

George M. Bodner
Thomas J. Greenbowe
and William R. Robinson
Purdue University
West Lafayette, IN 47907

The Introduction of Crystallographic Concepts Using Lap-Dissolve Slide Techniques

Our approach to subjects which deal with three-dimensional structure is often dictated by the visual aids available for use in the lecture. For many years, we at Purdue University have based our discussion of the structures of metals and ionic solids on a discussion of the location of atoms and the geometrical relationships within a unit cell, in large part because we had models of these unit cells which were more or less visible from the rear of the lecture hall (1). Our students may have developed some appreciation for the contents of the unit cell, the arrangement of ions in selected ionic solids, and the geometric relationships within the cell. They missed, however, the important relationships between structure and stoichiometry, the structural similarities between apparently unrelated compounds such as CsCl and CaF₂, and the regularity of extended structures in ionic solids in general. Indeed we often deliberately neglected the structure stoichiometry relationship because we felt that no effective visual technique was available for presenting this material in the lecture.

With the development of lap-dissolve slide techniques, we can now present visual effects which are clearly visible from the rear of a lecture hall, regardless of its size, and which can show structural features in extended arrays of atoms or ions involving up to several hundred atoms. Consequently, we have adopted a revised approach to the presentation of the structures of solids.

The Lap-Dissolve Technique

The lap-dissolve technique uses two (or more) matched slide projectors focused on a single screen so that their images overlap and a dissolve unit which fades out the image from one projector as it fades in the image from the other (2-3). By replacing the momentary blank between consecutive slides in a classical one-projector presentation with a controlled dissolve between visually related images, the lap-dissolve technique can provide a form of pseudo-animation which helps the viewer to maintain a correlation between the spatial relationships in one slide and the next. This technique can be particularly valuable when we try to lead the student through the three-dimensional relationships that can be found in extended arrays of atoms or ions.

There are several advantages of a lap-dissolve program compared with other visual media such as film or videotape. The instructor retains control over: (1) the selection of material to be included in the lecture, (2) the order of presentation of topics, (3) the rate with which information is introduced, and (4) the nature of the discussion which accompanies the visual display. Thus, the instructor can tailor the program to the students in a particular class. The materials discussed below are used at Purdue University in the extremes of the general chemistry and both undergraduate and graduate courses in inorganic chemistry.

The Description of the Structures of Metals and Ionic Solids

Before we can present the reasons for the formation of particular structures, and before we can begin to discuss the topics of non-stoichiometric substances, solid solutions, su-

perlattices, ionic mobility in crystalline solids, or the effects of lattice defects on the chemical and physical properties of solids, we need to tell our students how to represent the structures of simple solids.

The structures of most ionic solids can be described as efficiently packed, regular arrays of spherical anions with

An Introduction to the Structures of Crystalline Solids

- I. Extended arrays of spheres
 - A. The hexagonal closest packed array
 - B. The cubic closest packed array (face-centered cubic array)
 - C. The body centered cubic array
 - D. The simple cubic array
 - E. Structures of metals as arrays of spheres
- II. Structural features of ionic solids
 - A. Cations and anions differ in size
 - B. Cations occupy the space left over in an array of anions
 - C. Anions need not touch but may occupy positions of an extended array
 - D. Cations touch anions to maximize the efficiency of packing
 - E. Small cations tend to occupy tetrahedral holes, larger cations tend to occupy octahedral or cubic holes
- III. Octahedral holes in positions of closest packing
 - A. Location, geometry, and coordination number of octahedral holes
 - B. One octahedral hole per anion
 - C. Occupancy of holes reflects stoichiometry
 1. NaCl, NiO, MnS, KH: all octahedral holes occupied
 2. CdI₂: alternate planes of octahedral holes occupied
 3. TiO₂, MgF₂, NiF₂: one-half of octahedral holes in each plane occupied
- IV. Tetrahedral holes in positions of closest packing
 - A. Location, geometry, and coordination number of tetrahedral holes
 - B. Two tetrahedral holes per anion
 - C. Occupancy of holes reflects stoichiometry
 1. Li₂O, Na₂O, Li₂S, Na₂S: all tetrahedral holes occupied
 2. ZnS, ZnSe, BeO: one-half of tetrahedral holes occupied
- V. Cubic holes
 - A. There are no cubic holes in close packed arrays
 - B. Location, geometry and coordination number of cubic holes in anions in positions of a simple cubic array
 - C. One cubic hole per anion
 - D. Occupancy of holes reflects stoichiometry
 1. CsCl, CsBr, TiCl: all cubic holes occupied
 2. CaF₂, SrCl₂, SrH₂, UO₂: one-half of cubic holes occupied
- VI. Description of mixed structures
 - A. Tetrahedral and octahedral holes occupied simultaneously
 1. Spinels: one-eighth of tetrahedral and one-half of octahedral holes occupied
 2. Silicates, phosphates, etc.
 - a. Non-metal in tetrahedral hole, metal in octahedral hole, oxides in approximate close packed array
 - b. Non-metal covalently bonded to oxygen giving discrete polyatomic ions
 - B. Perovskites, ABX₃
 1. Large cations (B) and anions (X) occupy positions of cubic closest packing in the same array
 2. Small cations (A) occupy octahedral holes
- VII. Effect of radius ratio and covalency on hole selection
- VIII. Unit cells and crystal systems
 - A. Unit cell, the building block of an extended structure
 - B. Description of size and shape of unit cell
 - C. Contents of unit cells
 - D. Geometrical relationships within unit cells
- IX. Etc.

