 \\ \bar{6} & 2 & 4 \end{vmatrix} = -36 \neq 0.$$

(b) Using Eqn. 4.37,

$$\omega_{20\bar{6}} - \theta_{20\bar{6}} = 0.257^{\mathrm{o}} - 9.997^{\mathrm{o}} = -9.74^{\mathrm{o}}$$

$$\mathbf{z}_{20\bar{6}} = \frac{2\sin 9.997^{\mathrm{o}}}{0.71073} \times$$

$$\begin{bmatrix} \cos 70.621^{\mathrm{o}} \sin -9.74^{\mathrm{o}} - \sin 70.621^{\mathrm{o}} \cos 43.299^{\mathrm{o}} \cos -9.74^{\mathrm{o}} \\ \sin 70.621^{\mathrm{o}} \sin -9.74^{\mathrm{o}} + \cos 70.621^{\mathrm{o}} \cos 43.299^{\mathrm{o}} \cos -9.74^{\mathrm{o}} \\ \sin 43.299^{\mathrm{o}} \cos -9.74^{\mathrm{o}} \end{bmatrix}$$

$$= \begin{bmatrix} -0.3572 \\ 0.0384 \\ 0.3296 \end{bmatrix}, \text{ etc.}$$

$$\mathbf{Z} = \begin{bmatrix} -0.3572 & 0.2603 & 0.2560 \\ 0.0384 & -0.0145 & -0.2698 \\ 0.3296 & 0.5076 & 0.1234 \end{bmatrix}$$

$$\mathbf{A}^* = \mathbf{Z}\mathbf{H}^{-1} = \begin{bmatrix} 0.0265 & -0.0440 & 0.0634 \\ -0.0410 & -0.1486 & -0.0200 \\ 0.1601 & -0.0304 & -0.0016 \end{bmatrix}.$$

(c) Using Eqn. 4.46,

$$\begin{aligned}
\mathbf{A} &= \mathbf{A}^{*-1} = \begin{bmatrix} -0.2049 & -1.1646 & 5.9820 \\ -1.7746 & -5.9527 & -1.2301 \\ 13.5617 & -3.3805 & -3.1121 \end{bmatrix} \\
\mathbf{G} &= \mathbf{A}\mathbf{A}^T = \begin{bmatrix} 37.1869 & -0.0628 & -17.4598 \\ -0.0628 & 40.0974 & -0.1155 \\ -17.4598 & -0.1155 & 205.0339 \end{bmatrix} \\
a &= \sqrt{37.1869} = 6.098 \text{ Å} \\
b &= \sqrt{40.0974} = 6.332 \text{ Å} \\
c &= \sqrt{205.0339} = 14.319 \text{ Å} \\
\alpha &= \arccos\left(\frac{-0.1155}{bc}\right) = 90.07^{\text{o}} \\
\beta &= \arccos\left(\frac{-17.4598}{ac}\right) = 101.53^{\text{o}} \\
\alpha &= \arccos\left(\frac{-0.0628}{ab}\right) = 90.09^{\text{o}} \\
V &= \sqrt{|\mathbf{G}|} = 541.76 \text{ Å}^3.
\end{aligned}$$

7. Show that a c-glide plane perpendicular to the b axis has the same effect on the symmetry of the intensity weighted reciprocal lattice as a mirror plane perpendicular to the b axis (without the translational symmetry).

Solution:

For the mirror plane, the electron density at (x_f, y_f, z_f) is identical to that at $(x_f, -y_f, z_f)$. The scattered wave for the reflection with reciprocal lattice vector $\mathbf{h}' = [h' \ k' \ l']$ is

$$\begin{aligned}
\overrightarrow{\mathcal{E}}_{h'k'l'} &= D\int_0^{V_c} \rho(x_f, -y_f, z_f) e^{-2\pi i(h'x_f + k' - y_f + l'z_f)} dV. \\
&= D\int_0^{V_c} \rho(x_f, y_f, z_f) e^{-2\pi i(h'x_f - k'y_f + l'z_f)} dV.
\end{aligned}$$

Replacing $h' = h$, $k' = \bar{k}$ and $l' = l$,

$$\overrightarrow{\mathcal{E}}_{h\bar{k}l} = D\int_0^{V_c} \rho(x_f, y_f, z_f) e^{-2\pi i(hx_f + ky_f + lz_f)} dV = \overrightarrow{\mathcal{E}}_{hkl},$$

$\mathcal{E}^2_{h\bar{k}l} = \mathcal{E}^2_{hkl}$, and $I^2_{h\bar{k}l} = I^2_{hkl}$.

The glide plane has identical electron density at (x_f, y_f, z_f) and $(x_f, -y_f, z_f + 1/2)$, and

$$\begin{aligned}\overrightarrow{\mathcal{E}}_{h'k'l'} &= D\int_0^{V_c} \rho(x_f, -y_f, (z_f + 1/2))e^{-2\pi i(-h'x_f+k'-y_f+l'(z_f+1/2))}dV \\ &= D\,e^{-\pi i\,l}\int_0^{V_c} \rho(x_f, y_f, z_f)e^{-2\pi i(h'x_f-k'y_f+l'z_f)}dV.\end{aligned}$$

Replacing $h' = h$, $k' = \bar{k}$ and $l' = l$,

$$\overrightarrow{\mathcal{E}}_{h\bar{k}l} = e^{-\pi il}\overrightarrow{\mathcal{E}}_{hkl}.$$

As with the diad screw axis, the scattered wave has a modified phase, due to the presence of the translational symmetry in the crystal – but the intensity is proportional to $\mathcal{E}^2_{h\bar{k}l}$ and

$$\mathcal{E}^2_{h\bar{k}l} = \overrightarrow{\mathcal{E}}_{h\bar{k}l}\overrightarrow{\mathcal{E}}^*_{h\bar{k}l} = e^{-\pi i\,l}\overrightarrow{\mathcal{E}}_{hkl}\,e^{\pi i\,l}\overrightarrow{\mathcal{E}}^*_{hkl} = e^0\mathcal{E}^2_{hkl} = \mathcal{E}^2_{hkl}.$$

Again, $I_{hkl} = I_{h\bar{k}l}$ and $F_{hkl} = F_{h\bar{k}l}$. The glide plane produces the same reflection symmetry as the mirror plane.

8. The simplest tetragonal space group is $P4$, which represents the $4/m$ Laue group. (a) Referring to Sec. 2.4.7, determine the symmetry-equivalent positions in the $P4$ space group for the general direct lattice vector, $[x_f\ y_f\ z_f]$. (b) Determine the symmetry-equivalent intensities in the intensity-weighted reciprocal lattice for a general reciprocal lattice vector, $[h\ k\ l]$, in the $P4$ space group.

   Solution:

   (a) Referring to Fig. 2.82, the four equivalent positions are (1) $[x_f\ y_f\ z_f]$, (2) $[-y_f\ x_f\ z_f]$, (3) $[-x_f\ -y_f\ z_f]$, and (4) $[y_f\ -x_f\ z_f]$.

   (b) $\mathbf{R}(4^1)$ establishes symmetry-equivalent electron density at $(-y_f, x_f, z_f)$. For the general reciprocal lattice vector, $\mathbf{h}' = [h'\ k'\ l']$,

   $$\begin{aligned}\overrightarrow{\mathcal{E}}_{h'k'l'} &= D\int_0^{V_c} \rho(-y_f, x_f, z_f)e^{-2\pi i(h'-y_f+k'x_f+l'z_f)}dV. \\ &= D\int_0^{V_c} \rho(x_f, y_f, z_f)e^{-2\pi i(k'x_f-h'y_f+l'z_f)}dV.\end{aligned}$$

   Replacing $h' = \bar{k}$, $k' = h$ and $l' = l$,

   $$\overrightarrow{\mathcal{E}}_{\bar{k}hl} = \overrightarrow{\mathcal{E}}_{hkl} \Longrightarrow I_{\bar{k}hl} = I_{hkl}.$$

   Similarly, for $\mathbf{R}(4^2)$, $I_{\bar{h}\bar{k}l} = I_{hkl}$, and for $\mathbf{R}(4^3)$, $I_{k\bar{h}l} = I_{hkl}$.

9. Consider crystals of a small molecule (S) and a protein (P), each rectangular solids with dimensions 0.3mm × 0.4mm × 0.5mm. Both molecules pack in orthorhombic space groups. The unit cell dimensions for the small molecule lattice are $a = 8$ Å, $b = 10$ Å, and $c = 12$ Å, while the unit cell dimensions

for the protein lattice are $a = 48$ Å, $b = 50$ Å, and $c = 52$ Å. Suppose that a structure factor, F_{0k0}, fortuitously has the same value for both structures. Using the integrated intensity of this reflection as an estimate of the comparative "diffracting power" of the crystals, calculate the ratio $\mathcal{I}^{\mathrm{S}}_{0k0}/\mathcal{I}^{\mathrm{P}}_{0k0}$. For simplicity assume that $\sin 2\theta_{\mathrm{P}}/\sin 2\theta_{\mathrm{S}} \simeq \sin\theta_{\mathrm{P}}/\sin\theta_{\mathrm{S}}$.

Solution:

Let V_{S} be the volume of the small molecule unit cell and V_{P} the volume of the protein unit cell. The volume of each crystal, V_x, is the same for both. Using Eqn. 4.111,

$$\frac{\mathcal{I}^{\mathrm{S}}_{0k0}}{\mathcal{I}^{\mathrm{P}}_{0k0}} = \frac{\sin 2\theta_{\mathrm{P}}}{\sin 2\theta_{\mathrm{S}}}\left(\frac{V_{\mathrm{P}}}{V_{\mathrm{S}}}\right)^2 \simeq \frac{\sin\theta_{\mathrm{P}}}{\sin\theta_{\mathrm{S}}}\left(\frac{V_{\mathrm{P}}}{V_{\mathrm{S}}}\right)^2.$$

Since the unit cells are orthorhombic, $b^* = 1/b$, and $\mathrm{h}_{0k0} = 2\sin\theta/\lambda_{0k0} = kb^* = k/b$. Thus $\sin\theta_{\mathrm{P}}/\sin\theta_{\mathrm{S}} = (k/50)/(k/10) = 1/5$, and

$$\frac{\mathcal{I}^{\mathrm{S}}_{0k0}}{\mathcal{I}^{\mathrm{P}}_{0k0}} = \frac{1}{5}\left(\frac{48\ \text{Å}\times 50\ \text{Å}\times 52\ \text{Å}}{8\ \text{Å}\times 10\ \text{Å}\times 12\ \text{Å}}\right)^2 = 3380.$$

10. A data-to-parameter ratio in the vicinity of 10:1 is often cited as a criterion for a "good" (atomic resolution) crystal structure. Referring to Exercise 9, assume that the small molecule asymmetric unit contains seven non-hydrogen atoms, the protein asymmetric unit contains 1800 non-hydrogen atoms, and that data are collected with Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). (a) Determine the maximum value of the diffraction angle, 2θ, necessary to attain a 10:1 data-to-parameter ratio for the small molecule and protein structures. (b) Determine the data-to-parameter ratios for the protein crystal at 1 Å (atomic) resolution, 2.5 Å resolution, and 5 Å resolution.

Solution:

(a) For the small molecule structure, three positional and six displacement parameters per atom ⇒ 63 parameters. The 10:1 data-to-parameter ratio indicates that 630 unique reflections must be collected. The Laue group is *mmm*, with a degeneracy of 8, and the limiting sphere must therefore contain 630 × 8 = 5040 reflections. From Eqn. 4.122,

$$\mathrm{h}_{\max} = \left(\frac{3\times 5040}{4\pi\times 960\ \text{Å}^3}\right)^{1/3} = 1.08\ \text{Å}^{-1}$$

$$\frac{2\sin\theta_{\max}}{1.5418\ \text{Å}} = 1.08\ \text{Å}^{-1}$$

$$\theta_{\max} = 56.2^{\mathrm{o}}$$

$$2\theta_{\max} = 112.4^{\mathrm{o}}.$$

For the protein structure, three positional and a single displacement parameter per atom ⇒ 7200 parameters. For a 10:1 parameter ratio the limiting sphere must contain 7200 × 10 × 8 = 576 000 reflections:

$$\mathrm{h}_{\max} = \left(\frac{3\times 576\,000}{4\pi\times 124\,800\ \text{Å}^3}\right)^{1/3} = 1.03\ \text{Å}^{-1}$$

$$2\theta_{\max} = 105.1^{\mathrm{o}}.$$

(b) At 1 Å resolution, $\mathrm{h}_{max} = 0.917/1\ \text{Å} = 0.917\ \text{Å}^{-1}$.

$$M = \frac{4\pi}{3}(0.917\ \text{Å}^{-1})^3(124\,800\ \text{Å}^3) = 403\,098 \text{ reflections}$$

$$\text{number of unique reflections } = \frac{403\,098}{8} = 50\,387$$

$$\text{data to parameter ratio} = \frac{50\,387}{7200} = 7.0.$$

At 2.5 Å resolution, $\mathrm{h}_{max} = 0.917/2.5\ \text{Å} = 0.367\ \text{Å}^{-1}$.

$$M = \frac{4\pi}{3}(0.367\ \text{Å}^{-1})^3(124\,800\ \text{Å}^3) = 25\,840 \text{ reflections}$$

$$\text{number of unique reflections } = \frac{25\,840}{8} = 3230$$

$$\text{data to parameter ratio} = \frac{3230}{7200} = 0.4.$$

At 5 Å resolution, $\mathrm{h}_{max} = 0.917/5\ \text{Å} = 0.184\ \text{Å}^{-1}$.

$$M = \frac{4\pi}{3}(0.184\ \text{Å}^{-1})^3(124\,800\ \text{Å}^3) = 3224 \text{ reflections}$$

$$\text{number of unique reflections } = \frac{3224}{8} = 403$$

$$\text{data to parameter ratio} = \frac{403}{7200} = 0.06.$$

Chapter 5

Crystal Diffraction: Data

1. In a diffraction experiment the integrated intensity of a reflection is measured repeatedly and found to have an average value of 7500 counts per second (cps). Determine the probability that a single measurement of the intensity will provide a value less than or equal to (a) 7450 cps, (b) 7400 cps, (c) 7300 cps, and (d) 7200 cps.

Solution:

(a) The mean intensity: $\bar{I} = 7500$. Counting events are characterized by a Poisson distribution: $\sigma(I) = \sqrt{7500} = 86.60$. The number of counts observed in the X-ray experiment is nearly always large enough to render the Poisson distribution effectively symmetric, and closely approximated by a Gaussian distribution. Thus,

$$\begin{aligned} Pr(0 \leq I \leq 7450) &= \frac{\mathrm{erf}(t_{7450}) - \mathrm{erf}(t_0)}{2} \\ t_{7450} &= \frac{7450 - 7500}{86.60\sqrt{2}} = -0.408 \\ t_0 &= \frac{0 - 7500}{86.60\sqrt{2}} = -61.23 \end{aligned}$$

From Eqn. 5.66,

$$\begin{aligned} \mathrm{erf}(t_{7450}) &= \mathrm{erf}(-0.408) = -\mathrm{erf}(0.408) = -0.4362 \\ \mathrm{erf}(t_0) &= \mathrm{erf}(-61.23) = -\mathrm{erf}(61.23) = -1.0000 \\ Pr(0 \leq I \leq 7450) &= \frac{-0.4362 + 1.0000}{2} = 0.28\ (28\%). \end{aligned}$$

28 in 100 measurements will yield $I \leq 7450$.

(b) $t_{7400} = -0.816$; $Pr(0 \leq I \leq 7400) = 0.12$ (12%).

(c) $t_{7300} = -1.63$; $Pr(0 \leq I \leq 7300) = 0.01$ (1%).

(d) $t_{7200} = -2.45$; $Pr(0 \leq I \leq 7200) = 0.0003$ ($\sim 0\%$).

2. Determine the diffraction angles, 2θ, for which the polarization correction will be at a maximum and a minimum and the values of the correction factor at these angles. Ignore secondary polarization effects such as those arising from a monochromator.

Solution:

The polarization correction,

$$P = \frac{1}{2} + \frac{1}{2}\cos^2 2\theta,$$

has minima and maxima when $dP/d(2\theta) = 0$:

$$\frac{dP}{d(2\theta)} = \frac{1}{2}2(\cos 2\theta)(-\sin 2\theta) = -\cos 2\theta \sin 2\theta = 0.$$

There is no angle that simultaneously has a sine and cosine equal to zero. Thus there are two possibilities:

(a) $\cos 2\theta = 0 \Rightarrow 2\theta = 90^{\circ}$ and $P = 1/2 + 1/2(0) = 1/2$. The intensity is attenuated to half of its unpolarized magnitude.

(b) $\sin 2\theta = 0 \Rightarrow 2\theta = 0^{\circ}$, $\cos 2\theta = 1$, and $P = 1/2 + 1/2(1) = 1$ (no polarization).

3. The orientation matrix and X-ray wavelength for the data collected for the mercaptopyridine crystal discussed in Chapter 1 are given in Exercise 2 of Chapter 4. (a) Using the orientation matrix, determine the Lorentz correction factor for the $(2\ \bar{4}\ 11)$ reflection for the case in which the integrated intensity is collected with a serial detector. For comparative purposes, use the form of the factor that includes the wavelength. (b) Determine the Lorentz correction factor for the reflection when its intensity is measured using an area detector at $\omega = 9.41^{\circ}$, with χ fixed at 54.73° and φ set at 270°.

