AN EXAMPLE OF THE INTERPRETATION OF A DIFFERENCE PATTERSON PROJECTION

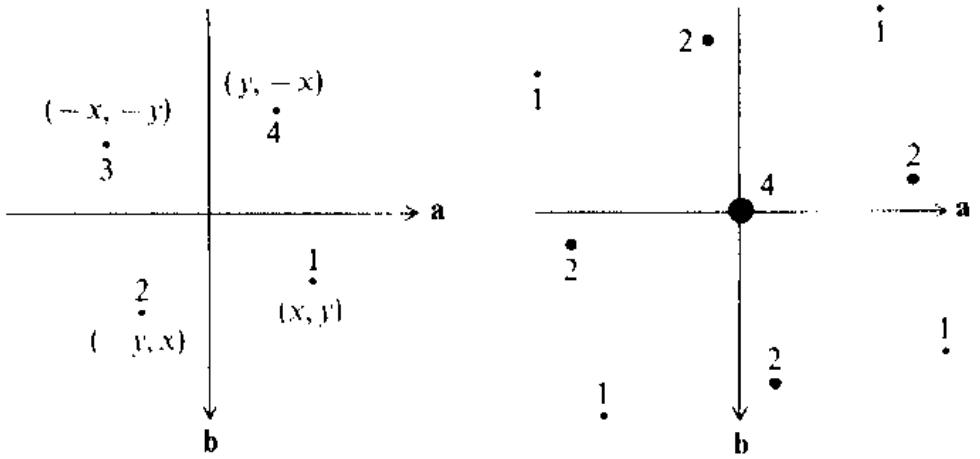
The difference Patterson map shown in Figure 13-36a was calculated for a projection into a plane perpendicular to the **c** axis of a tetragonal crystal of cytochrome *c* ($a = b = 58.45$ Å; $c = 42.34$ Å):

$$\Delta P(x, y) = (1/A) \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} [|F_{PH}(h, k, 0)| - |F_P(h, k, 0)|]^2 e^{-2\pi i(hx + ky)}$$

where $|F_{PH}|$ and $|F_P|$ are the square roots of the measured intensities of the heavy-atom isomorphous Pt derivative and the parent crystal, respectively. Thus, $\Delta P(x, y)$ can be calculated from data collected for a single layer of the reciprocal lattice.

The space group of these crystals is $P4_1$. The asymmetric unit is one molecule of cytochrome *c*. There are four molecules per unit cell, and these are related by a fourfold screw axis. The projection of the structure perpendicular to the **c** axis places all four molecules in the **a** **b** plane, where they are now related by a fourfold rotation axis. Because of this axis, the two-dimensional structure also has a center of symmetry.

We can use the symmetry to predict what the difference Patterson map should look like for a single heavy atom located at identical positions on each of the four molecules. For



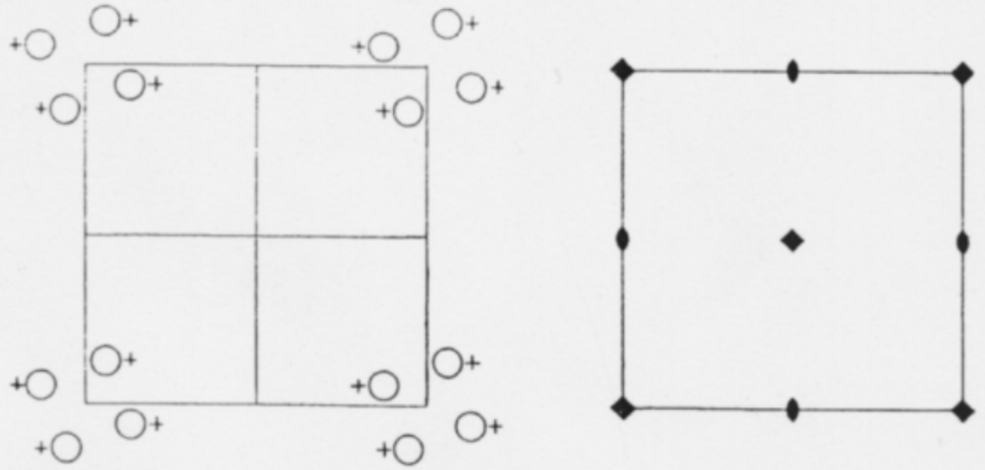
convenience, we choose the origin of the coordinate system right at the fourfold axis. Then, if the position of one heavy atom is $x\mathbf{a} + y\mathbf{b}$, the others must be located as shown in part a of the figure. The corresponding heavy atom–heavy atom vectors will be

