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.

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.

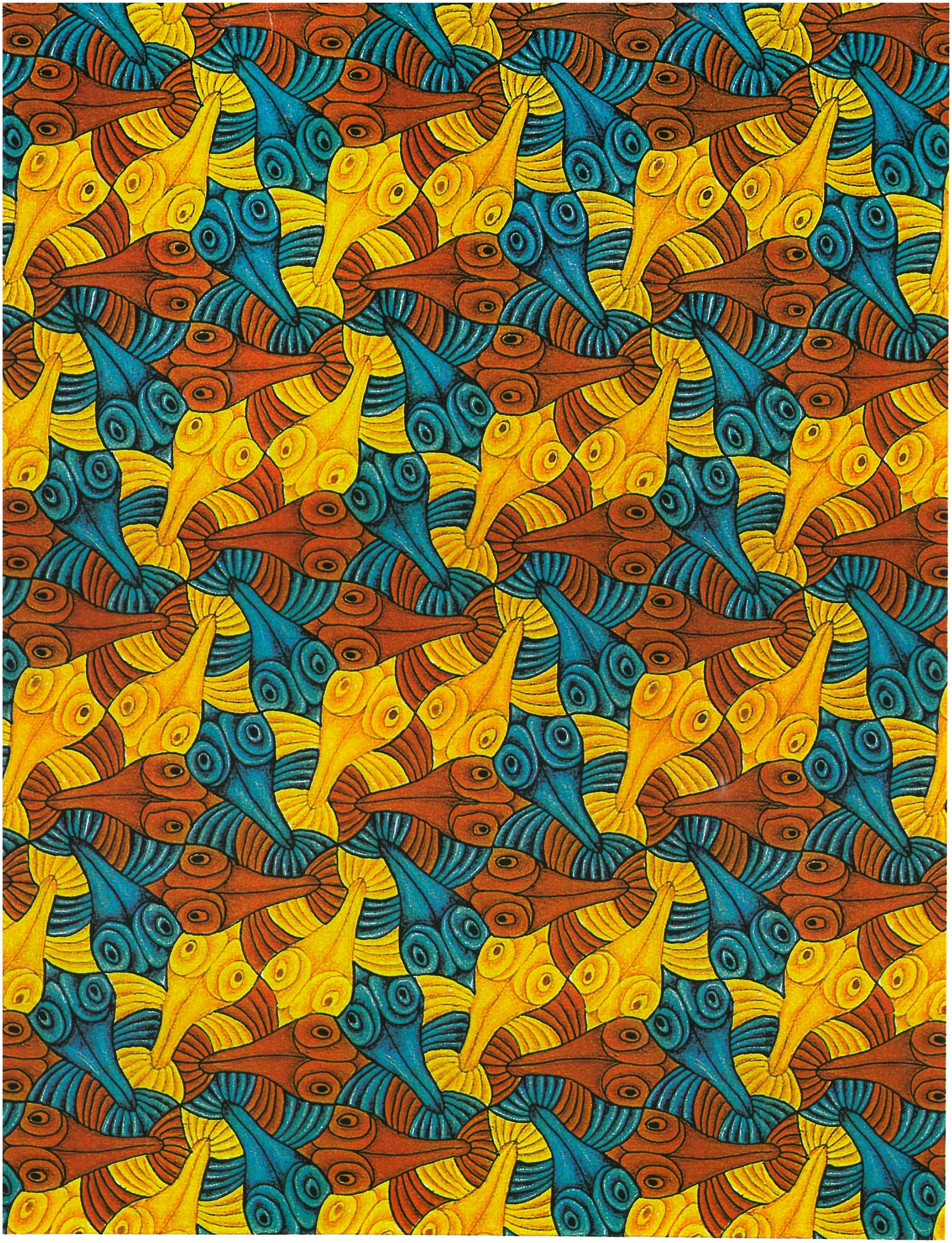

Figure 1. Escher Pattern #55 (*Fish*), reproduced with permission of Cordon Art.