Solution:

(a) $\mathbf{A}^*\mathbf{h} = \mathbf{h}_{\mathrm{l}}$ provides the Cartesian components of the reciprocal lattice vector for the reflection:

$$\mathbf{A}^* = \begin{bmatrix} 0.02650 & -0.04430 & 0.06840 \\ -0.04094 & -0.14859 & -0.02004 \\ 0.15986 & -0.03066 & -0.00154 \end{bmatrix} \begin{bmatrix} 2 \\ \bar{4} \\ 11 \end{bmatrix} = \begin{bmatrix} 0.9826 \\ 0.2920 \\ 0.4254 \end{bmatrix}.$$

The magnitude of the vector, $\mathrm{h} = 2\sin\theta/\lambda$, provides θ and the Lorentz correction factor:

$$\begin{aligned} \mathrm{h} &= (0.9826^2 + 0.2920^2 + 0.4254^2)^{1/2} = 1.110\ \text{Å}^{-1} \\ \theta &= \arcsin\left(\frac{1.110\ \text{Å}^{-1} 0.71073\ \text{Å}}{2}\right) = 23.23^{\circ} \\ L &= \frac{1}{h_y} = \frac{0.71073}{2\sin(23.23^{\circ})(\cos 23.23^{\circ})} = 0.98. \end{aligned}$$

(b) The y component of the reciprocal lattice vector in the diffractometer coordinate system is

$$\begin{aligned} h_y &= (\cos(270^o)\sin(9.41^o) - \sin(270^o)\cos(54.73^o)\cos(9.41^o)) \times 0.9826 \\ &+ (\sin(270^o)\sin(9.41^o) + \cos(270^o)\cos(54.73^o)\cos(9.41^o)) \times 0.2920 \\ &+ (\sin(54.73^o)\sin(9.41^o) \times 0.4254 = 0.8546. \\ L &= \frac{1}{h_y} = 1.17. \end{aligned}$$

4. The mercaptopyridine molecule, C_5H_4NSH, is a common ligand in organometallic chemistry. It often occurs as a bridging ligand, attaching itself to more than one metal center in a complex. For example, in the complex $Re_2Os_2\,((C_6H_5)_3P)_2(CO)_{11}(\mu\text{-}SNC_5H_4)$, the ligand bonds to an osmium atom and a rhenium atom through its sulfur atom, and another rhenium atom via its nitrogen atom (the "μ" indicates that the sulfur atom "bridges" two metal atoms). The unit cell for a crystal of the ligand has a volume of 542.3 Å^3; the space group is $P2_1/n$. The unit cell of a crystal of the complex has a volume of 4920.66 Å^3 in the $P2_1/c$ space group. The table below gives the mass absorption coefficients ($\mu_m = \mu_l/\rho$ (cm^2/g)) for the elements in these compounds for both copper and molybdenum radiation:

Element	Cu $K\alpha$	Mo $K\alpha$	Element	Cu $K\alpha$	Mo $K\alpha$
H	0.435	0.380	S	89.1	9.55
C	4.60	0.625	P	77.28	7.87
N	7.52	0.916	Re	178.1	98.7
O	11.5	1.31	Os	181.8	100.2

(a) Determine the linear absorption coefficients of crystals of the ligand for Cu $K\alpha$ and Mo $K\alpha$ radiation. (b) Determine the linear absorption coefficients of crystals of the complex for Cu $K\alpha$ and Mo $K\alpha$ radiation.

Solution:

(a) Molar mass of the ligand = 111.16 g/mol. Assuming $Z = 4$, the mass of a unit cell is

$$m_c = \frac{111.16}{6.022 \times 10^{23}} \text{ g/molecule} \times 4 \text{ molecules} = 7.385 \times 10^{-22} \text{ g}.$$

The density of the ligand crystal is therefore

$$\rho(\text{lig}) = \frac{7.385 \times 10^{-22} \text{ g}}{542.3 \times 10^{-24} \text{ cm}^3} = 1.36 \text{ g/cm}^3.$$

The fractional masses of the elements in the compound are

$$\begin{aligned} f_{\text{H}} &= \frac{5 \times 1.0079}{111.16} = 0.045 \qquad & f_{\text{N}} &= \frac{1 \times 14.007}{111.16} = 0.126 \\ f_{\text{C}} &= \frac{5 \times 12.011}{111.16} = 0.540 \qquad & f_{\text{S}} &= \frac{1 \times 32.065}{111.16} = 0.288. \end{aligned}$$

$$\begin{aligned}
&\mu_l = (f_H\mu_m^H + f_C\mu_m^C + f_N\mu_m^N + f_S\mu_m^S)\rho(\text{lig})\\
&\mu_l(\text{Cu}\,K\alpha) = 39.65\ \text{cm}^{-1}\\
&\mu_l(\text{Mo}\,K\alpha) = 4.38\ \text{cm}^{-1}
\end{aligned}$$

(b) Molar mass of the complex = 1695.60 g/mol. Assuming $Z = 4$,

$$m_c = \frac{1695.60}{6.022 \times 10^{23}}\ \text{g/molecule} \times 4\ \text{molecules} = 1.126 \times 10^{-20}\ \text{g}.$$

The density of the complex crystal is therefore

$$\rho(\text{cpx}) = \frac{1.126 \times 10^{-20}\ \text{g}}{4920.66 \times 10^{-24}\ \text{cm}^3} = 2.29\ \text{g/cm}^3.$$

The fractional masses of the elements in the compound are

$$\begin{aligned}
f_\text{H} &= \frac{34 \times 1.0079}{1695.6} = 0.020 & f_\text{Os} &= \frac{2 \times 190.23}{1695.6} = 0.224\\
f_\text{C} &= \frac{52 \times 12.011}{1695.6} = 0.368 & f_\text{P} &= \frac{2 \times 30.974}{1695.6} = 0.037\\
f_\text{N} &= \frac{1 \times 14.007}{1695.6} = 0.008 & f_\text{Re} &= \frac{2 \times 186.21}{1695.6} = 0.220\\
f_\text{O} &= \frac{11 \times 15.994}{1695.6} = 0.104 & f_\text{S} &= \frac{1 \times 32.065}{1695.6} = 0.0.019.
\end{aligned}$$

$$\begin{aligned}
&\mu_l = (f_\text{H}\mu_m^\text{H} + f_\text{C}\mu_m^\text{C} + f_\text{N}\mu_m^\text{N} + f_\text{O}\mu_m^\text{O} + f_\text{Os}\mu_m^\text{Os}\\
&\quad + f_\text{P}\mu_m^\text{P} + f_\text{Re}\mu_m^\text{Re} + f_\text{S}\mu_m^\text{S})\rho(\text{cpx})\\
&\mu_l(\text{Cu}\,K\alpha) = 200.18\ \text{cm}^{-1}\\
&\mu_l(\text{Mo}\,K\alpha) = 103.07\ \text{cm}^{-1}.
\end{aligned}$$

5. Iron pyrite, FeS_2, packs in a simple cubic lattice with four formula units per unit cell and $a = 5.4187$ Å. The crystals are often found in nature in the form of cubes. A cube of FeS_2 with edge length d is mounted between a Mo $K\alpha$ X-ray source and a detector that intercepts the beam. We assume that the beam has a comparatively negligible width, so that its cross-section uniformly passes through the cube as it is rotated. The mass absorption coefficients for Fe and S are 17.74 cm^2/g and 9.63 cm^2/g respectively. Calculate the ratio of the minimum and maximum intensities observed as the crystal is rotated in the beam for (a) $d = 0.1$ mm, (b) $d = 0.5$ mm, and (c) $d = 1.0$ mm.

Solution:

$$\frac{I}{I_0} = e^{-\mu_l\, x}$$

The maximum absorption (minimum intensity) will occur for the longest path through the crystal, along the cube diagonal, for which $x = d\sqrt{3}$. The maximum intensity will be observed with the beam parallel to the edge of the cube; $x = d$. Thus

$$\frac{I_{min}}{I_{max}} = \frac{I_{min}/I_0}{I_{max}/I_0} = \frac{e^{-\mu_l\, d\sqrt{3}}}{e^{-\mu_l\, d}} = e^{(1-\sqrt{3})\mu_l\, d} = e^{-0.732\mu_l\, d}.$$

$$
\begin{aligned}
V_c &= (5.4187^{-8}\text{ cm})^3 = 1.591\times10^{-22}\text{cm}^3\\
m_c &= \frac{119.98\text{ g/mol}}{6.022\times10^{23}\text{ fu/mol}}\times 4\text{ fu/cell} = 7.969^{-22}\text{g/cell.}\\
\rho(\text{FeS}_2) &= 5.01\text{g/cm}^3\\
f_{\text{Fe}} &= \frac{53.845}{119.98} = 0.465 \qquad f_{\text{S}} = \frac{2\times32.065}{119.98} = 0.535\\
\mu_l &= ((0.465\times17.72)+(0.535\times9.63))\text{cm}^2/\text{g}\times5.01\text{g/cm}^3\\
&= 67.09\ \mathbf{cm}^{-1}.
\end{aligned}
$$

(a)

$$\frac{I_{min}}{I_{max}} = e^{-0.732(67.09\text{ cm}^{-1})(0.01\text{ cm})} = e^{-0.491} = 0.61.$$

(b)

$$\frac{I_{min}}{I_{max}} = e^{-0.732(67.09\text{ cm}^{-1})(0.05\text{ cm})} = e^{-2.455} = 0.09.$$

(c)

$$\frac{I_{min}}{I_{max}} = e^{-0.732(67.09\text{ cm}^{-1})(0.10\text{ cm})} = e^{-4.910} = 0.01.$$

6. Although the carbon monoselenide molecule, CSe, is known only in the gas phase, its analog, carbon monosulfide, CS, tends to form $(\text{CS})_n$ polymers. Consider a hypothetical crystal of CSe containing a single molecule in a triclinic unit cell. The carbon atom is at the origin, and the selenium atom is at (0.375, 0,375, 0.375). Using the dispersion and scattering factor data below,

atom	f_{110}	$\Delta f'(\text{Cu } K\alpha)$	$\Delta f''(\text{Cu } K\alpha)$	$\Delta f'(\text{Mo } K\alpha)$	$\Delta f''(\text{Mo } K\alpha)$
C	5.4	0.017	0.009	0.002	0.002
Se	30.6	-0.879	1.139	-0.178	2.223

(a) determine the amplitudes and phases for $\mathbf{F}_{110}$ and $\mathbf{F}_{\bar{1}\bar{1}0}$ for Cu $K\alpha$ radiation, and (b) for Mo $K\alpha$ radiation.

Solution:

$$
\begin{aligned}
\xi_{\text{C}} &= -2\pi(1\cdot0+1\cdot0+0\cdot0) = 0\\
\xi_{\text{Se}} &= -2\pi(1\cdot0.375+1\cdot0.375+0\cdot0.375) = -2\pi\left(\frac{3}{4}\right) = -\frac{3\pi}{2} = \frac{\pi}{2}\\
A_{110} &= (f_{\text{C},110}+\Delta f'_{\text{C}})\cos(0) - \Delta f''_{\text{C}}\sin(0)\\
&\qquad +(f_{\text{Se},110}+\Delta f'_{\text{Se}})\cos\left(\frac{\pi}{2}\right) - \Delta f''_{\text{Se}}\sin\left(\frac{\pi}{2}\right)\\
&= f_{\text{C},110}+\Delta f'_{\text{C}} - \Delta f''_{\text{Se}}
\end{aligned}
$$

$$\begin{aligned}
B_{110} &= (f_{\mathrm{C},110} + \Delta\, f'_{\mathrm{C}}) \sin(0) + \Delta f''_{\mathrm{C}} \cos(0) \\
&\quad +(f_{\mathrm{Se},110} + \Delta\, f'_{\mathrm{Se}}) \sin\left(\frac{\pi}{2}\right) + \Delta f''_{\mathrm{Se}} \cos\left(\frac{\pi}{2}\right) \\
&= \Delta f''_{\mathrm{C}} + f_{\mathrm{Se},110} + \Delta\, f'_{\mathrm{Se}} \\
A_{\bar{1}\bar{1}0} &= (f_{\mathrm{C},110} + \Delta\, f'_{\mathrm{C}}) \cos(0) - \Delta f''_{\mathrm{C}} \sin(0) \\
&\quad +(f_{\mathrm{Se},110} + \Delta\, f'_{\mathrm{Se}}) \cos\left(-\frac{\pi}{2}\right) - \Delta f''_{\mathrm{Se}} \sin\left(-\frac{\pi}{2}\right) \\
&= f_{\mathrm{C},110} + \Delta\, f'_{\mathrm{C}} + \Delta f''_{\mathrm{Se}} \\
B_{\bar{1}\bar{1}0} &= (f_{\mathrm{C},110} + \Delta\, f'_{\mathrm{C}}) \sin(0) + \Delta f''_{\mathrm{C}} \cos(0) \\
&\quad +(f_{\mathrm{Se},110} + \Delta\, f'_{\mathrm{Se}}) \sin\left(-\frac{\pi}{2}\right) + \Delta f''_{\mathrm{Se}} \cos\left(-\frac{\pi}{2}\right) \\
&= \Delta f''_{\mathrm{C}} - f_{\mathrm{Se},110} - \Delta\, f'_{\mathrm{Se}}
\end{aligned}$$

(a) For Cu $K\alpha$ radiation,

$$\begin{aligned}
A_{110} &= 5.4 + 0.017 - 1.139 = 4.278 \\
B_{110} &= 0.009 + 30.6 - 0.879 = 29.73 \\
F_{110} &= (4.278^2 + 29.73^2)^{1/2} = 30.04 \\
\varphi_{110} &= \arctan\left(\frac{29.73}{4.278}\right) = 81.81^{\mathrm{o}} \\
A_{\bar{1}\bar{1}0} &= 5.4 + 0.017 + 1.139 = 6.556 \\
B_{\bar{1}\bar{1}0} &= 0.009 - 30.6 + 0.879 = -29.71 \\
F_{\bar{1}\bar{1}0} &= (6.556^2 + 29.71^2)^{1/2} = 30.42 \\
\varphi_{\bar{1}\bar{1}0} &= \arctan\left(\frac{-29.71}{6.556}\right) = -77.56^{\mathrm{o}}.
\end{aligned}$$

(b) For Mo $K\alpha$ radiation,

$$\begin{aligned}
A_{110} &= 5.4 + 0.002 - 2.223 = 3.179 \\
B_{110} &= 0.002 + 30.6 - 0.178 = 30.42 \\
F_{110} &= (3.179^2 + 30.42^2)^{1/2} = 30.58 \\
\varphi_{110} &= \arctan\left(\frac{30.42}{3.179}\right) = 84.03^{\mathrm{o}} \\
A_{\bar{1}\bar{1}0} &= 5.4 + 0.002 + 2.223 = 7.625 \\
B_{\bar{1}\bar{1}0} &= 0.002 - 30.6 + 0.178 = -30.42 \\
F_{\bar{1}\bar{1}0} &= (7.625^2 + 30.42^2)^{1/2} = 31.36 \\
\varphi_{\bar{1}\bar{1}0} &= \arctan\left(\frac{-30.42}{7.625}\right) = -75.92^{\mathrm{o}}.
\end{aligned}$$

7. A terminal oxygen atom in a typical metal carbonyl complex has the following displacement parameters when refined from data collected at 298 K: $U_{11} = 0.06396$, $U_{22} = 0.08275$, $U_{33} = 0.07527$, $U_{12} = -0.04411$, $U_{13} = -0.00590$, and $U_{23} = 0.01226$. A typical metal carbonyl complex with data collected at 100 K provides the following refined displacement parameters: $U_{11} = 0.04448$, $U_{22} = 0.03012$, $U_{33} = 0.03846$, $U_{12} = 0.01193$, $U_{13} = 0.01169$, and $U_{23} = 0.00365$. (a) Compute the equivalent squared isotropic displacement, u^2_{iso}, for the oxygen atoms observed at both temperatures. (b) For

the intensity of a reflection collected at $2\theta = 35^{\circ}$ with Mo $K\alpha$ radiation ($\lambda = 0.71073$) determine the percentage of the "scattering power" that is lost due to vibration by comparing the effective atomic scattering factor at both temperatures to that of a hypothetical oxygen at rest. The scattering factor parameters for oxygen (Eqn. 3.100) are given in Exercise 8 at the end of Chapter 3.

Solution:

(a)

$$u_{iso}^2(298) = \frac{0.06396 + 0.08275 + 0.07527}{3} = 0.074\ \text{Å}^2$$
$$u_{iso}^2(100) = \frac{0.04448 + 0.03012 + 0.03846}{3} = 0.038\ \text{Å}^2$$

(b) For the atom at rest, $\theta = 17.5^{\circ}$, $s = \sin(17.5^{\circ})/0.71073 = 0.423$, and

$$\begin{aligned} f_\theta &= 3.0485\, e^{-13.2771\, s^2} + 2.2868\, e^{-5.7011\, s^2} \\ &\quad +1.5463\, e^{-0.3239\, s^2} + 0.8670\, e^{-32.9089\, s^2} + 0.2508 \\ &= 2.820 \end{aligned}$$

For the vibrating atom,

$$\begin{aligned} T_{iso} &= 8\pi^2 u_{iso}^2 \frac{\sin^2\theta}{\lambda^2} = 8\pi^2 s^2 u_{iso}^2 = 14.127 u_{iso}^2 \\ f_{\theta,T} &= f_\theta\, e^{-T_{iso}}. \end{aligned}$$

For the atom vibrating at 298 K,

$$\begin{aligned} f_{\theta,T} &= f_\theta\, e^{-1.045} = 0.991 \\ \Delta f &= 1.828. \quad \text{loss} = \frac{1.828}{2.820} = 65\%. \end{aligned}$$

For the atom vibrating at 100 K,

$$\begin{aligned} f_{\theta,T} &= f_\theta\, e^{-0.537} = 1.649 \\ \Delta f &= 1.171. \quad \text{loss} = \frac{1.171}{2.820} = 42\%. \end{aligned}$$

8. The mercaptopyridine unit cell contains four C_5H_4NSH molecules. The table on the following page summarizes the intensity data for the crystal structure, collected with Mo $K\alpha$ radiation and divided into regions of approximately constant values of the diffraction angle, 2θ. The average intensity is listed for each region, along with the value of the atomic scattering factor, $f(\langle 2\theta \rangle)$, for each type of atom in the unit cell for each region. Create a Wilson plot of the data and determine the scale factor and the average atomic displacement.

