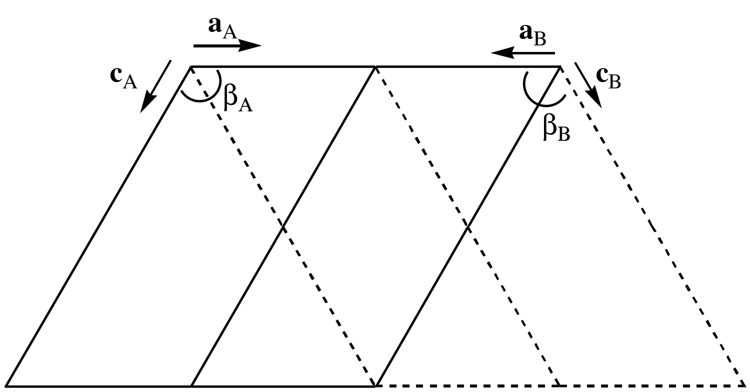
Chemistry 208—Spring 2009 **Problem Set 5**
Professor K. N. Raymond **Answer Key**

1)

a) The systematic absence observed is (*0k0*) $k = 2n$, which indicates a 2_1 axis parallel to **b**. While the hk0 photograph has mm symmetry, the *hk1* has only a single mirror plane – suggesting that the mm symmetry is an artifact the zero-layer photograph. The mirror symmetry observed is a direct consequence of the already-mentioned two-fold symmetry, and does not give any new information.

b) Without other systematic absences, a glide plane (or centering) must not be present – either $P2_1$ or $P2_1/m$ are possible. It isn't possible to decide between these two with the information given.

c) This introduction to the question suggests that a truly different **c** has been chosen by the other group. The most reasonable way to imagine this occurring is diagrammed below, with your cell constants (sub A) and theirs (sub B) delineated:



$$\vec{a}_B = -\vec{a}_A$$
$$\vec{b}_B = \vec{b}_A$$
$$\vec{c}_B = 2\vec{a}_A + \vec{c}_A$$

Verifying this analysis via independent calculation of c_B and β_B.

$$\vec{c}_B^{\ 2} = \vec{c}_B \cdot \vec{c}_B = (2\vec{a}_A + \vec{c}_A)\cdot(2\vec{a}_A + \vec{c}_A)$$
$$\vec{c}_B^{\ 2} = 4\vec{a}_A^{\ 2} + \vec{a}_A^{\ 2} - 4\vec{a}_A\vec{c}_A \cos\beta_A$$
$$\vec{c}_B^{\ 2} = 250.12$$
$$\Rightarrow \vec{c}_B = 15.82\text{Å}$$

$$\vec{a}_B\vec{c}_B \cos\beta_B = \vec{a}_B \cdot \vec{c}_B = -\vec{a}_A \cdot (2\vec{a}_A + \vec{c}_A)$$
$$= -2\vec{a}_A^{\ 2} - \vec{a}_A\vec{c}_A \cos\beta_B$$
$$= -(8.23)(15.82)\cos\beta_B = -86.97$$
$$\Rightarrow \beta_B = 132.2°$$

d) The transformation matrix representing the system of equations above is as follows:

$$\begin{pmatrix} \vec{a}_B \\ \vec{b}_B \\ \vec{c}_B \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 2 & 0 & 1 \end{pmatrix} \begin{pmatrix} \vec{a}_A \\ \vec{b}_A \\ \vec{c}_A \end{pmatrix}$$

e) The determinant of the transformation matrix is -1. The ratio of the volumes of the two cells is 1:1 – and the negative sign indicates that the handedness of the two cells is opposite.

2) The rhodium atoms must be located on mirror planes.
We know that Z = 4, so the rhodium atoms must be on special positions. If a rhodium atom were placed on an inversion center, an adjacent rhodium atom with the same x and z coordinates would be $b/2$ = 1.49Å away. Thus, the rhodium atoms are required to lie on mirror planes.

