

TRANSPARENT, PLASTIC-BALL, CRYSTAL STRUCTURE MODELS*

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ABSTRACT

A method is described for making crystal structure packing models from transparent, hollow, plastic balls. The special advantage of such models is their high degree of transparency which permits easy identification of the different constituent atoms on the basis of their color and size, and which facilitates the study of atomic arrangement in the interior of the model. The plastic model is easier to assemble than most types; it is light-weight, and it can be handled without undue fear of breakage. The principal structural features of the phlogopite mica model are illustrated in color plates.

INTRODUCTION

The development of the science of crystal structure analysis, based on x -ray diffraction measurements, has created a need for three-dimensional models to represent the geometric and bond relationships between the various atoms or ions constituting crystal structures. Experience has shown that these relationships cannot be represented adequately in all aspects by two-dimensional drawings. Indeed, models become increasingly valuable as the complexity of the structure increases, because the mind experiences great difficulty in visualizing the many-sided aspects of intricate geometric structures. The primary use for such models is for teaching the fundamentals of x -ray crystallography and crystal chemistry to students. However, their usefulness by no means ends here, for they are used to good advantage by crystallographers to solve structure problems that involve multiple choices. Additionally, scientists have found them indispensable for understanding the dependence of crystal chemistry and crystal physics on structure such as, for example, the extensive investigations on the nature of gliding mechanisms in crystals by Seifert (12).

TYPES OF MODELS

As might be expected, the need for crystal structure models has been met in a variety of ways, as attested by the many articles on the subject that have been published during the last 25 years. In most cases the sphere has been chosen to represent the atomic or ionic units comprising the structure because, to a reasonably good first approximation, atoms behave as if they were more or less rigid spheres in contact. The great

* Illustrated by phlogopite mica.

majority of the ball-unit models that have been described can be classified (6, 8) as ball-and-stick models (2, 3, 8, 9, 18, 19) or as geometric-packing models (4, 7, 10, 15, 16), although a third type, consisting of flattened spheres in contact, are preferred for models representing many types of organic compounds (6, 13, 14, 17).

Ball-and-stick models

Ball-and-stick models are constructed with small, widely-spaced balls which may represent the centers or nuclei of the atoms. The balls are usually held together by rods or wires representing the valence bonds, but sometimes they are strung on vertical wires stuck in a baseboard. Although models of this type are useful for showing atomic positions and elements of symmetry, they do not convey much of an idea of how the packing of the atoms controls the structure and many of the properties of the crystal. Nevertheless, ball-and-stick models are still popular, partly because they are relatively inexpensive and, in the case of a recently developed type (2), because they can very readily be constructed and taken apart. This agreeable state of affairs has been achieved by the use of rubber balls with molded holes in them, the balls being connected with plastic rods. An important feature of this type of model is its flexibility, making it especially useful for demonstrating distortion and strain effects.

Geometric-packing models

Geometric-packing models are constructed with spheres that are approximately proportional in size to the constituent atoms of the structures one wishes to represent. A second essential feature is that the spheres are packed together in contact with or in close proximity to each other, thus forming models that are similar in structure and proportional in size to the corresponding unit cells as determined from *x*-ray diffraction measurements. Consequently, such models, when carefully made, are very useful for semiquantitative measurements of dimensions, interplanar spacings, and angular relations of the structure as related to crystal form, growth peculiarities, cleavage, slip planes, twinning, polymorphism, and isomorphism. In addition, packing models are helpful in understanding the dependence of many physical properties on the structure such as density, hardness, refractive index, and thermal expansion, to mention a few of the more commonly measured ones.

A wide variety of materials are available for the construction of packing models, including metals, wood, cork, rubber, glass, celluloid "Ping-pong" balls, and various other kinds of plastics. Well-known models of this type have been made from wooden balls by Buerger (4) and his

students (7), the balls being joined together by metal pins. These models are very neat and strong, but they are time-consuming and expensive to build, especially those having complex structures. Although relatively inexpensive wooden balls suitable for the purpose may be purchased, their use involves considerable calculation and preparation, as indicated by the following steps in the procedure for constructing this type of model (4).

1. Calculation of the atomic environments in the actual crystals.
2. Adjustment of atomic environments to available material.
3. Calculation of drilling coordinates.
4. Painting the balls.
5. Drilling the balls.
6. Assembling the model.

