FROM 2D TO 3D: I. ESCHER DRAWINGS
CRYSTALLOGRAPHY, CRYSTAL CHEMISTRY, AND CRYSTAL "DEFECTS"

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PREFACE TO INSTRUCTOR

This set of exercises illustrates **A.** plane and space groups and **B.** crystal chemistry and "defects" in crystals. The problems are designed to present the material as puzzles that are visually attractive and intellectually challenging. Parts **A** and **B** can be covered independently of one another. Part **B** flows into the following problem set, "From 2D to 3D: II. HRTEM and AFM images" (Buseck, this volume), which provides examples of real crystals through high-resolution images from both transmission electron microscopy (HRTEM) and atomic-force microscopy (AFM). The exercises can be used either as take-home problem sets or as laboratory exercises.

Several exercises use drawings by M.C. Escher and one by I. Schaschl to take the students to another level of sophistication from that in many texts and to see whether they can draw mineralogical analogies from these drawings (a strange thought, considering these are just weird, artistic fantasies of animals and more abstract motifs). We also look at **deviations** from ideality as they occur in minerals. These are examples of the wide range of fascinating features that are encountered in real (as opposed to idealized) minerals.

There is too much material to be covered in a single laboratory session. However, it is possible to select from among the problems, choosing those that are most relevant to the particular topic being covered. The two problems of topic **A,** "Escher drawings as 3-D projections: analogies to real minerals," take the most time. They can be skipped if crystal chemistry and mineral defects are the topics of greatest interest.

Problems 3 to 6, grouped under topic **B** "Order/disorder relations," provide examples of features found in real minerals (superstructures, substitutions and structural "defects," and modulated and incommensurate structures). Only some of these complexities are covered in the typical introductory mineralogy course. Comments I received at the Workshop were encouraging. Some participants, themselves mineralogy instructors, commented that some of these mineralogical complexities made sense to them for the first time in the process of doing these problems.

Students should have prior familiarity with basic symmetry elements, unit cells (in two dimensions, even if not in three), and have been exposed to the concept of plane groups. These topics are covered in most mineralogy textbooks, and students may wish to consult those texts (a worthwhile goal in itself) in the course of doing these problems. The insights provided in these exercises are reinforced by comparison to the exercises in the following problem set ,"From 2D to 3D: II. HRTEM and AFM images," in which TEM and AFM images of real minerals are considered.

Materials: Escher drawings # 42, 55, 70, 78, and "*Birds in Space,*" plus "*Iselberg*" by I. Schaschl (Vienna Museum); transparent overlays (plastic overhead sheets do well); colored markers (I like Staedtler Lumocolors); a reference copy of the *International Tables for Crystallography* (ref. given below). I found it effective to use sequential overlays in demonstrations to explain the steps in figuring out the relationships in problems #1 and 2.

References: Two books that I found both useful and enjoyable for working with the art of Escher are (a) MacGillavry, Caroline H., 1965, *Symmetry Aspects of M.C. Escher's Periodic Drawings.* The International Union of Crystallography; and (b) Schattschneider, D., 1990, *Visions of Symmetry: Notebooks, Periodic Drawings, and Related Work of M. C. Escher.* W. H. Freeman and Company. N.Y., 354 pp. The ultimate reference for information regarding space groups is Hahn, T., *ed.*, 1985, *International Tables for Crystallography, Volume A, Space-group Symmetry*, D. Reidel Pub. Co., Boston, *for* The International Union of Crystallography. A "*Brief Teaching Edition*" of vol. A is also available; it lists selected space groups and is designed as an instructional aid.

A. ESCHER DRAWINGS AS 3-D PROJECTIONS: ANALOGIES TO REAL MINERALS

PLANE AND SPACE GROUPS

1. Escher pattern #55 ("**Fish**") can be viewed as a planar pattern (plane group) either (a) considering the colors or (b) ignoring them. It shows rather different symmetry depending on whether color is considered or ignored. It can also be considered as (c) a 3-dimensional (3D) projection with each color at a different level. Interestingly, for each of these cases we obtain a different symmetry.

