

1.

In order to fix the origin, arbitrary values must be assigned to the phases of the three reflections (preferably ones of high intensity). Pbc_a is centrosymmetric, so the phase should be equal to 0 or π . The reflections must be chosen such that the origin is uniquely determined by their respective phase assignments.

(reproduced from S&J, p267) o = odd value for *h*, *k*, or *l*. e = even value for *h*, *k*, or *l*

| Origin | Shift | Reflection Kind | | | | | | | |
|--------|--------------------------------------|-----------------|-----|-----|-----|-----|------|------|-----|
| | | eee | oee | oeo | eeo | ooe | o eo | eo o | ooo |
| 1 | 0 | + | + | + | + | + | + | + | + |
| 2 | <i>a</i> /2 | + | - | + | + | - | - | + | - |
| 3 | <i>b</i> /2 | + | + | - | + | - | + | - | - |
| 4 | <i>c</i> /2 | + | + | + | - | + | - | - | - |
| 5 | (<i>a</i> + <i>b</i>)/2 | + | - | - | + | + | - | - | + |
| 6 | (<i>a</i> + <i>c</i>)/2 | + | - | + | - | - | + | - | + |
| 7 | (<i>b</i> + <i>c</i>)/2 | + | + | - | - | - | - | + | + |
| 8 | (<i>a</i> + <i>b</i> + <i>c</i>)/2 | + | - | - | - | + | + | + | - |

First, we will look at the most intense reflection (3, 0, -4) = (oee). This restricts the possible choices of origin to options 1, 4, 5, or 8.

Second, we will look at the second most intense reflection (2, -2, 2) = (eee). This is of little assistance, as it is invariant with origin choice.

So, we turn to the third-most intense reflection (6, -2, 3) = (eeo). This restricts the origin to 1, 2, 3, or 5. Taking into consideration the previous triplet, we have narrowed the choice of origin to 1 or 5.

Last, we use the fourth reflection (2, 3, 6) = (eoe). This allows us to eliminate number 5 – assigning a phase value of +1 to (2, 3, 6), (3, 0, -4), and (6, -2, 3) will fix the origin at #1.

A triple meets the requirements of the Sayre equation if the indices of the two observed reflections add to give the indices of a third observed reflection. Remember that for a centrosymmetric structure states that $F_{hkl} = F_{\bar{h}\bar{k}\bar{l}}$, so from the six reflections given in the problem, we can generate a total of twelve reflections to work with.

The triplets that were provided are A, B, C, D, E, and F below. We can generate the following triplets (adding or subtracting to incorporate Friedel pairs):

| | h | k | l |
|---|---|----|----|
| A | 3 | 0 | -4 |
| B | 2 | 3 | 6 |
| C | 2 | -2 | 2 |
| D | 5 | 0 | 1 |
| E | 4 | -5 | -3 |
| F | 6 | -2 | 3 |

Looking at the additions:

| | h | k | l | |
|-----|----|----|----|---------|
| A+B | 5 | 3 | 2 | |
| A+C | 5 | -2 | -2 | |
| A+D | 8 | 0 | -3 | |
| A+E | 7 | -5 | -7 | |
| A+F | 9 | -2 | -1 | |
| | | | | |
| B+C | 4 | 1 | 8 | |
| B+D | 7 | 3 | 7 | |
| B+E | 6 | -2 | 3 | It's F! |
| B+F | 8 | 1 | 9 | |
| | | | | |
| C+D | 7 | -2 | 3 | |
| C+E | 6 | -7 | -1 | |
| C+F | 8 | -4 | 5 | |
| | | | | |
| D+E | 9 | -5 | -2 | |
| D+F | 11 | -2 | 4 | |
| | | | | |
| E+F | 10 | -7 | 0 | |

So, we can see that B, E, and F will satisfy the Sayre equation. Unsurprisingly, we can see this with the Friedel pairs as well:

| | h | k | l | |
|-----|----|----|-----|----------|
| A-B | 1 | -3 | -10 | |
| A-C | 1 | 2 | -6 | |
| A-D | -2 | 0 | -5 | |
| A-E | -1 | 5 | -1 | |
| A-F | -3 | 2 | -7 | |
| | | | | |
| B-C | 0 | 5 | 4 | |
| B-D | -3 | 3 | 5 | |
| B-E | -2 | 8 | 9 | |
| B-F | -4 | 5 | 3 | It's -E! |
| | | | | |
| C-D | -3 | -2 | 1 | |
| C-E | -2 | 3 | 5 | |
| C-F | -4 | 0 | -1 | |

| | | | | |
|-----|----|----|----|----------|
| D-E | 1 | 5 | 4 | |
| D-F | -1 | 2 | -2 | |
| E-F | -2 | -3 | -6 | It's -B! |

2. This is really a fairly simple vector addition problem. If position **n** has coordinates (x_n, y_n, z_n) :

Carbon 5 (x_5, y_5, z_5) : $(x_5, y_5, z_5) = (x_4, y_4, z_4) + (x_1, y_1, z_1) - (x_2, y_2, z_2)$

Carbon 6 (x_6, y_6, z_6) : $(x_6, y_6, z_6) = (x_4, y_4, z_4) + (x_1, y_1, z_1) - (x_3, y_3, z_3)$

3.

- (a) The multiplicity of position e is appropriate ($Z \cdot 4 = 64$). This does not truly fix the coordinates of the Ga (though it certainly reduces the number of parameters and provides a restriction), in that they may lie in any position (x, x, x) .