It is evident that steps 1, 2 and 6 are involved in the construction of packing models from any type of material but that steps 3, 4, and 5 are primarily characteristic of wooden-ball models. In any case, it is the latter set of operations that contribute substantially to the time and expense of building wooden-ball models, although step 5 is facilitated by the use of a special ball-orienting device (5) attached to the drill press.

Possibly the major disadvantage in using opaque balls in a packing model is that the arrangement of the atoms usually is not clearly visible. For simple structures this obstruction of view may not be particularly important, but for complex structures involving many different kinds of atoms, several of which may occupy equivalent positions, it can be a serious disadvantage. In other words, the ability to see the arrangement of the atoms and to trace rows and planes of atoms through the structure in all possible directions are deemed to be highly desirable features of a packing model.

It was such considerations as these that led to the idea of a transparent, plastic-ball, packing model. However, the authors make no claim for the originality of this idea. Undoubtedly it had occurred to many scientists, as for example, Badgeley (1) who illustrated and described the use of several types of three-dimensional plastic models.

TRANSPARENT PLASTIC-BALL PACKING MODELS

Development of the idea

The need for an improved type of crystal structure model became apparent during the early stages of the research on the synthetic analogues of mica, amphibole asbestos, and other complex silicate minerals currently being conducted at the Electrotechnical Laboratory. As a consequence, a method for making transparent plastic balls was developed at this laboratory during the early part of 1950, and models of phlogopite

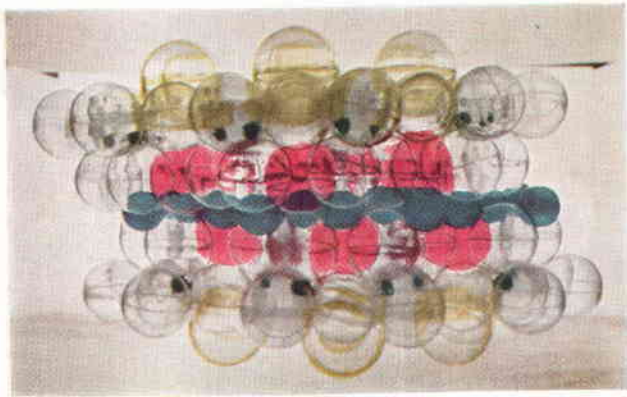


FIG. 1-A. A single layer of the phlogopite crystal structure viewed along the (130) direction, showing the layer structure and the "monoclinic shift" of $\text{AlSi}_3\text{O}_{10}\text{F}$ sheets. Yellow balls on top and bottom represent potassium in plane of cleavage; oxygen—colorless; fluorine or hydroxyl—pink; magnesium—blue; and silicon and aluminum—black.

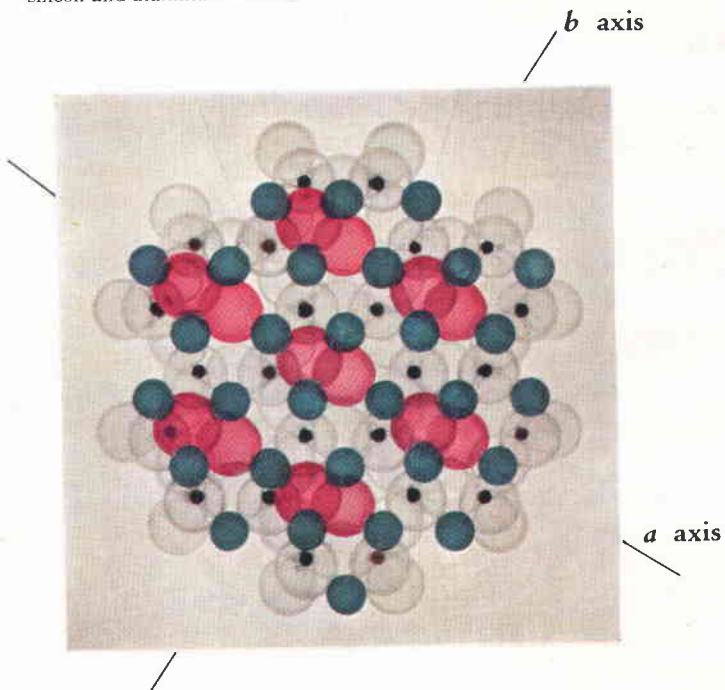


FIG. 1-B. A single sheet of the phlogopite structure viewed along the direction perpendicular to the layer structure, showing the hexagonal symmetry of the silicon-oxygen network, the trigonal symmetry resulting from the placement of magnesium between the sheets, and the monoclinic symmetry resulting from the shift of the fluorine (hydroxyl) ions.

mica and tremolite amphibole were assembled. Subsequently, the mica model was exhibited at the April 1950 meeting of the American Crystallographic Association at Pennsylvania State College, and the tremolite model was exhibited at the November 1950 meeting of the Mineralogical Society of America in Washington, D. C. The many expressions of interest in these models and requests for information on their construction, together with the fact that a review of the literature did not reveal any published description of models of this type, led to the preparation of this article.

