Memory Metal
Teacher Materials (includes Student Materials)

Curriculum Suggestions

Topics

Chemical Bonding	Chemical Equilibrium	Introduction to Chemistry
Crystal Structure	Equilibrium	Scientific Method
Structure of Solids	Phases-Phase Diagrams	Physical Properties
Metallic Bonding	LeChatelier's Principle	Observational Skills
Alloys		

Overview

This unit could stand alone with a scope that is limited to understanding memory metals. It could also be used as a supplement to an existing chemistry curriculum and provide for a unique way to introduce or reinforce the above topics. In the suggestions that follow, when a specific investigation or experiment is used as an example, it refers not only to the activity but also to the background information that is included within the Teacher Notes. These suggestions should in no way be considered complete.

Suggestions

Investigation 1 ----- This is an introduction to scientific observation. It could also be used to introduce any of the above topics.

Investigation 2 ----- This is an introduction to crystal structures (and the structure of solids), which are often included in a unit on the phases of matter. It can also be used to introduce the nature of alloys.

Investigation 3 ----- This is an introduction to reversible reactions and to heats of reaction.

Investigation 4 ----- This is an introduction to phase diagrams, equilibrium, LeChatelier's Principle, and to physical properties and their relationship to structure.

Investigation 5 ----- This is an extension of Investigation 4 topics with the introduction of sound propagation as an additional physical characteristic.

Experiment 1------- This experiment provides an opportunity for an open-ended problem solving activity, as well as an authentic assessment opportunity.

Sample Lesson Plan

DAY 1

Students should begin to work through the Exploring the Nanoworld Kit, completing the worksheet that accompanies this activity as they proceed. This will likely require more than one period.

DAY 2
15-20 min

Finish the activity from DAY 1. It is important that students complete this activity in a manner that allows them enough time to examine the materials in the kit thoroughly and to reflect upon their observations. It should not become a "busy work" activity.

5-10 min

Discuss the observations made by the students and clarify any questions on the worksheet as necessary. Avoid at this time a great deal of discussion as to the nature of these materials or "how they work".

20-30 min

Have students do Investigation 1.

DAY 3
15 min

Discuss the results of Investigation 1. Collect the observations on the board and use them to stress the difference between observation and inference as well as qualitative versus quantitative observations.

35 min

Use follow-up question (2) to begin a discussion of memory metals. You should present the material in the background information section of this unit through the treatment of structural defects.

DAY 4

Before students attempt Investigation 2, it is necessary that they have a good understanding of what constitutes a <u>unit cell</u>. Appendix A contains a development of this concept using traditional two-dimensional arrays. This topic is further extended in the Teacher Notes for Investigation 2.

Models or overhead projections of the unit cells will be helpful. Be sure to emphasize that some atoms in a structure are shared by more than one unit cell and the fraction belonging to a given cell must be determined.

DAY 5

Have students do Investigation 2.

DAY 6

Discuss Investigation 2. Questions 5 (b) and (c) will require that you point out that the difference between the two structures amounts to layers of atoms in the austenite structure experiencing both a sliding and shearing motion to arrive at their locations in the martensite structure. There is a <u>slight</u> change in density of the structure (<0.5%) and <u>substantial differences</u> in properties such as flexibility, hardness, and acoustic signature.

DAY 7 10-15 min	Have students do Investigation 3.
35-40 min	Class discussion of how the austenite-to-martensite transition occurs. Also discuss the mechanism of how the memory can be changed. See the Notes for the Instructor.
DAY 8	Have students do Investigation 4.
DAY 9	Discuss Investigation 4. See the Notes for the Instructor. You may want to do problem 1 from the Memory Metal Review Questions Worksheet.
DAY 10	Have students do Investigation 5.
DAY 11 5-10 min	Discuss the results of Investigation 5. See the notes for the Instructor.
45-50 min	Pre-lab Experiment 1. Review the steps in the scientific method and encourage your students to keep them in mind as they develop a procedure to determine the transition temperature range for a sample of NiTi. Provide class time for the students to "brainstorm" their procedures and make sure they understand that they are to show you their procedures for approval before proceeding.
DAY 12	After approval, have students do Experiment 1. If you have anticipated likely approaches to this problem, you will probably have most of the equipment that the students request already at hand. (See the Notes for the Instructor). It may, however still require more than one class period for everyone to finish.
DAY 13 15-20 min	Discuss the capabilities and uses of memory metals. Recall Investigation 1, question (4) and ask your students if any other applications have come to mind now that they have completed this unit. Also, distribute the Memory Metal Review Questions Worksheet and allow students the remainder of the period to discuss it in small groups.
DAY 14	Discuss the In-Class Discussion Question from the previous day. Have the small groups share their ideas with the entire class. Also, continue reviewing the unit by completing the Memory Metal Review Questions Worksheet.
DAY 15	Unit exam (See the Memory Metal Assessment at the end of the unit).

Nickel-Titanium Memory Metal

Overview

Nickel-titanium (NiTi) is a remarkable metal alloy that is representative of "smart materials" that respond to a stimulus in a predictable manner. The wire sample of NiTi used in this unit can be bent at room temperature, but will return to its linear shape when heated by hot air or water as its atoms move in a kind of "atomic ballet." Moreover, the wire can be heated to the much higher temperature of a candle flame (~500 degrees C), where it can be trained to "remember" a new shape. Subsequently, when the wire is distorted at room temperature and heated by hot air or water, it will return to this new shape. Rods of NiTi can be used to show that the flexibility, hardness, and even its acoustic characteristics are all affected by its temperature.

The unusual properties of this smart material are derived from the two crystal structures that can be interconverted by changes in temperature or pressure. At temperatures between about 0 and 100 degrees Celsius, there are two important phases or crystal structures of NiTi that can be referred to as the high temperature and low temperature phase, or as austenite and martensite, respectively. The austenite phase has the symmetry of a cube and is characterized by hardness and rigidity.

When cooled, the austenite phase transforms to martensite, which is less symmetric and in fact can have 24 different relative orientations (called variants) of groups of atoms comprising the crystal. When pressure is applied to this low temperature phase, groups of atoms can change their relative orientation to accommodate the pressure, causing the material to be softer and more flexible than the austenite phase. Furthermore, when a rod of NiTi in the austenite phase is dropped, a sound wave propagates relatively unimpeded through the material, yielding a ringing sound; in contrast, when a rod of NiTi in the martensite phase is dropped, its different orientations of groups of atoms act as sound absorbing boundaries and will create a muffled thud sound.