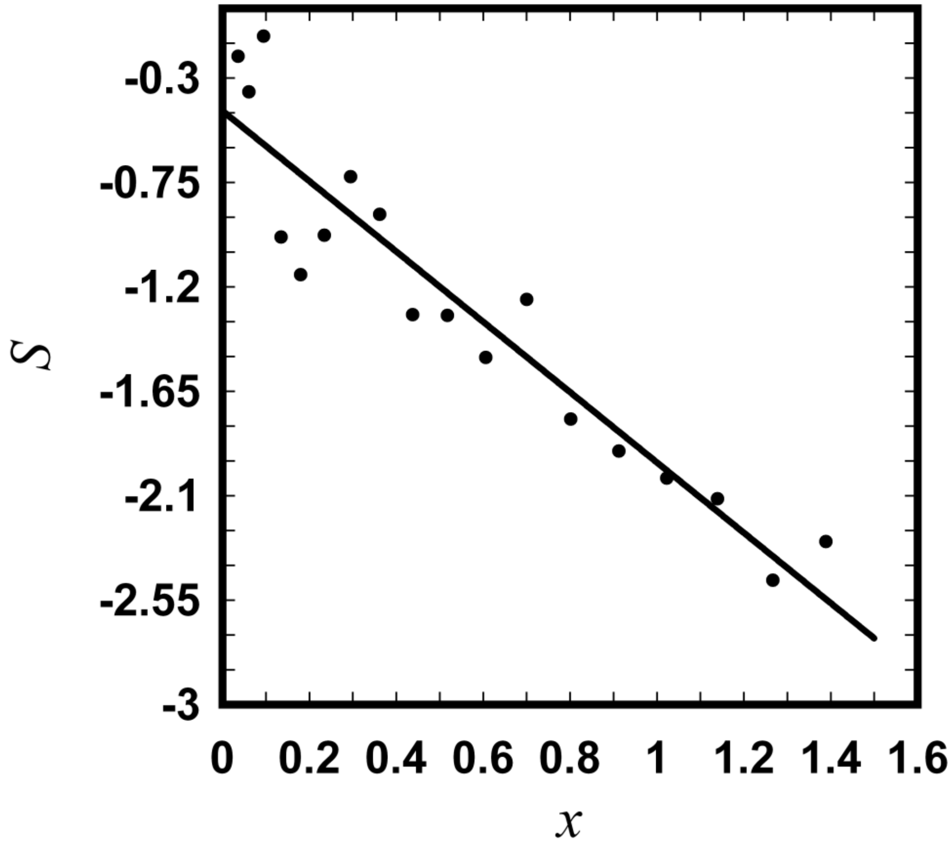
$\langle 2\theta \rangle$	$\langle I_{rel} \rangle$	f_{H}	f_{C}	f_{N}	f_{S}
7.71	1247.8	0.83	5.19	6.26	14.34
10.04	921.59	0.73	4.74	5.83	13.45
12.52	982.03	0.63	4.26	5.33	12.48
14.97	345.16	0.53	3.8	4.83	11.57
17.31	247.5	0.45	3.4	4.37	10.8
19.8	247.41	0.37	3.04	3.93	10.1
22.23	273.53	0.3	2.74	3.55	9.52
24.67	202.97	0.25	2.49	3.21	9.03
27.18	116.46	0.21	2.28	2.92	8.61
29.62	104.61	0.17	2.12	2.68	8.27
32.12	79.41	0.14	1.99	2.47	7.96
34.59	93.92	0.12	1.88	2.29	7.69
37.09	52.02	0.1	1.8	2.15	7.44
39.67	42.16	0.08	1.73	2.02	7.2
42.11	35.15	0.07	1.68	1.92	6.98
44.58	30.18	0.06	1.63	1.84	6.76
47.15	19.9	0.05	1.59	1.77	6.54
49.51	22.17	0.04	1.55	1.71	6.33

Solution:

Let $S_i = \langle I_{rel} \rangle_i / \sum_{j=1}^{48} f_i^2 \equiv \langle I_{rel} \rangle_i / \sum_i^2$ and $x_i = \langle h \rangle_i^2$, where $\langle h \rangle_i = 2 \sin\langle \theta \rangle_i / \lambda$. $\sum_i^2 = 20 f_{\mathrm{H},i}^2 + 20 f_{\mathrm{C},i}^2 + 4 f_{\mathrm{N},i}^2 + 4 f_{\mathrm{S},i}^2$, resulting in

$\langle h \rangle^2$	S	$\langle h \rangle^2$	S
0.04	-0.21	0.52	-1.32
0.06	-0.36	0.61	-1.50
0.09	-0.12	0.70	-1.25
0.13	-0.98	0.80	-1.77
0.18	-1.15	0.91	-1.91
0.23	-0.98	1.02	-2.02
0.29	-0.72	1.14	-2.11
0.36	-0.89	1.27	-2.46
0.44	-1.32	1.39	-2.30

and a Wilson Plot:



The slope and intercept of the least squares line provides the overall temperature factor and the scale factor, respectively. Treating $S_{o,i}$ as the "observed" parameter, and $S_{c,i}$ as the "calculated" parameter, the method of linear least squares minimizes $\sum_i (S_{c,i} - S_{o,i})^2$, where $S_{c,i} = mx_i + b$. Referring to Appendix G, by analogy, for $n = 18$,

$$\begin{bmatrix} m \\ b \end{bmatrix} = \begin{bmatrix} \sum_i x_i^2 & \sum_i x_i \\ \sum_i x_i & n \end{bmatrix} \begin{bmatrix} \sum_i x_i S_{o,i} \\ \sum_i S_{o,i} \end{bmatrix} = \begin{bmatrix} -1.515 \\ -0.4412 \end{bmatrix}.$$

$$\begin{aligned} \ln K &= -0.4412 \\ K' &= \frac{1}{K} = 1.555 \\ -2\mathrm{B}' &= -1.515 \\ \langle u \rangle^2 &= \frac{\mathrm{B}'}{2\pi^2} = 0.038\ \text{Å}^2 \\ \langle u \rangle &= 0.19\ \text{Å}. \end{aligned}$$

9. Derive the reflection conditions for (a) an I-centered crystal, (b) a crystal with a triad screw axis parallel to the c axis.

Solution:

(a) Symmetry-equivalent atoms at (x_f, y_f, z_f) and $((x_f + \frac{1}{2}), (y_f + \frac{1}{2}), (z_f + \frac{1}{2}))$. The structure factor for a *general* reflection is

$$\begin{aligned}
\mathbf{F}_{c,hkl} &= \sum_{j=1}^{n/2} f_j e^{-2\pi\, i(hx_j+ky_j+lz_j)} \\
&\quad + \sum_{m=1}^{n/2} f_m e^{-2\pi\, i(h(x_m+1/2)+k(y_m+1/2)+l(z_m+1/2)} \\
&= \sum_{j=1}^{n/2} f_j e^{-2\pi\, i(hx_j+ky_j+lz_j)} \\
&\quad + \sum_{m=1}^{n/2} f_m e^{-2\pi\, i(hx_m+ky_m+lz_m)}\, e^{-(h+k+l)\pi i}.
\end{aligned}$$

When $h+k+l$ is odd, $e^{-(h+k+l)\pi i} = -1$, $\mathbf{F}_{c,hkl} = \mathbf{0}$ and $I_{hkl} = 0$. The reflection conditions for a general reflection if the lattice is I centered require that $h+k+l = 2n$.

(b) The triad screw axis has symmetry equivalent positions at (x_f, y_f, z_f), $(\bar{y}_f, x_f - y_f, z_f + \frac{1}{3})$, and $(y_f - x_f, \bar{x}_f, z_f + \frac{2}{3})$. For reflections with $(00l)$ indices,

$$\mathbf{F}_{c,00l} = \sum_{j=1}^{n/3} f_j e^{-2\pi\, i\, l y_j} + \sum_{j'=1}^{n/3} f_{j'} e^{-2\pi\, il(y_{j'}+1/3)} + \sum_{j''=1}^{n/3} f_{j''} e^{-2\pi\, il(y_{j''}+2/3)}.$$

To simplify, set $Q = \sum_{j=1}^{n/3} f_j e^{-2\pi\, i\, l y_j}$:

$$\begin{aligned}
\mathbf{F}_{c,00l} &= Q + e^{(-2\pi\, i\, l)/3} Q + e^{(-4\pi\, i\, l)/3} Q \\
&= Q\left(1 + e^{(-2\pi\, i\, l)/3} + e^{(-4\pi\, i\, l)/3}\right)
\end{aligned}$$

All l indices can take on values of $3n+m$, $m = 1$, 2, or 3 (divisible by 3), and n is an integer:

$$\begin{aligned}
\mathbf{F}_{c,00l} &= Q\left(1 + e^{(-2\pi\, i)(3n/3)} e^{(-2\pi\, i)(m/3)} + + e^{(-4\pi\, i)(3n/3)} e^{(-4\pi\, i)(m/3)}\right) \\
&= \left(1 + e^{(-2\pi\, i)(m/3)} + e^{(-4\pi\, i)(m/3)}\right) \\
&= Q(1 + \cos(-2\pi m/3) + i\sin(-2\pi m/3) \\
&\qquad + \cos(-4\pi m/3) + i\sin(-4\pi m/3).
\end{aligned}$$

$$\begin{aligned}\mathbf{F}_{c,00(3n+1)} &= Q\left(1-\frac{1}{2}-i\frac{\sqrt{3}}{2}-\frac{1}{2}+i\frac{\sqrt{3}}{2}\right)=0\\ \mathbf{F}_{c,00(3n+2)} &= Q\left(1-\frac{1}{2}+i\frac{\sqrt{3}}{2}-\frac{1}{2}-i\frac{\sqrt{3}}{2}\right)=0\\ \mathbf{F}_{c,00(3n+3)} &= Q(1+1+0+1+0)=3Q.\end{aligned}$$

Intensities are observed for $00l$ reflections only where $l=3n+3$, with systematic absences for $l=3n+1$ and $l=3n+2$.

10. The relatively small difference between the expected values of $\langle E_{\mathbf{h}}\rangle$ for the centric and acentric E distributions has prompted the use of other "E-statistics" to assist in ascertaining the presence or absence of a center of symmetry in the unit cell. In particular, expected values of $\langle |E^2_{\mathbf{h}}-1|\rangle$ are commonly employed for this purpose. The absolute value is taken, since $E^2_{\mathbf{h}}-1$ can be negative. (a) Determine the expected value of $\langle |E^2_{\mathbf{h}}-1|\rangle_1$ for the acentric distribution. (Note: Because $E^2_{\mathbf{h}}-1$ is negative for $0\le E_{\mathbf{h}}<1$, the probability integral must be evaluated separately from 0 to 1, then added to the integral from 1 to ∞.) (b) Determine the expected value of $\langle |E^2_{\mathbf{h}}-1|\rangle_{\bar{1}}$ for the centric distribution by evaluating the probability integral numerically, or estimating it graphically using trapezoidal integration.

Solution:

(a)

$$\langle |E^2_{\mathbf{h}}-1|\rangle_1=\int_0^\infty |E^2_{\mathbf{h}}-1|\left(2E_{\mathbf{h}}e^{-E^2_{\mathbf{h}}}\right)dE_{\mathbf{h}}.$$

Substituting $u=E^2_{\mathbf{h}}\Rightarrow dE_{\mathbf{h}}=du/(2E_{\mathbf{h}})$,

$$\begin{aligned}\langle |E^2_{\mathbf{h}}-1|\rangle_1 &= \int_0^\infty |u-1|e^{-u}du\\ &= \int_0^1 -(u-1)e^{-u}du+\int_1^\infty (u-1)e^{-u}du\\ &= \int_0^1 e^{-u}du-\int_0^1 ue^{-u}du+\int_1^\infty ue^{-u}du-\int_1^\infty e^{-u}du.\end{aligned}$$

Using the two indefinite integrals,

$$\int e^{au}du=\frac{1}{a}e^{au}+C \quad\text{and}\quad \int ue^{au}du=\left(\frac{u}{a}-\frac{1}{a^2}\right)e^{au}+C,$$

and noting that $\lim_{u\to\infty}(ue^{-u})=0$ (since the exponential converges to zero rapidly as u becomes large),

$$\begin{aligned}
\int_0^1 e^{-u}du &= -e^{-u}\Big|_0^1 = 1-\frac{1}{e}\\
-\int_0^1 ue^{-u}du &= (u+1)e^{-u}\Big|_0^1 = \frac{2}{e}-1\\
\int_1^\infty ue^{-u}du &= -(u+1)e^{-u}\Big|_1^\infty = \frac{2}{e}\\
-\int_1^\infty e^{-u}du &= -e^{-u}\Big|_1^\infty = -\frac{1}{e}\\
\langle|E_{\mathbf{h}}^2-1|\rangle_1 &= 1-\frac{1}{e}+\frac{2}{e}-1+\frac{2}{e}-\frac{1}{e}=\frac{2}{e}=0.736.
\end{aligned}$$

(b)

$$\begin{aligned}
\langle|E_{\mathbf{h}}^2-1|\rangle_{\bar{1}} &= \int_0^\infty |E_{\mathbf{h}}^2-1|\left(\frac{2}{\sqrt{2\pi}}e^{-E_{\mathbf{h}}^2/2}\right)dE_{\mathbf{h}}\\
&= \frac{2}{\sqrt{2\pi}}\int_0^\infty |E_{\mathbf{h}}^2-1|e^{-E_{\mathbf{h}}^2/2}dE_{\mathbf{h}}.
\end{aligned}$$

As in part (a), an analytical solution requires integration of the function from 0 to 1 and from 1 to ∞. This results in indefinite integrals of the form $\int x^2\exp(-x^2)dx$, which, like the Gaussian function, cannnot be evaluated analytically. However, a numerical evaluation of the integral is straightforward, using a programmable calculator or computer. The following simple program, written in BASIC, is readily adaptable to any programming language:

```
pi = 3.1415927
dE = 0.001
integral = 0
E = −dE
Do While E <= 5
   E = E + dE
   integral = integral + Abs(E ∧ 2 − 1) * Exp(−E ∧ 2 / 2) * dE
Loop
integral = (2 / Sqr(2 * pi)) * integral
```

The result: integral = $\langle|E_{\mathbf{h}}^2-1|\rangle_{\bar{1}} = 0.968$.

Chapter 6

Crystal Structure Solution: Experimental

1. Representing each peak in a Fourier map as a single point, determine the "peak density" (the average number of peaks per unit volume) for an electron density map (D_e) and a Patterson map (D_P) for each of the following (ignore the hydrogen atoms): (a) C_5H_4NSH, V_{cell} = 542.3 Å^3, $Z = 4$, (b) Re_2Os_2 $((C_6H_5)_3P)_2(CO)_{11}(\mu\text{-}SNC_5H_4)$, V_{cell} = 4920.7 Å^3, $Z = 4$, and (c) Rat Short Chain Acyl-CoA Dehydrogenase (RSCAD)*, asymmetric unit consisting of 6330 non-hydrogen atoms, V_{cell} = 1 383 302 Å^3, $Z = 6$.

Solution:

(a) C_5H_4NSH: 7 atoms per asymmetric unit × 4 asymmetric units per unit cell = 28 atoms/cell.

$$D_e = \frac{28 \text{ peaks}}{542.3 \text{ Å}^3} = 0.05 \text{ peaks/ Å}^3.$$

Every atom in the unit cell has a Patterson vector to every other atom, resulting in $n \times (n-1)$ peaks, plus an additional peak for the origin:

$$D_P = \frac{(28 \times 27) + 1 \text{ peaks}}{542.3 \text{ Å}^3} = 1.4 \text{ peaks/ Å}^3.$$

(b) Re_2Os_2 $((C_6H_5)_3P)_2(CO)_{11}(\mu\text{-}SNC_5H_4)$: 71 atoms per asymmetric unit × 4 asymmetric units per unit cell = 284 atoms/cell.

$$\begin{aligned} D_e &= \frac{284 \text{ peaks}}{4920.7 \text{ Å}^3} = 0.06 \text{ peaks/ Å}^3 \\ D_P &= \frac{(284 \times 283) + 1 \text{ peaks}}{4920.7 \text{ Å}^3} = 16.3 \text{ peaks/ Å}^3. \end{aligned}$$

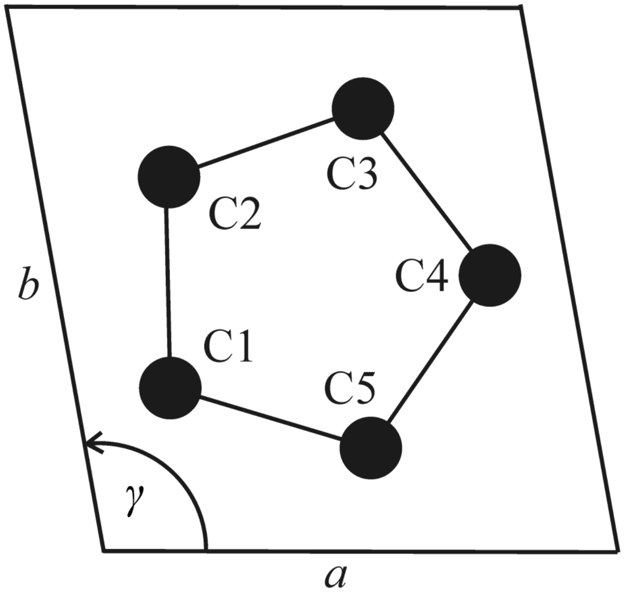
---

[*] Battaile, K.P., Molin-Case, J., Paschke, R., Wang, M. , Bennett, D.W., Vockley, J., and Kim, J.J.P., *J. Biol. Chem.*, 277(14), 12200 (2002).