General description

The most important features of the plastic crystal structure model can be illustrated to best advantage by natural color photographs such as those of the phlogopite mica structure reproduced in Fig. 1, *A* and *B*. It can be seen readily that the one feature that is new and unique to this type of model is its high degree of transparency. In this case, transparency was achieved by using colorless, transparent, plastic balls to represent the oxygen atoms that constitute about 72 per cent of the total volume occupied by the atoms in the mica structure. The other cations and anions represented in the model are distinguishable from the oxygen balls on the basis of color and usually by size. Thus, the fluorine or hydroxyl anions, whose ionic radii are nearly identical to that of oxygen, are represented by the pink balls; the potassium ions in (K-O_{12}) coordination are represented by the large yellow balls at the top and bottom of the model as viewed in Fig. 1-*A*; the magnesium ions in ($\text{Mg-O}_4\text{F}_2$) coordination are represented by the medium-sized blue balls; and the silicon plus aluminum ions in (Si, Al-O_4) coordination are represented by the small black balls. The sizes of the various balls are approximately proportional to the ionic radii of the atoms they represent. However, it should be noted that the mica model is not scaled to unit cell dimensions; several unit cells of the single-layer structure are represented.

The plastic model possesses other features and advantages that are not so readily evident from an inspection of the color reproduction. For example, the model is light in weight in spite of its relatively large size because the balls used in its construction are hollow and thin-walled. The mica model is 16" in diameter by $9\frac{3}{4}$ " high, and it weighs 4 pounds. Because it is light in weight and relatively strong, the plastic model is readily transportable if normal precautions are practiced.

Considered as a structural problem, the strength of a packing model depends chiefly on the bonds or fastenings that hold the balls together. The plastic model differs from most types in that the balls are cemented together at their points of contact instead of threaded with wire or fast-

ened with pegs. Although a single, cemented bond is relatively weak, the model is sufficiently strong and rigid for practical purposes owing to the fact that each ball usually is bonded to six to eight neighbors. Those occupying corner or edge positions have fewer bonds, therefore, they are more likely to break loose. However, ordinary care in handling the model virtually eliminates this source of trouble. And even though breaks may occur occasionally, it is one of the advantages of the cemented bond that repairs are quickly and easily made.

Assembling the model

It has been indicated that the use of colored plastic balls and the cemented bond between balls eliminates steps 3, 4, and 5 followed by Buerger and Butler (4) in the construction of their wooden-ball models. As the other steps involved in the construction of packing models are adequately described in their paper, to which the reader is referred, present remarks are confined to those aspects of assembling the model that are peculiar to the plastic-ball type.

Assuming that the atomic environments in the actual crystal already have been calculated, and that a sufficient number of plastic balls of the proper sizes are available, the next step is that of assemblage. On the basis of the authors' limited experience, there appear to be two general approaches to the problem. Models of layered structures usually are prepared most easily by assembling layer by layer. With other structural types, it is usually convenient to first assemble small units, such as clusters, rows, or chains of atoms, and then to attach these together, thereby completing the model. Regardless of the procedure followed, it should be noted that serious distortion of the model can result from the use of imperfectly shaped balls unless proper compensation is made. In any case, minor imperfections in a model are difficult to avoid, but in general they do not detract significantly from its value. For example, small deviations from perfect alignment of the blue "magnesium" balls may be seen in Fig. 1-B of the mica model.

The cemented bonds are made by applying one or two drops of a suitable solvent to each of the points of contact between the plastic balls. Within a few seconds the solvent softens the plastic, and a circular area of contact $\frac{1}{8}$ to $\frac{1}{4}$ inch in diameter is formed. Within a minute or two the bond is strong enough to support the weight of several balls. However, several hours are required for the complete evaporation of the solvent and attainment of full bond strength. A suitable solvent for the acrylic resin type of plastic used in these models (Lucite or Plexiglas) is ethylene dichloride.