Because martensite is also slightly denser than austenite, by LeChatelier's principle, which states that an increase in pressure favors the denser phase of multiple phases at equilibrium, pressure can be used to convert austenite to martensite. This is analogous to the pressure from ice skates helping to melt the ice: application of pressure from the skate helps transform the less dense ice to denser liquid water.

The ability to change the shape of this "smart" material stems from defects, irregularities in the packing of atoms, that occur in samples of the material. The defects, which can be altered at the high temperature of a candle flame where NiTi is in the austenite phase, are used to create the shape to be "remembered" by forcing groups of atoms to have particular positions relative to one another.

This collection of unusual properties possessed by NiTi has enabled it to be used in a wide variety of applications. Some of the more common uses are as the arch wires of orthodontic braces, bendable eyeglass frames, and anti-scald faucets.

Memory Metal

What is memory metal?

Memory metal is an alloy that can be "trained" to take on a predetermined shape in response to a stimulus such as a change in temperature. For example, a linear wire can be twisted and bent, yet will return to its original shape when heated above a characteristic temperature.* Many alloys exhibit this characteristic, although the effects are not always as dramatic. Some examples of shape-memory alloys include copper-zinc-aluminum, iron-manganese-silicon, gold-cadmium, copper-aluminum, copper-aluminum-nickel, and the subject of this module, nickel-titanium (NiTi).

*There are some limits to the distortions that the wire will accommodate; for example, if bent into a knot, the wire typically cannot return to its linear shape.

Nitinol

Nickel-titanium shape memory alloy, Nitinol, was discovered in 1965. Nitinol is an acronym for **Ni**ckel **Ti**tanium **N**aval **O**rdnance **L**aboratory, where the alloy's remarkable properties were discovered. Nitinol is an alloy containing nearly equal numbers of nickel and titanium atoms, leading to its common compositional representation as NiTi. The relative amounts of Ni and Ti can be varied by a few percent in order to control the temperature of the phase change responsible for its "smart" behavior. A more accurate representation of its composition is Ni_xTi_{1-x}.

Nitinol and the BB Board Analogy

Through an analogy to the atomic scale, structural changes that Nitinol undergoes can be shown with a transparent, empty plastic CD case and BB's.

A. B.

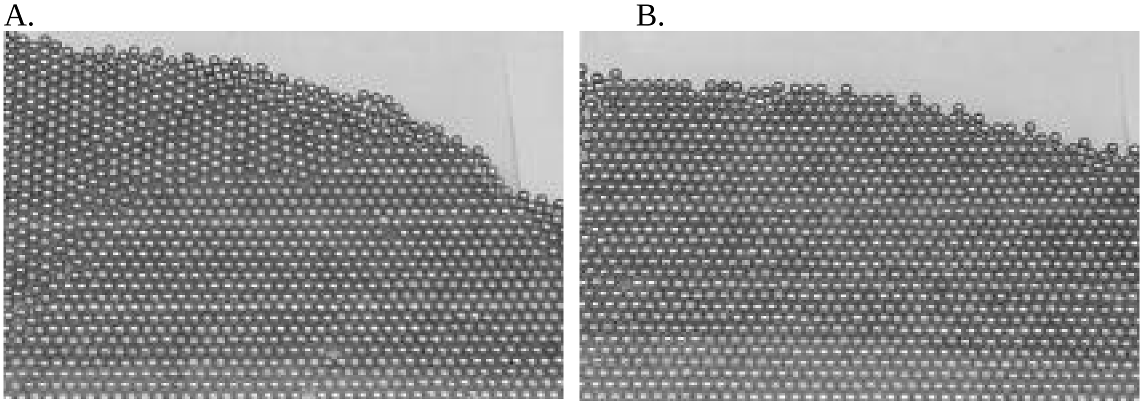

Figure 1. BB board with defects (IDENTIFY SOME WITH ARROWS)(A), and without defects (B).

Fill the case with a single layer of BB's until it is two-thirds full. Observe the pattern of BB's while holding the case almost horizontal. (Using an overhead projector to display this is also a good method of illustrating it to a class.) Several small groups of BB's, each with a regular internal pattern, are separated from each other by gaps. These gaps form defects. Analogous defects in Nitinol are composed of myriad three-dimensional crystalline regions called grains. Similar to the two-dimensional groups of BB's in the CD case, these grains are of random size, shape, and orientation. When Nitinol is heated to 500-550 degrees Celsius to fix the shape, the defects are minimized but not eliminated. Shifting atoms minimizes the defects as the grains are re-shaped. This shifting allows the atoms to fit closer together. You can use the CD case filled with BB's to illustrate how the atoms create this new arrangement. Shaking the CD case gently will add energy to the system (analogous to adding heat), and a new arrangement of BB's results. During heating, Nitinol's grains are restructured into the high-temperature austenite phase.

Uses and Capabilities

Since Nitinol has the capability of remembering its shape, this "smart" material can sense changes in its environment. It can respond to disturbances in a pre-programmed way. This new high-tech solid can consequently be used in a variety of artistic, medical, and engineering applications. These include eyeglass frames, golf clubs, coffee pot thermostats, electrical connectors, aircraft de-icers, solar collectors, clamps, sculptures, and structural damping elements, which are used to lessen the damage caused by earthquakes. For the practical joker, a magic spoon that bends when placed into a hot beverage cup also exists. The biocompatibility of NiTi allows it to be used in medical applications such as vascular stents for holding arteries open, anchors for attaching tendons to bone, medical guidewires, medical guidepins, root canal files, bendable surgical tools, and devices for closing holes in the heart as well as the common archwire for braces. Research that uses memory metal to deploy solar arrays, to create antennae on satellites and to control the balance on helicopter rotor blades is underway. Currently, these as well as many other uses are being developed.

There are four properties of unit cells that may be generalized.