$$\mathbf{r}_{12} = (x + y, y - x) \qquad \mathbf{r}_{21} = (-x - y, x - y)$$
$$\mathbf{r}_{13} = (2x, 2y) \qquad \mathbf{r}_{31} = (-2x, -2y)$$
$$\mathbf{r}_{14} = (x - y, x + y) \qquad \mathbf{r}_{41} = (y - x, -x - y)$$
$$\mathbf{r}_{23} = (x - y, x + y) \qquad \mathbf{r}_{32} = (y - x, -x - y)$$
$$\mathbf{r}_{24} = (-2y, 2x) \qquad \mathbf{r}_{42} = (2y, -2x)$$
$$\mathbf{r}_{34} = (-x - y, x - y) \qquad \mathbf{r}_{43} = (x + y, y - x)$$

plus four heavy-atom self-vectors, which will lie at the origin.

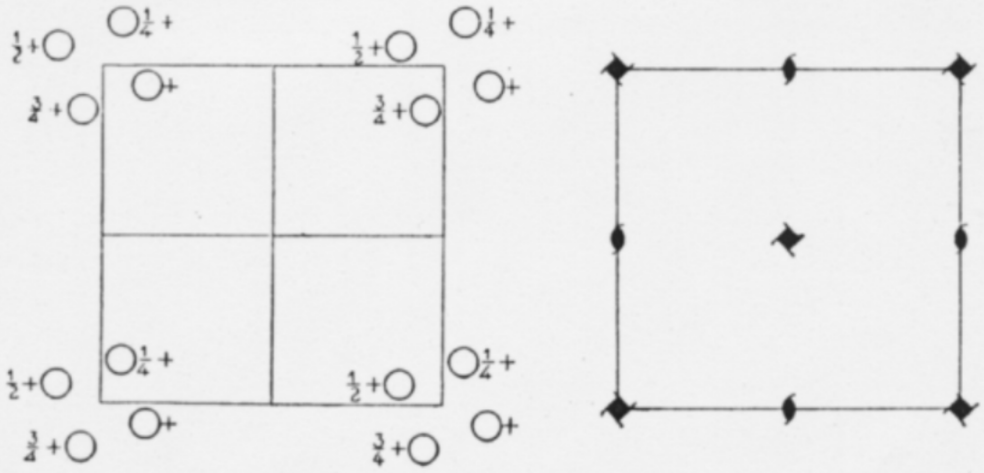
The resulting difference Patterson map will be that shown in part b of the figure (for the relative values of x and y shown in part a of the figure), where the number adjacent to each peak gives its relative weight. Notice that the map has the same fourfold rotational symmetry as the structure that generated it. Concentrate just on the quadrant at lower right, and compare the result with Figure 13-36a. Notice the doubly-weighted peak near the vertical axis. This peak must correspond to the nearly vertical vector that forms two sides of the square of heavy atoms in the structure. The singly-weighted peak (near the lower right of Fig. 13-36a) is produced from a diagonal of the square. The hint of a peak near the horizontal axis arises from the nearby doubly-weighted vector in the upper right-hand quadrant of the map. Thus, a square structure of heavy atoms is fully consistent with the observed difference Patterson map. Once the vectors have been assigned, their locations yield the values of x and y, and thus the actual heavy-atom positions.

It would be a useful exercise for the reader to interpret the Hg difference map in Figure 13-36b and then, using the results of both maps, to attempt to explain the results shown in Figure 13-36c for the Hg, Pt double derivative.