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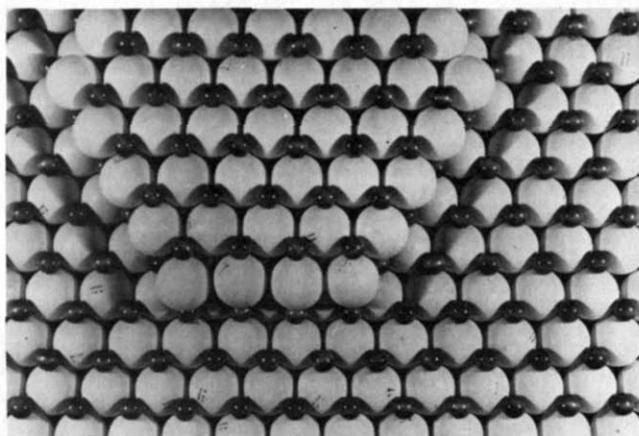


Figure 1. A portion of the idealized structure of NaCl showing the filling of all octahedral holes.

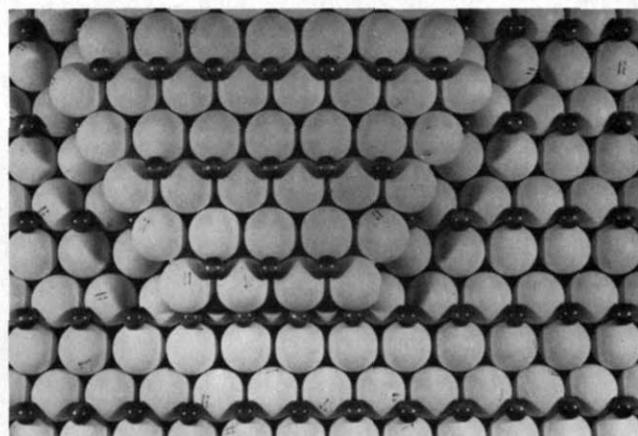


Figure 2. A portion of the idealized structure of TiO_2 showing the filling of one-half of the octahedral holes.

spherical cations occupying holes in these anion arrays. With this simple concept and some elementary ideas of what constitutes an efficiently packed array of spheres and the empty space available in such an array, a student can correlate and organize a great deal of information on the structures of metals and many ionic solids. A syllabus which describes this approach to the description of the structures of solids is presented in the table. Our purpose is not to discuss each of these points in detail; more information can be found elsewhere (4–11). However, several points should be noted.

The geometrical relationships between hexagonal closest packed and cubic closest packed arrays of spheres are among the most difficult that introductory chemistry students are asked to grasp. In general, they do not have sufficient experience with the use of two-dimensional representations of three-dimensional concepts, so the use of diagrams to present these concepts is complicated by the necessity for concomitant training of the student in their interpretation. Models are obviously a better visual aid for the introduction of these concepts. Unfortunately, models are not always visible to all students in the classroom, and they are difficult to handle, especially when they are large enough to be seen clearly and if they are extensive enough to represent a close packed array. We have found, though, that slides of models can be used in a very effective presentation. The pseudo-animation available from lap-dissolve techniques further enhances the presentation, allowing us, for example, to show the structural relationships between successive close packed planes in these arrays. Photographing the models on a light box, with the resulting illumination of the triangular voids between the spheres in a close packed plane, makes a particularly striking series of slides.

Having introduced the common types of arrays of spheres (hexagonally and cubic closest packed, body centered cubic, and simple cubic), we next turn to the packing of spheres of unequal sizes found in ionic crystals. At this point the concept of an ionic crystal as an extended array of efficiently packed anions with cations occupying the remaining space is introduced. Note that in crystals such as NaCl and ZnS the anion array should not be described as closest packed. The cations are too large to fit into holes in a closest packed array of anions. In these crystals, the anions can be regarded as occupying the positions of closest packing.

The lap-dissolve technique is particularly effective in presenting the location of octahedral and tetrahedral holes in arrays of anions in positions of closest packing, and of cubic

holes in arrays of anions in positions of simple cubic packing, as well as showing the geometry and coordination number of such holes. The technique allows us to dissolve, for example, from a model of an extended array of several hundred atoms to a single octahedron. This ability to single out a particular structural feature in a complex model is one of the more powerful aspects of the technique.

The student can now be introduced to the relationship between the stoichiometry of a salt and the fraction of octahedral, tetrahedral, or cubic holes which are occupied in the crystal structure, as well as the factors which affect the choice of the holes to be used. After the concept of the repetitive nature of solids has been established through extensive exposure to slides such as those shown in Figures 1 and 2, the student is prepared for the idea of a unit cell. The concept of the unit cell as the "building block" which can be used to describe such a repetitive array, and the relationship of a single unit cell to such an array, is readily perceptible.

At this stage, the student should be ready to move on to more advanced concepts, thus the "Etc." in item IX of the table. However, we have one final suggestion. Slides or photographs of models should be mixed with slides which present diagrammatic representations of these models, to train the students to use two-dimensional representations of three-dimensional structures. Unlike the more elementary concepts, slide sets of more advanced concepts may not be available.

Crystal Structure Slide Sets

The authors have developed the capability of producing registered copies of the lap-dissolve slides that we use to introduce crystallographic concepts in our lectures. Individuals who are interested in obtaining copies of these slides should contact the authors for further information.

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