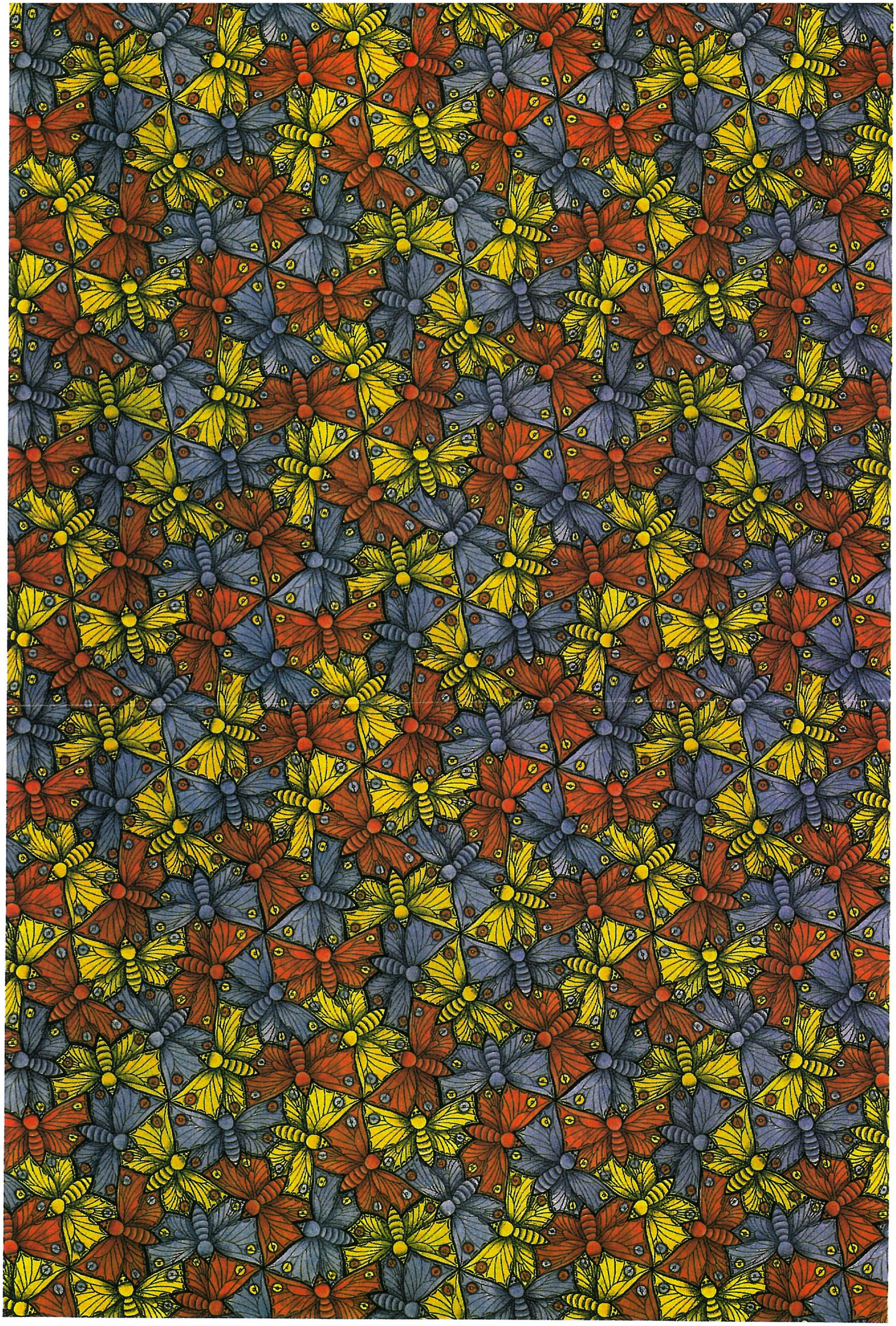

Figure 2. Escher Pattern #70 (*Butterfly*), reproduced with permission of Cordon Art.

Figure 3. Escher Pattern #78 (*Unicorn*), reproduced with permission of Cordon Art.

