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**SOLID-STATE
GENERAL-CHEMISTRY
MOLECULAR VISIONS™
MODELS**

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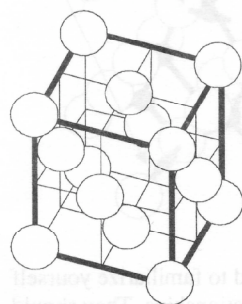
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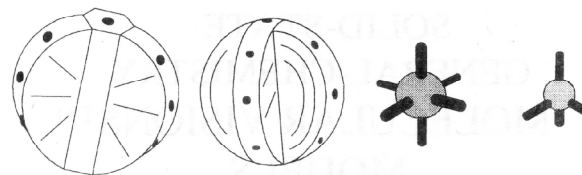
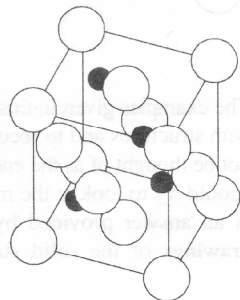
SOLID-STATE GENERAL-CHEMISTRY MOLECULAR VISIONS™ MODELS

Visualization of things we can not see but know to exist is a very important part of learning. Solid hand held models provide tactile and visual aids to assist the mind in exploring the nature of matter. Models which are built from a minimum of pieces by association in the manner of bonding will provide the greatest help. Textbooks try to represent structures of three dimensional objects with two dimensional pictures having some perspective. Unless the viewers eye can capture this perspective the picture remains on the page as a flat picture. Adding to the confusion are the lines used to connect the balls representing atoms and supposedly providing perspective. These are often mistaken by the beginner as bonds. An examination of the face-centered-cubic lattice of anions, clear circles, shown here



should bring to the viewer the realization that anions would not attract each other or bond. Yet many modeling systems represent such lines by rods used to support the structure, thereby giving a false impression of bonds.

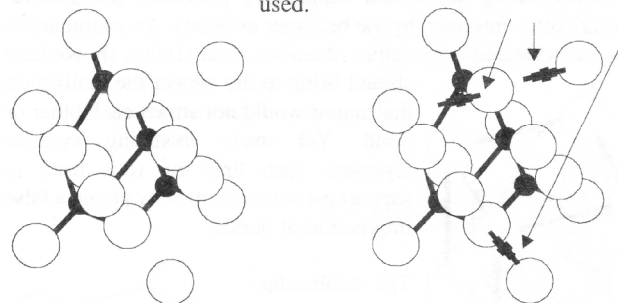
The Molecular Visions™ solid-state models consist of anions with



ANIONS

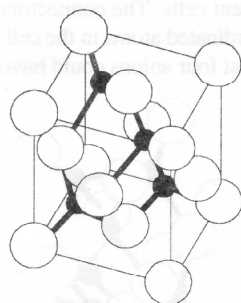
CATIONS

Crystal lattices and other covalent structures are produced when the rods and tubes of their respective atoms are joined. This produces a self supporting system from which to create solid-state models without the fiction of supports. There is one exception and that is the artificial volume called a unit cell. The cell shown below consisting of anions, clear circles, and cations, black circles with bonds, contains four corner anions which are not shown coordinated to any cation. They are of course associated with cations in an adjacent cell but to support them in the cell shown, four connectors below are used.

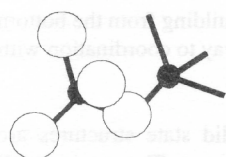
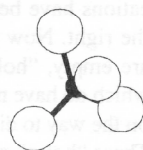


The examples given in this text are to be used to familiarize yourself with structures and to recognize familiar relationships. They should not be thought of as the end, such as building a ship in a bottle. You should try to look at the model and ask questions. Then see if there is an answer provided by the model. With these models various drawings of the solid state may be interpreted to yield a three

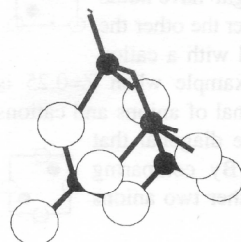
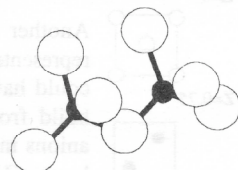
dimensional model.



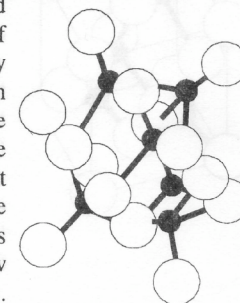
The cells given above provide examples of how to convert to a model. We see in this cell that the cations are tetrahedral and there are four anions surrounding each cation, as shown by the black lines representing bonds. Start at the bottom, in this case the lower left. We need a tetrahedral cation and a general anion (because the cell is cubic and the general anion is used for the construction of cubic and hexagonal cells with tetrahedral cations).



Construct a tetrahedron of anions around a cation. Align the anions so they are parallel. Next notice that there is another cation that makes a diagonal across the bottom face of the cell and shares an anion with the tetrahedron just made. Add that tetrahedral cation and continue building. You may eventually notice that this diagonal arrangement of anions and cations is very common in face-centered-cubic-cells containing tetrahedral cations. Continuing with the model, notice that the cations above the first two are also arranged in a diagonal that is perpendicular to the first group. Note that they also share anions from the structure just built. Add these two new cations. The addition of three more anions to these newly added cations forms another diagonal of anions and cations. Keep the



anions parallel as you build. All that remains to finish the cell is to attach four more anions. Because there are no more cations in this cell to bond with, they must be from adjacent cells. The connectors are used in these situations to anchor uncoordinated atoms in the cell. At this point you might recognize that the last four anions could have been anchored to this cell if there had been four more cations. Ask yourself if there is a place for these cations. You may see that there are unfilled "holes" between four anions which would accommodate tetrahedral cations. Several of these cations have been added to the model at the right. Now you might ask why these are empty, "holes", or are there crystals which do have more cations. You are now on the way to discovery using the models. These "holes" may make interpretation of some drawings confusing, but if you start building from the bottom layer the cation rods will usually point the way to coordination with an anion.



Z=0



Z=0.75



Z=0.5



Z=0.25



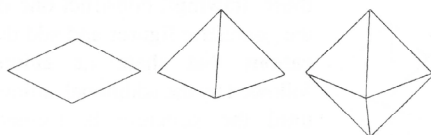
Z=0



Another way in which solid state structures are represented is by the use of layers. The previous cell could have been shown as a series of layers. To build from this diagram you would lay out the anions in Z=0 and attach the tetrahedral cations of layer Z=0.25. You should note that two of the anions are not coordinated, leave them until the end of the model building to decide what to do. You might have noted that if you lay one layer over the other the anions that are associated with a cation are made clearer. For example when Z=0.25 is placed over Z=0 a diagonal of anions and cations appears. This is the same diagonal that was constructed above. By comparing Z=0.25 with Z=0.5 the other two anions

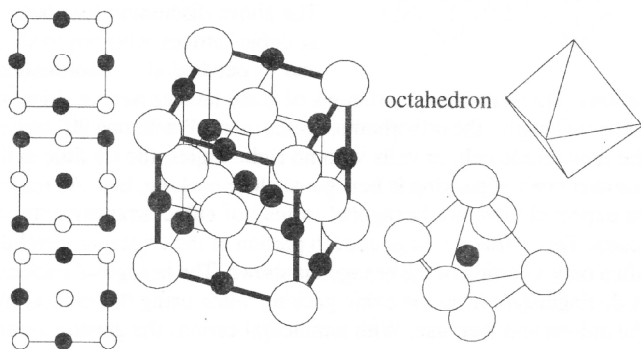


around each tetrahedral cation become visible. A comparison of $Z=0.5$ and $Z=0.75$ will bring out the placement of the other cations and anions.



One other representation of the solid state is the use of geometric figures as a shorthand for a

coordinated cation. Examples are squares, pyramids, and octahedra for square planar, tetrahedral, and octahedral coordination of the cations.



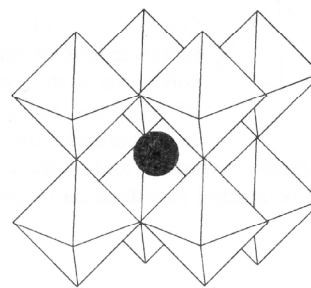
NaCl cell layers

NaCl cell

NaCl core

Sodium chloride is a face-centered-cubic cell made up of octahedral coordinated chloride and sodium ions. The central sodium ion is shown at the right surrounded by six chloride ions, and finally by an octahedron. The cell contains one complete octahedron and many truncated figures. Sometimes textbooks show the complete geometric figure to construct not just a cell but a portion of the crystal. Several examples of building these models are given in the latter part of this book. A classic structure that is usually portrayed with these octahedra is perovskite, a titanium oxide lattice, which contains a calcium cation in the central cavity. The actual unit cell contains only

the oxygen atoms of the shared vertices of the octahedra. It is of current interest because many of the recent superconducting solids are believed to mimic this structure. When building models from



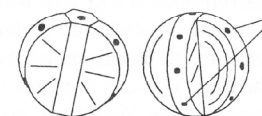
these drawings, construct one of the geometric figures and add the cations that share its anions followed by the additional anions until the structure is formed. Model building requires some experimentation to see how the atoms fit.

The above discussion has looked at cubic lattices with tetrahedral and octahedral coordinated

cations. There are many variations of these lattices having sides of different lengths, the orthorhombic cells, or a cell with one 90° angle, the monoclinic cell, or cells with no right angles, the triclinic cell. Another class of packing is hexagonal close packing, hcp. As might be expected there are hexagonal instead of cubic arrangements of atoms. This is true if a large enough portion of the crystal is seen but often only a portion of the hexagon is shown. The hexagonal packing is distinguished from the cubic packing when using the models by the anions and their use. With tetrahedral cations the general anion is used but the cations are arranged at 109° .

109°

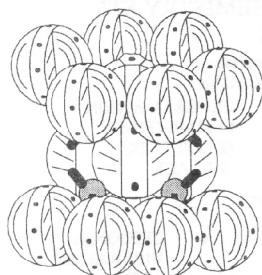
The octahedral cation requires a new anion, the hexagonal anion, to accommodate the new angles.



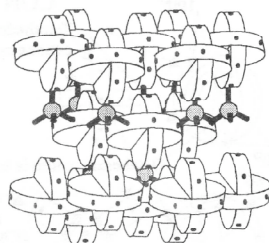
Hexagonal anion

General anion

The classic hcp cells are that of NiAs which looks like a hexagon of anions coordinated to octahedral cations and Wurtzite, ZnS, which has tetrahedral cations.