1. The opposite sides of a unit cell are parallel.

2. Each unit cell contains an integer number of structural units (circles, atoms, ions, etc.) - in this case, one.

3. The unit cells fit together so as to fill space completely, and they are identical to one another.

4. The corners of the unit cell can be anywhere.

Memory Metal

memory metal - metal that remembers its shape

examples: NiTi, Cu-Zn-Al, Fe-Mn-Si, Au-Ca, Cu-Al-Ni, Cu-Al, etc.

smart material-responds to a stimulus in a predictable manner

Characteristics of NiTi

1. bent at room temp. but return to linear shape when heated by hot air or water

   -"atomic ballet"

   -some limits

2. can be "trained" to remember new shape by heating in candle flame (500°C)

3. NiTi consists of 2 structures interconverted by changes in temp. or pressure
   - between 0-100°C there are 2 phases
     1. Austenite
        - high temp. phase
        - cubic symmetry
        - hard, rigid
     2. Martensite
        - low temp. phase
        - less symmetrical
        - flexible

Martensite + energy === Austenite
(more dense) (less dense)

Martensite can have 24 varients
- flexibility of martensite due to varients in structure & ability to re-orient these varients = mecahnical flexibility

Nickel-Titanium = Nitinol = Nickel Titanium Naval Ordinance Laboratory
- nitinol discovered in 1965

- contains nearly equal amounts of Ni & Ti atoms

NiTi common composition but relative amounts of Ni & Ti varied to control temp. of the phase change responsible for its smart behavior

Ni_xTi_{1-x}

ex. $Ni_{0.5}Ti_{0.5}$ $Ni_{0.3}Ti_{0.7}$

BB board analogy
- case = solid, BB's = atoms
- groups of atoms (BB's) = small groups with regular internal pattern separated from each other by gaps
- gaps = defects

Nitinol composed of 3-D crystalline regions = grains
- grains have random shapes, sizes, orientations

heat to 500-550°C to fix shape, linear defects are minimized, not eliminated
-defects minimized by atoms moving & reshaping grains
-allows atoms to fit closer together

Crystallography-study of the structure of crystals, including ways of describing the crystal structure, the principles that govern the various structures, & methods of determining a crystal's structure

3 parts to crystallography

1. ways that spheres pack into a 3-D array that can be extended indefinitely in all directions

2. the smallest unit that can be associated with a solid

3. determining planes & directions in crystal structures

unit cell-an imaginary box that can be constructed from arrays of atoms, ions, or molecules-basic unit of a crystal structure

valid unit cells-used to represent the array

See Appendix A or overheads

Note: Each unit cell contains 1 complete circle, & only the shaded portion of the circle lies in the unit cell. If any of the unit cells is moved along its edges the entire pattern is produced.

Simple Cubic Face-centered cubic Body-centered cubic

See Figure 2 in Investigation 2 (Notes for the Instructor)

valid unit cell vs. invalid unit cell

coordination number - number of nearest neighbors

Thermochemical equation to represent transition between phases

martensite + energy === austenite

-energy of a few kJ/mol to change from martensite to austenite

Ni & Ti atoms within the grain(crystalline region) in a sample of memory metal in austenite phase are almost perfectly arranged with few imperfections

-memory from defects in austenite phase & grain boundaries

-to give metal a new shape, new defects must be created - goes to new set of defects, rather than old

-new defects obtained by heating metal 500℃ while securing shape

-thermal energy allows atoms to relax into lower energy positions = defects formed

-if heated too long, memory metal feature of wire destroyed because if atoms around defects have enough energy they relax & a defect free structure results

-defects created in austenite phase (altered by candle flame) create new memory by forcing groups of atoms to have particular positions relative to one another

Uses and Capabilities

-sense changes in environment & respond to disturbances in a pre-programmed way so used for...

For example:

Artistic medical engineering
eyeglass frames
golf clubs
clamps
practical jokes
See background information for more.

archwire for braces
coffee pot thermostats
electrical connectors
sculptures
medical applications

Austenite	Martensite
1. high temp. phase	1. low temp. phase
2. rigid/hard	2. flexible
3. symmetrical	3. less symmetrical
4. ring	4. thud
5. uniform structure allows sound waves to travel through it easily	5. boundaries between regions with different orientations reduce vibrations & muffle the sound
6. less dense	6. more dense

Hysteresis Effect - the phase changes in the 2 directions do not have the same temperature dependence-phase change from austenite to martensite occurs over a lower temp. range than that from martensite to austenite

Graph of figure 9.9 from Companion

Explanation: one solid phase needs to grow within the region of the other-elastic strain in region around new crystal growth

Overall effect: displacement of heating curve to higher temps.
therefore, whether it was heated or cooled makes a difference

Equilibrium - system in which the rates of forward & reverse processes are equal
-processes can be chemical or physical

-system must be closed

closed vs. steady state

LeChatelier's Principle - when a system at equilibrium is subjected to a stress (change in temperature, pressure, concentration), the equilibrium will shift in the direction that tends to counteract or relieve the stress

Straining material causes NiTi to change from one phase to another

-as rod is bent some atoms compressed & some pulled apart

Figure 9.7 from Companion

-therefore, pressure exerted on atoms
-material favors matensite (more dense phase) formation under high pressure

Transistion temperature (TTR) - temperature at which a phase transformation occurs

Memory Metal

memory metal -

examples: NiTi, Cu-Zn-Al, Fe-Mn-Si, Au-Ca, Cu-Al-Ni, Cu-Al, etc.

smart material-

<u>Characteristics of NiTi</u>

1.

-"atomic ballet"

-some limits

2.

3. NiTi consists of 2 structures interconverted by changes in temp. or pressure

-between 0-100°C there are 2 phases

1.

2.

+ energy ===

(more dense) (less dense)

Martensite can have _____ varients

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<u>3 parts to crystallography</u>

1.

2.

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______________-an imaginary box that can be constructed from arrays of atoms, ions, or molecules-basic unit of a crystal structure

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coordination number - ______________________________

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Uses and Capabilities

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__________________ __________________

__________________	__________________
1. high temp. phase	1. low temp. phase
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__________________ - system in which the rates of forward & reverse processes are equal
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Figure 9.7 from Companion

-therefore, pressure exerted on atoms

-material favors matensite (more dense phase) formation under high pressure

Transistion temperature (TTR) -

PURPOSE

To allow students to investigate NiTi memory wire.

METHOD

You should allow students adequate time both to follow the instructions as outlined on page 18 of the "Exploring the Nanoworld" guide and to experiment freely with other ideas that come to mind as they ponder what they have observed. Encourage them to write down not only their observations, but also questions that arose as they completed the activity. See the sample lesson plan for recommended time allocations.

MATERIALS

Samples of NiTi wire either from the "Exploring the Nanoworld" kit or from the suppliers listed in the appendix.

400 mL beaker

hot plate or Bunsen burner (you may want to pre-heat the water in a coffee pot, in which case these are not necessary).

ringstand, ring, and wire gauze, if burner is used.