(c) RSCAD: 6330 atoms per asymmetric unit × 6 asymmetric units per unit cell = 37 980 atoms/cell.

$$
\begin{aligned}
D_e &= \frac{37\,980 \text{ peaks}}{1\,383\,302 \text{ Å}^3} = 0.03 \text{ peaks/ Å}^3 \\
D_P &= \frac{(37\,980 \times 37\,979) + 1 \text{ peaks}}{1\,383\,302 \text{ Å}^3} = 1043 \text{ peaks/ Å}^3.
\end{aligned}
$$

2. A two dimensional unit cell for the *very* hypothetical ion pair, $H^+ \ C_5H_5^-$ is shown below (ignoring the hydrogen atoms and ion):



The unit cell parameters are $a = 3.5$ Å, $b = 3.8$ Å, and $\gamma = 100^o$. The fractional coordinates of the carbon atoms: C1(0.1951, 0.3110), C2(0.2586, 0.6847), C3(0.6595, 0.8065), C4(0.8438, 0.5079) and C5(0.5568, 0.2017). Calculate the Cartesian components of the Patterson vectors and the four origins that encompass the unit cell. Plot the predicted locations of the Patterson maxima.

Solution:

The fractional coordinates of the Patterson vectors are determined as $u_f(\overrightarrow{\text{CACB}}) = x_f(\text{CB}) - x_f(\text{CA})$ and $v_f(\overrightarrow{\text{CACB}}) = y_f(\text{CB}) - y_f(\text{CA})$. In order to place each vector in the same unit cell, 1 is added to any component less than zero, and −1 is added to any component greater than 1, resulting in

vector	u_f	v_f	vector	u_f	v_f
$\overrightarrow{\mathrm{C1C2}}$	0.0635	0.3737	$\overrightarrow{\mathrm{C2C1}}$	0.9365	0.6263
$\overrightarrow{\mathrm{C1C3}}$	0.4644	0.4955	$\overrightarrow{\mathrm{C3C1}}$	0.5356	0.5045
$\overrightarrow{\mathrm{C1C4}}$	0.6487	0.1969	$\overrightarrow{\mathrm{C4C1}}$	0.3513	0.8031
$\overrightarrow{\mathrm{C1C5}}$	0.3617	0.8907	$\overrightarrow{\mathrm{C5C1}}$	0.6383	0.1093
$\overrightarrow{\mathrm{C2C3}}$	0.4009	0.1218	$\overrightarrow{\mathrm{C3C2}}$	0.5991	0.8782
$\overrightarrow{\mathrm{C2C4}}$	0.5852	0.8232	$\overrightarrow{\mathrm{C4C2}}$	0.4148	0.1768
$\overrightarrow{\mathrm{C2C5}}$	0.2982	0.5170	$\overrightarrow{\mathrm{C5C2}}$	0.7018	0.4830
$\overrightarrow{\mathrm{C3C4}}$	0.1843	0.7014	$\overrightarrow{\mathrm{C4C3}}$	0.8157	0.2986
$\overrightarrow{\mathrm{C3C5}}$	0.8973	0.3952	$\overrightarrow{\mathrm{C5C3}}$	0.1027	0.6048
$\overrightarrow{\mathrm{C4C5}}$	0.7130	0.6938	$\overrightarrow{\mathrm{C5C4}}$	0.2870	0.3062

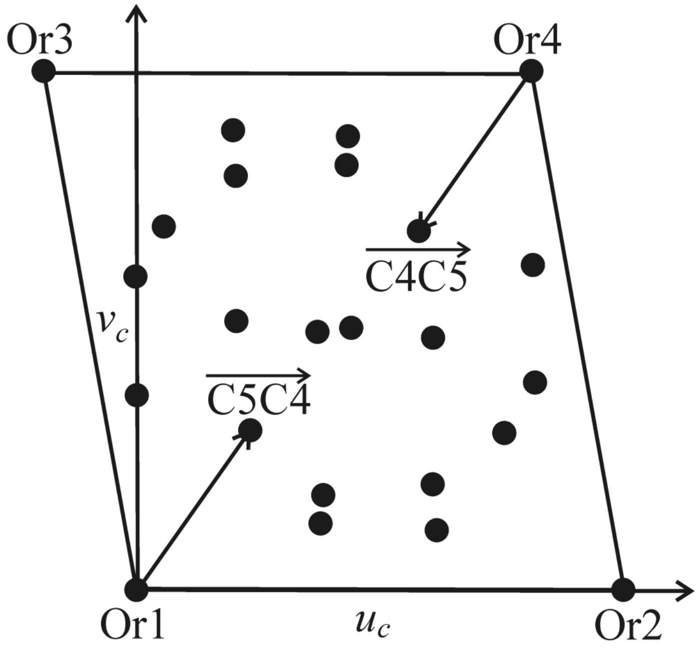
The matrix to convert these vectors to Cartesian coordinates is

$$\mathbf{B} = \begin{bmatrix} a & b\cos\gamma \\ 0 & b\sin\gamma \end{bmatrix} = \begin{bmatrix} 3.5 & -0.6599 \\ 0 & 3.7423 \end{bmatrix}; \quad \mathbf{B}\begin{bmatrix} u_f \\ v_f \end{bmatrix} = \begin{bmatrix} u_c \\ v_c \end{bmatrix}.$$

Cartesian coordinates of predicted Patterson maxima and origins in Å:

vector	u_c	v_c	vector	u_c	v_c
$\overrightarrow{\mathrm{C1C2}}$	−0.0243	1.3985	$\overrightarrow{\mathrm{C2C1}}$	2.8645	2.3438
$\overrightarrow{\mathrm{C1C3}}$	1.2984	1.8543	$\overrightarrow{\mathrm{C3C1}}$	1.5417	1.8880
$\overrightarrow{\mathrm{C1C4}}$	2.1405	0.7369	$\overrightarrow{\mathrm{C4C1}}$	0.6996	3.0054
$\overrightarrow{\mathrm{C1C5}}$	0.6782	3.3332	$\overrightarrow{\mathrm{C5C1}}$	2.1619	0.4090
$\overrightarrow{\mathrm{C2C3}}$	1.3228	0.4558	$\overrightarrow{\mathrm{C3C2}}$	1.5174	3.2865
$\overrightarrow{\mathrm{C2C4}}$	1.5050	3.0806	$\overrightarrow{\mathrm{C4C2}}$	1.3351	0.6616
$\overrightarrow{\mathrm{C2C5}}$	0.7026	1.9348	$\overrightarrow{\mathrm{C5C2}}$	2.1376	1.8075
$\overrightarrow{\mathrm{C3C4}}$	0.1822	2.6248	$\overrightarrow{\mathrm{C4C3}}$	2.6579	1.1174
$\overrightarrow{\mathrm{C3C5}}$	2.8798	1.4789	$\overrightarrow{\mathrm{C5C3}}$	−0.0396	2.2633
$\overrightarrow{\mathrm{C4C5}}$	2.0377	2.5964	$\overrightarrow{\mathrm{C5C4}}$	0.8024	1.1459
Or1	0.0000	0.0000	Or2	3.5000	0.0000
Or3	−0.6599	3.7423	Or4	2.8401	3.7423

The resulting plot should look something like this:



3. Extend the Patterson map created in Exercise 2 so that there are four unit cells arranged about a common origin (e.g., Fig. 6.8). Overlay the plot with a sheet of paper that is transparent enough to provide a view of the points underneath and carefully mark an "x" at the center of each point on the plot. Use this template to demonstrate by Patterson superposition that there are numerous images of the H^+ $C_5H_5^-$ structure in the Patterson map.

Solution:

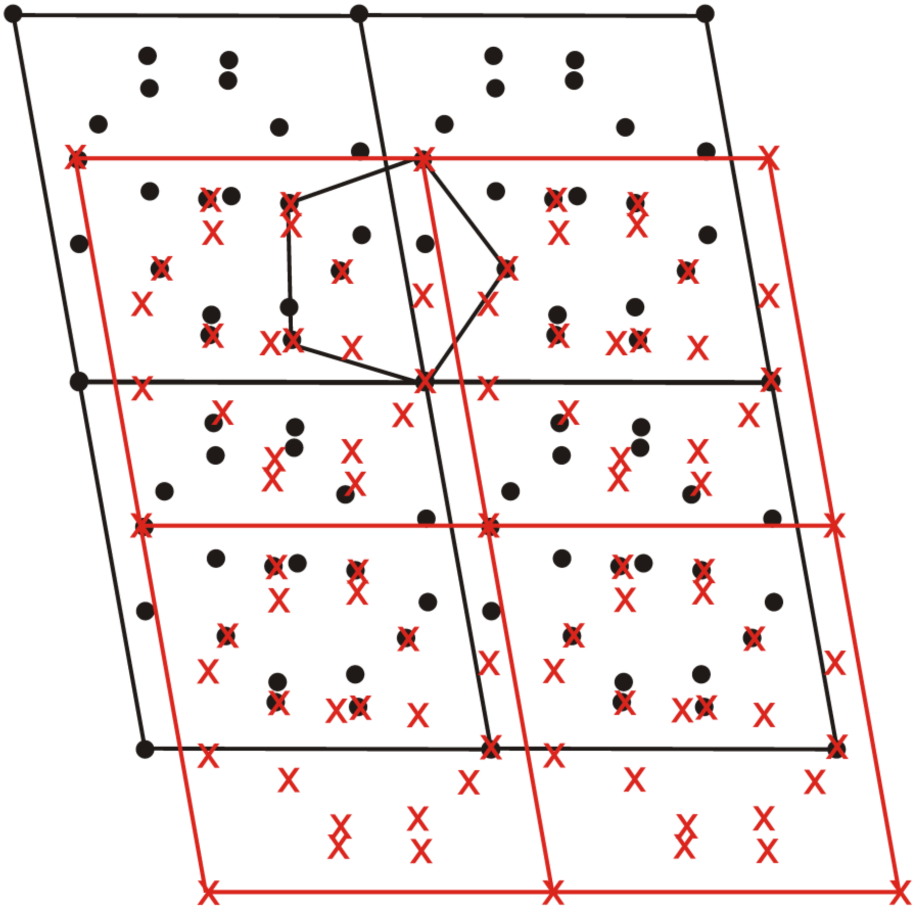
The figure on the following page illustrates one of many superpositions.

4. Predict the lines and/or planes in the Patterson unit cell upon which Patterson maxima tend to accumulate (in Harker lines and sections) for the following space groups: (a) $P2/c$, (b) $P2_1/c$, (c) $P2_12_12$, (d) $P2_12_12_1$, (e) $P3_1$, and (f) $P4_1$.

Solution:

(a) $P2/c$: Symmetry-equivalent positions at (1) (x, y, z), (2) $(\bar{x}, y, 1/2 - z)$, (3) $(\bar{x}, \bar{y}, \bar{z})$, and (4) $(x, \bar{y}, 1/2 + z)$.

$$\left.\begin{aligned} u_{12} &= x - \bar{x} = 2x \\ v_{12} &= y - y = 0 \\ w_{12} &= z - \tfrac{1}{2} + z = 2z - \tfrac{1}{2} \end{aligned}\right\} \quad \text{Harker section at } \Big(u,\ 0,\ w \Big)$$



$$\left.\begin{aligned} u_{14} &= x - x = 0 \\ v_{14} &= y - \bar{y} = 2y \\ w_{14} &= z - \tfrac{1}{2} - z = -\tfrac{1}{2} \equiv \tfrac{1}{2} \end{aligned}\right\} \quad \text{Harker line at } \left(0,\ v,\ \tfrac{1}{2}\right)$$

(b) $P2_1/c$: Symmetry-equivalent positions at (1) (x, y, z), (2) $(\bar{x}, 1/2{+}y, 1/2{-}z)$, (3) $(\bar{x}, \bar{y}, \bar{z})$, and (4) $(x, 1/2 - y, 1/2 + z)$.

$$\left.\begin{aligned} u_{12} &= x - \bar{x} = 2x \\ v_{12} &= y - \tfrac{1}{2} - y = -\tfrac{1}{2} \equiv \tfrac{1}{2} \\ w_{12} &= z - \tfrac{1}{2} + z = 2z - \tfrac{1}{2} \end{aligned}\right\} \quad \text{Harker section at } \left(u,\ \tfrac{1}{2},\ w\right)$$

$$\left.\begin{aligned} u_{14} &= x - x = 0 \\ v_{14} &= y - \tfrac{1}{2} + y = 2y - \tfrac{1}{2} \\ w_{14} &= z - \tfrac{1}{2} - z = -\tfrac{1}{2} \equiv \tfrac{1}{2} \end{aligned}\right\} \quad \text{Harker line at } \left(0,\ v,\ \tfrac{1}{2}\right)$$

(c) $P2_12_12$: Symmetry-equivalent positions at (1) (x, y, z), (2) $(\bar{x}, \bar{y}, z)$, (3) $(1/2 - x, 1/2 + y, \bar{z})$, and (4) $(1/2 + x, 1/2 - y, \bar{z})$.

$$\left.\begin{aligned} u_{12} &= x - \bar{x} = 2x \\ v_{12} &= y - \bar{y} = 2y \\ w_{12} &= z - z = 0 \end{aligned}\right\} \quad \text{Harker section at } \Big(\, u,\ v,\ 0 \,\Big)$$

$$\left.\begin{aligned} u_{13} &= x - \tfrac{1}{2} + x = 2x - \tfrac{1}{2} \\ v_{13} &= y - \tfrac{1}{2} - y = -\tfrac{1}{2} \equiv \tfrac{1}{2} \\ w_{13} &= z - \bar{z} = 2z \end{aligned}\right\} \quad \text{Harker section at } \Big(\, u,\ \tfrac{1}{2},\ w \,\Big)$$

$$\left.\begin{aligned} u_{14} &= x - \tfrac{1}{2} - x = -\tfrac{1}{2} \equiv \tfrac{1}{2} \\ v_{14} &= y - \tfrac{1}{2} + y = 2y - \tfrac{1}{2} \\ w_{14} &= z - \bar{z} = 2z \end{aligned}\right\} \quad \text{Harker section at } \Big(\, \tfrac{1}{2},\ v,\ w \,\Big)$$

(d) $P2_12_12_1$: Symmetry-equivalent positions at (1) (x, y, z), (2) $(1/2 - x, \bar{y}, 1/2 + z)$, (3) $(1/2 + x, 1/2 - y, \bar{z})$, and (4) $(\bar{x}, 1/2 + y, 1/2 - z)$.

$$\left.\begin{aligned} u_{12} &= x - \tfrac{1}{2} + x = 2x - \tfrac{1}{2} \\ v_{12} &= y - \bar{y} = 2y \\ w_{12} &= z - \tfrac{1}{2} - z = -\tfrac{1}{2} \equiv \tfrac{1}{2} \end{aligned}\right\} \quad \text{Harker section at } \Big(\, u,\ v,\ \tfrac{1}{2} \,\Big)$$

$$\left.\begin{aligned} u_{13} &= x - \tfrac{1}{2} - x = -\tfrac{1}{2} \equiv \tfrac{1}{2} \\ v_{13} &= y - \tfrac{1}{2} + y = 2y - \tfrac{1}{2} \\ w_{13} &= z - \bar{z} = 2z \end{aligned}\right\} \quad \text{Harker section at } \Big(\, \tfrac{1}{2},\ v,\ w \,\Big)$$

$$\left.\begin{aligned} u_{14} &= x - \bar{x} = 2x \\ v_{14} &= y - \tfrac{1}{2} - y = -\tfrac{1}{2} \equiv \tfrac{1}{2} \\ w_{14} &= z - \tfrac{1}{2} + z = 2z - \tfrac{1}{2} \end{aligned}\right\} \quad \text{Harker section at } \Big(\, u,\ \tfrac{1}{2},\ w \,\Big)$$

(e) $P3_1$: Symmetry-equivalent positions at (1) (x, y, z), (2) $\bar{y}, x - y, 1/3 + z)$, and (3) $(\bar{x} + y, \bar{x}, 2/3 + z)$.

$$\left.\begin{aligned} u_{12} &= x - \bar{y} = x + y \\ v_{12} &= y - x + y = 2y - x \\ w_{12} &= z - \tfrac{1}{3} - z = -\tfrac{1}{3} \equiv \tfrac{1}{3} \end{aligned}\right\} \quad \text{Harker section at } \Big(\, u,\ v,\ \tfrac{1}{3} \,\Big)$$

(f) $P4_1$: Symmetry-equivalent positions at (1) (x, y, z), (2) $(\bar{x}, \bar{y}, 1/2 + z)$, (3) $(\bar{y}, x, 1/4 + z)$, (4) $(y, \bar{x}, 3/4 + z)$

$$\left.\begin{aligned} u_{12} &= x - \bar{x} = 2x \\ v_{12} &= y - \bar{y} = 2y \\ w_{12} &= z - \tfrac{1}{2} - z = -\tfrac{1}{2} \equiv \tfrac{1}{2} \end{aligned}\right\} \quad \text{Harker section at } \Big(\, u,\ v,\ \tfrac{1}{2} \,\Big)$$

$$\left.\begin{aligned} u_{13} &= x - \bar{y} = x + y \\ v_{13} &= y - x \\ w_{13} &= z - \tfrac{1}{4} - z = -\tfrac{1}{4} \equiv \tfrac{1}{4} \end{aligned}\right\} \quad \text{Harker section at } \Big(\, u,\ v,\ \tfrac{1}{4} \,\Big)$$

5. A sharpened Patterson map for the mercaptopyridine structure, space group $P2_1/n$, revealed the following peak locations, heights, and vector lengths:

peak	u_f	v_f	w_f	height	length
1	0.0000	0.0000	0.0000	999	0.00
2	0.5000	0.3730	0.5000	339	7.58
3	0.9764	0.5000	0.3130	282	5.51
4	0.0666	0.5000	0.1778	184	4.03
5	0.5189	0.1243	0.1880	144	4.44
6	0.7005	0.5000	0.2653	143	5.53
7	0.3194	0.0000	0.4201	141	5.94
8	0.8408	0.0000	0.0399	132	1.22
9	0.5136	0.5000	0.0481	123	4.49
10	0.5000	0.0000	0.5000	119	7.20

Determine the location of the sulfur atom in the unit cell and verify that its location is consistent with that listed in Sec. 1.5.3, found by direct methods.