NiAs

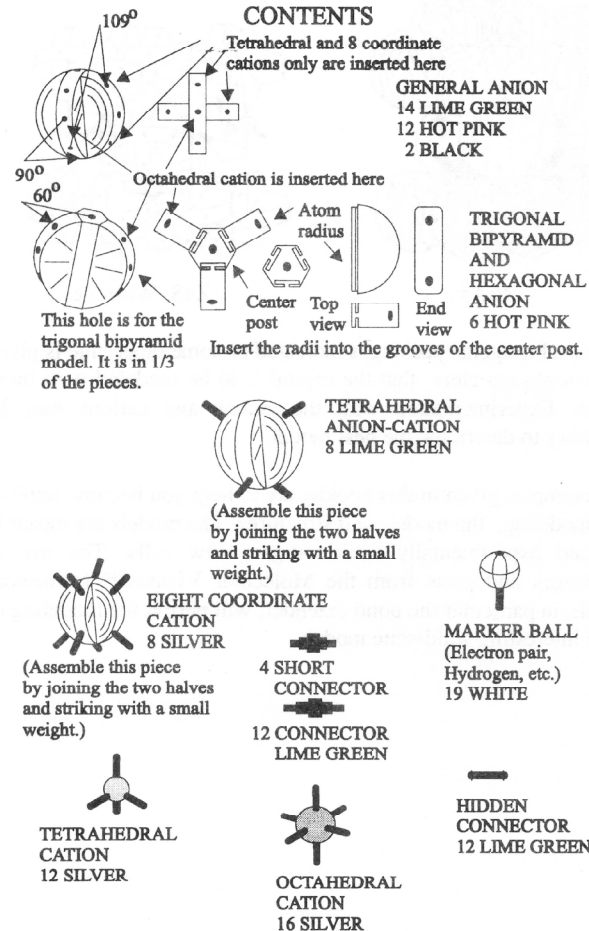


ZnS, Wurtzite

Unless a hexagonal packing is indicated or some other clue is given it is not always clear that the crystal is to be modeled with these anions. Experimentation with the anions and cations may be necessary to determine the best model.

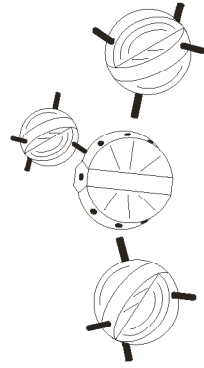
The examples given in this booklet are to help you become familiar with modeling, the models and structures. The models are meant to be used experimentally to investigate new cells. The use of connectors and parts from the Molecular Visions™ framework models, in particular the bond extender, will permit the modeling of many interesting solid-state models.

SOLID STATE-GENERAL CHEMISTRY KIT CONTENTS

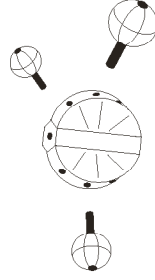


VSEPR MODELS

AX₃

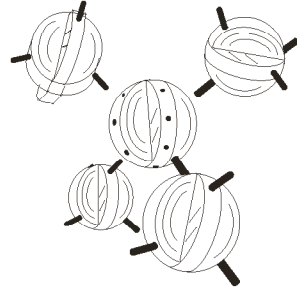


Trigonal, boron trichloride

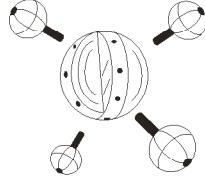


Trigonal, borane

AX₄

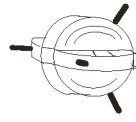


Tetrahedral, carbon tetrachloride

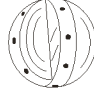


Tetrahedral, methane

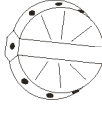
Pieces required



Tetrahedral
anion-cation



General
anion

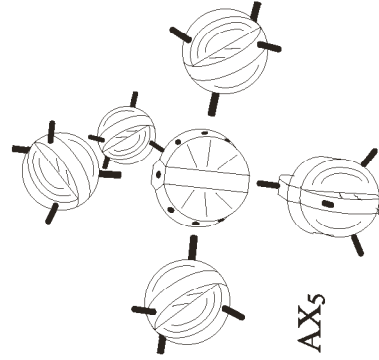


Hexagonal
anion



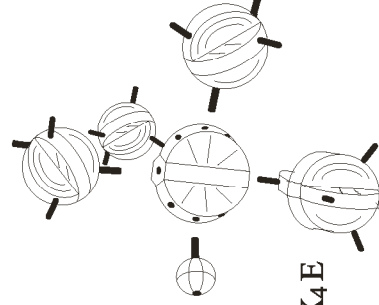
Marker ball
(Hydrogen)

VSEPR MODELS

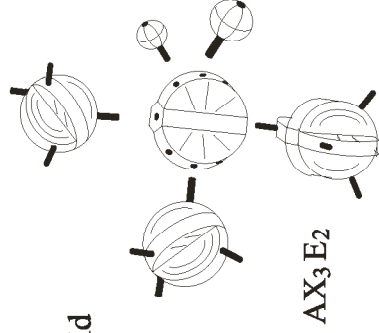


AX₅

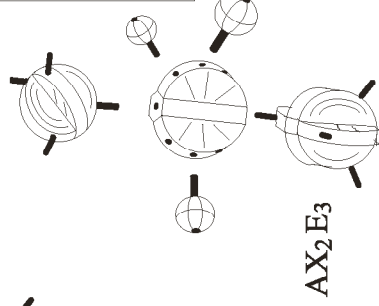
Trigonal bipyramid



AX₄E



AX₃E₂



AX₂E₃

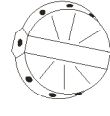
Pieces required



Marker ball
(electrons)



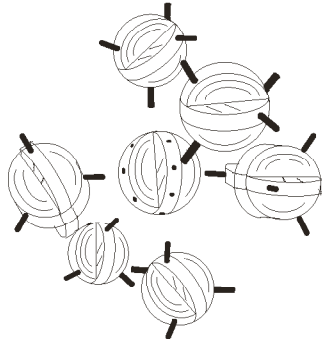
Tetrahedral
anion-cation



Hexagonal
anion

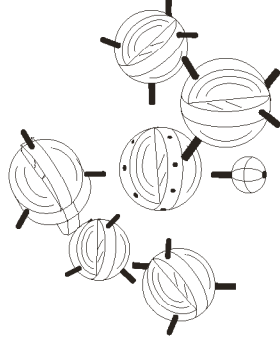
VSEPR MODELS

AX_6



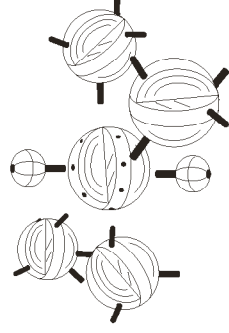
Octahedral

AX_5E



Square pyramid

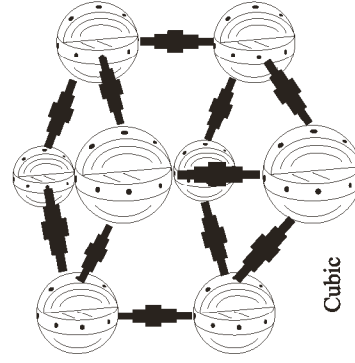
AX_4E_2



Square planar

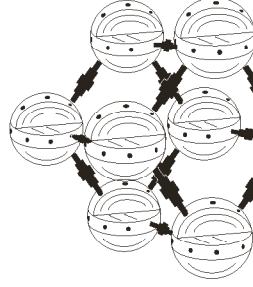
Pieces required			
	General anion	1	
	Tetrahedral anion-cation	6	
	Marker ball (electrons)	2	

BRAVAIS LATTICES



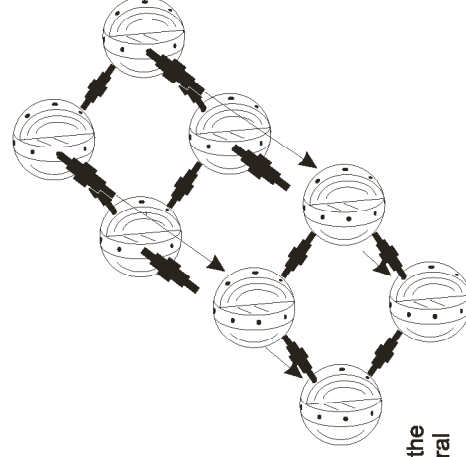
Cubic

Place the connectors only in the octahedral holes of the general anion.



Triclinic

Place the connectors only in the tetrahedral holes of the general anion.

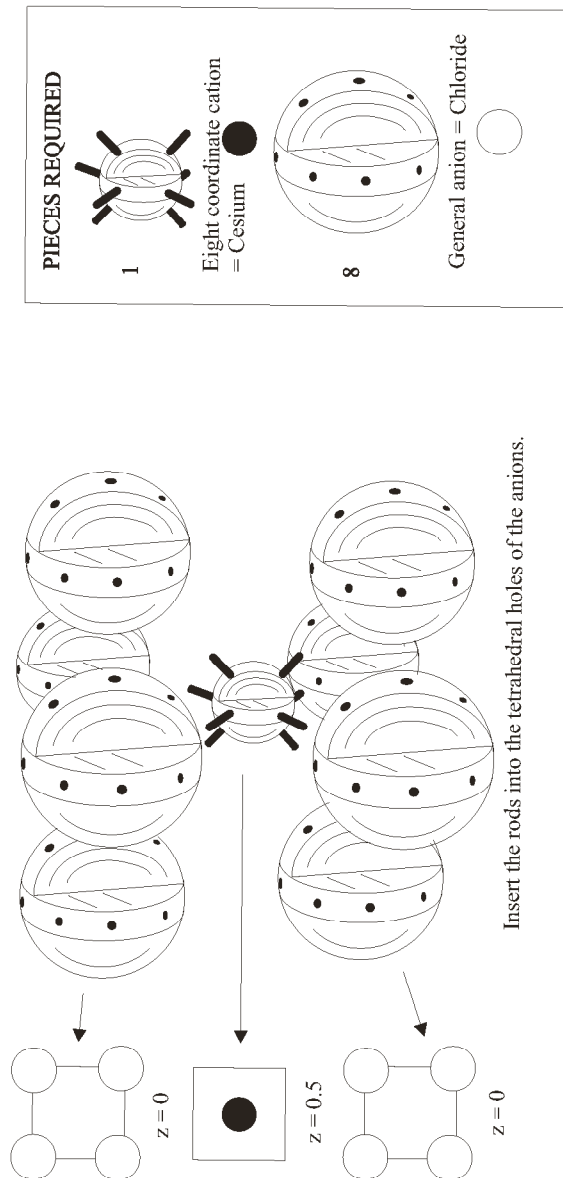


Monoclinic

Place the connectors in the tetrahedral holes between four of the general anions. Make two pieces and join them with connectors in the octahedral holes.