PROCEDURE

a. Observe the piece of wire that has been provided by your instructor. Note its outward characteristics, especially its shape. (Draw its initial shape in your notebook.) Fill a 400 mL beaker 2/3 full of tap water and place it on a wire screen on a ring stand or a hot plate as directed by your instructor. NOTE: Your instructor may provide you with hot water.
b. Make several coils in the wire by wrapping it around your pencil several times.
c. If you are to heat water, place the wire into the beaker and begin slowly heating the water while carefully observing the wire. Stop heating after any significant changes to the wire have been observed.
d. Record your observations.

ANSWERS TO FOLLOW-UP QUESTIONS

1. List your observations before and after deforming the wire. Also list your observations as you heated the wire. Specifically, what happened when the deformed wire was exposed to hot water?

Wire returns to its original shape. Note: Be sure to include in a post-investigation discussion the difference between an observation and an inference/interpretation.

2. What questions came to mind as you performed this experiment? Invariably, good observations lead to many questions; recall what being a good observer entails.

Student responses will vary and should probably be collected and recorded during a class discussion. They may include:
1) Why did this happen?
2) How did this happen?
3) Do all metals do this? If not, why is this one special?
4) Does the temperature of the water make any difference?
5) Does the length or diameter of the wire matter?
6) What uses could metals of this nature have?

You may want to demonstrate with a paper clip for comparison. A simultaneous demonstration with multiple pieces of wire is also quite dramatic!

3. Why do you think these wires fall into a category called “smart materials”?

Because they “remember” their original shapes and respond to changes in their environment.

4. What possible uses could materials similar to these have?

Student responses will vary, but this should lead to a lively and entertaining class discussion. This should also be viewed as an opportunity for you to encourage the class to design experiments to answer some of their previous questions with further investigation.

INVESTIGATION 1

PURPOSE

To investigate the piece of wire that has been provided by your instructor. Everyone thinks of himself or herself as a good observer. Yet there is much more to being a good observer than meets the eye! It takes concentration, alertness to detail, ingenuity, and often, great patience. It even takes practice! As you make your observations, keep an open mind and also consider any conditions during the experiment that may be important to its outcome. Can any of these conditions be controlled?

PROCEDURE

a. Observe the piece of wire that has been provided by your instructor. Note its outward characteristics, especially its shape. (Draw its initial shape in your notebook.) Fill a 400 mL beaker 2/3 full of tap water and place it on a wire screen on a ring stand or a hot plate as directed by your instructor. NOTE: Your instructor may provide you with hot water.
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FOLLOW-UP QUESTIONS

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2. What questions came to mind as you performed this experiment? Invariably, good observations lead to many questions; recall what being a good observer entails.

3. Why do you think these wires fall into a category called “smart materials”?

4. What possible uses could materials similar to these have?

PURPOSE

To have students begin to understand that the behavior of the wire that they observed in Investigation 1 can ultimately be explained in terms of the transformations that occur between two subtly different structures (phases) of the NiTi alloy from which the wires were made. To have students build or view a number of structures and elucidate unit cells within them. To relate unit cell characteristics to properties like density.

METHOD

Since an understanding of the features of the shape-memory metal cycle is dependent upon the relationship between the structures of the high- and low-temperature phases of this material, it is suggested that these structures be discussed at an early stage of this unit. This may be accomplished in one of two ways: 1) make an overhead transparency of the figure below; or 2) better yet, have some or all students build models of both the austenite (high temperature) and martensite (low temperature) structures using the Solid State Model Kit* that the entire class may view.

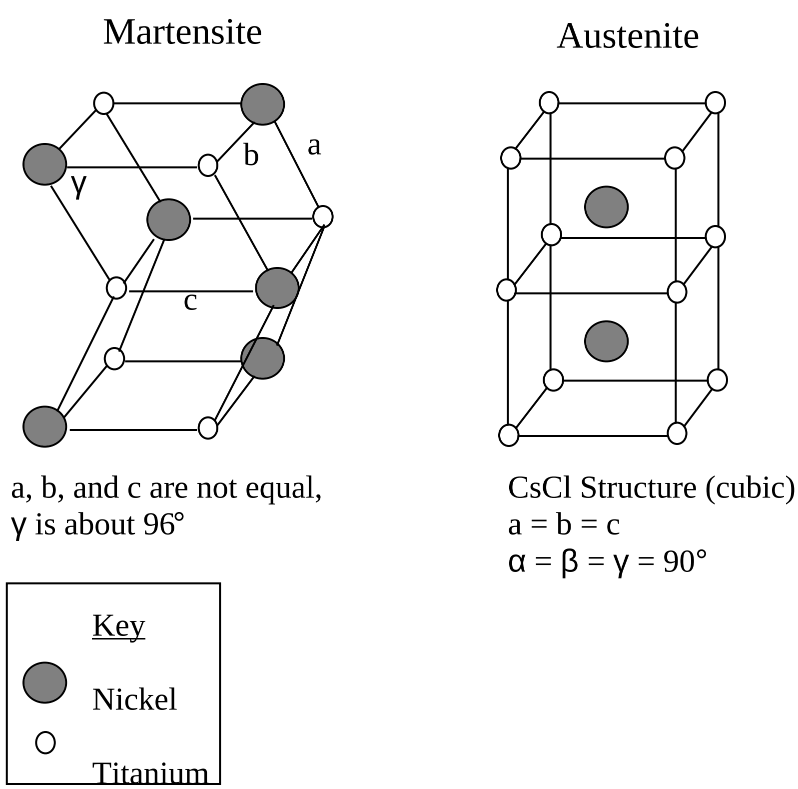
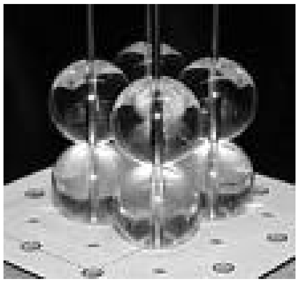


Figure 1. Unit cell of NiTi in the martensite and austenite phases.

*Available from the Institute for Chemical Education (ICE), University of Wisconsin-Madison Department of Chemistry, 1101 University Avenue, WI 53706-1396, Phone: 608/262-3033, 800/991-5534, Fax: 608/265-8094, ICE@chem.wisc.edu, http://ice.chem.wisc.edu/. Less complicated models may also be assembled from styrofoam spheres (or oranges) appropriately cut.