Solution:

The sulfur-sulfur vectors will have the largest intensities, since sulfur is the only heavy atom in the structure. Intense peaks should be found on the Harker line and plane determined from the symmetry-equivalent positions: (1) (x, y, z), (2) $1/2 - x, 1/2 + y, 1/2 - z)$, (3) $(\bar{x}, \bar{y}, \bar{z})$, and (4) $(1/2 + x, 1/2 - y, 1/2 + z)$.

$$\left.\begin{aligned} u_{12} &= x - \tfrac{1}{2} + x = 2x - \tfrac{1}{2} \\ v_{12} &= y - \tfrac{1}{2} - y = -\tfrac{1}{2} \equiv \tfrac{1}{2} \\ w_{12} &= z - \tfrac{1}{2} + z = 2z - \tfrac{1}{2} \end{aligned}\right\} \quad \text{Harker section at } \left(u,\ \tfrac{1}{2},\ w \right)$$

$$\left.\begin{aligned} u_{14} &= x - \tfrac{1}{2} - x = -\tfrac{1}{2} \equiv \tfrac{1}{2} \\ v_{14} &= y - \tfrac{1}{2} + y = 2y - \tfrac{1}{2} \\ w_{14} &= z - \tfrac{1}{2} - z = -\tfrac{1}{2} \equiv \tfrac{1}{2} \end{aligned}\right\} \quad \text{Harker line at } \left(\tfrac{1}{2},\ v,\ \tfrac{1}{2} \right)$$

Peak 1 is the origin peak. Peak 2 represents the S − S vector on the Harker line at $(1/2, (2y - 1/2), 1/2) \Rightarrow$

$$2y - \tfrac{1}{2} = 0.3730 \qquad y = 0.4365.$$

Peak 3 represents the S−S vector on the Harker plane at $((2x-1/2), 1/2, (2z-1/2)) \Rightarrow$

$$\begin{aligned} 2x - \tfrac{1}{2} &= 0.9764 \qquad x = 0.7382 \\ 2z - \tfrac{1}{2} &= 0.3130 \qquad z = 0.4065. \end{aligned}$$

When solved by direct methods, the sulfur atom position refines to $(0.7403, 0.0629, 0.4073)$. The y positions are shown to be consistent by noting that there is an equivalent $\mathrm{S} - \mathrm{S}$ vector at $(-1/2, -0.3730, -1/2) \Rightarrow$

$$2y - \tfrac{1}{2} = -0.3730 \qquad y = 0.0635.$$

The structure is solved by difference Fourier synthesis from the initial sulfur atom position, which refines to $(0.7402, 0.4370 \equiv 0.0630, 0.4074)$.

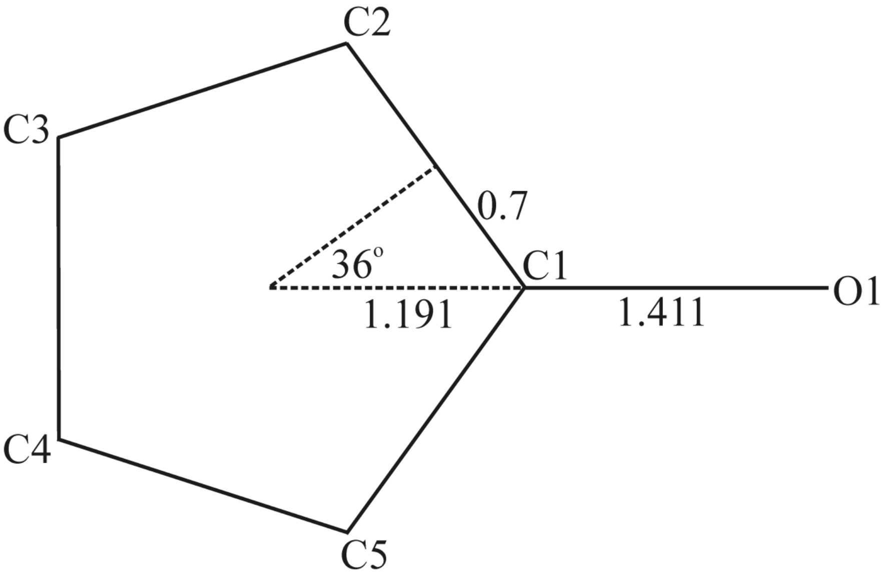
6. The unit cell parameters for the hypothetical two-dimensional $\mathrm{C_5H_4OH}$ structure illustrated in Fig. 6.8(a) are $a = 7$ Å, $b = 6$ Å, and $\gamma = 110^{\mathrm{o}}$. The following table lists the $6 \times 5 = 30$ Patterson vectors, centered about the origin, due to the six non-hydrogen atoms:

vector	u_f	v_f	vector	u_f	v_f
$\overrightarrow{\mathrm{O1C1}}$	0.2130	0.1136	$\overrightarrow{\mathrm{C1O1}}$	−0.2130	−0.1136
$\overrightarrow{\mathrm{O1C2}}$	0.3164	0.3589	$\overrightarrow{\mathrm{C2O1}}$	−0.3164	−0.3589
$\overrightarrow{\mathrm{O1C3}}$	0.5253	0.3976	$\overrightarrow{\mathrm{C3O1}}$	−0.5253	−0.3976
$\overrightarrow{\mathrm{O1C4}}$	0.5511	0.1763	$\overrightarrow{\mathrm{C4O1}}$	−0.5511	−0.1763
$\overrightarrow{\mathrm{O1C5}}$	0.3581	0.0008	$\overrightarrow{\mathrm{C5O1}}$	−0.3581	−0.0008
$\overrightarrow{\mathrm{C1C2}}$	0.1034	0.2453	$\overrightarrow{\mathrm{C2C1}}$	−0.1034	−0.2453
$\overrightarrow{\mathrm{C1C3}}$	0.3123	0.2840	$\overrightarrow{\mathrm{C3C1}}$	−0.3123	−0.2840
$\overrightarrow{\mathrm{C1C4}}$	0.3381	0.0627	$\overrightarrow{\mathrm{C4C1}}$	−0.3381	−0.0627
$\overrightarrow{\mathrm{C1C5}}$	0.1451	−0.1128	$\overrightarrow{\mathrm{C5C1}}$	−0.1451	0.1128
$\overrightarrow{\mathrm{C2C3}}$	0.2089	0.0387	$\overrightarrow{\mathrm{C3C2}}$	−0.2089	−0.0387
$\overrightarrow{\mathrm{C2C4}}$	0.2347	−0.1826	$\overrightarrow{\mathrm{C4C2}}$	−0.2347	0.1826
$\overrightarrow{\mathrm{C2C5}}$	0.0417	−0.3581	$\overrightarrow{\mathrm{C5C2}}$	−0.0417	0.3581
$\overrightarrow{\mathrm{C3C4}}$	0.0258	−0.2213	$\overrightarrow{\mathrm{C4C3}}$	−0.0258	0.2213
$\overrightarrow{\mathrm{C3C5}}$	−0.1672	−0.3968	$\overrightarrow{\mathrm{C5C3}}$	0.1672	0.3968
$\overrightarrow{\mathrm{C4C5}}$	−0.1930	−0.1755	$\overrightarrow{\mathrm{C5C4}}$	0.1930	0.1755

A model Patterson map can be created by orienting a model of the molecule in a convenient location in the unit cell. The orientation of the "actual" molecule in the structure can then be determined by superimposing the origin of the two maps and rotating the model map until the maxima in both maps are superimposed — emulating a rotation search. Using a C−C bond length of 1.400 Å, and a C−O bond length of 1.411 Å, create a model Patterson map by placing the center of the five carbon pentagon at the origin and the oxygen atom coincident with the a (x) axis. Plot the Patterson maxima for both maps on semi-transparent paper and determine the angle at which the molecule is rotated in the unit cell with respect to the orientation of the model.

Solution:

The carbon atom (C1) on the x axis is located at $x = 0.7/\sin 36^{\mathrm{o}} = 1.191$ Å. The oxygen atom (O1) is located at $1.191 + 1.411 = 2.602$ Å. The Cartesian



coordinates of the remaining carbon atoms are determined by rotating the C1 vector by $\eta = n \times (360^o/5)$, $n = 1, 2, 3,$ and 4:

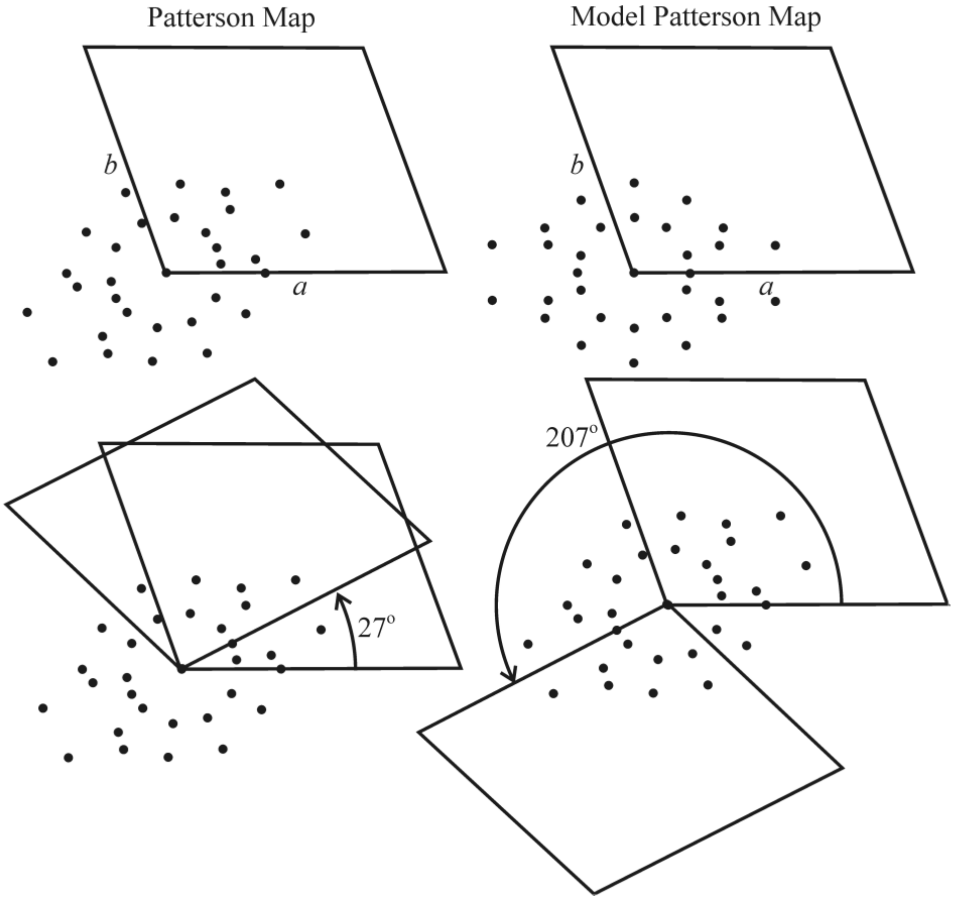
$$\begin{bmatrix} x_c \\ y_c \end{bmatrix} = \begin{bmatrix} \cos\eta & \sin\eta \\ -\sin\eta & \cos\eta \end{bmatrix} \begin{bmatrix} 1.191 \\ 0 \end{bmatrix}.$$

The fractional coordinates of the model are determined by transforming the Cartesian vectors with the inverse of the **B** matrix:

$$\begin{aligned} \mathbf{B} &= \begin{bmatrix} a & b\cos\gamma \\ 0 & b\sin\gamma \end{bmatrix} = \begin{bmatrix} 7.000 & -2.052 \\ 0 & 5.638 \end{bmatrix} \\ \mathbf{B}^{-1} &= \frac{1}{|\mathbf{B}|} \begin{bmatrix} 5.638 & 2.052 \\ 0 & 7.000 \end{bmatrix} = \begin{bmatrix} 0.143 & 0.052 \\ 0 & 0.177 \end{bmatrix} \\ \begin{bmatrix} x_f \\ y_f \end{bmatrix} &= \mathbf{B}^{-1} \begin{bmatrix} x_c \\ y_c \end{bmatrix}. \end{aligned}$$

Patterson vectors are generated for the model by calculating the 30 difference vectors: $u_f(AB) = x_f(B) - x_f(A)$, $v_f(AB) = y_f(B) - y_f(A)$. The Patterson vectors and origin locations for both maps are converted to Cartesian coordinates and plotted:

$$\begin{bmatrix} u_c \\ v_c \end{bmatrix} = \mathbf{B} \begin{bmatrix} u_f \\ v_f \end{bmatrix}$$



The plot on the upper left illustrates the Patterson maxima from the table, the plot on the upper right the Patterson map of the model molecule. The inversion center in the Patterson maps invokes two-fold symmetry in two dimensions, giving two possible rotational angles for the molecule, 27° and 207°. The "actual" rotational angle is 207°. The addition of a third dimension removes this ambiguity.

7. Intensities for the (1 2 2) reflection are collected from two isomorphous crystals containing cobalt amine transition metal complex ions, one with ammonium ions, Crystal A, the other with rubidium ions, Crystal B, located in the same site (site 1). The intensity from a third isomorphous crystal, Crystal B', containing an ammonium ion in site 1, is formed from an iridium amine complex, in which an iridium atom has replaced the cobalt atom inside the complex (at site 2 in the crystal). After scaling, the structure factor amplitudes of the reflection from each crystal are: $F_A = 43.23$, $F_B = 76.16$, $F_{B'} = 103.81$. From a Patterson map generated from data collected from Crystal B, the rubidium ion is located at $\mathbf{r}_R$; a Patterson map generated from data collected

from Crystal B' provides the location of the iridium atom at $\mathbf{r}_I$. Based on these locations and their three symmetry-equivalents, the structure factor contributions for each of these heavy atoms can be calculated:

$$\begin{aligned}
\mathbf{F}_{R,122} &= f_{Rb}\sum_{i=1}^{4} e^{-2\pi\, i(\mathbf{h}_{122}\cdot\,\mathbf{r}_{R,i})}, \quad F_R = 46.25,\ \varphi_R = 188^{\mathrm{o}} \\
\mathbf{F}_{I,122} &= f_{Ir}\sum_{i=1}^{4} e^{-2\pi\, i(\mathbf{h}_{122}\cdot\,\mathbf{r}_{I,i})}, \quad F_R = 97.88,\ \varphi_R = 185^{\mathrm{o}}
\end{aligned}$$

Determine the phase of the (1 2 2) reflection for Crystal A.

Solution:

The first isomorphous replacement generates a pair of possible phases for the reflection. The second isomorphous replacement removes the ambiguity. Presuming that the nitrogen atom of the ammonium ion is at the same location as the rubidium ion, scattering with the same phase, we can calculate its contribution to the structure factor:

$$\begin{aligned}
\mathbf{F}_{N,122} &= f_N\sum_{i=1}^{4} e^{-2\pi\, i(\mathbf{h}_{122}\cdot\,\mathbf{r}_{R,i})}, \quad F_N = 8.25,\ \varphi_N = 188^{\mathrm{o}} \\
\mathbf{F}_D &= \mathbf{F}_R - \mathbf{F}_N = 38.00\, e^{i\varphi_R} = 38.00(\cos 188^{\mathrm{o}} + i\sin 188^{\mathrm{o}}) \\
&= (-37.63) + i(-5.29) = x_D + iy_D. \\
D &= 2x_D = -75.26 \qquad E = 2y_D = -10.58 \\
G &= x_D^2 + y_D^2 = F_D = 1444.00 \qquad H = F_B^2 - F_A^2 = 3991.52 \\
I &= H - G = 2487.51 \\
\frac{E^2}{D^2} + 1 &= 1.01 \qquad \frac{2IE}{D^2} = -9.29 \qquad \frac{I^2}{D^2} - F_A^2 = -776.38 \\
& 1.01y_A^2 + 9.29y_A - 776.38 = 0 \\
y_A(1) &= 23.49 \\
y_A(2) &= -32.67 \\
x_A &= \left(-\frac{1}{75.26}\right)(2487.51 + 10.58y_A) \\
x_A(1) &= -36.35 \\
x_A(2) &= -28.46 \\
\varphi(1) &= \arctan\left(\frac{23.49}{-36.35}\right) = 147^{\mathrm{o}} \\
\varphi(2) &= \arctan\left(\frac{-32.67}{-28.46}\right) = 229^{\mathrm{o}}.
\end{aligned}$$

For the third isomorphous replacement, the Co atom in Crystal A is in the same location as the Rb atom in Crystal B', scattering with the same phase.