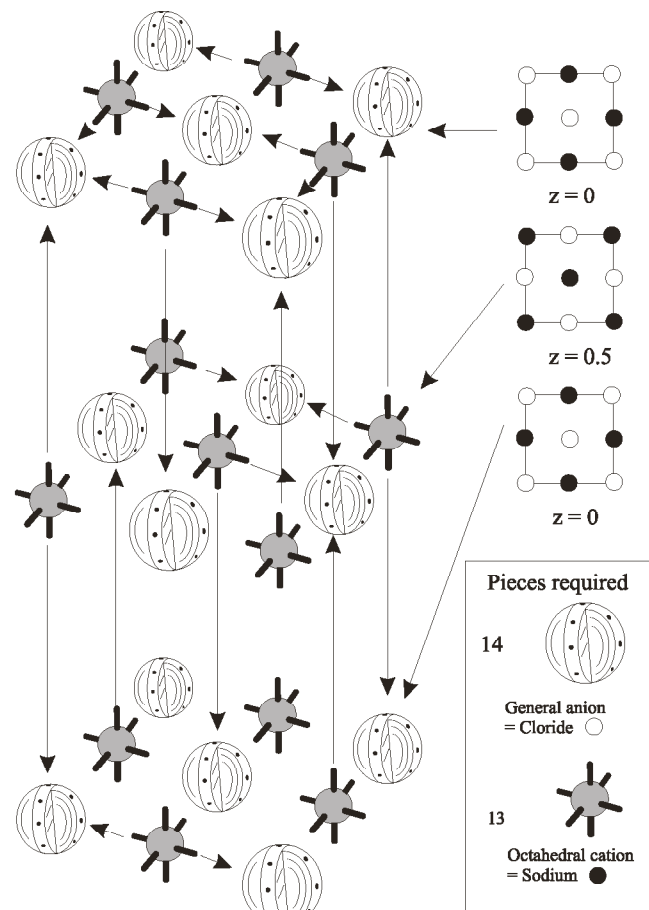
PIECES REQUIRED	
	General anion
	Connector

**CESIUM CHLORIDE (CsCl).
BODY CENTERED CUBIC PACKING WITH 8 COORDINATE CATION.**

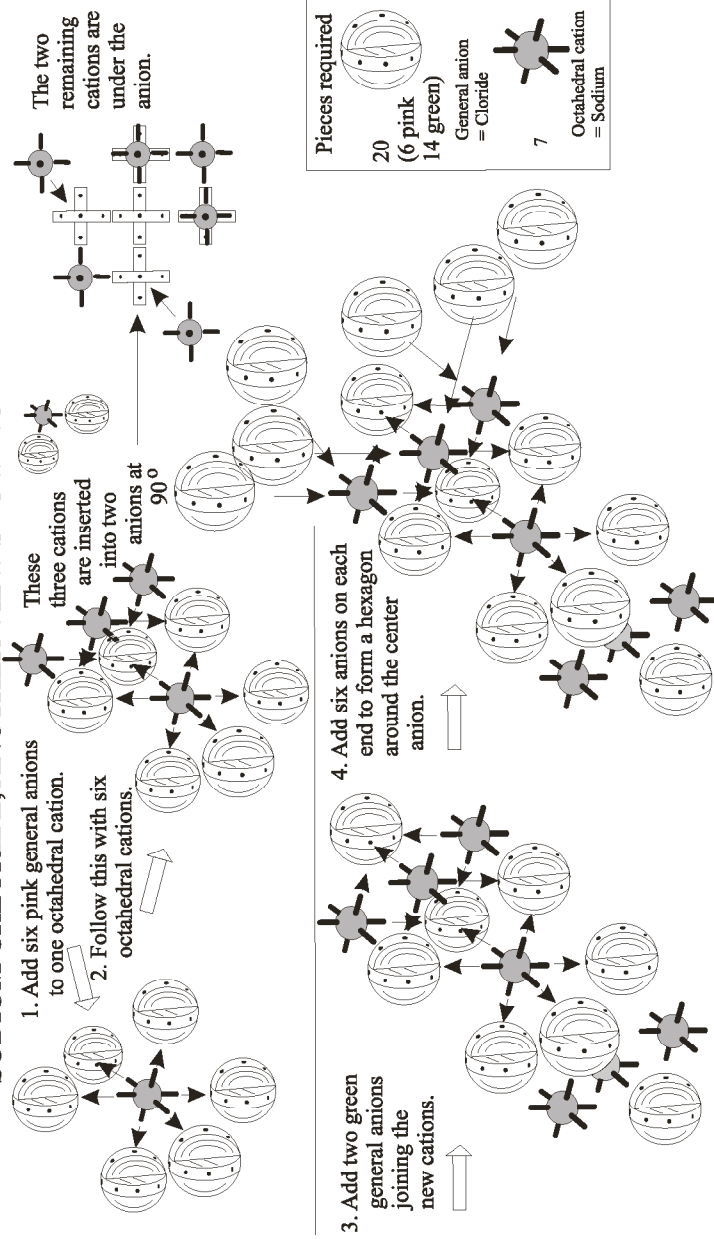


**SODIUM CHLORIDE (NaCl). CUBIC CLOSE
PACKING WITH OCTAHEDRAL CATIONS.**

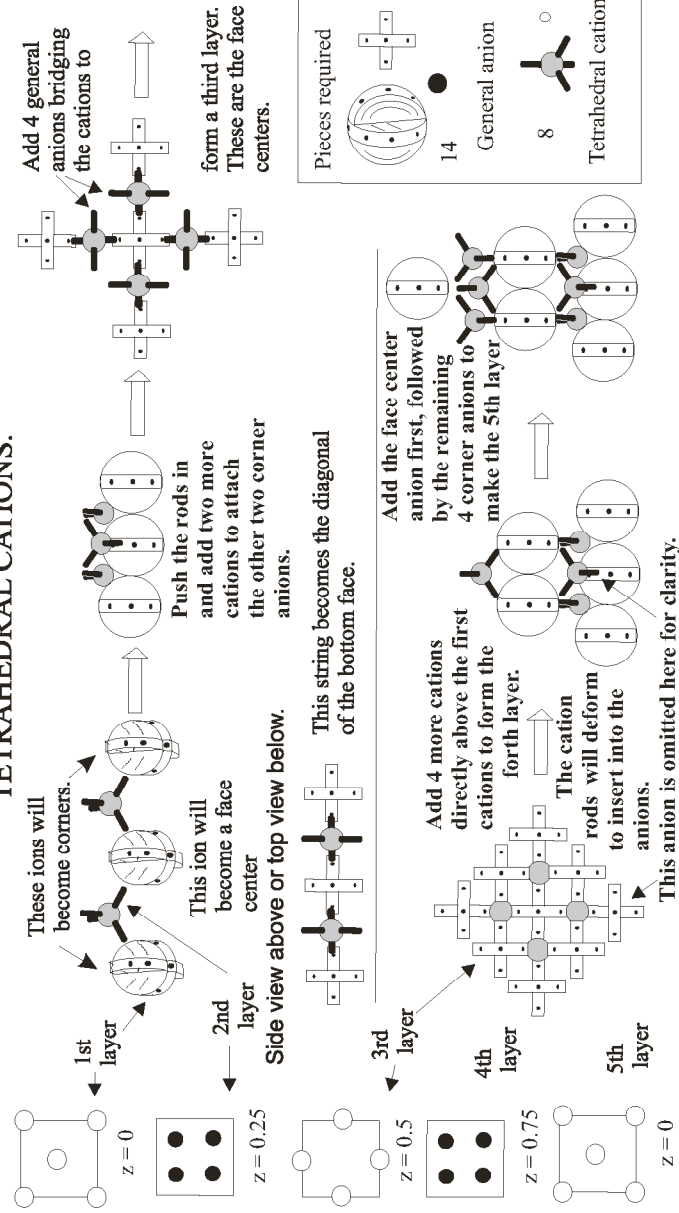
BEGIN CONSTRUCTION BY FORMING THE LAYERS.
JOIN THE LAYERS TO COMPLETE THE CELL.



SODIUM CHLORIDE, ANOTHER VIEW SHOWING A REPEAT LAYER

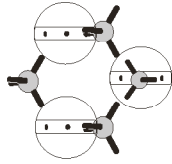


ANTIFLUORITE, A CUBIC CLOSE PACKING CRYSTAL LATTICE WITH 8 TETRAHEDRAL CATIONS.

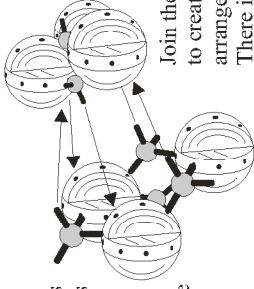


CUBIC CLOSE PACKING (ANTIFLUORITE) ALTERNATIVE CONSTRUCTION STRATEGIES.

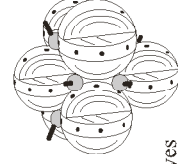
THE CCP CORE (The six face centered ions)



Join three hot pink general anions with four tetrahedral cations. Use only the tetrahedral holes. Make 2 of these.



Push the rods into the holes and rotate one group 180 deg. relative to the other.

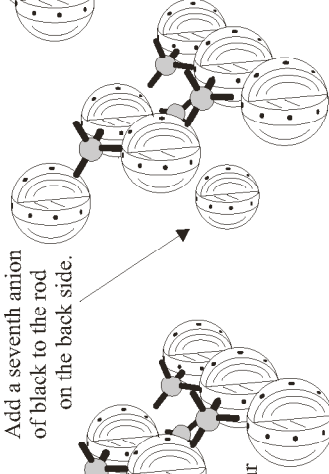


Join the two halves to create an octahedral arrangement of the anions. There is an empty octahedral hole in the center.

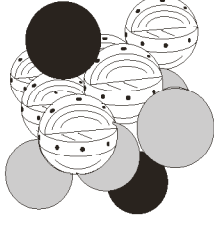
These six anions are the face center ions of a ccp lattice. Add eight more green general anions to the remaining rods to give the complete cell. Look for this arrangement in other cells as a clue to their arrangement.

THE TRICOLORED CCP LAYERS

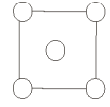
Prepare two groups of 3 anions as above, one green and one hot pink. Add 3 more anions of the same color as shown here to form a triangular plane.



Join the two halves.



ZINC BLEND, ZnS , A CUBIC CLOSE PACKING CRYSTAL LATTICE WITH 4 TETRAHEDRAL CATIONS.

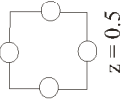


These ions will become corners.

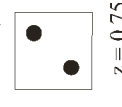


This ion will become a face center

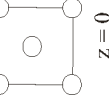
Side view above or top view below.



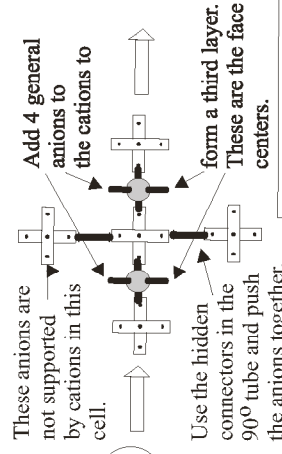
This string becomes the diagonal of the bottom face.