PART I – PLANAR SYMMETRY (2D)

a) Does this pattern have any symmetry elements (such as rotation axes or reflection lines) oriented perpendicular to the plane? Do **not** overlook the color differences. If so, mark these elements onto your overlay.
b) Considering the color differences, mark a unit cell.
c) What is the plane group?
d) Now assume you are color blind. Mark the symmetry onto an overlay ignoring color differences. What symmetry changes occur and where are the new symmetry elements located?.
e) Does the unit cell change dimensions? Orientation? If so, mark the new unit cell.
f) What is the plane group?

PART II – 3D CONSIDERATIONS

Now assume that the pattern represents a projection of a 3D structure that consists of three parallel layers. Each color then corresponds to a motif occurring at a different height (blue on one level, yellow on another, red on a third). Lets consider each of these in turn.

a) How many levels are there? Let's (arbitrarily) pick one of the colors as the "0" level and the others at 1/3 multiples perpendicular to the plane. For example: blue = 0; red = 1/3; yellow = 2/3.
b) **Locating the unit cell.** As a first assumption, search for points located at sites of maximum symmetry and use them to define the unit cell (the assumption will prove correct in this instance). Draw this cell onto an overlay.
c) **Determining the symmetry perpendicular to the pattern**. It is convenient to do this in steps.
   [1] **At cell corners.**
   What is the "fold" of the rotation axes perpendicular to the pattern? Does more than one level have to be considered for a rotation?
   If so, how many?
   In radians, what is the rotation angle? What type of rotation axis has this characteristic?

[2] **At cell edges** (but still perpendicular to the pattern).

What is the "fold" of the rotation axes? Does more than one level have to be considered for a rotation?

If so, how many?

In radians, what is the rotation angle? What type of rotation axis has this characteristic?

[3] **Within the cells.**

What is the "fold" of the rotation axes? Does more than one level have to be considered for a rotation?

If so, how many?

In radians, what is the rotation angle? What type of rotation axis has this characteristic?

[4] **Other symmetry**.

Mirrors? If so, how many?

d) **Determining the space group**. We now have enough information to search for possible space groups. Consider the symmetry elements you determined above. They lead to a space group symbol of the type $\_X_y\ \_\ \_$, where you have determined the values of X and y, both of which are small integers.

It turns out that there are few space groups having these characteristics.

[1] Consult the *International Tables* to locate possible candidates. Give their full symmetry and space group number(s).

[2] What is the relationship between these space groups?

2. Escher pattern #70 ("**Butterfly**") contains blue, yellow, and red butterflies that are identical except in color. Consider the colors, but assume that this pattern represents a projection of a 3-dimensional (3D) structure consisting of three parallel layers. Each color then corresponds to motifs occurring at different heights (blue on one level, yellow on another, red on a third). When the colors of the dots on the wings are considered, we actually have six layers, and such an array also fits one of the space groups quite well. The problem is to find this space group by considering the symmetry of the pattern. We will then relate the pattern and its symmetry to some common minerals.

PART I – PLANAR SYMMETRY (2D)

a) Does this pattern have any symmetry elements oriented perpendicular to the plane (consider color differences)? If so, mark it onto your overlay.
b) Considering the color differences, mark a unit cell.
c) Do all symmetry elements of the same "fold" occur in identical "environments"?
d) If not, how many distinct environments are there?
e) What is the plane group?
f) Now assume you are color blind. Mark the symmetry onto an overlay ignoring color differences. What symmetry changes occur and where are the new symmetry elements located?
g) Does the unit cell change dimensions? Orientation? If so, mark the new unit cell.
h) Which has the larger unit cell? By what factor?
i) What is the plane group?

PART II – 3D CONSIDERATIONS

a) What additional symmetry elements and operations are introduced perpendicular to the pattern when this is considered as a 3D structure?

b) Show where these new symmetry elements occur by marking them onto a transparent overlay and by giving their fractional *xy* coordinates (e.g., 0, 0; 1/2, 1/2; 0, 1/3, etc.).

c) What is the relevant Bravais lattice of this projected 3D pattern?

We now have a 3D array that can be described as a ***space group*** rather than one of the 2D ***plane groups***. Such a 3D array might also have new symmetry elements that are oriented horizontally, either within the plane of the pattern or above it, and they are required to recognize exactly which space group is represented. With the experience at hand, it would be difficult to identify each of these new symmetry elements. However, it is possible to use the available information to identify *possible* space groups.

d) Using the *International Tables for Crystallography*, name and give the space group number (marked at the top of the page in the *IT*) of one or more space groups that are compatible with this symmetry? For purposes of this problem, it is acceptable to hypothesize the presence (or absence) of inversion centers and horizontal axes of rotation, but no other symmetry elements that are not evident upon inspection.