Thus its contribution to the structure factor is

$$\begin{aligned}
\mathbf{F}_{C,122} &= f_{Co}\sum_{i=1}^{4} e^{-2\pi\, i(\mathbf{h}_{122}\cdot\,\mathbf{r}_{I,i})}, \quad F_C = 31.53,\ \varphi_C = 185^{\circ} \\
\mathbf{F}'_D &= \mathbf{F}_I - \mathbf{F}_C = 66.35\, e^{i\varphi_I} = 66.35(\cos 185^{\circ} + i\sin 185^{\circ}) \\
&= (-66.10) + i(-5.78) = x'_D + iy'_D. \\
D' &= 2x'_D = -132.20 \qquad E' = 2y'_D = -11.56 \\
G' &= {x_D}'^2 + {y_D}'^2 = F'_D = 4402.32 \qquad H' = F^2_{B'} - F^2_A = 8907.68 \\
I' &= H' - G' = 4505.36 \\
\frac{E'^2}{D'^2} + 1 &= 1.01 \qquad \frac{2I'E'}{D'^2} = -5.96 \qquad \frac{I'^2}{D'^2} - F^2_A = -707.39 \\
&\ 1.01{y'}^2_A + 5.96y'_A - 707.39 = 0 \\
y'_A(1) &= 23.70 \\
y'_A(2) &= -29.62 \\
x'_A &= \left(-\frac{1}{132.20}\right)(4505.36 + 11.56y'_A) \\
x'_A(1) &= -36.15 \\
x'_A(2) &= -31.53 \\
\varphi'(1) &= \arctan\left(\frac{23.70}{-36.15}\right) = 147^{\circ} \\
\varphi'(2) &= \arctan\left(\frac{-29.62}{-31.53}\right) = 223^{\circ}. \\
\varphi_{122} &= 147^{\circ}.
\end{aligned}$$

8. Given the following scattering factor parameters for Eqn. 3.100,

	a_1	b_1	a_2	b_2	a_3	b_3	a_4	b_4	c
H	0.4899	20.6593	0.2620	7.7404	0.1968	49.5519	0.0499	2.2016	0.0013
C	2.3100	20.8439	1.0200	10.2075	1.5886	0.5687	0.8650	51.6512	0.2156
N	12.2126	0.0057	3.1322	9.8933	2.0125	28.9975	1.1663	0.5826	−11.5290
O	3.0485	13.2771	2.2868	5.7011	1.5463	0.3239	0.8670	32.9089	0.2508
S	6.9053	1.4679	5.2034	22.2151	1.4379	0.2536	1.5863	56.1720	0.8669

Determine the Fourier weighting factors, $w(\mathbf{h})$, following location of the sulfur atom from a Patterson map for: (a) The (1 2 1) reflection for 2-dimethylsulfuranylidene–indan 1,3 dione, $C_{11}H_{10}O_2S$, which packs in the $P2_12_12_1$ space group. The observed structure factor magnitude for the (1 2 1) reflection, collected at $2\theta = 25.21^{\circ}$ with CuKα radiation ($\lambda = 1.5418\mathring{A}$), is $F_o = 76.19$. The sulfur atom alone produces a calculated structure factor magnitude of $F_c = 19.92$ for the reflection. (The modified Bessel functions needed are discussed in Appendix F); (b) the (1 1 2) reflection for the 2-mercaptopyridine structure, collected at $2\theta = 11.76^{\circ}$ with MoKα radiation

($\lambda = 0.71073\mathring{A}$). The observed structure factor is $F_o = 120.30$, and the calculated structure factor, based on the sulfur atom alone is $F_c = 40.73$.

Solution:

(a) The structure is non-centrosymmetric, with $Z = 4 \Rightarrow 44$ C, 40 H, 8 O, and 4 S atoms in the unit cell. $\theta = 12.61^o$ and $s = \sin\theta/\lambda = 0.14159$ Å^{-1}. From Eqn. 3.100,

$$\begin{aligned} f_H &= 0.670 \\ f_C &= 4.446 \\ f_O &= 6.622 \\ f_S &= 12.850 \\ \sum f^2 &= 40 \times 0.670^2 + 44 \times 4.446^2 + 8 \times 6.622^2 + 4 \times 12.850^2 = 1897.71 \\ X &= \frac{F_o F_c}{1897.71} = 0.799. \end{aligned}$$

The modified Bessel functions are determined from the summation over 5 terms:

$$I_n(0.799) = \sum_{m=0}^{4} \frac{1}{m!(m+n)!}\left(\frac{0.799}{2}\right)^{2m+n} \tag{6.1}$$

$$I_0(0.799) = 1.166 \tag{6.2}$$

$$I_1(0.799) = 0.432. \tag{6.3}$$

The Fourier weighting factor is therefore

$$w(\mathbf{h}) = \frac{I_1(0.799)}{I_0(0.799)} = 0.37.$$

(b) The structure is centrosymmetric, with $Z = 4 \Rightarrow 20$ C, 20 H, 4 N, and 4 S atoms in the unit cell. $\theta = 5.88^o$ and $s = \sin\theta/\lambda = 0.14414$ Å^{-1}. From Eqn. 3.100,

$$\begin{aligned} f_H &= 0.661 \\ f_C &= 4.404 \\ f_N &= 5.486 \\ f_S &= 12.768 \\ \sum f^2 &= 20 \times 0.661^2 + 20 \times 4.404^2 + 4 \times 5.486^2 + 4 \times 12.768^2 = 1169.29 \\ X &= \frac{F_o F_c}{1169.29} = 4.190 \end{aligned}$$

$$w(\mathbf{h}) = \tanh\left(\frac{4.190}{2}\right) = 0.97.$$

Chapter 7

Crystal Structure Solution: Statistical

1. The triplet phase relationship (TPR) for strong reflections, $\varphi_{\mathbf{h}} \approx \varphi_{\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}}$, is seen in the literature in various forms. (a) Show that $\varphi_{-\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}} \approx 0$ is equivalent. (b) Show that $\varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} - \varphi_{\mathbf{h}+\mathbf{k}} \approx 0$ is equivalent.

   Solution:

   (a) $\varphi_{\mathbf{h}} \approx \varphi_{\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}} \Rightarrow \varphi_{\mathbf{h}} - \varphi_{\mathbf{k}} - \varphi_{\mathbf{h}-\mathbf{k}} \approx 0$. From Fig. 4.21, $\varphi_{\mathbf{h}} = -\varphi_{-\mathbf{h}}$, and

   $$\begin{aligned} -\varphi_{-\mathbf{h}} - \varphi_{\mathbf{k}} - \varphi_{\mathbf{h}-\mathbf{k}} &\approx 0 \\ \varphi_{-\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}} &\approx 0. \end{aligned}$$

   (b) Let $\mathbf{h}' = -\mathbf{h}$, $\mathbf{k}$, and $-\mathbf{h}' - \mathbf{k}$ be the indices of three reflections in a triplet relationship. Then

   $$\begin{aligned} \varphi_{\mathbf{h}'} - \varphi_{\mathbf{k}} - \varphi_{\mathbf{h}'-\mathbf{k}} &\approx 0 \\ \varphi_{-\mathbf{h}} - \varphi_{\mathbf{k}} - \varphi_{-\mathbf{h}-\mathbf{k}} &\approx 0 \\ -\varphi_{\mathbf{h}} - \varphi_{\mathbf{k}} - \varphi_{-(\mathbf{h}+\mathbf{k})} &\approx 0 \\ \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{-(\mathbf{h}+\mathbf{k})} &\approx 0 \\ \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} - \varphi_{\mathbf{h}+\mathbf{k}} &\approx 0. \end{aligned}$$

2. Triplet relationships are analyzed with conditional probabilities since the phase of a given reflection is *not* independent of the phases of the other reflections in the relationship. To gain an idea of the difference between a simple probability and a conditional probability, solve the following two problems: (a) You are told that your new neighbor has two children. What is the probability that the older child's sibling is a brother? (b) You discover that the older child's name is John. What is the probability that the older child's sibling is a brother?

Solution:

(a) Denoting $P(m_2)$ as the probability that child number 2 (the sibling) is a male, consider randomly selecting a large number of families with two children. Assuming that male and female children are evenly distributed throughout the population, the probability that a random child selected from a random family will be a male is $P(m_2) = 1/2$.

(b) It may at first appear that a family with one male child will still have a 1/2 probability of having a second male child. However, distinguishing the children by older/younger, there are four equally probable family arrangements: male/male, male/female, female/male and female/female. Only one of these arrangements has two male children. The probability that the sibling is a male, subject to the condition that the older child is also a male is $P(m_2|m_1) = 1/4$.

3. Show that the tangent formula provides the expected value for a single triplet relationship.

Solution:

The predicted value of $\varphi_{\mathbf{h}} \approx \beta_{\mathbf{h}}$ gives

$$\begin{aligned} \tan\varphi_{\mathbf{h}} &\approx& \tan\beta_{\mathbf{h}} = \frac{X_{\mathbf{hk}}\sin\alpha}{X_{\mathbf{hk}}\cos\alpha} = \frac{X_{\mathbf{hk}}\sin(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h-k}})}{X_{\mathbf{hk}}\cos(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h-k}})} \\ &=& \tan(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h-k}}) \\ &\Longrightarrow& \varphi_{\mathbf{h}} \approx \varphi_{\mathbf{k}}+\varphi_{\mathbf{h-k}}, \end{aligned}$$

which is the phase predicted by the triplet relationship.

4. The E values for the strong reflections for the bikitaite structure, $\mathrm{Li[AlSi_2O_6]\cdot H_2O}$, are given in Table 7.3. The (7 1 0) reflection is found in a number of triplet relationships. During the structural solution process the (4 0 7) and ($\bar{3}$ 1 7) are assigned phases of 0° and 30°, respectively. (a) Determine the phase of the (7 1 0) reflection predicted by the triplet relationship among these reflections. (b) Based on this single relationship, determine the probability that φ_{710} lies within $\pm 10^{\circ}$ of the predicted phase.

Solution:

(a) For $\varphi_{\mathbf{h}} \approx \varphi_{\mathbf{k}} + \varphi_{\mathbf{h-k}}$, The $\mathbf{h}-\mathbf{k}$ reflection must have indices (3 1 $\bar{7}$), which, according to Eqn. 7.169, has an assigned phase of $\pi + 30^{\circ} = 210^{\circ}$. Thus,

$$\varphi_{710} \approx 0^{\circ} + 210^{\circ} = 210^{\circ}.$$

(b) The conditional probability integral for a single triplet relationship, evaluated between φ_1 and φ_2, is

$$Pr(\varphi_{\mathbf{h}}|E_{\mathbf{h}}, \mathbf{E_k}, \mathbf{E_{h-k}}) = \frac{1}{2\pi I_0(X_{\mathbf{hk}})}\int_{\varphi_1}^{\varphi_2} e^{X_{\mathbf{hk}}\cos(\varphi_{\mathbf{h}}-\varphi_{\mathbf{k}}-\varphi_{\mathbf{h-k}})}d\varphi_{\mathbf{h}}.$$

$$\sigma_2 = \sum_j Z_j^2 = 4 \times 1^2 + 14 \times 8^2 + 2 \times 3^2 + 2 \times 13^2 + 4 \times 14^2 = 2040$$

$$\sigma_3 = \sum_j Z_j^3 = 4 \times 1^3 + 14 \times 8^3 + 2 \times 3^3 + 2 \times 13^3 + 4 \times 14^3 = 22\,596$$

$$\frac{2\sigma_3}{(\sigma_2)^{3/2}} = 0.4905$$

$$X_{\mathbf{hk}} = 0.4905 \times E_{\mathbf{h}} E_{\mathbf{k}} E_{\mathbf{h-k}} = 3.569$$

$$Pr(\varphi_{710}|E_{\mathbf{h}}, \mathbf{E_k}, \mathbf{E_{h-k}})_{200}^{220} = \frac{1}{2\pi I_0(3.569)} \int_{200^{\circ}}^{220^{\circ}} e^{3.569\cos(\varphi_{\mathbf{h}} - 210^{\circ})} d\varphi_{\mathbf{h}}.$$

The modified Bessel function value is determined from the summation over six terms (Appendix F):

$$I_0(3.569) = \sum_{m=0}^{6} \frac{1}{m!(m+0)!} \left(\frac{3.569}{2} \right)^{2m+0} = 7.82$$

$$Pr(\varphi_{710}|E_{\mathbf{h}}, \mathbf{E_k}, \mathbf{E_{h-k}})_{200}^{220} = 0.020 \int_{200^{\circ}}^{220^{\circ}} e^{3.569\cos(\varphi_{\mathbf{h}} - 210^{\circ})} d\varphi_{\mathbf{h}}.$$

The integral cannot be evaluated analytically, but it can be evaluated graphically by trapezoidal integration — or numerically, using a programmable calculator or computer. The following simple program, written in BASIC, is readily adaptable to any programming language:

```
pi = 3.1415927
dr = pi / 180
dphase = 0.001
integral = 0
phase = (200 * dr)
alpha = 210 * dr
Xhk = 3.569
N = 0.02
Do While phase <= (220* dr)
   phase = phase + dphase
   integral = integral + (Exp(Xhk* Cos((phase − alpha)))) * dphase
Loop
integral = N * integral
```

The result: integral = $Pr(\varphi_{710}|E_{\mathbf{h}}, \mathbf{E_k}, \mathbf{E_{h-k}})_{200}^{220} = 0.24$.

5. As the solution of the bikitaite structure described in Exercise 4 continues, the phases of a number of reflections involved in triplet relationships with the (7 1 0) reflection emerge (listed in ($\mathbf{h}$, $\mathbf{h-k}$) pairs, one for each triplet):

h	k	l	E	φ	h	k	l	E	φ	h	k	l	E	φ	h	k	l	E	φ
4	0	7	1.96	0	4	4	1	1.92	24	$\bar{3}$	3	2	1.94	120	3	3	0	1.90	288
$\bar{3}$	1	7	1.56	30	$\bar{3}$	3	1	1.91	144	4	2	2	1.73	74	4	2	0	1.63	69
$\bar{5}$	2	5	2.02	226	$\bar{8}$	1	10	2.12	24	$\bar{9}$	0	8	1.92	0	$\bar{3}$	3	2	1.94	120
2	1	5	1.62	188	$\bar{1}$	0	10	2.09	0	$\bar{2}$	1	8	1.73	202	$\overline{10}$	2	2	1.81	254

(a) Determine the expected value of φ_{710} based upon the assigned phases of these reflections. (b) Determine the probability that φ_{710} lies within ±10° of the predicted phase (Note: The modified Bessel function that determines the normalization constant tends to require a large number of terms in the series expansion when the argument becomes large. Since the probability integral itself must be evaluated numerically, in such cases it is much easier to evaluate the normalization integral numerically as well.)

Solution:

(a) The expected value of φ_{710} is β_{710}, determined from the tangent formula:

$$\tan\beta_{710} = \frac{\sum_{i=1}^{8} X_{\mathbf{hk}_i}\sin\alpha_i}{\sum_{i=1}^{8} X_{\mathbf{hk}_i}\cos\alpha_i}, \qquad \alpha_i = \varphi_{\mathbf{k}_i} + \varphi_{\mathbf{h}-\mathbf{k}_i}.$$

The triplet pairs, $(\mathbf{h}, \mathbf{h}-\mathbf{k})$, related to the indices of the reflection pairs above by symmetry — along with their phases, are:

h	k	l	E	φ	h	k	l	E	φ	h	k	l	E	φ	h	k	l	E	φ
4	0	7	1.96	0	4	4	1	1.92	24	3	3	$\bar{2}$	1.94	300	3	3	0	1.90	288
3	1	$\bar{7}$	1.56	210	3	$\bar{3}$	$\bar{1}$	1.91	216	4	$\bar{2}$	2	1.73	286	4	$\bar{2}$	0	1.63	291
5	2	$\bar{5}$	2.02	226	8	1	$\overline{10}$	2.12	204	9	0	$\bar{8}$	1.92	0	$\bar{3}$	3	2	1.94	120
2	$\bar{1}$	5	1.62	352	$\bar{1}$	0	10	2.09	0	$\bar{2}$	1	8	1.73	202	10	2	$\bar{2}$	1.81	106

From the solution to Exercise 4, $X_{\mathbf{hk}_i} = 0.4905 \times E_{\mathbf{h}}E_{\mathbf{k}_i}E_{\mathbf{h}-\mathbf{k}_i}$, giving

$$\beta_{710} = 225^{\circ}.$$

(b) The conditional probability integral for the eight triplet relationships, evaluated between φ_1 and φ_2, is

$$Pr(\varphi_{\mathbf{h}}) = \frac{1}{2\pi I_0(Y_{\mathbf{h}})}\int_{\varphi_1}^{\varphi_2} e^{Y_{\mathbf{h}}\cos(\varphi_{\mathbf{h}}-\beta_{\mathbf{h}})}d\varphi_{\mathbf{h}},$$

$$\begin{aligned} Y_{\mathbf{h}} &= \left(\left(\sum_{j=1}^{8} X_{\mathbf{hk}_j}\cos(\alpha_j)\right)^2 + \left(\sum_{j=1}^{8} X_{\mathbf{hk}_j}\sin(\alpha_j)\right)^2\right)^{1/2} \\ &= 26.56. \end{aligned}$$

Forty terms in the series expansion to generate $I_0(Y_{\mathbf{h}})$ provides a value of 26 652 716 750, and a normalization constant of $N = 1/2\pi I_0(Y_{\mathbf{h}}) = 5.97 \times 10^{-12}$. Numerical evaluation (see the program below) results in

$$N = \frac{1}{\displaystyle\int_0^{2\pi} e^{26.56\cos(\varphi_{\mathbf{h}})} d\varphi_{\mathbf{h}}} = 5.96 \times 10^{-12} \quad \text{and}$$

$$Pr(\varphi_{\mathbf{h}})_{215}^{235} = 5.96 \times 10^{-12} \int_{215^{\circ}}^{235^{\circ}} e^{26.56\cos(\varphi_{\mathbf{h}} - 225^{\circ})} d\varphi_{\mathbf{h}}.$$

The following simple program, written in BASIC, is readily adaptable to any programming language:

```
pi = 3.1415927
dr = pi / 180
dphase = 0.001
Yhk = 26.56
phase = 0
normintegral = 0
Do While phase <= 2 * pi
   phase = phase + dphase
   normintegral = normintegral + (Exp(Yhk * Cos((phase)))) * dphase
Loop
N = 1 / normintegral
integral = 0
phase = (215 * dr)
beta = (225 * dr)
Do While phase <= (235 * dr)
   phase = phase + dphase
   integral = integral + (Exp(Yhk * Cos((phase - beta)))) * dphase
Loop
integral = N * integral
```

The result: integral $= Pr(\varphi_{710})_{215}^{235} = 0.63$.