Crystalline materials like NiTi have a patterned arrangement of atoms that extend in all directions to the surfaces of the sample. A useful way of describing this pattern is to consider a three-dimensional cube, which, when reproduced and moved along each of its edges by a length equal to that of the edge, generates the entire structure of atoms in the crystal. Such a cube is called a unit cell and it provides a template for the atoms and the empty spaces between the atoms in the structure.*


Simple Cubic


Face Centered Cubic

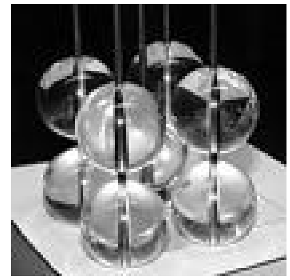

Body Centered Cubic

Figure 2. Examples of unit cell structures.

*See Appendix A for a more detailed discussion of unit cells.

Of course, not all crystals are in the form of cubes, which are a special kind of parallelepiped having exclusively 90^o angles and equal edge lengths, but this approach will allow students to better understand what unit cells are and some of their features. Make sure that students understand the concept of coordination numbers from Part 1 of the Investigation. **Size does not make a difference if all the spheres are the same size. If the spheres are of different sizes, as the size of the central sphere increases so can the coordination number. In the austenite and martensite stuctures the nearest neighbors would be spheres of the other color.** Cereal boxes or matchboxes may be used to show other kinds of non-cubic 3-D unit cells.

MATERIALS

Either overheads of Figures 1 and 2 above or several Solid-State Model Kits from ICE.

PROCEDURE

PART 1: General Considerations.

Determine how many larger spheres you can pack around a marked sphere in the same plane. It may be easier to hold the spheres in the palm of your hand while doing this. If all the spheres are the same size does the coordination number depend on size? What if the central sphere is smaller? Larger ? Check your predictions. **Note: Students may find a chart helpful in organizing the data for this part.**

PART 2: This part of the investigation requires that teams work together, using the Solid State Model Kits or following alternate procedures outlined by your instructor. Each team will build one of the following structures. All teams will then compare and contrast their structures and together answer questions.

Team A: Following the instructions in the kit, assemble the Simple Cubic Structure.
Team B: Following the instructions in the kit, assemble the Body Centered Cubic Structure.
Team C: Following the instructions in the kit, assemble the CsCl Structure with the Cl atoms at the corners.

Team D: Following the instructions in the kit, assemble the CsCl Structure with the Cs atoms at the corners.
Team E: Following the instructions in the kit, assemble the Austenite Structure.
Team F: Following the instructions in the kit, assemble the Martensite Structure.

ANSWERS TO FOLLOW-UP QUESTIONS

1. For each structure complete the table below, indicating HOW MANY SPHERES LIEWITH THEIR CENTERS AT THE _________________OF THE UNIT CELL.

Structure	Corners	Edges	Faces	Inside
A	**8**	**0**	**0**	**0**
B	**8**	**0**	**0**	**1**
C	**8**	**0**	**0**	**1**
D	**8**	**0**	**0**	**1**
E	**8**	**0**	**6**	**0**
F	**8**	**0**	**6**	**0**

2. With how many other unit cells are the spheres at the ___________of the cell shared?

a) corners___**7**___cells b) edges___**3**___cells c) faces___**1**___cells

3. What fraction of each sphere lying with their center at the ____is part of that cell?

a) corner ___**1/8**___ b) edge ___**1/4**___ c) face ___**1/2**___

4. For each structure complete the table below, indicating HOW MANY TOTAL SPHERES OCCUPY EACH SITE.

Structure	Corners	Edges	Faces	Inside	Total in Cell
A	**1**	**0**	**0**	**0**	**1**
B	**1**	**0**	**0**	**1**	**2**
C	**1**	**0**	**0**	**1**	**2**
D	**1**	**0**	**0**	**1**	**2**
E	**1**	**0**	**3**	**0**	**4**
F	**1**	**0**	**1**	**2**	**4**

5. Compare the models of austenite and martensite.

a) What packing arrangement is used in the austenite structure?

Simple cubic with respect to a given atom.

b) How is the austenite structure altered to yield the martensite structure?

It is distorted; some 90° angles are lost.

c) Compare the number of spheres per unit cell for each structure. How does the density of martensite compare to that of austenite?

Based on the number of atoms per cell; densities are the same. Packing efficiency, however, makes the martensite marginally denser.

d) From what you have learned about these structures, which do you think would be the more flexible low-temperature phase of the wire in Investigation 1? Explain.

The explanations to date have been over-simplified. Students will have a difficult time adequately answering this question and a class discussion would be appropriate in trying to explain this answer. Ultimately, the answer lies in the fact that during the transformation from austenite to martensite there are 24 different ways this may be carried out. This leads to 24 different "variants" within the martensite phase and the ability to re-orient these variants leads to mechanical flexibility. See Appendix B for examples of variants.

INVESTIGATION 2

PURPOSE

To construct portions of extended three-dimensional solids; to identify unit cells and determine the number of atoms in each cell; to determine the coordination number (number of nearest neighbors) in each of several different structures; to relate structure to some physical properties.

INTRODUCTION

A crystalline structure consists of a repeating arrangement of atoms, molecules, or ions. In this experiment we will use the ICE Solid-State Model Kit. You will study some of the ways that the building blocks of matter can be packed to form some typical crystals as well as two specific arrangements that are unique to the wire that you researched in Investigation 1.

A useful way of describing the basic pattern of an extended structure is to imagine a three-dimensional, six-sided figure having parallel faces that encloses only a portion of the interior of the extended structure. A cube is the simplest of these "unit cells" and will be used in this investigation. If the proper unit cell is selected, then when it is moved along any of its edges by a distance equal to the length of that edge, it should generate an identical unit cell. Repetition of this process will generate the entire structure of the crystal.

PROCEDURE

PART 1: General Considerations.

Determine how many larger spheres you can pack around a marked sphere in the same plane. It may be easier to hold the spheres in the palm of your hand while doing this. If all the spheres are the same size does the coordination number depend on size? What if the central sphere is smaller? Larger ? Check your predictions.

PART 2:

This part of the investigation requires that teams work together, using the Solid State Model Kits or following alternate procedures outlined by your instructor. Each team will build one of the following structures. All teams will then compare and contrast their structures and together answer questions.

Team A: Following the instructions in the kit, assemble the Simple Cubic Structure.
Team B: Following the instructions in the kit, assemble the Body Centered Cubic Structure.
Team C: Following the instructions in the kit, assemble the CsCl Structure with the Cl atoms at the corners.
Team D: Following the instructions in the kit, assemble the CsCl Structure with the Cs atoms at the corners.
Team E: Following the instructions in the kit, assemble the Austenite Structure.
Team F: Following the instructions in the kit, assemble the Martensite Structure.