More specific directions for assembling plastic ball models, which

would be applicable to all types, cannot be formulated. Each structural type presents its own peculiar problems which are best mastered by the experience gained during the actual construction of a model.

THE MANUFACTURE OF PLASTIC BALLS

Before undertaking the development of plastic crystal structure models, an attempt was made to obtain suitable plastic balls from a dozen or more companies that manufacture or fabricate plastics. Failing to locate a source of supply of plastic balls of the desired sizes and colors, there seemed to be no alternative but to make them ourselves. As other investigators who wish to construct this type of model may encounter the same difficulty, a brief description of the method used at this laboratory may prove useful.

The essential steps in the process were as follows: The plastic material (Lucite or Plexiglas) was obtained in the form of transparent and translucent sheets of various colors. The colors were selected on the following basis: A colorless, transparent plastic was used for the principal anion, for example, oxygen in oxides and silicates; light-colored, transparent plastics were used for large cations, such as potassium; darker-colored, transparent plastics for the cations of intermediate size, such as magnesium; and dark- or light-colored, translucent plastics for the small cations, such as silicon and aluminum. After choosing an appropriate set of colors for the particular model to be built, circles for forming hemispheres were cut from the plastic sheets (Fig. 2-A), each circle having a diameter $\frac{1}{4}$ inch larger than the intended sphere diameter. Balls that were larger than 1 inch in diameter were made from $\frac{1}{8}$ inch sheet, whereas smaller balls were made from $1/16$ inch sheet.

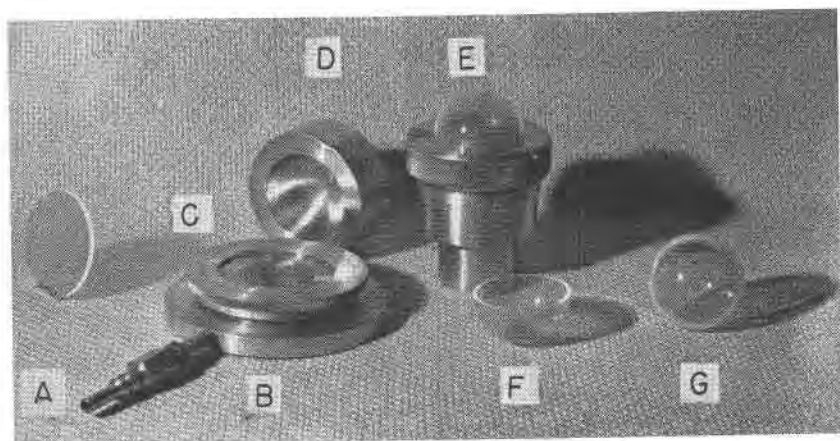


FIG. 2. Apparatus for the manufacture of transparent, hollow, plastic balls.

A plastic disk was clamped tightly in an assembly machined from aluminum, consisting of a base plate (Fig. 2-B) threaded to receive a clamping ring (Fig. 2-C). Each size ball required a different clamping ring bored to the correct diameter (2 inches for the oxygen ball illustrated in Fig. 2). The base plate contained an air inlet to a pressure chamber which was sealed on one side by the plastic disk. This entire assembly was placed in an oven and heated at about 300° F. for 5 to 6 minutes to soften the plastic. Then (1) the assembly was removed quickly from the oven (wearing asbestos gloves), (2) a cold, hemispherical, aluminum mold (Fig. 2-D) whose diameter was the same as that of the hole in the ring plate was fitted into a recess machined in the ring plate, (3) an air line was attached to the inlet by means of a quick-acting air coupler, and (4) a plastic hemisphere was blown into the cold mold, which was manually held in place. The mold contained several very small holes to prevent the trapping of air between the plastic and the mold. After several seconds, the air pressure was reduced and the entire assembly was quenched in water to cool and harden the plastic. The resulting dome of plastic material had a rim, similar to that on a derby hat, which had to be cut off to form a true hemisphere. This operation was done on a lathe using the usual cut-off tool and a special holder (Fig. 2-E), which was chucked in the lathe. The plastic dome was clamped around its rim to the end of the holder by means of a threaded ring, which was bored to the correct diameter.