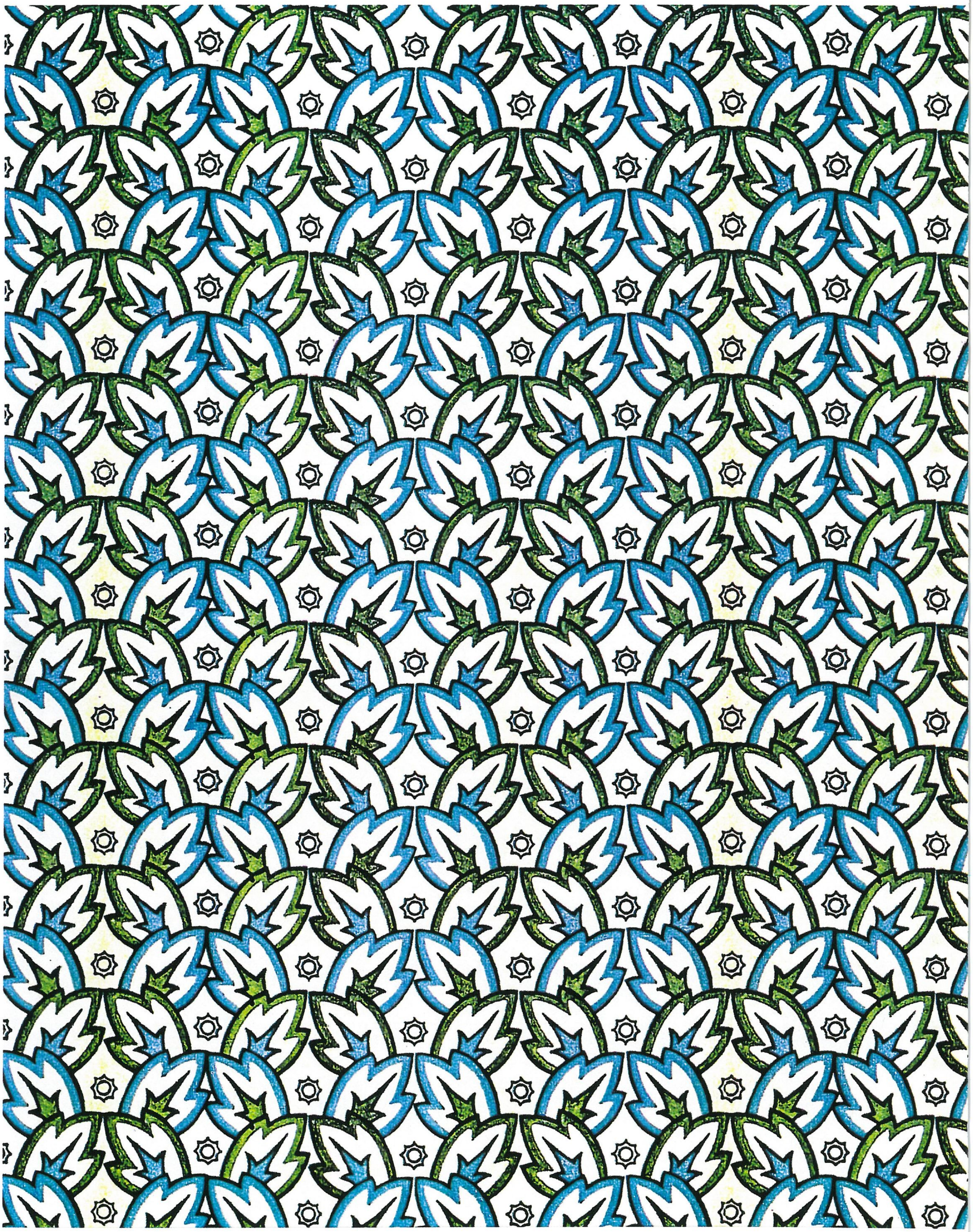

Figure 4. *Iselberg* by Irene Schaschl, reproduced with permission of MAK.

Figure 5. Escher Pattern #43 (*Shells and Starfish*), reproduced with permission of Cordon Art.