Add 2 more cations diagonal to the first cations to form the forth layer.



The cation rods will deform to insert into the anions.



These anions are not supported by cations in this cell. Use the hidden connectors in the 90° tube and push the anions together.

Pieces required

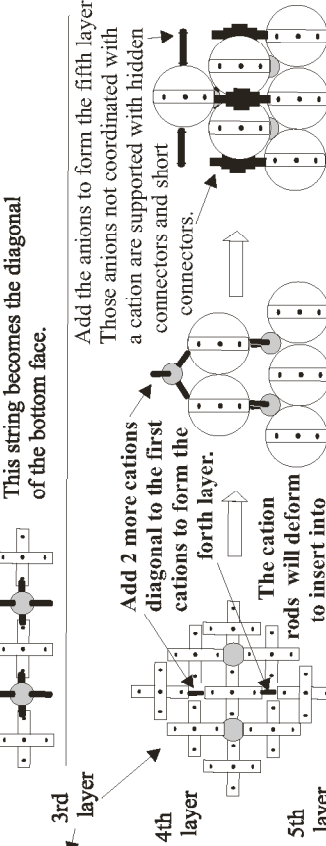
14 = 14

General anion, Sulfur 4

Tetrahedral cation, Zinc 4

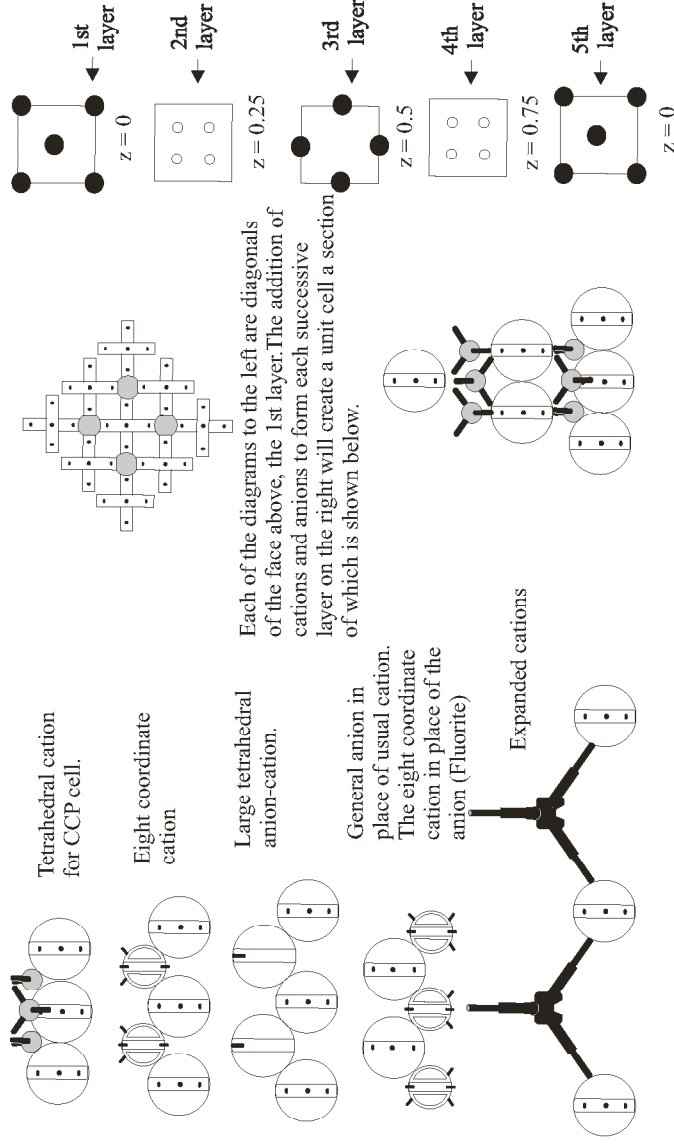
Hidden connector 4

Short connector 4



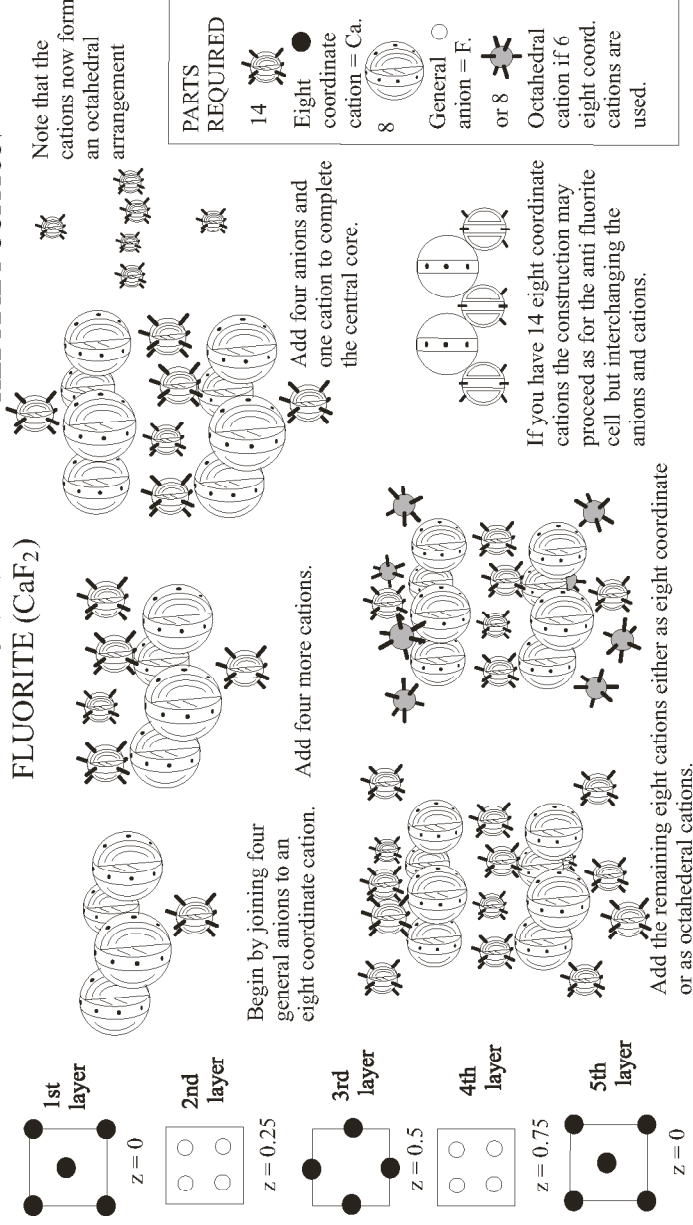
Add the anions to form the fifth layer. Those anions not coordinated with a cation are supported with hidden connectors and short connectors.

THE USE OF DIFFERENT CATIONS TO CREATE FACE CENTERED CUBIC CELLS



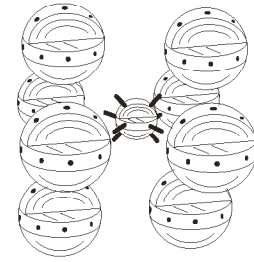
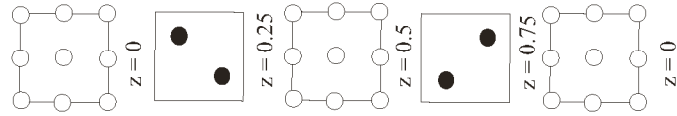
21

CCP OF THE CATION WITH THE ANION IN THE TETRAHEDRAL POSITION

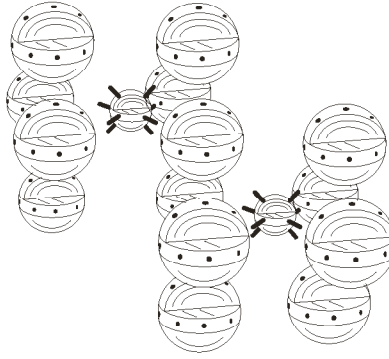


22

AN ALTERNATIVE FLUORITE CELL, MADE OF CUBIC AND BODY CENTERED CELLS



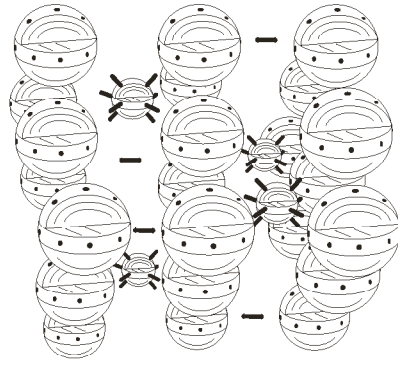
Begin with a body centered cube. You will need to use all of the anions in your kit. One color scheme to do this is suggested here. Use lime green for the first two cubes.



Add the second cube sharing an edge.

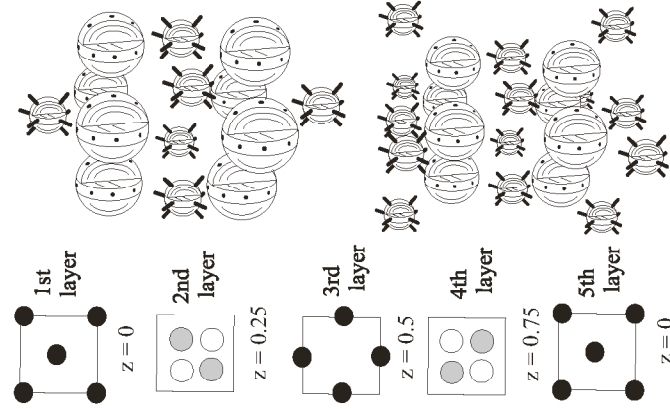
PIECES REQUIRED	14 lime green	12 hot pink	1 black
General anion = F.	○	●	●
Eight coordinate cation = Ca.	●	●	●
Hidden connector	→	→	→

Add hot pink anions and one black anion to the cations and attach the corners with hidden connectors to complete the cell. Compare this cell with the fluorite face centered cell. By filling out this latter cell with anions on three faces to create planes of nine anions you should be able to see that these two cells are part of the same matrix. This illustrates that there may be more than one way to look at crystal lattices.



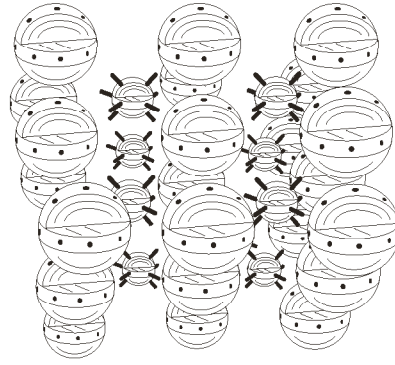
Add the remaining cations attached to three of the anions. These new cubes will share faces. Note the corner anion of the cubic cell is attached with a hidden connector.