6. Referring to Table 7.3 in order of descending values of E: (a) show that the first three reflections in the table do *not* constitute a potential set of origin-defining reflections; (b) proceeding down the table, determine the first set of three reflections that would be suitable for origin-definition.

Solution:

(a) The $(\bar{6}\ 0\ 2)$ reflection has eee parity, and cannnot be used to define the origin. The $(\bar{5}\ 2\ 10)$ planes cross the b axis in two locations – the origin will not be uniquely defined since $k \neq 1$.

(b) The $(\bar{5}\ 0\ 5)$ reflection has oeo parity, and is the first candidate in the list for origin-definition. $(7\ 1\ 0)$ reflection has $k = 1$ and is a second candidate. The third reflection must now be an $h0l$ reflection. The $(\bar{1}\bar{1}\ 0\ 7)$, $(\bar{7}\ 0\ 7)$, and $(\bar{9}\ 0\ 3)$ reflections all have oeo parity, and are not linearly independent of the $(\bar{5}\ 0\ 5)$ reflection. The $(\bar{1}\ 0\ 10)$ reflection has oee parity — linearly independent of $(\bar{5}\ 0\ 5)$. Thus the $(\bar{5}\ 0\ 5)$, $(\bar{1}1\ 0\ 7)$, and $(7\ 1\ 0)$ reflections constitute a potential set of origin-defining reflections.

7. Assigning phases of 0 to the $(\bar{5}\ 0\ 5)$, $(\bar{1}1\ 0\ 7)$, and $(7\ 1\ 0)$ reflections in Table 5.3 (defining the origin) , and symbolic phases, s_1, s_2, and s_3 to the $(\bar{2}\ 0\ 2)$, $(\bar{5}\ 2\ 5)$, and $(\bar{3}\ 3\ 2)$ reflections, respectively, assign the symbolic phases of the (a) $(\bar{6}\ 0\ 2)$, (b) $(\bar{7}\ 0\ 7)$, (c) $(\bar{8}\ 3\ 5)$, and (d) $(\bar{6}\ 2\ 2)$ reflections.

Solution:

To assign the phase of each reflection a triplet relationship must be found involving reflections with previously assigned symbolic phases:

(a)

$$\begin{aligned}
\mathbf{h} &= (\bar{6}\ 0\ 2) \\
\mathbf{k} &= (5\ 0\ \bar{5}) \\
\mathbf{h}-\mathbf{k} &= (\bar{1}1\ 0\ 7) \\
\varphi_{\bar{6}02} &\approx \varphi_{50\bar{5}} + \varphi_{\bar{1}1\,07} \\
\varphi_{50\bar{5}} &= -\varphi_{\bar{5}05} = 0 \\
\varphi_{\bar{6}02} &\approx 0 + 0 = 0.
\end{aligned}$$

(b)

$$\begin{aligned}
\mathbf{h} &= (\bar{5}\ 0\ 5) \\
\mathbf{k} &= (\bar{7}\ 0\ 7) \\
\mathbf{h}-\mathbf{k} &= (2\ 0\ \bar{2}) \\
\varphi_{\bar{5}05} &\approx \varphi_{\bar{7}07} + \varphi_{20\bar{2}} \\
\varphi_{20\bar{2}} &= -\varphi_{\bar{2}02} = -s_1 \\
0 &\approx -s_1 + \varphi_{\bar{7}07} \\
\varphi_{\bar{7}07} &\approx s_1.
\end{aligned}$$

(c)

$$\begin{aligned}
\mathbf{h} &= (\bar{1}1\ 0\ 7) \\
\mathbf{k} &= (\bar{3}\ 3\ 2) \\
\mathbf{h}-\mathbf{k} &= (\bar{8}\ \bar{3}\ 5) \\
\varphi_{\bar{1}1\,07} &\approx \varphi_{\bar{3}32} + \varphi_{\bar{8}\bar{3}5} \\
\varphi_{\bar{8}\bar{3}5} &= \pi - \varphi_{\bar{8}35} \\
0 &\approx s_3 + \pi - \varphi_{\bar{8}35} \\
\varphi_{\bar{8}35} &\approx s_3 + \pi.
\end{aligned}$$

(d)

$$\begin{aligned}
\mathbf{h} &= (\bar{1}\bar{1}\ 0\ 7) \\
\mathbf{k} &= (\bar{5}\ 2\ 5) \\
\mathbf{h}-\mathbf{k} &= (\bar{6}\ \bar{2}\ 2) \\
\varphi_{\bar{1}\bar{1}\,07} &\approx \varphi_{\bar{5}25} + \varphi_{\bar{6}\bar{2}2} \\
\varphi_{\bar{6}\bar{2}2} &= -\varphi_{\bar{6}22} \\
0 &\approx s_2 - \varphi_{\bar{6}22} \\
\varphi_{\bar{6}22} &\approx s_2.
\end{aligned}$$

8. Using the origin-defining and symbolic phases assigned in the previous exercise, show that triplet relationships involving the $(\bar{5}\ 0\ 5)$, $(\bar{5}\ 2\ 5)$, $(7\ 1\ 0)$, and $(0\ 2\ 0)$ reflections predict that s_2 is approximately π.

Solution:

The $(\bar{5}\ 0\ 5)$ and $(\bar{5}\ 2\ 5)$ phases predict that the $(0\ 2\ 0)$ reflection has a symbolic phase of $\varphi_{020} \approx s_2$:

$$\begin{aligned}
\mathbf{h} &= (\bar{5}\ 0\ 5) \\
\mathbf{k} &= (\bar{5}\ 2\ 5) \\
\mathbf{h}-\mathbf{k} &= (0\ \bar{2}\ 0) \\
\varphi_{\bar{5}\,05} &\approx \varphi_{\bar{5}25} + \varphi_{0\bar{2}0} \\
\varphi_{020} &= -\varphi_{0\bar{2}0} \\
0 &\approx s_2 - \varphi_{020} \\
\varphi_{020} &\approx s_2.
\end{aligned}$$

The $(7\ 1\ 0)$ reflection, combined with its symmetry relative, the $(7\ \bar{1}\ 0)$ reflection, predicts that the $(0\ 2\ 0)$ reflection has a phase of $\varphi_{020} \approx \pi$:

$$\begin{aligned}
\mathbf{h} &= (7\ 1\ 0) \\
\mathbf{k} &= (7\ \bar{1}\ 0) \\
\mathbf{h}-\mathbf{k} &= (0\ 2\ 0) \\
\varphi_{710} &\approx \varphi_{7\bar{1}0} + \varphi_{020} \\
\varphi_{7\bar{1}0} &= \pi - \varphi_{710} \\
0 &\approx \pi - 0 + \varphi_{020} \\
\varphi_{020} &\approx -\pi \equiv \pi.
\end{aligned}$$

Thus, based on these two triplets, $s_2 \approx \pi$.

Chapter 8

Crystal Structure Refinement

1. Consider a spring suspended from a horizontal support beam with a weight with mass m attached to the end of the spring. The weight is pulled downward and released, setting it into oscillatory (harmonic) motion, oscillating at frequency ν. If the mass of the spring is negligible, the frequency is determined by the force constant of the spring, k, and the mass of the weight:

   $$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}.$$

   The period — the time that it takes for a single oscillation to occur — is the reciprocal of the frequency:

   $$T = 2\pi\sqrt{\frac{m}{k}}.$$

   Since the spring has mass, in order to be rigorous, the formula must also contain the "effective mass" of the spring, m_s:

   $$T = 2\pi\sqrt{\frac{m + m_s}{k}}.$$

   In a series of experiments, various weights are attached to the spring and the oscillation frequency is measured in each case:

m (g)	10	20	30	40	50	60	70	80	90	100
ν (s^{-1})	1.778	1.463	1.263	1.137	1.036	0.950	0.899	0.838	0.795	0.759

   (a) Derive a relationship that is linear in m (the equation of a line with m as the independent variable). (b) Use the relationship and the method of least squares to determine the effective mass and force constant of the spring (assume that the masses are exact and that the values of the dependent variable are equally weighted).

Solution:

(a) The equation for the period can be made linear in m by squaring both sides:

$$T^2(m) = y(m) = \frac{4\pi^2}{k} m + \frac{4\pi^2 m_s}{k} = sm + y_0.$$

(b) The slope, s, and the intercept, y_0, of the least squares line will provide the values of m_s and k. From Eqn. G.3,

$$\begin{aligned}
\begin{bmatrix} s \\ y_0 \end{bmatrix} &= \begin{bmatrix} \sum_{i=1}^{10} m_i^2 & \sum_{i=1}^{10} m_i \\ \sum_{i=1}^{10} m_i & 10 \end{bmatrix}^{-1} \begin{bmatrix} \sum_{i=1}^{10} m_i y_i \\ \sum_{i=1}^{10} y_i \end{bmatrix} \\
&= \begin{bmatrix} 1.212 \times 10^{-4} & -6.667 \times 10^{-3} \\ -6.667 \times 10^{-3} & 4.667 \times 10^{-1} \end{bmatrix} \begin{bmatrix} 692.050 \\ 10.204 \end{bmatrix} \\
&= \begin{bmatrix} 1.584 \times 10^{-2} \\ 0.1485 \end{bmatrix} \\
\frac{4\pi^2}{k} &= 1.584 \times 10^{-2}\,\mathrm{s}^2/\mathrm{g} \Rightarrow \\
k &= 2490\,\mathrm{g/s}^2 \equiv 2490\,\mathrm{dyne/cm}. \\
\frac{4\pi^2}{k} m_s &= 0.1485\,\mathrm{s}^2 \\
m_s &= 9.37\,\mathrm{g}.
\end{aligned}$$

2. The unweighted linear least-squares solution of Exercise 1 can be refined by including appropriate weights for each of the residuals. If the error in the measurement of each frequency is entirely random, then these weights are the reciprocals of the variances of the dependent variables, $y_i = T_i^2$. The weighted sum of the squares of the residuals, $\sum_1^n w_i(sm_i + y_0 - y_i)^2$, is minimized, where $w_i = 1/\sigma^2(y_i)$. (a) Derive a matrix solution for the slope and intercept of a weighted least-squares line for the data in Exercise 1. (b) Assuming that the variance of the frequency (and therefore the period) is the same for each data point (independent of ν and T), show that the weights in part (a) are *not* independent of T. (c) Determine the weighted least-squares values for the force constant and effective mass of the spring in Exercise 1. (d) Given the following repeated measurements of the frequency of the oscillating 50 g weight (in s^{-1}): 1.038, 1.033, 1.029, 1.029, 1.034, 1.027, 1.028, 1.037, 1.028, 1.034, 1.032, 1.030, 1.037, 1.031, 1.033, 1.035, 1.031, 1.031, 1.035, and 1.035, determine the estimated standard deviations of the force constant and effective mass of the spring in Exercise 1.

Solution:

(a) Referring to Appendix G,

$$\frac{\partial \sum_i^n w_i(sm_i + y_0 - y_i)^2}{\partial s} = 0 \quad \text{and} \quad \frac{\partial \sum_i^n w_i(sm_i + y_0 - y_i)^2}{\partial y_0} = 0 \Longrightarrow$$

$$\left(\sum_{i=1}^n w_i m_i^2\right) s + \left(\sum_{i=1}^n w_i m_i\right) y_0 = \sum_{i=1}^n w_i m_i y_i$$

$$\left(\sum_{i=1}^n w_i m_i\right) s + \left(\sum_{i=1}^n w_i\right) y_0 = \sum_{i=1}^n w_i y_i$$

$$\begin{bmatrix} s \\ y_0 \end{bmatrix} = \begin{bmatrix} \sum_i^n w_i m_i^2 & \sum_i^n w_i m_i \\ \sum_i^n w_i m_i & \sum_i^n w_i \end{bmatrix}^{-1} \begin{bmatrix} \sum_i^n w_i m_i y_i \\ \sum_i^n w_i y_i \end{bmatrix}.$$

(b) Assuming that $\sigma^2(T_i)$ is the same for all data points,

$$\begin{aligned} y_i &= T_i^2 \\ \sigma^2(y_i) &= \left(\frac{\partial y_i}{\partial T_i}\right)^2 \sigma^2(T_i) \\ &= (2T_i^2)\sigma^2(T_i) = 4T_i^2\sigma^2(T_i) = 4y_i\sigma^2(T_i) \Longrightarrow \\ w_i &= \frac{1}{(4\sigma^2(T_i))y_i} = \frac{C}{y_i}; \quad C = \frac{1}{4\sigma^2(T_i)}. \end{aligned}$$

(c) The weights from part (b) are inserted into the solution from part (a):

$$\begin{aligned} \begin{bmatrix} s \\ y_0 \end{bmatrix} &= \begin{bmatrix} \sum_{i=1}^{10} \frac{C}{y_i} m_i^2 & \sum_{i=1}^{10} \frac{C}{y_i} m_i \\ \sum_{i=1}^{10} \frac{C}{y_i} m_i & \sum_{i=1}^{10} \frac{C}{y_i} \end{bmatrix}^{-1} \begin{bmatrix} \sum_{i=1}^{10} \frac{C}{y_i} m_i y_i \\ \sum_{i=1}^{10} \frac{C}{y_i} y_i \end{bmatrix} \\ &= C^{-1}C \begin{bmatrix} \sum_{i=1}^{10} \frac{m_i^2}{y_i} & \sum_{i=1}^{10} \frac{m_i}{y_i} \\ \sum_{i=1}^{10} \frac{m_i}{y_i} & \sum_{i=1}^{10} \frac{1}{y_i} \end{bmatrix}^{-1} \begin{bmatrix} \sum_{i=1}^{10} m_i \\ 10 \end{bmatrix} \\ &= \begin{bmatrix} 1.017 \times 10^{-4} & -4.019 \times 10^{-3} \\ -4.019 \times 10^{-3} & 2.364 \times 10^{-1} \end{bmatrix} \begin{bmatrix} 550 \\ 10 \end{bmatrix} \\ &= \begin{bmatrix} 1.577 \times 10^{-2} \\ 0.1532 \end{bmatrix} \\ \frac{4\pi^2}{k} &= 1.577 \times 10^{-2}\,\mathrm{s}^2/\mathrm{g} \Rightarrow \\ k &= 2504\,\mathrm{dyne/cm}. \\ \frac{4\pi^2}{k} m_s &= 0.1532\,\mathrm{s}^2 \\ m_s &= 9.72\,\mathrm{g}. \end{aligned}$$

(d) After conversion of the frequencies to periods, the mean of the measured periods is $\langle T\rangle = 0.969$ s. The estimated variance of the period is given by

$$\sigma^2(T) = \frac{1}{(20-1)}\sum_{i=1}^{20}(T_i - \langle T\rangle)^2 = 9.40\times 10^{-6}\mathrm{s}^2.$$

The estimated standard deviations of the slope, intercept, force constant and effective mass are determined by error propagation.

$$\begin{aligned}
y_i &= sm_i + y_0 \Longrightarrow s = \frac{y_i}{m_i} - \frac{y_0}{m_i} \quad \text{and} \quad y_0 = y_i - sm_i. \\
\sigma^2(s) &= \sum_{i=1}^{10}\left(\frac{\partial s}{\partial y_i}\right)^2\sigma^2(y_i) = \sum_{i=1}^{10}\frac{\sigma^2(y_i)}{m_i^2} \\
&= \sum_{i=1}^{10}\frac{4y_i\sigma^2(T)}{m_i^2} = 3.76\times 10^{-5}\sum_{i=1}^{10}\frac{y_i}{m_i^2} \\
&= 5.44\times 10^{-7}\mathrm{s}^2/\mathrm{g}. \\
\sigma^2(y_0) &= \sum_{i=1}^{10}\left(\frac{\partial y_0}{\partial y_i}\right)^2\sigma^2(y_i) = \sum_{i=1}^{10}\sigma^2(y_i) \\
&= \sum_{i=1}^{10}4y_i\sigma^2(T) = 3.76\times 10^{-5}\sum_{i=1}^{10}y_i \\
&= 3.532\times 10^{-4}\,\mathrm{s}^2. \\
k &= \frac{4\pi^2}{s} \\
\sigma^2(k) &= \left(\frac{\partial k}{\partial s}\right)^2\sigma^2(s) = \left(\frac{16\pi^4}{s^4}\right)\times 5.44\times 10^{-7}\,\mathrm{s}^2/\mathrm{g} \\
&= 13708\,\mathrm{dyne}^2/\mathrm{cm}^2. \\
\sigma(k) &= 117\,\mathrm{dyne/cm}. \\
m_s &= \frac{y_0 k}{4\pi^2} \\
\sigma^2(m_s) &= \left(\frac{\partial m_s}{\partial y_0}\right)^2\sigma^2(y_0) + \left(\frac{\partial m_s}{\partial k}\right)^2\sigma^2(k) \\
&= \left(\frac{k}{4\pi^2}\right)^2\sigma^2(y_0) + \left(\frac{y_0}{4\pi^2}\right)^2\sigma^2(k) \\
&= 1.63\,\mathrm{g}^2. \\
\sigma(m_s) &= 1.27\,\mathrm{g}.
\end{aligned}$$

3. In a chemical kinetics experiment a compound, compound X, is known to form slowly along a zero-order pathway, and decompose more rapidly along an independent first-order pathway. The concentration of X can be modeled as a function of time as

$$[\mathrm{X}](t) = p_1 t + p_2 e^{-p_3 t}.$$

In the experiment, [X] is measured in intervals of 0.1 h, and we seek the values of the parameters, p_1, p_2, and p_3 that will provide a “best fit” (a least-squares fit) to the data:

t (h)	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
[X](mM)	190.6	109.1	65.7	40.7	35.7	7.9	18.8	12.1	1.7	9.9	5.3

(a) Determine initial guesses for p_1, p_2, and p_3 by selecting data points with appropriate values of t. (b) Using a Taylor series approximation to the function, determine optimal least squares values for p_1, p_2, and p_3. (c) Plot the least squares model function and the data in the table.