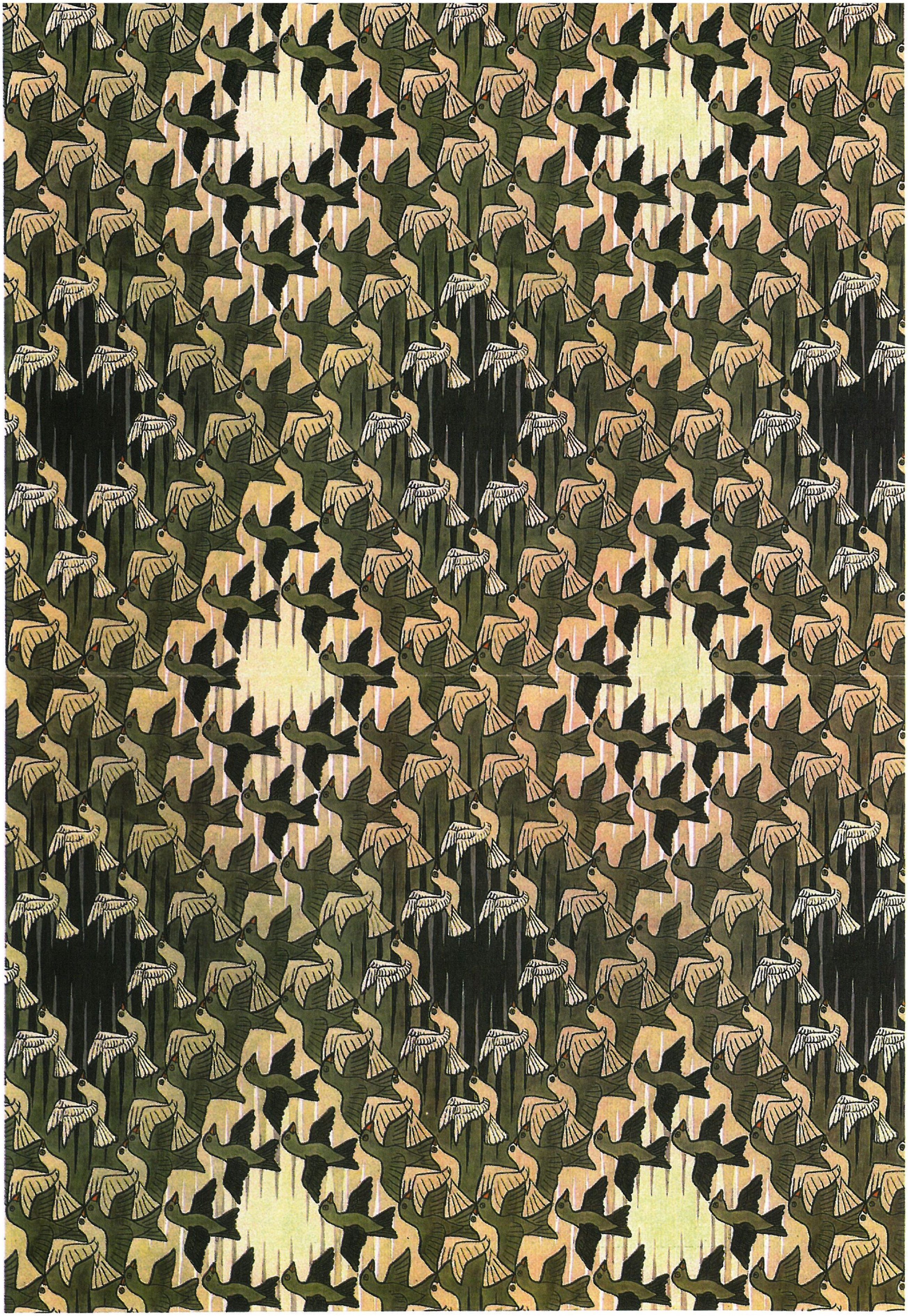

Figure 6. *Birds in Space* by M.C. Escher, reproduced with permission of Cordon Art.

(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:

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?