Hint: note that in the *IT* the space groups are organized by crystallographic system: # 1 and 2 - **triclinic**; 3 to 15 - **monoclinic**; 16 to 74 - **orthorhombic**; 75 to 142 - **tetragonal**; 143 to 194 - **hexagonal**; 195 - 230 - **isometric**. Within each crystal system they are arranged in order of increasing symmetry.

e) Explain your reasoning in arriving at the space groups you selected.

[It may be useful to generate cross sections that show the types of drawings at each level, e.g., red butterflies with blue dots, etc. Only a stacking of color pairs is needed to show the sequence.]

f) Note that these groups correspond to some important minerals. Name a common mineral that corresponds to a space group given above. [It may be necessary to hypothesize inversion centers or horizontal axes, as specified in d).]

g) If mirrors or glides were added, which additional common minerals would be included?

h) Two-fold axes occur in the "color-blind" pattern but not in the colored 2-D pattern. What is their status in the 3-D pattern?

B. ESCHER & SCHASCHL DRAWINGS: ORDER/DISORDER RELATIONS

SUPERSTRUCTURES

3. Escher pattern #78 ("**Unicorn**") contains red, yellow, and green unicorns that are identical except in color.

a) Ignoring the color differences, determine the symmetry, mark a unit cell, and determine the plane group

b) Now repeat a) considering the color differences.

c) Does the colored or "color-blind" pattern have the larger unit cell? By what factor?

d) Has the plane group changed? If so, to what?

e) The relation between these two cells is that one could be called a ***supercell*** and the other is then the ***subcell.*** Structures formed in this way are called ***superstructures.*** Which structure (colored or "color-blind") defines the **subcell**, which the **supercell,** and which is the **superstructure**?

f) Assume that parts of one pattern represent the atoms or atom groups in a mineral structure that formed at high temperatures and then transformed during cooling to a structure that is stable at low temperature. Many common oxide, sulfide, and silicate minerals display such transformations. Which pattern would be the more appropriate one for low temperatures? Explain your answer.

(A mineralogical analog might be that of a mineral such as chalcopyrite, in which the Cu and Fe atoms are randomly distributed onto the metal sites at high temperatures and then ordered at low temperatures to produce a new cell having different dimensions. [In the case of pattern #78, the analogy would be with a mineral having three cations (e.g., Cu, Fe, Zn; Fe, Mg, Mn; etc.) in solid solution at high temperatures which then order upon cooling.])

4. This pattern ("Iselberg" by Irene Schaschl) provides another example of a feature having a longer periodicity than what by first (and second) glance appears to be the basic repeat unit, although it is more subtle to see. Note that the tips of the leaves touch in some vertical rows and do not in others.

   a) Draw unit cells:

      (i) ignoring the above subtlety, i.e., assume the touching leaves are just a mistake by the artist, and

      (ii) considering that there is a real difference between the touching and non-touching leaves.

   b) What is the dimensional (metric) relationship between cells for assumptions (i) and (ii)?

   c) The following patterns contain repeating units that also can be considered on two scales, easiest seen by noting the periodicity first of the squares (❑ representing, for example, anions) and then of the squares plus intervening symbols (▲◆) representing cations.

      Assume that none of the ordered repeat units for the following patterns extend across more than half of the page (so that at least two repeat units are shown). Indicate the width of the unit cell and give its pattern. Recall that a disordered cell can be considered to have "average" site occupancies.

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repeat unit:

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repeat unit:

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repeat unit:

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repeat unit:

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repeat unit:

d) Which, if any, of the above sequences are analogous to the "Iselberg" pattern? If none are, then sketch one that is.

One approach would be to designate each of the "kissing" leaves as ▲, the other leaves as ◆, and the small circles surrounded by scalloping as ❑.

e) The sub- and super-periodicity should be evident in the "structure" drawn for d). If a ▲ represents a Mg atom, ◆ a Ca, and the ❑ as two (CO_3) units, then what mineral intergrowths can be inferred from this abstraction?