VARIATIONS ON THE FLUORITE CELL, MgAgAs AND Cu_2AlMn

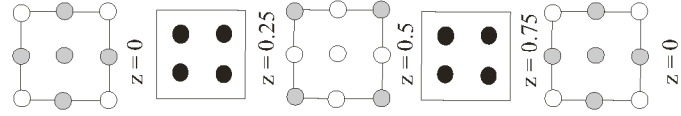


PARTS REQUIRED for MgAgAs	14	12	1
Eight coordinate cation = As	●	●	●
4 hot pink	○	○	○
General anion = Mg.	○	○	○
4 lime green	○	○	○
General anion = Ag.	○	○	○

Follow the instructions for building a FLUORITE cell and substitute 4 hot pink anions.



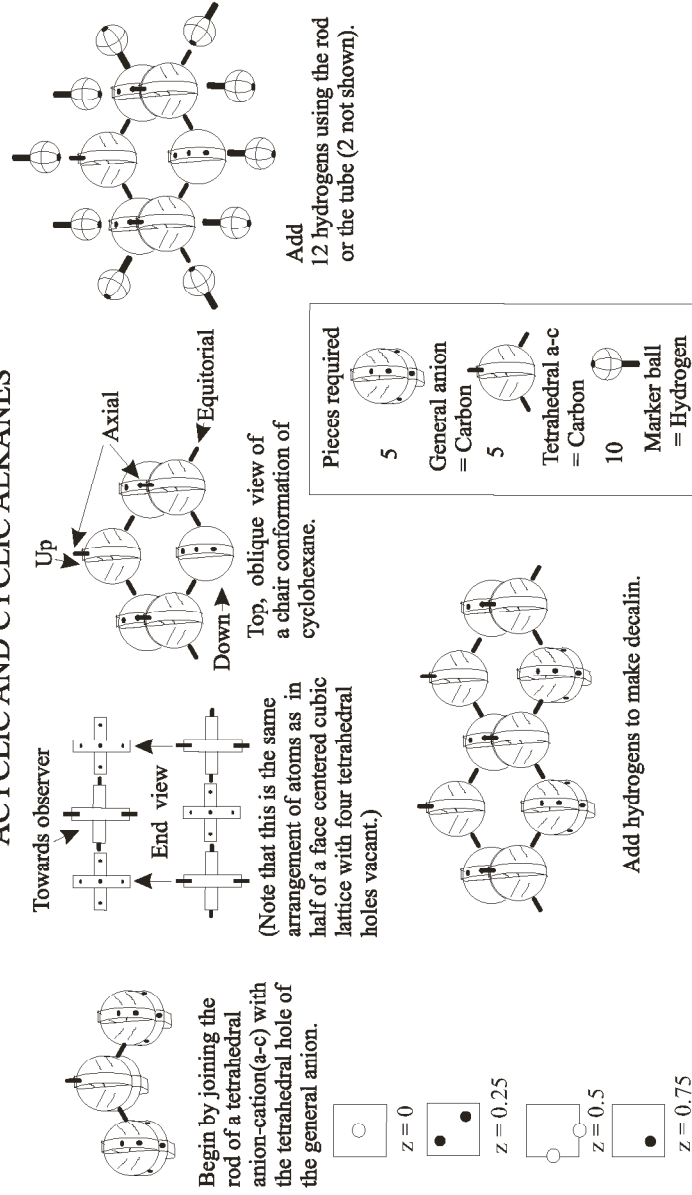
Follow the instructions for building an alternate FLUORITE adding 4 more cations and rearranging the colors.



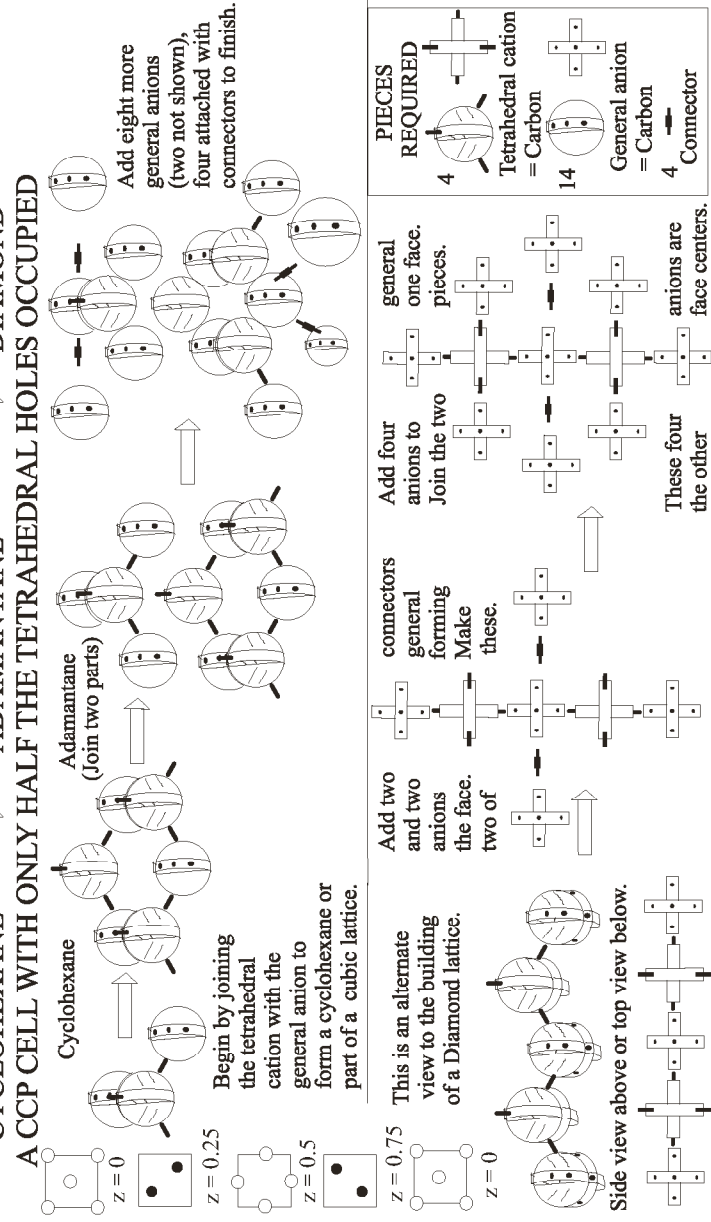
PIECES REQUIRED for Cu_2AlMn

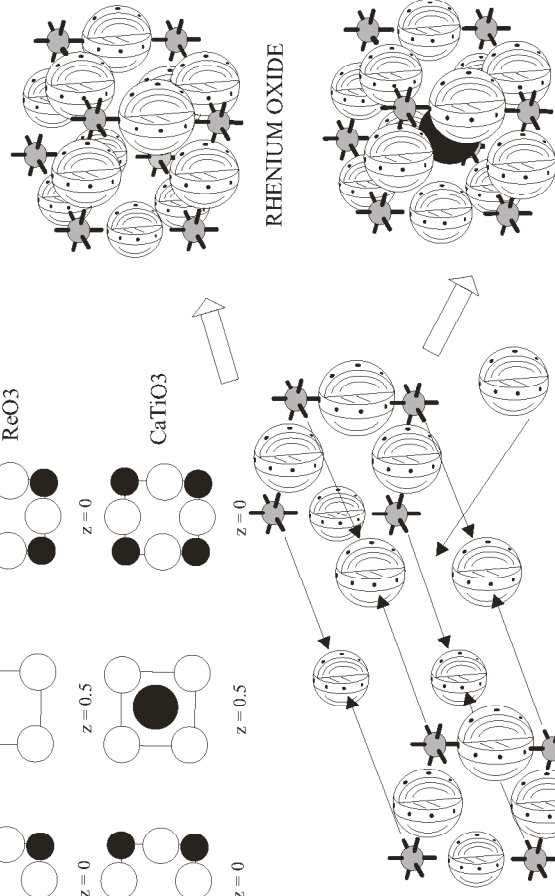
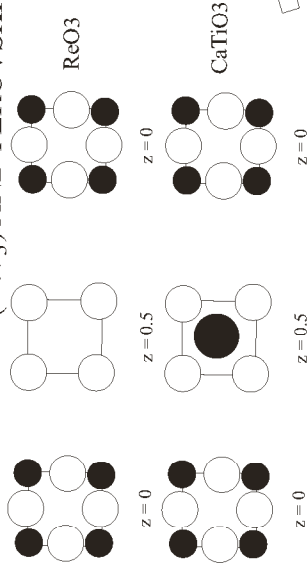
14 lime green = Mn	●
12 hot pink = Al	○
1 black = Al	○
(center, $z = 0.5$)	
General anion	○
Eight coordinate cation = Cu.	●

ACYCLIC AND CYCLIC ALKANES



CYCLOHEXANE → ADAMANTANE → DIAMOND



RHENIUM OXIDE (ReO_3) AND PEROVSKITE (CaTiO_3) CRYSTAL LATTICES

Place a black general anion into the cavity of the cell before closing to give Perovskite.