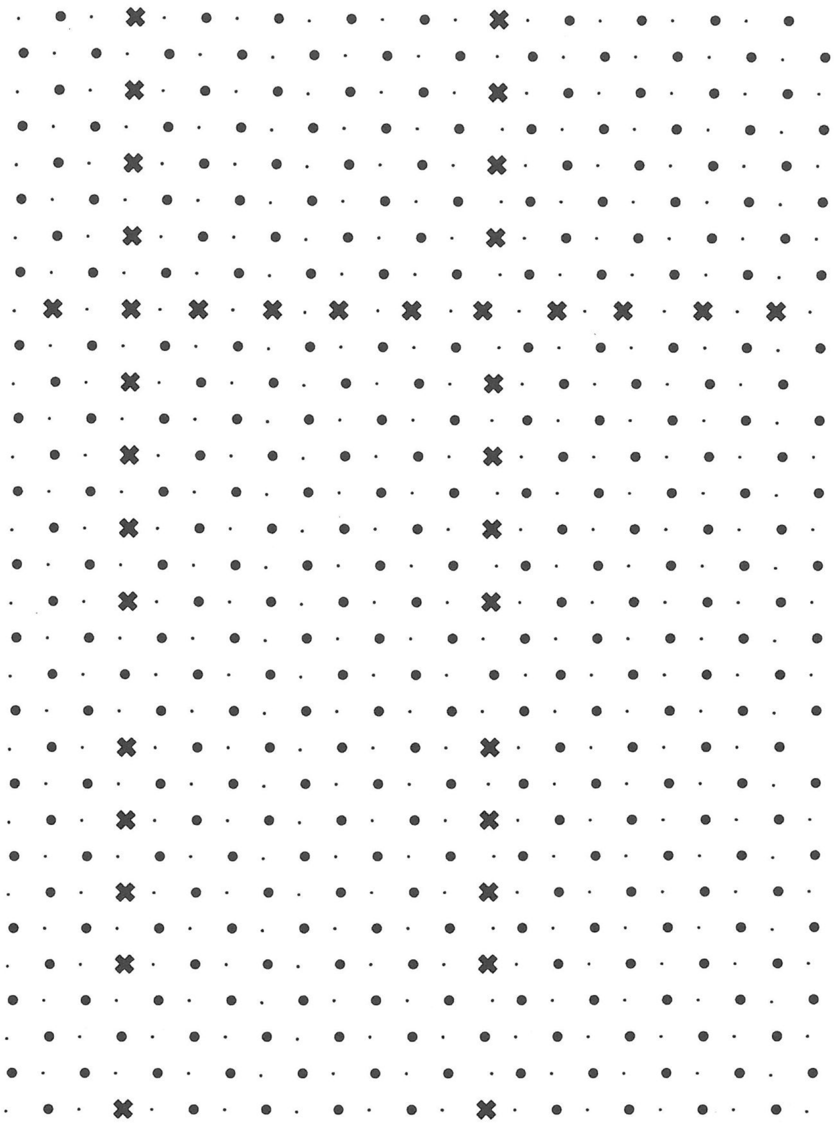
Answers for "FROM 2D TO 3D: I. ESCHER DRAWINGS"

1. **PART I** – **a)** yes – 2-fold rotation axes at the corners of the unit cell and midway along each cell edge and in the center of the cell; **c)** p2; **d)** 2's at tails --> 6's; 2's at eyes --> no change; 3's appear next to other eyes, i.e., along the long body diagonal at 1/3, 2/3 and 2/3, 1/3; **e)** no, no; **f)** p6. **PART II** – **a)** 3; **b)** the cell corners are located at the intersection of the 6_2 or 6_4 screw axes with the pattern; **c)** [**1**] 6, yes, 3, 2p/6, 6_2 or 6_4 screw axes; [**2**] 2, no, 1, 2p/2, 2-folds; [**3**] 3, yes, 3, 2p/3, 3_1 or 3_2 screw axes; [**4**] none; **d)** [**1**] $P6_2$ - # 171 & $P6_4$ - # 172 *or* $P6_222$ - # 180 & $P6_422$ - # 181; [**2**] they are enantiomorphic pairs.

