

3.60 Symmetry, Structure and Tensor Properties of Materials

Problem Set 8

- (1) Show that the body-centered and side-centered monoclinic lattices are not distinct.
- (2) In contrast to the above, the body-centered and side-centered orthorhombic lattices are distinct. Why?
- (3) A side-centered tetragonal lattice is impossible. Why?
- (4) A face-centered tetragonal lattice is not unique. Why?
- (5) A two-dimensional crystal has plane group $p2gg$ and $a=3$, $b=6$. The structure contains two cations, A and B, and two crystallographically-independent anions, X(1) and X(2), which occupy the following positions in the plane group:

A	in	2a		
B	in	4c	$x = .500$	$y = .200$
X(1)	in	4c	$x = .167$	$y = .167$
X(2)	in	4c	$x = .333$	$y = -.083$

X(1) and X(2) are not necessarily the same chemical species.

(Although concocted, this structure turns out to be a not unreasonable two-dimensional analogue of an ionic structure.)

- (a) On the basis of the rank of the equipoints that are occupied, how many ions are contained within the cell? What is the composition of this compound?
- (b) Using the equipoints tabulated for plane group $p2gg$, generate the coordinates of all ions contained within the unit cell. Plot the structure on a piece of graph paper showing enough of the structure outside of the boundaries of the cell to complete the arrangement of anions around each cation.
- (c) Connect each cation with bonds to nearest-neighbor anions. What is the shape of the coordination polyhedron formed by the anions about each of the two types of cations? How are these polyhedra linked to form the structure?

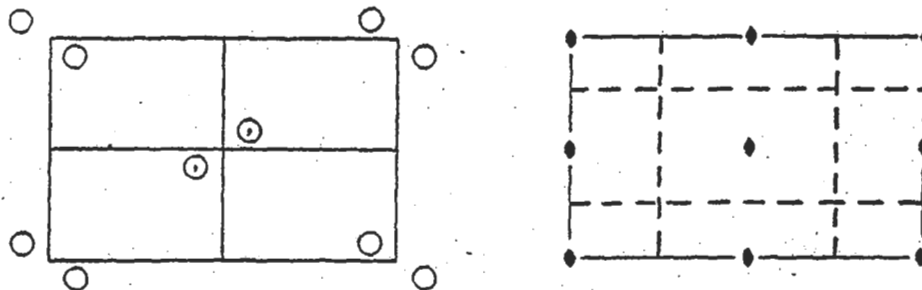
- (d) Pauling summarized the criteria for the formation of a stable ionic structure in five statements that are generally known as "Pauling's rules". The second rule gives a nice quantitative embodiment of the principle that a stable configuration of ions should be electrostatically neutral on an atomic scale as well as on a macroscopic scale. It views each cation as "donating" bonds to the neighboring anions and defines the strength of each bond, s , as

$$s = \frac{+q}{N}$$

where q is the charge on the cation and N , the coordination number of the cation, is the number of surrounding nearest-neighbor anions (regardless of their charge or slight variations in their distance from the cation). The rule then states, if we now switch our attention to an anion, that in a stable structure the sum of all of the bonds contributed to the anion from the surrounding cations should be equal to the charge on that anion.

Let us now apply Pauling's rule concerning bond strength to the present structure to see if this is, indeed, a reasonable ionic structure.

- (i) Can X1 and X2 have the same valence?
 - (ii) Is there some assignment of integer charges to A, B, X(1) and X(2) for which Pauling's rule is satisfied?
- (6) Sketch patterns of objects produced by 6_2 and 6_4 and show that they are enantiomorphous.
- (7) List the crystallographic screw axes that have no enantiomorphic equivalent.
- (8) List the symbols for the screw axes that can be based upon an 8-fold rotation axis. Sketch a representative pattern for each. It is strongly suggested that, for clarity, you show the patterns either in projection along the rotation axis (with labels showing the elevation of the objects) or, better yet, by means of the "unrolled cylinder" device.
- (9) Is a screw axis a candidate location for a special position in a space group? Consider carefully, and explain.



Origin at 2

Number of positions,
Wyckoff notation,
and point symmetry

Co-ordinates of equivalent positions

Conditions limiting
possible reflections

4 *c* 1 $x, y; \bar{x}, \bar{y}; \frac{1}{2}+x, \frac{1}{2}-y; \frac{1}{2}-x, \frac{1}{2}+y.$

General:

hk: No conditions

h0: $h=2n$

0k: $k=2n$

2 *b* 2 $\frac{1}{2}, 0; 0, \frac{1}{2}.$

Special: as above, plus

2 *a* 2 $0, 0; \frac{1}{2}, \frac{1}{2}.$

hk: $h+k=2n$