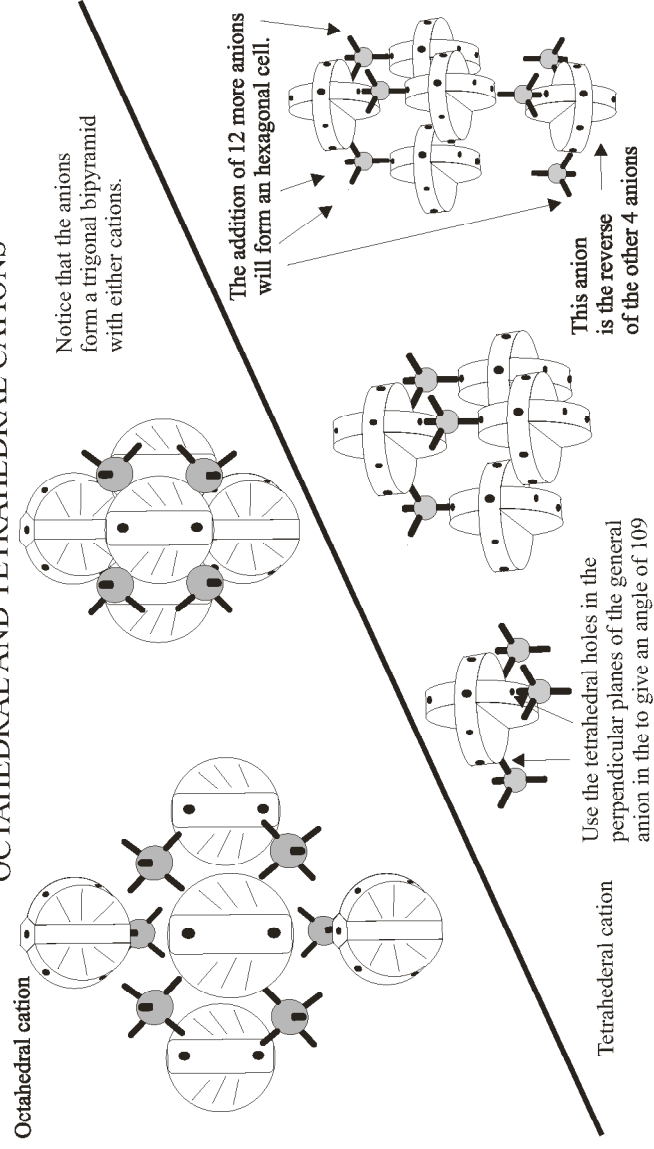
PEROVSKITE

© 1997 Stephen D. Darling

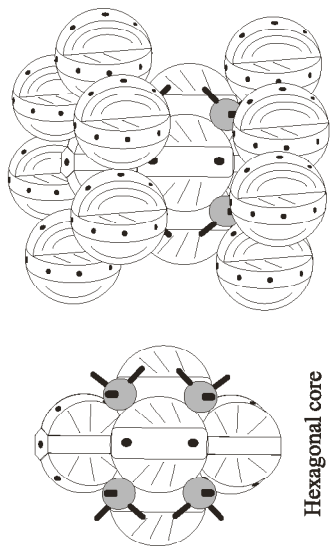
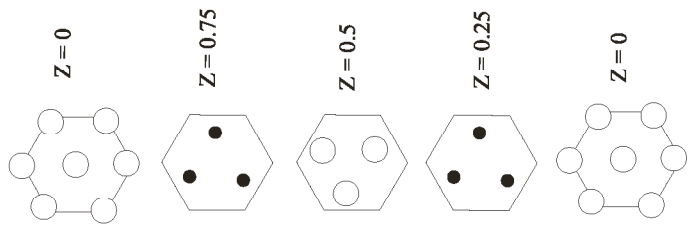
Pieces Required

13

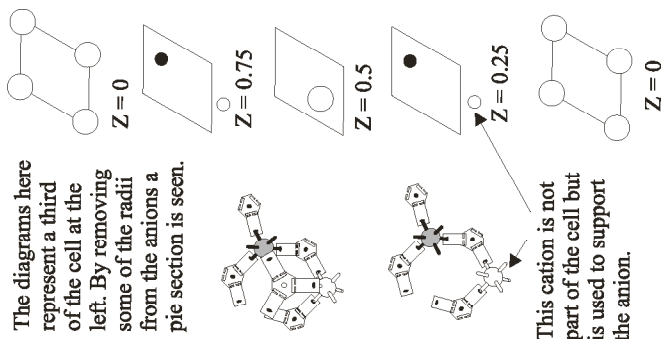
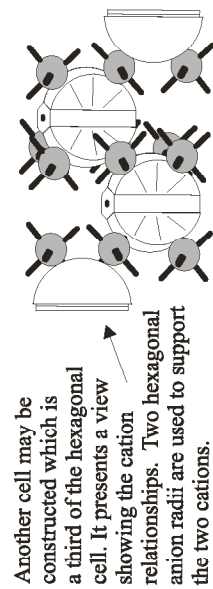
General anion
12 Hot pink as
oxygen, 1 black
as the Ca in
Perovskite

 ∞ Octahedral
cation = Re
or TiHEXAGONAL CLOSE PACKING CORES WITH
OCTAHEDRAL AND TETRAHEDRAL CATIONS

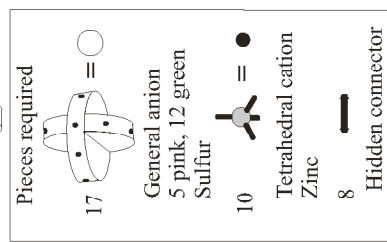
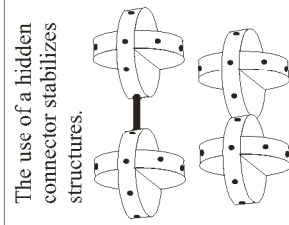
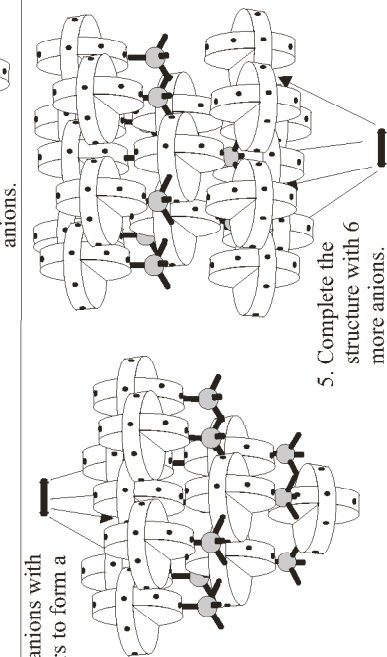
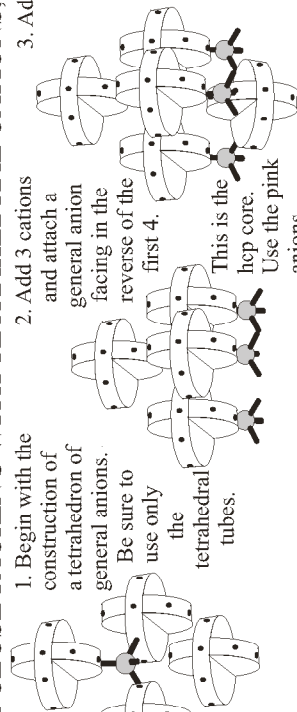
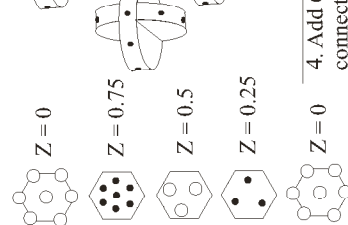
NICKEL ARSENIDE ,HEXAGONAL CLOSE PACKING WITH OCTAHEDRAL CATIONS



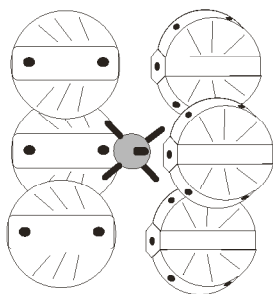
The NiAs hexagonal cell is built from an hexagonal core containing octahedral cations by adding 12 general anions to form a hexagon around the central hexagonal anion. The rods of the octahedral cations are inserted into the tetrahedral hole of the general anion.



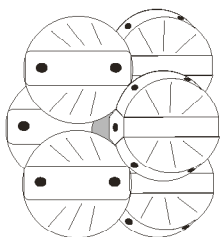
HEXAGONAL CLOSE PACKING WITH TETRAHEDRAL CATIONS, WURTZITE ZnS



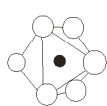
RUTILE, TITANIUM DIOXIDE TiO_2



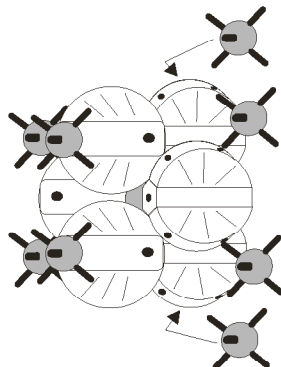
The rutile anion-cation relationship requires a hexagonal anion.



Construct an octahedral group of hexagonal anions around a octahedral cation. Be sure the anions are all parallel.

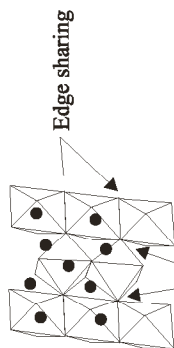


This is an octahedral representation of the anions on the left.



Add eight octahedral cations to form a cubic arrangement of the cations.

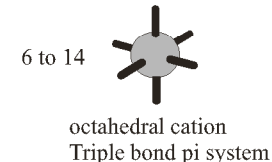
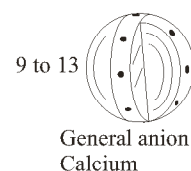
The rutile cell does not show the true structure of the rutile crystal. It consists of edge shared octahedrons that form strings. Each string shares vertices with adjacent strings. The crystal may be constructed from these models by building the strings and joining them with the central octahedral cation. The black circles represent the body centered cubic arrangement of the cations in the cell above.



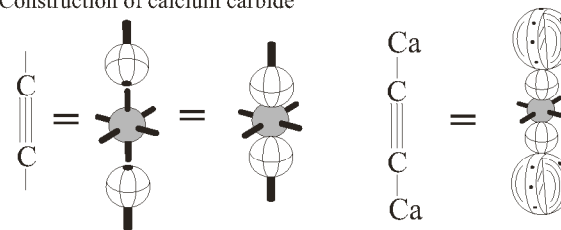
Vertex sharing

CALCIUM CARBIDE (CaC_2)