FOLLOW-UP QUESTIONS

1. For each structure complete the table below, indicating HOW MANY SPHERES LIE WITH THEIR CENTERS AT THE __________________OF THE UNIT CELL.

Structure	Corners	Edges	Faces	Inside
A				
B				
C				
D				
E				
F				

2. With how many other unit cells are the spheres at the ____________of the cell shared?
   a) corners_______cells   b) edges______cells   c) faces______cells

3. What fraction of each sphere lying with their center at the _____is part of that cell?
   a) corner ______   b) edge ______   c) face _______

4. For each structure complete the table below, indicating HOW MANY TOTAL SPHERES OCCUPY EACH SITE.

Structure	Corners	Edges	Faces	Inside	Total in Cell
A					
B					
C					
D					
E					
F					

5. Compare the models of austenite and martensite.

   a) What packing arrangement is used in the austenite structure?

   b) How is the austenite structure altered to yield the martensite structure?

   c) Compare the number of spheres per unit cell for each structure. How does the density of martensite compare to that of austenite?

   d) From what you have learned about these structures, which do you think would be the more flexible low temperature phase of the wire in Investigation 1? Explain.

PURPOSE

To allow students to reshape a piece of memory metal and to further stimulate them to think about the changes taking place at the atomic level that allow this to happen.

METHOD

Questions may arise as to how the memory was imparted to the metal in the first place or whether or not the memory may be altered. It should first be noted that if the transition between phases were represented by the thermochemical equation below:

$$\text{Martensite} \quad + \quad \text{energy} \quad \rightarrow \quad \text{Austenite}$$

the energy required would be in the neighborhood of only a few kJ/mol. The Ni and Ti atoms within one of the many crystalline regions (called grains) within a sample of memory metal in the austenite phase are almost perfectly arranged with a few imperfections here and there. (A piece of galvanized metal clearly shows such crystals, and the BB board discussed earlier shows defects within the crystal) These defects in the austenite phase along with the grain boundaries, another kind of defect, are responsible for giving the austenite its “remembered” shape. To give the metal a new shape it is necessary to create a new set of defects that will in turn force the metal to return to this new shape upon mild heating through the martensite-to-austenite phase change. This new set of defects can only be obtained by heating the metal sample to approximately 500^{o}C while it is secured in the new shape. This large amount of thermal energy allows atoms to relax into lower energy positions, thus creating a new set of defects.

The procedure simply involves having the students bend the wire into a new shape: they hold it at its ends and heat the center in the flame of a candle. The wire resists bending until it reaches the temperature of the flame at which point it yields and can be bent into a V-shape.

MATERIALS

NiTi wire from kit or supplier listed in the Appendix (3 inches of wire per group)

Candle and matches

Hot water bath like the one used in Investigation 1

PROCEDURE

a. Holding the wire at its ends (CAUTION, the ends may be sharp!), bend it into a V-shape and place the middle of the V into the center of a candle flame.
b. After cooling by blowing on the wire, Investigation 1 may be repeated with the deformed wire.
c. Holding the wire at its ends (CAUTION, the ends may be sharp!), try straightening it back into its original, linear shape as you place the middle of the wire into the center of a candle flame.

ANSWERS TO FOLLOW-UP QUESTONS

1. Why can't you use hot water to retrain the wire to "remember" a new shape?

   The energy required for the martensite-to-austenite transition is far lower than that required to "move" defects in the structure.

2. Describe any similarities or differences in the wire from its original condition after heating it in the flame.

   Student responses will vary. They may notice slightly slower response times after annealing several times. Discoloration may also be observed.

EXTENSIONS

If a metal frame of some type is available, it is possible to produce more complicated shapes (even your name) with the memory metal. This would require that you have access to some sort of metal rack or basket capable of withstanding the annealing temperatures and a heat source capable of providing those temperatures. The kiln in the art department would certainly be adequate; or perhaps the physics department has a muffle furnace that would work as well. The wire would have to be secured to the template and the entire assembly placed in the heat source for a period of about 15 minutes, removed, and allowed to cool. Longer heating may destroy the memory feature of the wire. Annealing produces the "remembered" shape by creating a new set of defects. Prolonged heating, however, will destroy the shape memory feature that relies on these defects. When the atoms surrounding the defects are supplied with sufficient energy, they relax into an almost defect-free structure.

INVESTIGATION 3

PURPOSE

To reflect upon Investigation 1 and to discover how a new shape may be given to the NiTi wire. In addition, as you carry out this experiment, be thinking about the results of Investigation 2 and how those results can explain the "new learning" the wire experienced in this investigation.

PROCEDURE

a. Holding the wire at its ends (CAUTION, the ends may be sharp!), try bending it into a V-shape as you place the middle of the wire into the center of a candle flame.
b. After cooling by blowing on the wire, Investigation 1 may be repeated with the deformed wire.
c. Holding the wire at its ends (CAUTION, the ends may be sharp!), try straightening it back into its original, linear shape as you place the middle of the wire into the center of a candle flame.

FOLLOW-UP QUESTIONS

1. Why can't you use hot water to retrain the wire to "remember" a new shape?

2. Describe any similarities or differences in the wire from its original condition after heating it in the flame.

PURPOSE

To investigate some of the mechanical properties of the two NiTi phases and to try to relate these properties to the structure of each phase.

METHOD

So far, the phase transformation of NiTi has been accomplished by temperature cycling, but straining the material by applying stress also can initiate these transitions. Martensite is favored under high applied stress because it is marginally denser than austenite, a fact that was brought out in Investigation 2. Therefore, if we consider the composition of the alloy to be an equilibrium between these two phases, LeChatelier’s Principle should govern the behavior of the equilibrium under applied stress. LeChatelier's Principle predicts that an increase in pressure favors the denser phase. A bending motion applied to a metal rod would result in some atoms being compressed and some pulled apart. A force per unit area, or pressure, is exerted on the atoms in the region of the compression. As a result, this increase in pressure should result in a transition to the more dense, martensite phase, as predicted by LeChatelier’s Principle.

An analogy would be to consider the phase diagram for water. The line that separates the liquid and gaseous phases exhibits a positive slope, and any point on that line represents an equilibrium between the two phases. Therefore, at any point on this line, if, at constant temperature, the pressure were to increase, the equilibrium would shift toward the liquid or denser phase. Releasing the stress will allow the reverse transformation to occur.

The two NiTi structures display markedly different mechanical properties. The cubic crystal structure of austenite results in its being relatively hard and inflexible, whereas the less symmetric structure of martensite with the ability to reorient variants in its structure, displays a greater flexibility and malleability. NiTi rods can illustrate the different mechanical properties of the two structures. Consider the idealized figure below.