- (b) This limits, but does not fix (see above), the coordinates of the Ga, in that they may lie in any position (x, x, x) . It does impose 3-fold symmetry on the metal center.

- (c) First, we will calculate the Ga-Ga distance. The coordinates of the four symmetry-related centers will be (x, x, x) , $(x, -x, -x)$, $(-x, x, -x)$ and $(-x, -x, x)$. Calculation of the distance between any of these two points suggests that it will be $[(2x)^2 + (2x)^2]^{1/2} = x \cdot 2\sqrt{2}$. This gives a Ga-Ga distance of 0.25198 in fractional coordinates or 12.6002 angstroms.

In order to determine the error, we must first deal with the fractional coordinates.

$$\ell = 2\sqrt{2}x$$

$$\frac{\partial \ell}{\partial x} = 2\sqrt{2}$$

$$\frac{\sigma(\ell)}{\sigma(x)} \approx \frac{\partial \ell}{\partial x} \approx 2\sqrt{2}$$

$$\therefore \sigma(\ell) = 2\sqrt{2}(0.00003) = 0.000084$$

But this is still in fractional coordinates, so we need to multiply by a to get the distance esd

$$\sigma(\ell) = 0.0042 \text{ \AA}$$

Therefore, the Ga-Ga distance would be reported as 12.6002(42) \AA

- d) The Ga atoms lie on (x, x, x) , and so we first must identify the symmetry operation which leaves their position unchanged. While looking at the 48 symmetry operations might seem daunting, there are only two attractive options – (5) and (9). These are the positive and negative 3-fold symmetry operations, and our choice should be irrelevant. We then examine how each of the operations $(x_2, y_2, z_2, xy, xz, yz)$ transform in the symmetry operation of our choice. (I will here use (5) – (z, x, y) .)

x^2 becomes z^2 , therefore $\beta_{11} = \beta_{33}$.
 y^2 becomes x^2 , therefore $\beta_{22} = \beta_{11}$.
 z^2 becomes y^2 , therefore $\beta_{33} = \beta_{22}$. (which was, of course, already implied by the above.)
 xy becomes xz , therefore $\beta_{12} = \beta_{13}$.
 yz becomes xy , therefore $\beta_{23} = \beta_{12}$.
 xz becomes yz , therefore $\beta_{13} = \beta_{23}$. (again, already implied)

So, we obtain the restrictions $\beta_{11} = \beta_{22} = \beta_{33}$ and $\beta_{12} = \beta_{13} = \beta_{23}$.

4. First, let us write (algebraically) the symmetry operations given for each of these space groups. The coordinates given are the result of applying the operation to the general positions. All planes and axes intersect the origin for simplicity.

a) Pbam

b) Pbcm

(b glide \perp to a): $(-x, y + 1/2, z)$

(b glide \perp to a): $(-x, y + 1/2, z)$

(a glide \perp to b): $(x + 1/2, -y, z)$

(c glide \perp to b): $(x, -y, z + 1/2)$

(m \perp to c): $(x, y, -z)$

(m \perp to c): $(x, y, -z)$

To identify the other symmetry operations in these groups, we'll need to find the products of the operations we've already identified.

a) Pbam

b) Pbcm

$b^*a = (-x + 1/2, -y + 1/2, z) = 2\text{-fold } \parallel \text{ to } c$

$b^*c = (-x, -y + 1/2, z + 1/2) = 2_1 \text{ axis } \parallel \text{ to } c$

$a^*m = (x + 1/2, -y, -z) = 2_1 \text{ axis } \parallel \text{ to } a$

$c^*m = (x, -y, -z + 1/2) = 2\text{-fold } \parallel \text{ to } a$

$b^*m = (-x, y + 1/2, -z) = 2_1 \text{ axis } \parallel \text{ to } b$

$b^*m = (-x, y + 1/2, -z) = 2_1 \text{ axis } \parallel \text{ to } b$

In addition, the products of the 2-fold axes with their associated mirror planes will produce inversion centers (with an offset of $1/4$ in each dimension).

5. Evaluate the following statements for accuracy, providing the corrected statement if appropriate.

a) All centrosymmetric space groups are achiral.

This is absolutely true. The presence of an inversion center (which is an improper symmetry operation) precludes centrosymmetric groups from being chiral.

b) All non-centrosymmetric space groups are chiral.

This is not true – it is possible to incorporate improper elements of symmetry without introducing a center of symmetry. The simplest counterexample for this statement would be Pm.

c) Anomalous scattering can be used to determine the absolute configuration of a chiral molecule and its enantiomer in Pbca.

This statement has a number of problems. First of all, determining the absolute configuration of a molecule and its enantiomer makes no sense, and there's no reason you

would want to do this. Secondly, anomalous scattering is only useful in non-centrosymmetric space groups. (Note that these two statements are related – anomalous scattering is applicable when you have an enantiopure sample crystallized in a chiral space group. That space group must be non-centrosymmetric.)

d) The parameter n in the expression $f_0^{anom} = f_0 + \Delta f' + i\eta\Delta f''$ is refined to a value between 0 (racemic) and 1 (enantiopure), allowing crystallographic determination of the enantiomeric excess in a chiral crystal.

The parameter n is refined to -1 (incorrect handedness) or +1 (correct handedness). It tends strongly towards these values, not towards zero (anomalous scattering is used on resolved, not racemic samples).