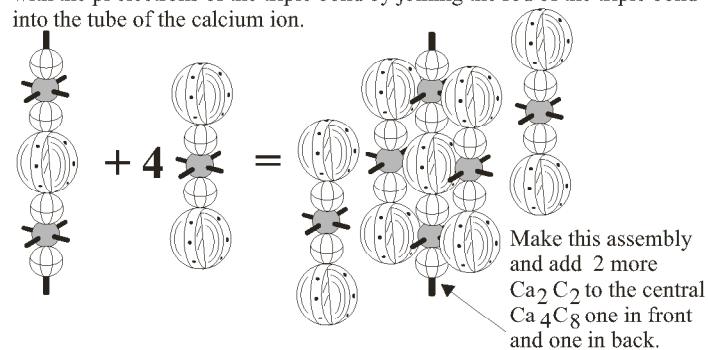
Pieces required



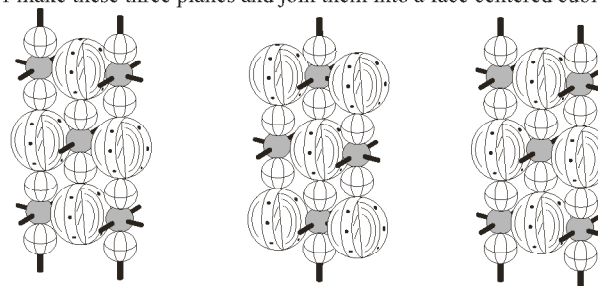
Construction of calcium carbide



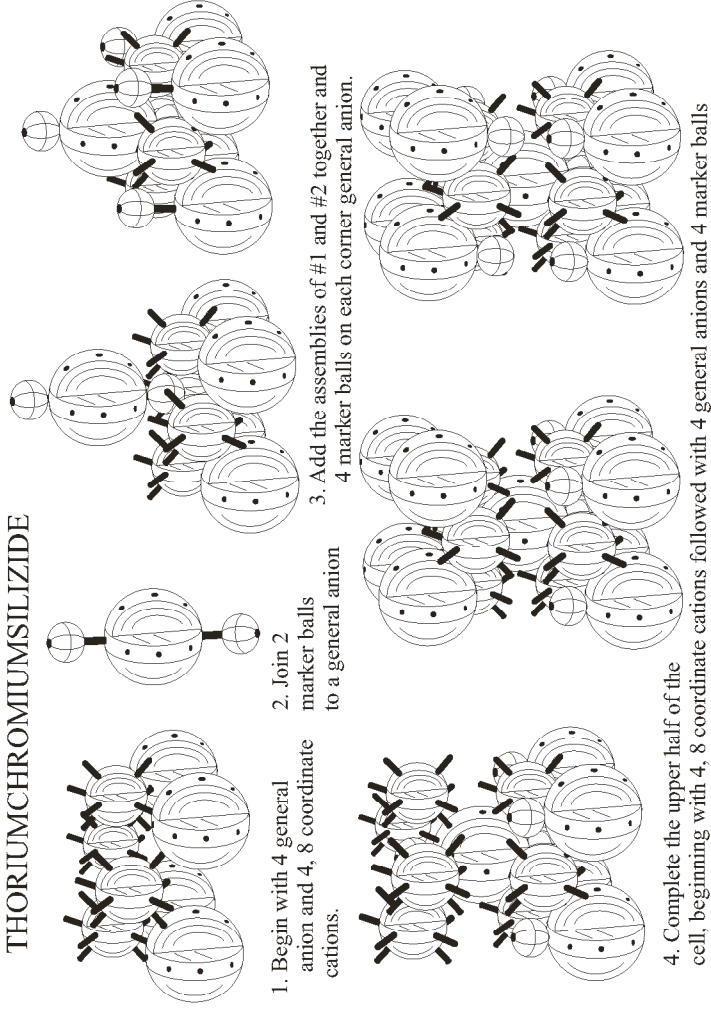
Construction of calcium carbide unit cell(s). Coordinate the calcium cation with the pi electrons of the triple bond by joining the rod of the triple bond into the tube of the calcium ion.



Or make these three planes and join them into a face centered cubic cell.



THORIUMCHROMIUMSILIZIDE

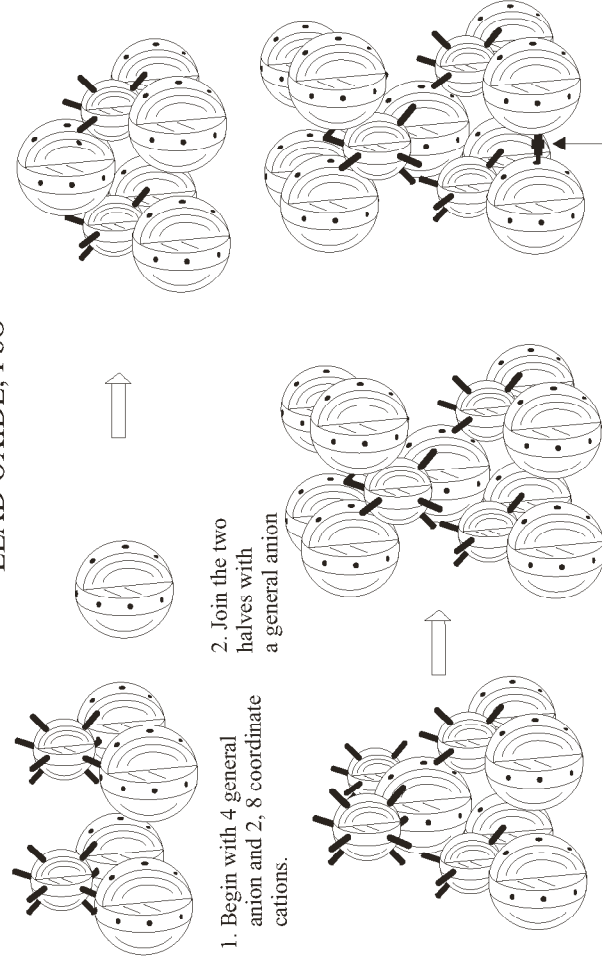


8
Marker ball,
Chromium

9
General anion,
Silicon

8
Coordinate
cation, Thorium

LEAD OXIDE, PbO



Parts required

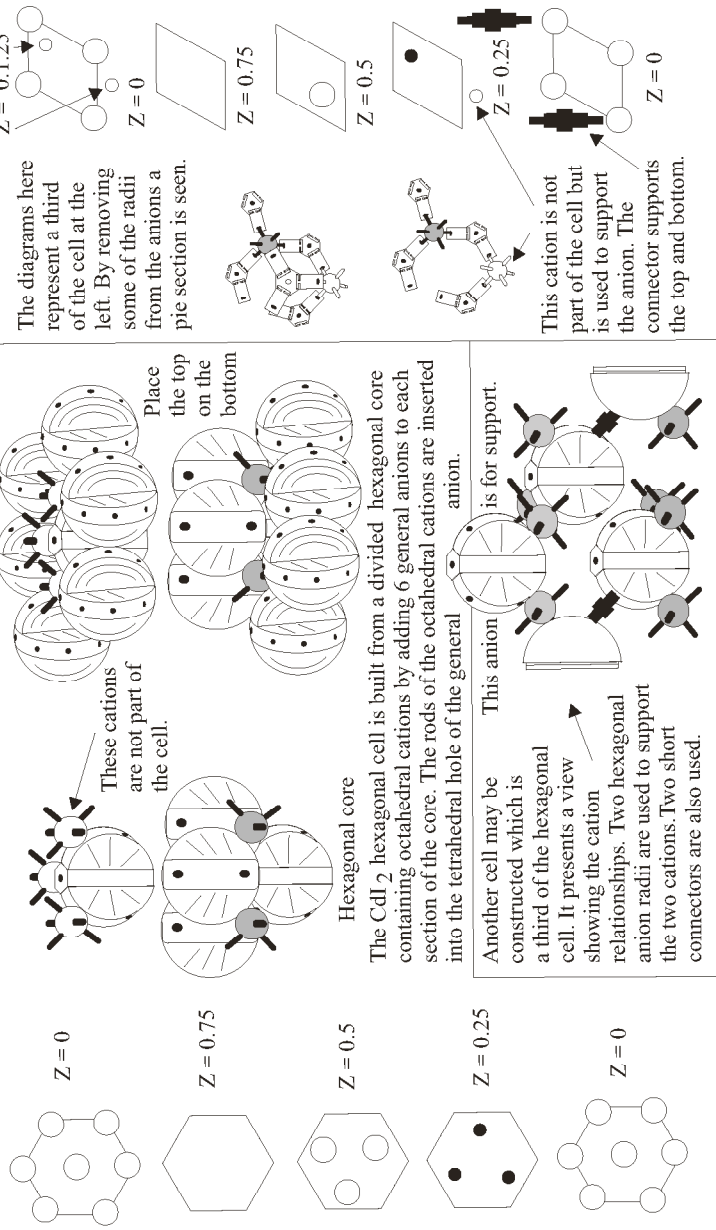
8
General anion,
Oxygen

4
Coordinate
cation, Lead

4
Short connector

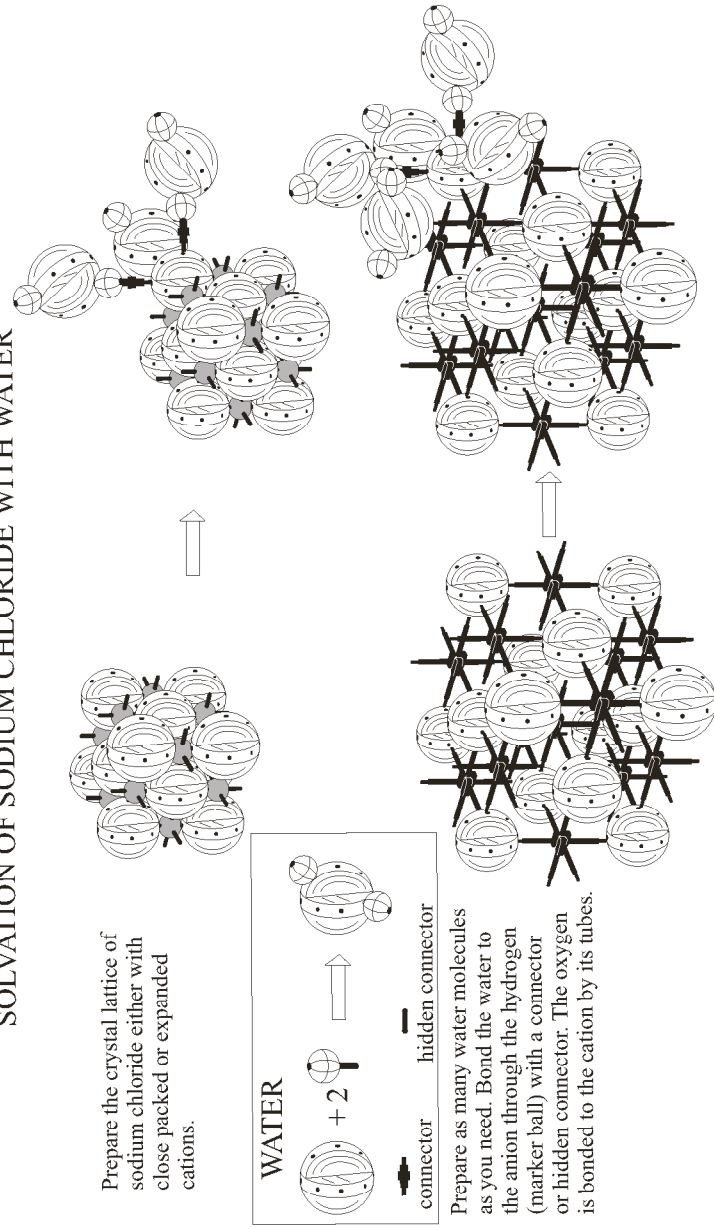
4. The general anions may be joined with a short connector for stabilization.