Comment: the ordering of vacancies in pyrrhotite, $Fe_{1-x}S$, and many other sulfide minerals provide examples of an effect such as is seen above (although the metrical details differ).

SUBSTITUTIONS AND STRUCTURAL "DEFECTS"

5. Escher pattern #42 ("**Shells and starfish**") consists of an intriguing array of clams, shells and starfish. Note that there are green and brownish snails, and they display different orientations. Ignore, for now, these differences in orientation.

a) Note that the brownish snails can have either of two orientations (tip up or tip down, resulting from a 2-fold rotation) and still fit into the pattern.

Using the array on the next page, show where, if anywhere, on the pattern there is a disruption of the symmetry caused by a "misorientation" of brown snails. Assume the small points correspond to the spots where the four clamshells or the four green snails meet, and the heavier points correspond to the positions of the brown snails. Place bold red marks to show the positions where the brown snails are misoriented.

b) Is this pattern perfectly periodic or is it not, i.e., how good a match is it to a real crystal such as we might find in a mineral? Here are some leading questions:

[1] If the brown snails represent cations, which of the following pairs are feasible? Use your knowledge of crystal chemistry to explain your answers.

K^+ and Cs^+

Ti^{+4} and Fe^{+2}

Fe^{+2} and Fe^{+3}

Fe^{+2} and Mg^{+2}

Ca^{+2} and Mg^{+2}

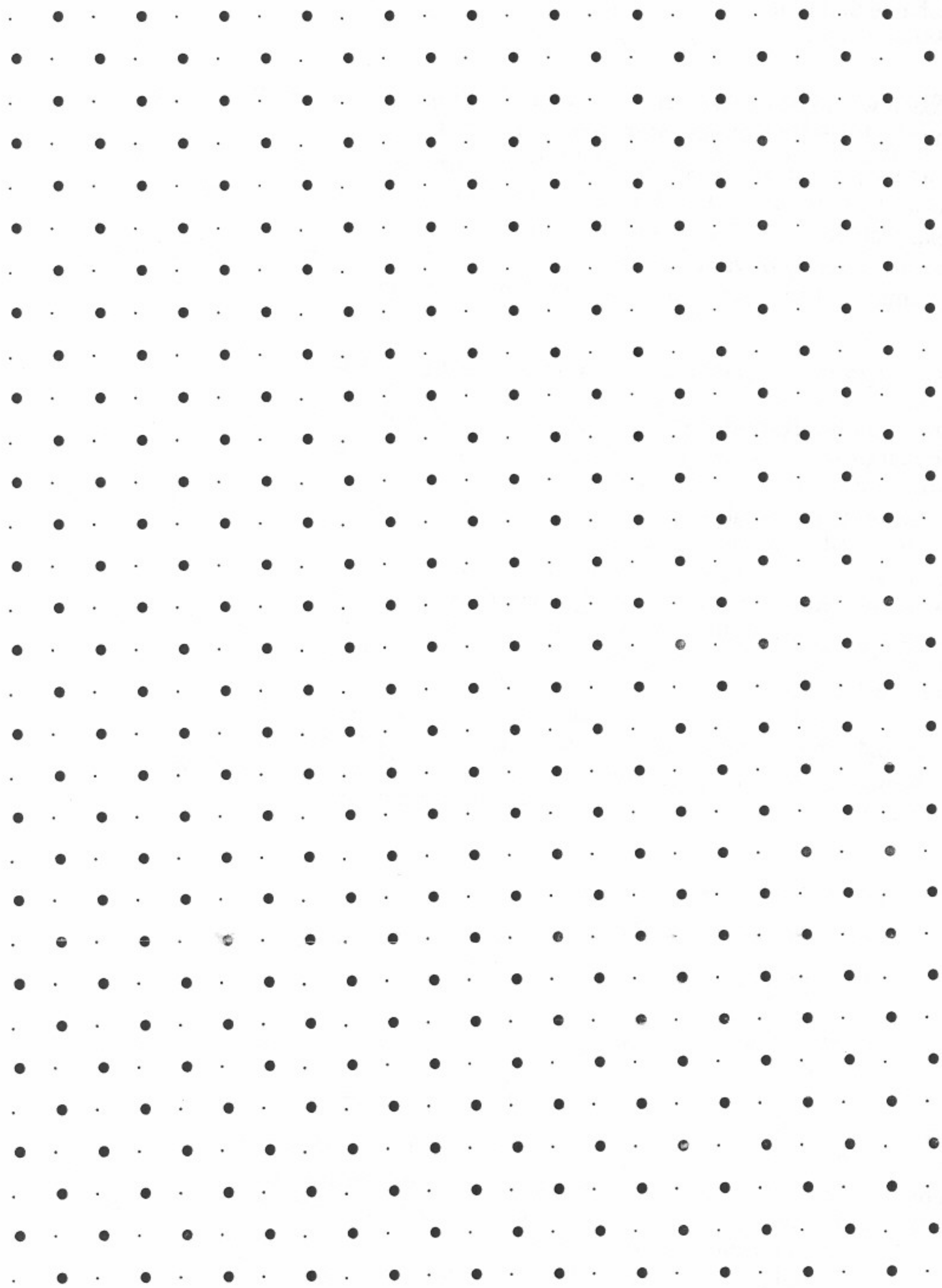
Si^{+4} and Al^{+3}

Cu^{+2} and Zn^{+2}

[2] In what respects is this structure periodic and in what respects is it disordered?

"Problems" such as this occur throughout ***real*** crystals and are what make minerals so interesting and useful as geological indicators. It is features such as these that can record the origin and conditions of formation and transformation of the minerals.

[3] What experimental techniques might be used to observe features such as are considered in this problem?



MODULATED AND INCOMMENSURATE STRUCTURES

6. Escher pattern of **Birds in space** is truly fascinating and reflects a type of disorder that is becoming increasingly apparent as our methods for studying minerals (and other crystals) become more sophisticated. It shows the two types of birds changing into one another as the pattern is traversed. The large black and white areas can be seen as isolated point defects (perhaps more realistically, clustered point defects), and they are periodically arrayed.

The result is the analog of a superstructure. Supercells have dimensions that are multiples of the subcell.