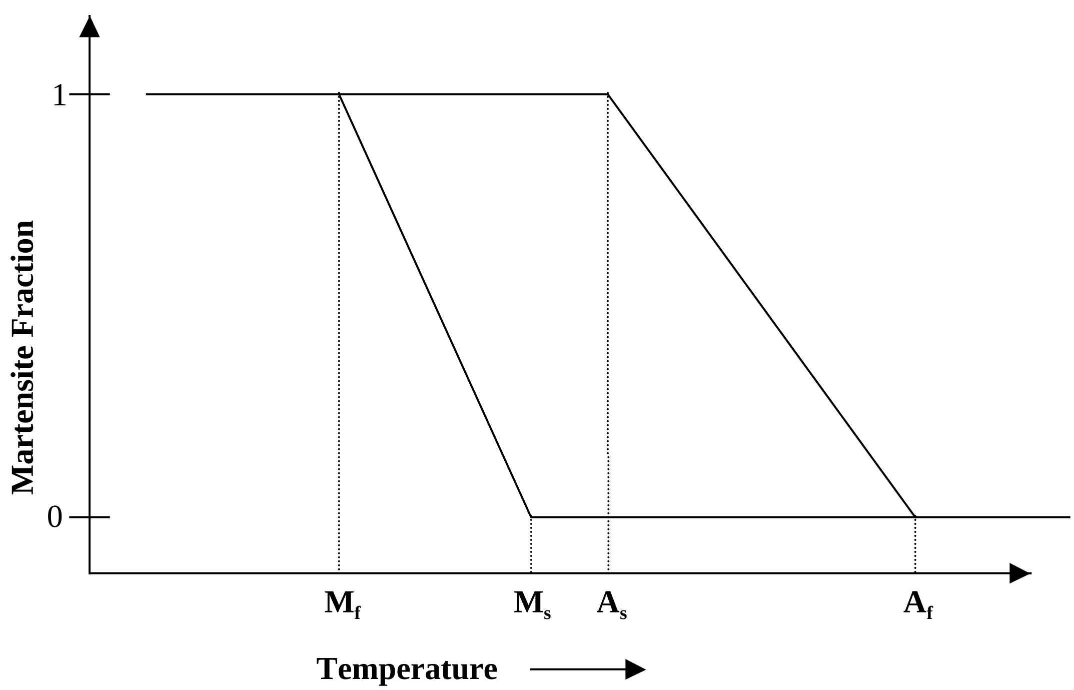


Figure 3: Taken from http//www.sma-inc.com/ttrmeas.html#dsc Smart Sheet #11:
There are four characteristic temperatures defining the martensite transformation. Starting at a high temperature in which the NiTi sample is exclusively in the austenite structure, the martensite start temperature, $\mathbf{M_s}$, is the temperature at which martensite first appears in the austenite. The transformation proceeds with further cooling and is complete at the martensite finish temperature, $\mathbf{M_f}$. Below $\mathbf{M_f}$, the entire structure is in the martensite phase, and a specimen typically consists of many regions each containing a different variant of martensite. The boundaries between the variants are mobile under small applied stresses. With heating, the austenite start temperature, $\mathbf{A_s}$, is the temperature at which austenite first appears in the martensite. With further heating, the sample continues its transformation into austenite, and this transformation is complete at the austenite finish temperature, $\mathbf{A_f}$. Above $\mathbf{A_f}$ the specimen is in the original undistorted state.

The samples used in this activity can be made to exist in either of the two phases at room temperature by carefully adjusting the composition of the rods. The Ni/Ti ratio is nominally 1:1, but the ratio may be modified by a few percent to control the temperatures at which the phase transformations occur.

MATERIALS

NiTi rods-one of each type per group (See supplier information in the Appendix)

hot water bath

liquid nitrogen (local sources include dermatologists, welders, universities, hospitals, research institutions). An alternative would be to use a dry ice and acetone bath.

tongs

gloves

heat gun (hair dryer)

PROCEDURE

Part I

a. Try bending each of the two rods provided by your instructor into a V-shape. Identify the rod that is inflexible. **Note: Caution students that the thickness of the rod prevents it from being bent into a complete V-shape.**

b. Cool the less flexible rod in liquid nitrogen or an alternative cooling bath (CAUTION), as directed by your instructor. Use tongs and gloves.

c. Remove the rod from the liquid nitrogen or alternative cooling bath. Then, while wearing gloves, bend the rod into a V-shape.

d. Allow the rod to warm back to room temperature.

Part II

e. Warm the flexible rod in water that has been heated to near the boiling point. Remove with tongs, and, while wearing gloves, try to bend it.

f. Allow the rod to cool and then try to bend it again.

Part III

g. Using the appropriate methods, return both rods to their original linear shapes.

h. Try scratching each rod with the other. **Note: Tell the students to expect a light scratch, not a gouge.**

ANSWERS TO FOLLOW-UP QUESTIONS

1. State your observations for step (a) of the procedure.

   One-rod bends easily, the other does not.

2. State your observations for step (d) of the procedure.

   The bent rod returns to its original shape when warmed to room temperature.

3. State your observations for step (e).

   The more flexible rod becomes difficult to bend.

4. State your observations for step (f).

   The rod is inflexible when warm and flexible when it returns to room temperature.

5. State your observations for step (g).

   Student responses. Need to heat the bent, low temperature rod.

6. State your observations for step (h).

   Austenite scratches martensite.

7. Based upon your observations, which rod was in the low temperature martensite phase and which was in the high temperature austenite phase?

   Flexible-martensite. Inflexible-austenite.

8. a) Which rod was harder than the other?

   Inflexible-austenite.

   b) Is this consistent with your answer to question (5)? Explain.

   Yes, inflexibility and hardness are related, at least, to a certain extent.

9. If you were to make a pair of eye-glass frames that could be easily restored to their original shape if accidentally sat upon:

   a) In which phase would you manufacture them?

Austenite for rigidity and strength.

b) Where would you adjust the transition temperature- above or below room temperature?

Below room temperature to ensure that the austenite phase is dominant at room temperature.

c) If your glasses were bent, what, if anything, would you do to return them to their original shape? Explain.

Nothing. The applied stress allowed them to transform into martensite and become flexible. Relieving the stress will allow them to return to their original shape.

d) What if they didn't fit exactly right? What would you need to do to adjust them?

Heat them to candle flame temperature. Reshape them, then let them cool to room temperature.