After cutting off the rim on the plastic dome, the trimmed edge of each hemisphere (Fig. 2-F) was ground flat by rubbing it on a sheet of fine emery paper. Before cementing pairs of hemispheres together, each one was cleaned with a rag to remove dust and grease. The final step in making a ball was to press together two hemispheres and apply several drops of ethylene dichloride along the edge of the crack. The solvent was drawn rapidly around the crack by capillary attraction, welding the halves within a few seconds. The finished ball (Fig. 2-G) should not deviate significantly from a true sphere, otherwise it will introduce distortions in the model.

Although it appeared that the above-described method of making plastic balls was one of the simplest that could be devised, the number of balls made per man-hour was quite limited, averaging about ten. As a result, the cost of manufacturing them was undesirably high. This serious disadvantage can be overcome only by the adoption of a mass-production method. A step in this direction would be the use of gang molds, in which several hemispheres were blown at one time. Even more desirable would be the development of a technique whereby a complete ball could be formed in one operation. As such techniques as these

require more elaborate and costly equipment, especially molds of different sizes, they would be practical only if one desires to manufacture a large number of balls at an efficient rate. It is to be hoped that some company will undertake this development to supply scientists with transparent plastic balls in sizes and colors suitable for use in crystal structure models.

UTILITY OF THE MODEL

As stated earlier, the ability to see the arrangement of the atoms and to trace rows and planes of atoms through the structure in all possible directions is deemed to be a highly desirable feature of a packing model. To illustrate the utility of transparent models, several structural relationships that can be observed on a packing model of phlogopite, such as the one shown in Fig. 1, are described briefly.

One sees that a single layer of the phlogopite structure is composed of two $(\text{AlSi}_4\text{O}_{10})_n$ sheets which, together with hydroxyl or fluorine anions, are bound together by magnesium cations. Especially worth noting is the virtual hexagonal arrangement of the oxygen anions in the individual sheets, yet the single-layered mica structure as a whole is monoclinic. The lower symmetry is the result of a displacement of one sheet over the other by an amount approximately equal to one-sixth of the a unit cell dimension (indicated by the displacement of the pink fluorine anions in Fig. 1). The model shows that such a displacement is necessary to stabilize the structure. The shift minimizes the repulsion between the apex oxygen anions in opposing sheets and makes it possible for each magnesium to be octahedrally coordinated as $\text{Mg-O}_4\text{F}_2$.

Hendricks (11) has shown that polymorphism occurs rather commonly among micas of the phlogopite-biotite subfamily. He described hexagonal, monoclinic, and triclinic multi-layer forms and showed how they might be derived from the single-layer form by the application of various combinations of symmetry operations. Not only is the transparent model useful for illustrating these symmetry operations, but also it shows clearly the structural basis for the origin of multi-layer mica polymorphs. During the growth of phlogopite crystal, the magnesium ions continually have a choice of occupying one or the other of two sets of positions between the sheets, each position being related to the other by a rotation of 180° about an axis perpendicular to the sheet. For each set of positions, the displacement of one sheet over the other may take place in any one of three equivalent directions 120° apart, or a total of six equivalent directions 60° apart. Thus, a large number of multi-layered mica polymorphs are possible owing to the simple fact that certain ions in the mica structure have a choice of several equivalent posi-

tions in that structure during crystal growth. It is to be expected, however, that the frequency of occurrence of phlogopite polymorphs composed of many layers should be small compared with the frequency of single-, double-, and three-layer forms.

The geologist long has made use of percussion and pressure figures (glide planes or secondary cleavages) to determine the crystallographic directions of sheet mica and for the purpose of relating common structural imperfections to these directions. Due to the ease with which one can visually trace rows and planes of atoms through the transparent model, it is readily apparent that the orientation of percussion figures parallel to (010), (110), and ($1\bar{1}0$) is controlled by the rows of densely packed oxygen atoms in the basal hexagonal network. On the other hand, the orientation of pressure figures parallel to (13 l) and 10 l (planes that are inclined about 67° to the prominent basal cleavage of mica) is controlled by the densely packed planes of inner or "apex" oxygen and magnesium atoms.

Although many other geometric and structural relationships can be observed on the mica model, those described above will serve to illustrate the special advantages inherent in the use of transparent, packing models for the study of crystal structures. A detailed description of the structural features and the defects found in mica will be given in a later paper. In the meantime, it is hoped that this description will serve to stimulate the interest of teachers, students, and scientists in the construction and use of transparent, plastic models. If a demand for such models can be created, the problem of finding a manufacturer for plastic balls in the necessary sizes and colors will be greatly simplified.

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