Solution:

(a) At $t = 0.0\,\mathrm{h}$, the experimental value of [X] approximates p_2:

$$[\mathrm{X}]_i \;=\; p_1 t_i + p_2 e^{-p_3 t_i} \Longrightarrow 190.6 \simeq p_1 \times 0.0 + p_2 e^0 \simeq p_2^o.$$

At $t = 1.0\,\mathrm{h}$, the concentration approaches zero, indicating that $e^{-p_3 t}$ is close to zero, and that $p_1 t$ is also close to zero. This implies that p_1 must be very small, and we will approximate it as $p_1^o \simeq 0$. Using these values, and selecting the data point at $t = 0.5\,\mathrm{h} = 1/2\,\mathrm{h}$ gives

$$\begin{aligned} [\mathrm{X}] &= 7.9 \simeq 190.6\, e^{-p_3/2} \\ p_3^o &\simeq -2\ln\left(\frac{7.9}{190.6}\right) = 6.37 \end{aligned}$$

(b) Using the method described in Sec. 8.3 as a model, the ith observed concentration is given by $[\mathrm{X}]_{o,i}$. The parameter vector is $\mathbf{p} = [p_1\ p_2\ p_3]$, and the ith concentration predicted from the model is $[\mathrm{X}(\mathbf{p})]_{c,i}$. A least squares fit of the model to the observed data will minimize

$$R(\mathbf{p}) = \sum_{i=1}^{11} ([\mathrm{X}]_{o,i} - [\mathrm{X}(\mathbf{p})]_{c,i})^2.$$

Expanding the model function as a Taylor series about the initial approximations, $\mathbf{p}_o = [p_1^o\ p_2^o\ p_3^o]$, and discarding the the higher terms, gives

$$[\mathrm{X}(\mathbf{p})]_{c,i} = ([\mathrm{X}(\mathbf{p})]_{c,i})_{\mathbf{p}_o} + \sum_{j=1}^{3} \left(\frac{\partial [\mathrm{X}(\mathbf{p})]_{c,i}}{\partial p_j}\right)_{\mathbf{p}_o} \Delta p_j.$$

Setting $\Delta X_i = [\mathrm{X}]_{o,i} - ([\mathrm{X}(\mathbf{p})]_{c,i})_{\mathbf{p}_o}$, and $\mathbf{\Delta p} = [\Delta p_1\ \Delta p_2\ \Delta p_3] = [(p_1 - p_1^o)\ (p_2 - p_2^o)\ (p_3 - p_3^o)]$, results in

$$\begin{aligned} \mathrm{t}_{kj} &= \sum_{i=1}^{11} \left(\frac{\partial [\mathrm{X}(\mathbf{p})]_{c,i}}{\partial p_j}\ \frac{\partial [\mathrm{X}(\mathbf{p})]_{c,i}}{\partial p_k}\right)_{\mathbf{p}_o} \quad \text{and} \\ d_j &= \sum_{i=1}^{11} \Delta X_j \left(\frac{\partial [\mathrm{X}(\mathbf{p})]_{c,i}}{\partial p_j}\right)_{\mathbf{p}_o}, \quad j = 1,2,3;\ k = 1,2,3. \end{aligned}$$

The derivatives with respect to each of the parameters, evaluated at p_o are:

$$\left(\frac{\partial[\mathrm{X}(\mathbf{p})]_{c,i}}{\partial p_1}\right)_{\mathbf{p}_o} = t_i$$
$$\left(\frac{\partial[\mathrm{X}(\mathbf{p})]_{c,i}}{\partial p_2}\right)_{\mathbf{p}_o} = e^{-p_3^o t_i}$$
$$\left(\frac{\partial[\mathrm{X}(\mathbf{p})]_{c,i}}{\partial p_3}\right)_{\mathbf{p}_o} = -p_2^o t_i e^{-p_3^o t_i}.$$

The matrix elements for $\mathbf{T}$ are therefore

$$\begin{aligned}
\mathrm{t}_{11} &= \sum_{i=1}^{11} t_i^2 \\
\mathrm{t}_{12} &= \mathrm{t}_{12} = \sum_{i=1}^{11} t_i e^{-p_3^o t_i} \\
\mathrm{t}_{13} &= \mathrm{t}_{31} = \sum_{i=1}^{11} -t_i^2 p_2^o e^{-p_3^o t_i} \\
\mathrm{t}_{22} &= \sum_{i=1}^{11} e^{-2p_3^o t_i} \\
\mathrm{t}_{33} &= \sum_{i=1}^{11} t_i^2 p_2^o e^{-2p_3^o t_i}.
\end{aligned}$$

The $\mathbf{d}$ vector is given by

$$\begin{aligned}
d_1 &= \sum_{i=1}^{11} \Delta X_i t_i \\
d_2 &= \sum_{i=1}^{11} \Delta X_i e^{-p_3^o t_i} \\
d_3 &= \sum_{i=1}^{11} -\Delta X_i p_2^o t_i e^{-p_3^o t_i},
\end{aligned}$$

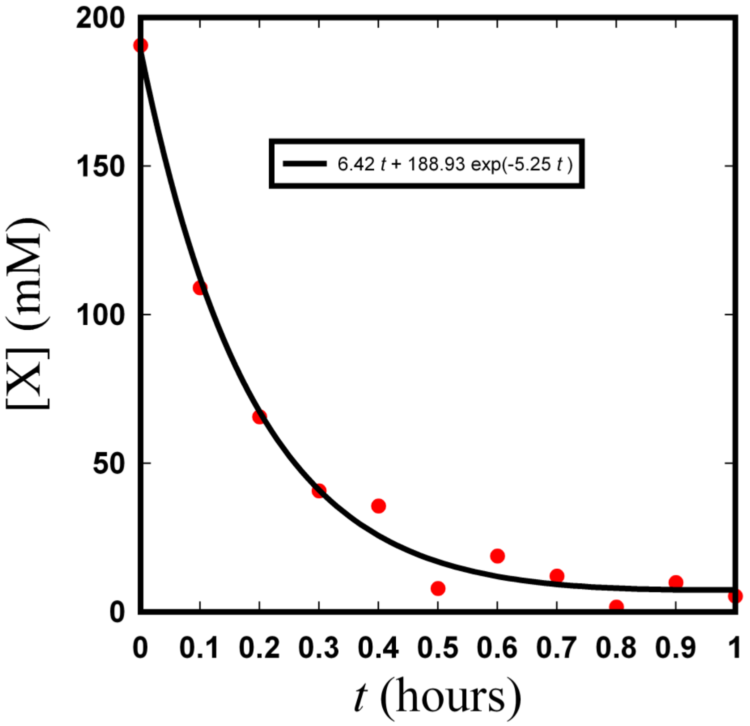
allowing for the determination of the parameter change vector:

$$\mathbf{\Delta p} = \mathbf{T}^{-1}\mathbf{d}.$$

New values for the parameters are generated by adding Δp_1, Δp_2, and Δp_2 to p_1^o, p_2^o, and p_3^o, and the process is repeated iteratively until only negligible changes in the parameters are observed. The algorithm outlined here converges in 15 iterations, and is essentially complete after 10 iterations. The following table lists the parameters computed after each iteration:

iteration	p_1	p_2	p_3	iteration	p_1	p_2	p_3
0	0.00	190.60	6.37	10	6.46	188.87	5.26
1	6.90	197.94	5.20	11	6.41	188.98	5.25
2	8.46	187.92	5.54	12	6.44	188.90	5.26
3	6.07	191.77	5.21	13	6.42	188.94	5.25
4	7.10	188.29	5.35	14	6.43	188.92	5.26
5	6.21	189.92	5.23	15	6.42	188.93	5.25
6	6.67	188.62	5.29	16	6.43	188.92	5.26
7	6.33	189.29	5.24	17	6.43	188.93	5.25
8	6.52	188.79	5.27	18	6.43	188.92	5.25
9	6.39	189.06	5.25	19	6.43	188.93	5.25

(c) Non-linear least-squares fit of model function (black) to concentration data (red):



4. The pyridine ring in Fig. 1.32 can be approximated by a hexagon with an edge length of 1.36 Å. Given the fractional coordinates of S(1), C(1), and N(1), calculate the fractional coordinates of the remaining atoms based on this approximation, retaining the original locations of C(1) and S(1).

Solution:

The calculated positions are determined in the following sequence:

(a) Create the **B** matrix and convert the positions of S(1), C(1), and N(1) to crystal Cartesian coordinates. The results are given on page 59:

Atom	x_c	y_c	z_c
S(1)	3.359	0.398	5.712
N(1)	1.036	1.655	6.022
C(1)	2.258	1.650	5.414

(b) Translate the origin to C(1) by subtracting its coordinates from those of S(1), C(1), and N(1):

Atom	x'_c	y'_c	z'_c
S(1)	1.101	-1.252	0.298
N(1)	-1.222	0.005	0.608
C(1)	0.000	0.000	0.000

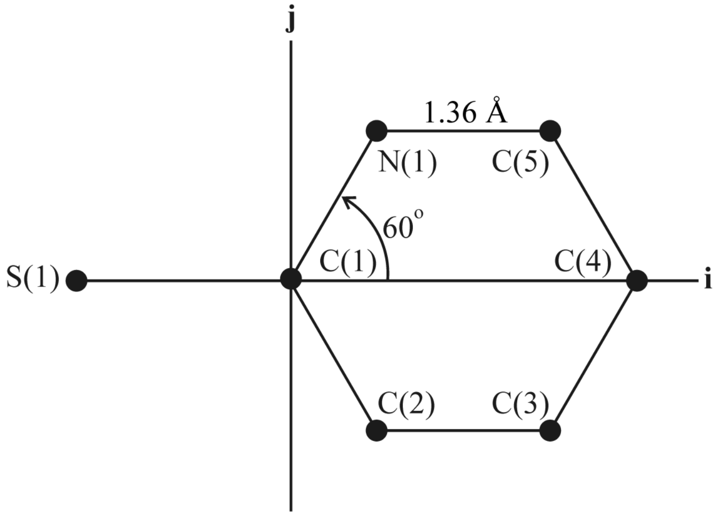
(c) Create a unit vector in the local x direction — in the direction opposite to the $\overrightarrow{\mathrm{C(1)(S(1)}}$ vector (see the figure on the following page): $\mathbf{v}_{xa} = [-1.101, 1.252, -0.298]$; $v_{xa} = 1.694$ Å. $\mathbf{i}_g = \mathbf{v}_{xa}/v_{xa} = [-0.650, 0.739, -0.176]$.

(d) Create a unit vector in the local z direction: $\mathbf{v}_{xy} = [-1.222, 0.005, 0.608]$. $\mathbf{v}_z = \mathbf{i}_g \times \mathbf{v}_{xy} = [0.450, 0.610, 0.900]$; $\mathbf{k}_g = \mathbf{v}_z/v_z = [0.382, 0.518, 0.765]$.

(e) Create a unit vector in the local y direction:$\mathbf{j}_g = \mathbf{k}_g \times \mathbf{i}_g = [-0.657, -0.430, 0.619]$.

(f) Determine coordinates of the atoms in the local system. Referring to the figure on the following page,

$$\begin{aligned}
\mathrm{S(1)} &: [-1.694, 0.000, 0.000]\\
\mathrm{C(1)} &: [0.000, 0.000, 0.000]\\
\mathrm{C(2)} &: [1.36\cos 60^o, -1.36\sin 60^o, 0.000] = [0.680, -1.178, 0.000]\\
\mathrm{C(3)} &: [1.36\cos 60^o + 1.36, -1.36\sin 60^o, 0.000] = [2.040, -1.178, 0.000]\\
\mathrm{C(4)} &: [2.72, 0.000, 0.000]\\
\mathrm{C(5)} &: [1.36\cos 60^o + 1.36, 1.36\sin 60^o, 0.000] = [2.040, 1.178, 0.000]\\
\mathrm{N(1)} &: [1.36\cos 60^o, 1.36\sin 60^o, 0.000] = [0.680, 1.178, 0.000].
\end{aligned}$$



(g) Transform each of these vectors back into the translated crystal Cartesian system: $[\mathbf{i}_g\ \mathbf{j}_g\ \mathbf{k}_g]\mathbf{v}'' = \mathbf{v}'$:

Atom	x'_c	y'_c	z'_c
S(1)	1.101	−1.252	0.298
N(1)	−1.216	−0.004	0.610
C(1)	0.000	0.000	0.000
C(2)	0.332	1.009	−0.849
C(3)	−0.552	2.014	−1.008
C(4)	−1.768	2.010	−0.479
C(5)	−2.099	1.001	0.370

(h) Transform the Cartesian vectors back to the unit cell origin by adding the crystal Cartesian coordinates of C(1) to each vector. Then transform them back to fractional coordinates with $\mathbf{B}^{-1}$:

Atom	x_f	y_f	z_f
S(1)	0.7403	0.0629	0.4073
N(1)	0.3715	0.2602	0.4295
C(1)	0.5501	0.2608	0.3860
C(2)	0.5761	0.4203	0.3255
C(3)	0.4262	0.5792	0.3142
C(4)	0.2449	0.5786	0.3519
C(5)	0.2191	0.4191	0.4124

5. Given the following multiple isomorphous replacement data for the (0 6 0) reflection from a protein crystal,[*] estimate φ_P for the native protein:
   native protein: $F_P = 858$,
   Pt derivative: $F_{HP} = 756$, $F_H = 141$, $\varphi_H = 78^{\text{o}}$,
   U derivative: $F_{HP} = 856$, $F_H = 154$, $\varphi_H = 63^{\text{o}}$,
   I derivative: $F_{HP} = 940$, $F_H = 100$, $\varphi_H = 146^{\text{o}}$.

Solution:

(a) For the Pt derivative,

$$\begin{aligned}\varphi_P &\simeq 78^{\text{o}} - \arccos\left(\frac{756^2 - 858^2 - 141^2}{2 \times 141 \times 858}\right) = 78^{\text{o}} \pm 140^{\text{o}} \\ \varphi(1) &\simeq 218^{\text{o}} \\ \varphi(2) &\simeq 298^{\text{o}}.\end{aligned}$$

(b) For the U derivative,

$$\begin{aligned}\varphi_P &\simeq 63^{\text{o}} - \arccos\left(\frac{856^2 - 858^2 - 154^2}{2 \times 154 \times 858}\right) = 63^{\text{o}} \pm 90^{\text{o}} \\ \varphi(1) &\simeq 159^{\text{o}} \\ \varphi(2) &\simeq 327^{\text{o}}.\end{aligned}$$

(c) For the I derivative,

$$\begin{aligned}\varphi_P &\simeq 146^{\text{o}} - \arccos\left(\frac{940^2 - 858^2 - 100^2}{2 \times 100 \times 858}\right) = 146^{\text{o}} \pm 37^{\text{o}} \\ \varphi(1) &\simeq 183^{\text{o}} \\ \varphi(2) &\simeq 109^{\text{o}}.\end{aligned}$$

The phases that agree most closely are the $\varphi(1)$ values for each derivative. An average value gives $\varphi_P \simeq 187^{\text{o}}$.

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[*] Ladd, M. and Palmer, R., *Structure Determination by X-ray Crystallography*, 4th ed., Plenum Press, New York, (2003).