In some minerals, the supercells are integral multiples (e.g., n = 2, 3, 4, ...) of the subcell. They are then called ***commensurate***. Sulfides such as chalcopyrite, silicates such as long-period polytypes of mica and chlorite, and oxides such as hollandites form commensurate superstructures.

In other superstructures the supercells are not integral multiples of the subcell. They are then called ***incommensurate***. Many sulfide and sulfosalts (e.g., pyrrhotite, franckeite), silicates (e.g., plagioclase, antigorite serpentine), and oxides (e.g., intermediate tridymite) form incommensurate superstructures.

Incommensurate superstructures have also been called "vernier" materials because their units mesh like a vernier on surveying or measuring instruments (e.g., transit, theodolite, alidade).

Superstructures such as are mentioned above are becoming of increasing mineralogical and industrial interest. Their utility for industrial purposes is that it is possible to make "designer" materials whose properties depend on subtle variations in structure such as is possible when there are slight dimensional or motif mismatches.

Back to the Escher drawing, it can be difficult to define a unique subcell.

The most unambiguous periodicity in this pattern is the large repeat defined by the large black (and white) "holes" or "defects" in the pattern. We shall call the cell defined by these "holes" a supercell and place its origin in the center of the "hole."

There is also an underlying periodicity of intermediate spacing (and so described as a subcell), although it is more difficult to recognize and define because of its inexactness. Viewing the pattern from a distance while squinting helps make the subcell periodicity evident.

a) On an overlay mark a subcell with a horizontal cell edge that is defined by the white birds. What is the relation of the width of the subcell to the supercell in terms of numbers of birds – if the origin of the supercell is placed (i) on the center of the black holes? (ii) on the center of the white holes?

b) As a further complexity, consider a line in a southeast direction from the black to the white holes. How many white birds do you count?

c) Now count in a northeast direction from the black to the white holes. What number of white birds do you come up with? This difficulty in defining the repeating unit is characteristic of incommensurate structures where there is not a perfect dimensional match between the component parts.

d) Draw a unit cell of the substructure. Note that you will have to assume a uniformity that does not really exist in detail, only in shape. Indicate where you chose the origin and how you decided on that choice.

e) Draw a unit cell of the superstructure. What are its dimensions in terms of subcell repeats?