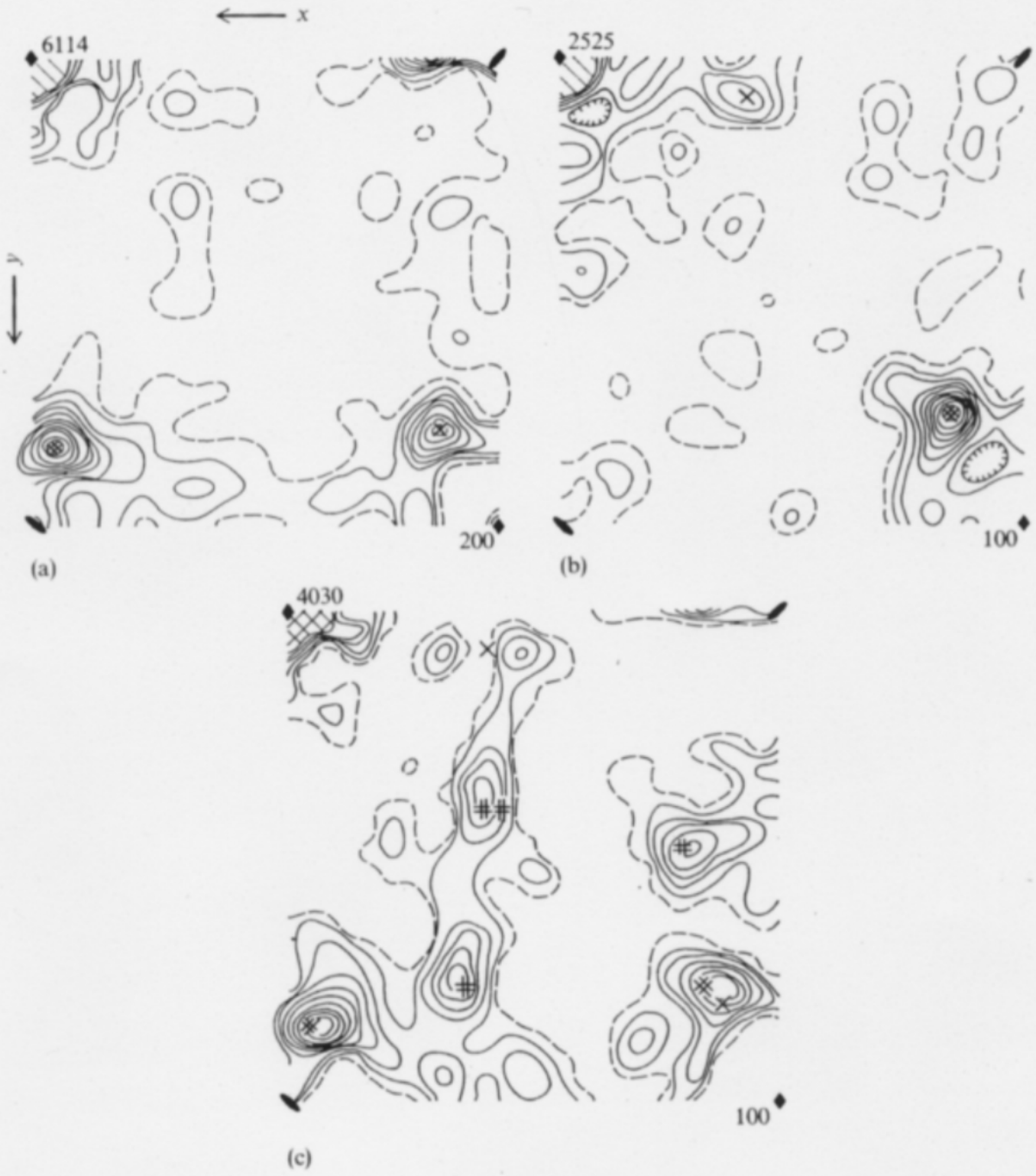
Origin on 4

Number of positions, Wyckoff notation, and point symmetry			Co-ordinates of equivalent positions	Conditions limiting possible reflections
				General:
4	*d*	1	x,y,z; $\bar{x},\bar{y},z$; $y,\bar{x},z$; $\bar{y},x,z$.	hkl: No conditions $00l$: No conditions
				Special:
2	*c*	2	$0,\frac{1}{2},z$; $\frac{1}{2},0,z$.	hkl: $h+k=2n$
1	*b*	4	$\frac{1}{2},\frac{1}{2},z$.	No conditions
1	*a*	4	$0,0,z$.	No conditions



Origin on 4_1

				General:
4	*a*	1	x,y,z; $\bar{x},\bar{y},\frac{1}{2}+z$; $\bar{y},x,\frac{1}{4}+z$; $y,\bar{x},\frac{3}{4}+z$.	hkl: No conditions $00l$: $l=4n$



Difference Patterson maps, calculated for projections of crystals of cytochrome *c* into the *x*–*y* plane. The origin is at the upper left of each map. All maps are drawn to the same scale; contour intervals are marked at the lower right-hand corners; the height of the peak at the origin is indicated at the upper left-hand corners. The zero contours are dashed. The *x* and *y* coordinates are indicated; they run only from the origin to one-half the unit-cell dimensions. Single-weight Patterson peaks are shown by X, double-weight Patterson peaks by ⋇. **(a)** A platinum derivative. **(b)** A mercury derivative. **(c)** A derivative containing both heavy metals; platinum–mercury cross-vectors are shown by #. [From R. E. Dickerson et al., *J. Mol. Biol.* 29:77 (1967).]