$x, \frac{1}{4}, z,$ $\frac{1}{2} - x, \frac{3}{4}, z + \frac{1}{2},$ $-x, \frac{3}{4}, -z,$ $x + \frac{1}{2}, \frac{1}{4}, \frac{1}{2} - z.$

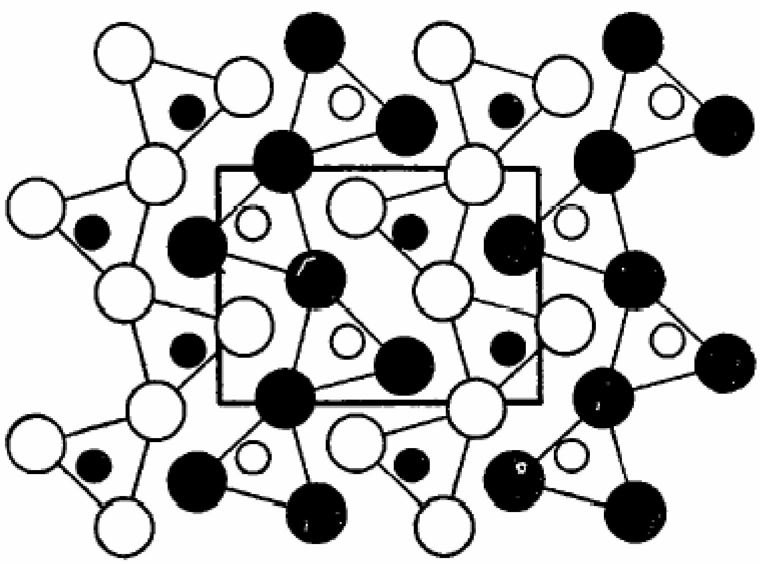
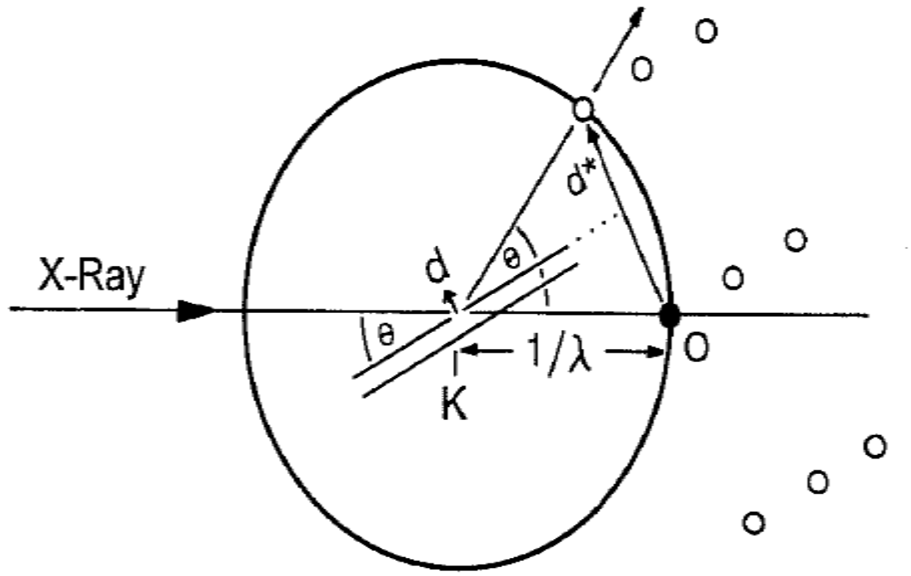


Fig. 2. Projection of the Rh_2B structure down the b axis. Large circles represent Rh atoms; small circles, B atoms. The solid circles are located on the $y = \frac{1}{4}$ plane; the others, on the $y = \frac{3}{4}$ plane. The unit cell is shown by the heavy lines. The light lines between metal atoms illustrate the triangular nature of this structure.

3.

a) The Ewald Sphere represents the conditions for diffraction as a spatial construction. While we have seen many illustration of the reciprocal relationships between real diffraction object spacings and the spacing between diffraction spots, the Ewald Sphere is a three-dimensional amalgamation of these concepts.



b) The reciprocal lattice points will be rotated about the reciprocal lattice origins in 'all' directions, producing reciprocal lattice 'spheres' instead of discrete points.
c) The intersection between two spheres will always be a circle (or a point). As a resule, we could expect to see circles, or rings (which are concentric with the center of our diffraction pattern.
d) While symmetry information will be obliterated by the imposed circular symmetry, the distances between rings will still reflect the distance between reciprocal lattice points, and so will give information about the size of the unit cell.

4. This tetragonal space group will produce the following characteristics in each of the desired precession photographs:

$0kl$: All $k = 2n$ will be absent.
$1kl$: No systematic absences.
$h0l$: All $h = 2n$ along the $l = 0$ axis (the a* axis)
$h1l$: No systematic absences.

Normalized, the distances on the graphs should represent a (a*:b*:c*) of (3:3:1).
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