HCP WITH WITH HALF THE OCTAHEDRAL" HOLES" OCCUPIED, CADMIUM IODIDE



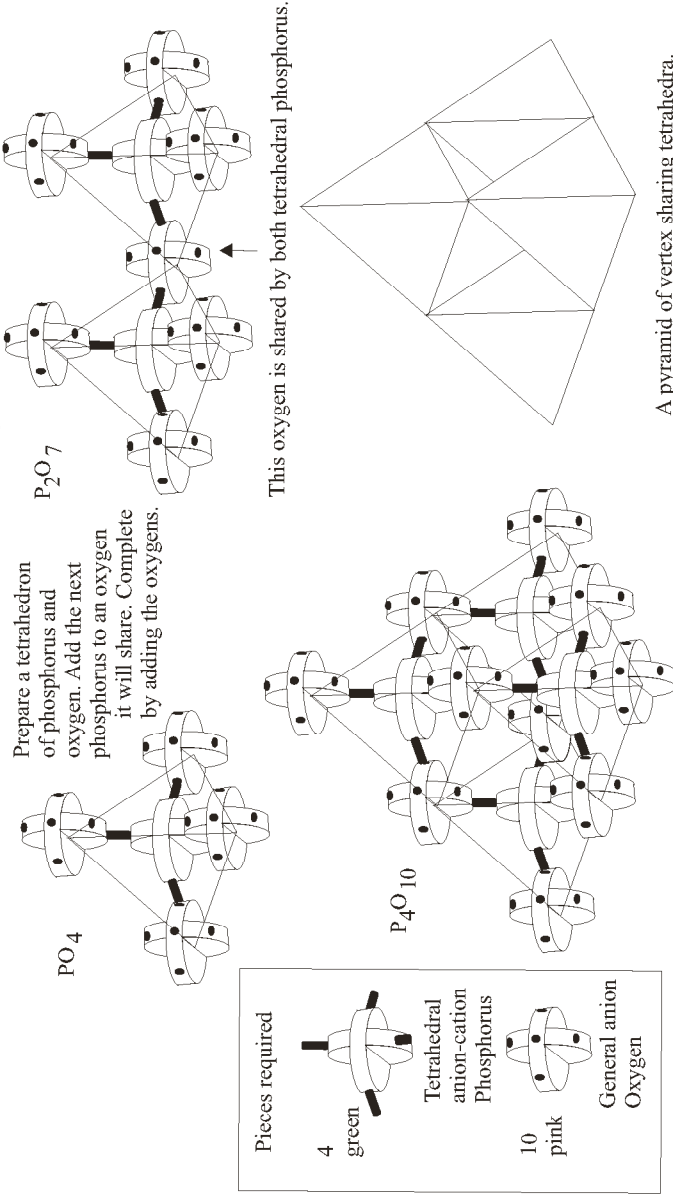
35

SOLVATION OF SODIUM CHLORIDE WITH WATER

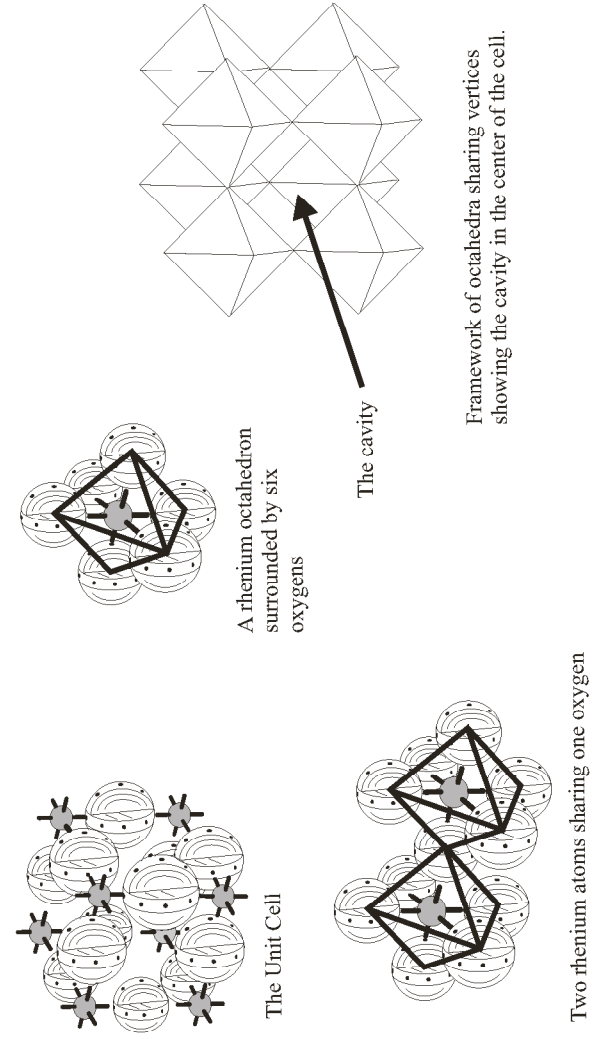


36

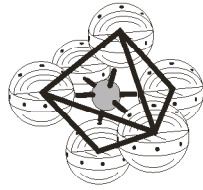
VERTEX SHARING TETRAHEDRA, P_4O_{10}



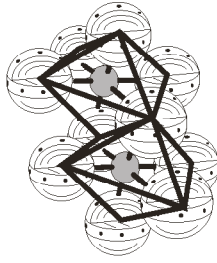
SHARED VERTICES (OXYGEN) IN THE RHENIUM OXIDE CRYSTAL



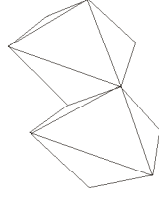
EDGE-SHARING OCTAHEDRA, AlCl_3



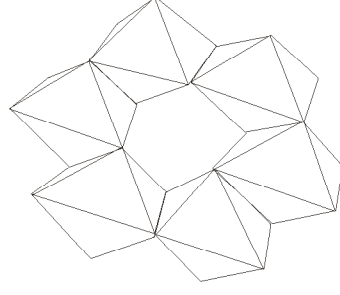
An aluminum octahedron surrounded by six chlorides



Two aluminum chloride octahedra sharing an edge.

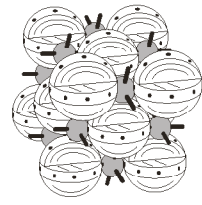


A shorthand drawing of the two octahedra.

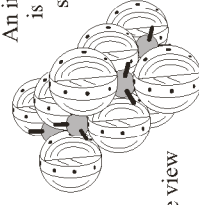


A ring of six edge shared octahedra.

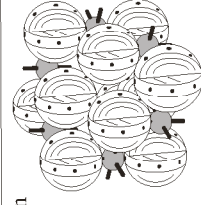
39



The sodium chloride cell



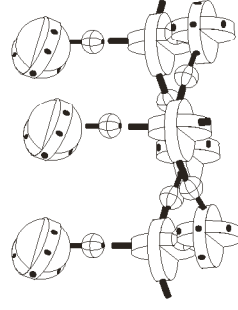
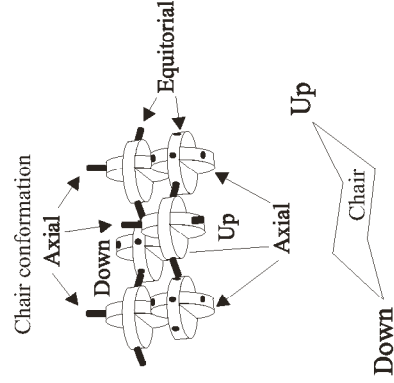
Edge view



Frontal view

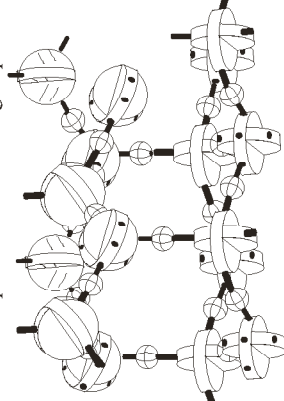
An interesting color pattern is created if the anions shown here are green and the remaining coordination is pink.

The aluminum chloride ring of six aluminum atoms with only the shared chlorides, showing the relationship to the sodium chloride cell. There are two chlorides absent and seven cations.

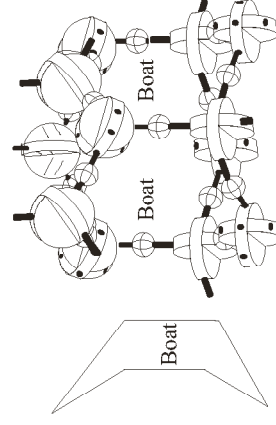


ICE

Build a chair arrangement using the general anion and tetrahedral anion-cation with a marker ball as a spacer. Add the axial groups.



Add 2 more general anions and 2 tetrahedral anion-cations and 4 marker balls to complete the cell. (A general anion and a hidden connector will substitute for the tetrahedral anion-cation.)



Connect the axial general anions with 3 tetrahedral anion-cations and 6 marker ball spacers forming the boat shaped rings vertically. This is the same conformation of the rings as in the beta form of diamond.

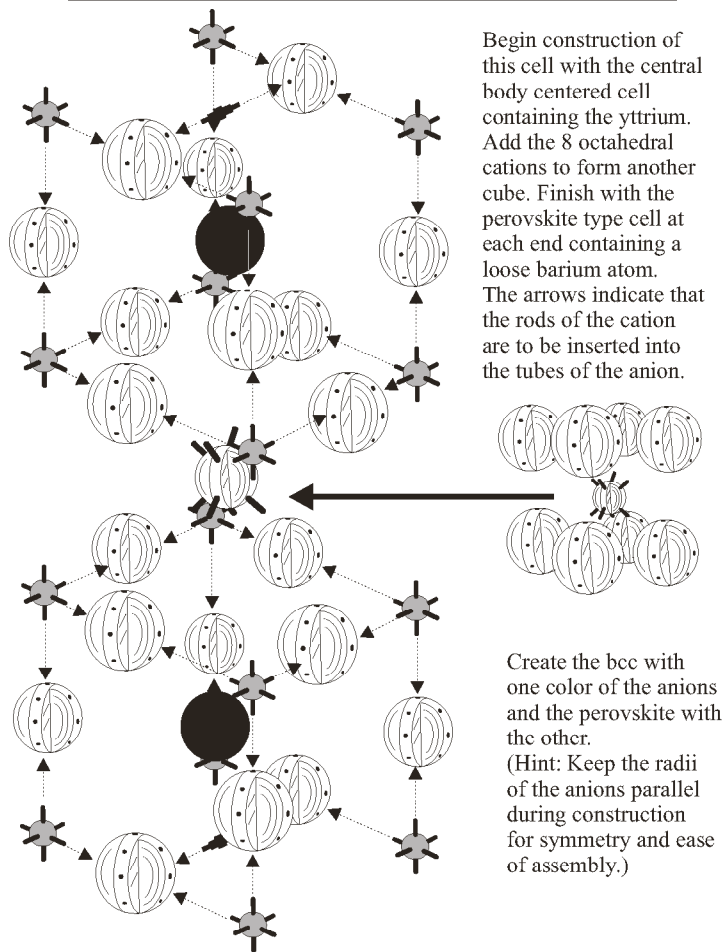
Pieces required	8 Tetrahedral anion-cation Pink, Oxygen	8 General anion Pink, Oxygen	19 Marker ball, hydrogen
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40

YBa₂Cu₃O₇, A SUPERCONDUCTOR

PARTS REQUIRED

1		22		16		2	
Eight coordinate cation = Y.		General anion 20, Pink = O 2, Black = Ba		Octahedral cation = Cu		Short connector	



A MODEL OF A HYPERCUBE, A CUBE IN THE 4TH DIMENSION