2. **PART I** – **a)** yes – 3-fold rotation axes at the corners of the unit cell and along the long body diagonal at 1/3, 2/3 and 2/3, 1/3; **c)** no; **d)** three for the 3's, i. e., there are three distinct color combinations around the 3 folds; **e)** p3; **f)** 3's --> 6's; new 2's between the 6's; new 3's along the long body diagonal at 1/2, 1/2; 1/3, 2/3; and 2/3, 1/3; **g)** yes; yes; it becomes rhomb shaped with its long body diagonal along the cell edge of the "colored" unit cell; h) the p3 cell with color is 3 times larger than the (colorblind) p6 cell i) p6.
PART II – **a)** 3-fold screw axes; **b)** at 1/3 and 2/3 along each cell edge, i.e., at 1/3, 0; 2/3, 0; 0, 1/3; 0, 2/3 and at 1/3, 1/3; 2/3, 2/3 within the cell; **c)** R; **d)** R3, #146, *or* $R\bar{3}$, #148, if inversion centers are present *or* R 32, #155, if horizontal 2-folds are present; **e)** the R lattice and 3-fold screws limit the answer to the above; R3m, #160; R3c, #161; $R\bar{3}$ m, #166; and $R\bar{3}$ c, #167 are not possibilities because no mirrors or glides are evident; **f)** $R\bar{3}$ – dolomite, ilmenite; for dolomite: At 3s at cell corners (lattice nodes): red butterflies with blue spots represent oxygens along the top of Ca octahedra and yellow butterflies with blue spots represent oxygens along the bottoms of Ca octahedra. At 3s along the long body diagonal: 2/3, 1/3 – blue butterflies with red spots represent oxygens along the top of Ca octahedra, and 1/3, 2/3 – blue butterflies with yellow spots represent oxygens along the bottoms of Ca octahedra **g)** R3m – tourmaline; $R\bar{3}$ c – hematite, corundum, calcite; **h)** they are absent – the butterflies at the positions of these presumptive 2-folds are at levels separated by 1/3 and there is no 2-fold that has that property.

3. **a)** there are vertical glide planes; the position of the unit cell is defined by the glide planes; pg; **b)** the same as a) *except that* the unit cell is three times as high; **c)** colored; x3; if the color differences are ignored, then a unit cell 1/3 the size of the "color-inclusive" cell is defined; **d)** it is still pg; **e)** colored – supercell & superstructure; "color-blind" – subcell; **f)** the larger cell is the result of ordering of atoms (here represented by motifs) upon cooling. Such formation of superstructures at low temperatures is common among all minerals, and especially among ore minerals such as sulfides.

4. **a)** note the every third pair of leaves along horizontal rows is touching, and there are narrow gaps between the tips of intervening leaves; **b)** cell ii has triple the area (triple the length) of cell i; **c)** repeat units: ▲ ◆ ❑ ; ▲ ◆ ❑ ◆ ▲ ❑ ; ***disordered;*** ▲ ◆ ❑ ***or*** ◆ ▲ ❑ ; ▲ ◆ ❑ ◆ ▲ ❑ ▲ ◆ ❑ ; ▲ ◆ ❑ ▲ ◆ ❑ ◆ ▲ ❑ ; **d)** ▲ ▲ ❑ ◆ ◆ ❑ ◆ ◆ ❑ ▲ ▲ ❑ ◆ ◆ ❑ ◆ ◆ ❑ ▲ ▲ ; **e)** if ◆ ❑ ◆ are used to approximate a calcite layer while ▲ ❑ ◆ approximates a dolomite layer, then we have repeating layers of dolomite, calcite, calcite, ..., i.e., a Mg-rich calcite or a calcic "dolomite.

5. **a)** 

b) the pattern is not perfectly periodic because some brown snails have reversed orientations; however, the positions of the components of the drawing are perfectly periodic; **[1]** K^+ & Cs^+: probably not since size differences would produce structural distortions; Ti^{+4} & Fe^{+2} : no – charge differences; would probably structural distortions; Fe^{+2} & Fe^{+3}: no – size & charge differences; would produce structural distortions; Fe^{+2} & Mg^{+2}: OK; Ca^{+2} & Mg^{+2}: probably not – size differences; would produce structural distortions; Si^{+4} & Al^{+3}: perhaps; they do substitute for one another in tetrahedral sites; Cu^{+2} & Zn^{+2}: OK; **[2]** the lattice is perfectly periodic, and most parts of the motifs are periodic. It is only the brown snails that disrupt the perfect periodicity. Technically, there is local order and overall disorder with respect to the brown snails; **[3]** TEMy, but even then, only if the brown snails generate sufficient contrast, as might occur if they were heavy metals. Mineralogical examples include vacancies in pyrrhotite or clusters in digenite

6. **a)** the supercell is (i) 4x that of the subcell when the supercell origin is placed on the center of the black holes, and (ii) 4x when on the white holes; **b)** ~4; **c)** ~4; **d)** there is no symmetry, so there is freedom in where to choose the origin; the dimensions are those from one bird to another either horizontally or along the diagonals; **e)** 4 x 5.