INVESTIGATION 4

PURPOSE

To investigate some of the mechanical properties of the two phases of the NiTi alloy and to relate these properties to the structures of these phases.

PROCEDURE

Part I

a. Try gently bending each of the two rods provided by your instructor into a V-shape. Identify the rod that is inflexible.

b. Cool the less flexible rod in liquid nitrogen or an alternative cooling bath (CAUTION), as directed by your instructor. Use tongs and gloves.

c. Remove the rod from the liquid nitrogen or alternative cooling bath. Then, while wearing gloves, bend the rod into a V-shape.

d. Allow the rod to warm back to room temperature.

Part II

e. Warm the flexible rod in water that has been heated to near the boiling point. Remove with tongs, and, while wearing gloves, try to bend it.

f. Allow the rod to cool and then try to bend it again.

Part III

g. Using the appropriate methods, return both rods to their original linear shapes.

h. Try scratching each rod with the other.

FOLLOW-UP QUESTIONS

1. State your observations for step (a) of the procedure.

2. State your observations for step (d) of the procedure.

3. State your observations for step (e).

4. State your observations for step (f).

5. State your observations for step (g).

6. State your observations for step (h).

7. Based upon your observations, which rod was in the low temperature martensite phase and which was in the high temperature austenite phase?

8. a) Which rod was harder than the other?

   b) Is this consistent with your answer to question (5)? Explain.

9. If you were to make a pair of eye-glass frames that could be easily restored to their original shape if accidentally sat upon:

   a) In which phase would you manufacture them?

   b) Where would you adjust the transition temperature- above or below room temperature?

   c) If your glasses were bent, what, if anything, would you do to return them to their original shape? Explain.

   d) What if they didn't fit exactly right? What would you need to do to adjust them?

PURPOSE

To investigate the acoustic properties of the two phases of the NiTi alloy.

METHOD

It is not surprising that the two NiTi phases also exhibit a different "acoustic signature" as well as other physical properties. The propagation of sound is affected by a number of factors but most certainly depends upon structure. The uniform structure of austenite allows sound waves to travel through it readily. In martensite, on the other hand, the boundaries between regions with different orientations of the less symmetric monoclinic structure act to reduce the vibrations and muffle the sound. The net result is a noticeable "ringing" sound when the austenite rod is dropped, compared to a dull "thud" for the martensite.

MATERIALS

NiTi rods (one of each phase per group)	string
hot plate	400 mL beaker
thermometer	ring-stand and ring
meterstick	

PROCEDURE

a. Determine which of the rods is in the martensite phase (recall Investigation 4).

b. Using the rod that you selected in (a), tie one end to a string and suspend it in a beaker of water on a hot plate by tying the other end of the string to a ring on the stand at the appropriate height. After several minutes, remove the rod and drop it on the counter-top from a height of 50 cm. The rod should be held parallel to the counter as it is dropped. Note the nature of the sound that the rod produces (thud, ring, intermediate). Record the temperature of the water.

c. Return the rod to the beaker, and turn on the hot plate at its lowest setting. Remove and test the rod at approximately 10 ^{o}C intervals. Continue until a noticeable change in sound is detected.

d. Repeat the above procedure until the water cools to just above room temperature.

ANSWERS TO FOLLOW-UP QUESTIONS

1. How did you decide which rod was martensite?

Probably by the "bend test" from Investigation 4.

2. Describe the changes in sound produced as the rod was slowly heated.

   The sound progressed from a "thud", through an intermediate sound, to a "ring".

3. Do the sounds produced at each temperature depend upon whether the rod is being heated or cooled?

   It may be difficult for the students to detect this "hysteresis effect", but the phase changes in the two directions do not have the same temperature dependence. The phase change from austenite to martensite occurs over a lower temperature range than that from martensite to austenite. This is simply explained by noting that one soild phase needs to grow within the region of the other. This creates elastic strain in the region surrounding the new crystal growth. which results in a thermodynamic increase in the free energy necessary to continue the growth of the crystal. The overall effect is a displacement of the heating curve to higher temperatures. The thermal history of the rod does then make a difference.

4. How do you account for this observed change in sound?

   See the teacher notes above. Students will have difficulty in answering this question completely. Most will realize it has to do with structure, but will not be able to fully explain just how. This should be a good topic for a class discussion.

INVESTIGATION 5

PURPOSE

To investigate the acoustic properties of the two rods that you used in Investigation 4.

PROCEDURE

a. Determine which of the rods is in the martensite phase (recall Investigation 4).

b. Using the rod that you selected in (a), tie one end to a string and suspend it in a beaker of water on a hot plate by tying the other end of the string to a ring on the stand at the appropriate height. After several minutes, remove the rod and drop it on the counter-top from a height of 50 cm. The rod should be held parallel to the counter as it is dropped. Note the nature of the sound that the rod produces (thud, ring, intermediate). Record the temperature of the water.

c. Return the rod to the beaker, and turn on the hot plate at its lowest setting. Remove and test the rod at approximately 10 ^{o}C intervals. Continue until a noticeable change in sound is detected.

d. Repeat the above procedure until the water cools to just above room temperature.

FOLLOW-UP QUESTIONS

1. How did you decide which rod was martensite?

2. Describe the changes in sound produced as the rod was slowly heated.

3. Do the sounds produced at each temperature depend upon whether the rod is being heated or cooled?

4. How do you account for this observed change in sound?

PROBLEM

Determine the Transformation Temperature for a sample of a shape memory metal.

METHOD

The preceding investigations should have given your students a good understanding of what memory metals are and basically how they "work". As they did the investigations, they may have thought about the conditions that caused these phase changes to take place. Pose the following question: "What is the transition temperature range for your sample of NiTi?" Say very little in the way of how they should proceed, but the following provides an outline of procedures that might be used.

A.
1. Using a thermometer clamp or 1-hole stopper, suspend a thermometer in a 400 mL beaker that is 2/3 full of water, and set the beaker atop a hot plate.
2. Bend a piece of NiTi wire and suspend it from the clamp that is holding the thermometer in the water bath. Take care that the bend in the wire and bulb of the thermometer are next to one another.
3. With constant stirring, slowly warm the water and note the temperature at which the wire returns to its original shape.

B. Utilize the same procedure as Investigation 5.

C. Hang a weight on the wire and monitor its deformation and shape recovery simultaneously as the material is cooled and heated through the transformation range. The idealized figure below shows the elongation and contraction of shape memory wire under tensile loading as the temperature is lowered and then subsequently raised.

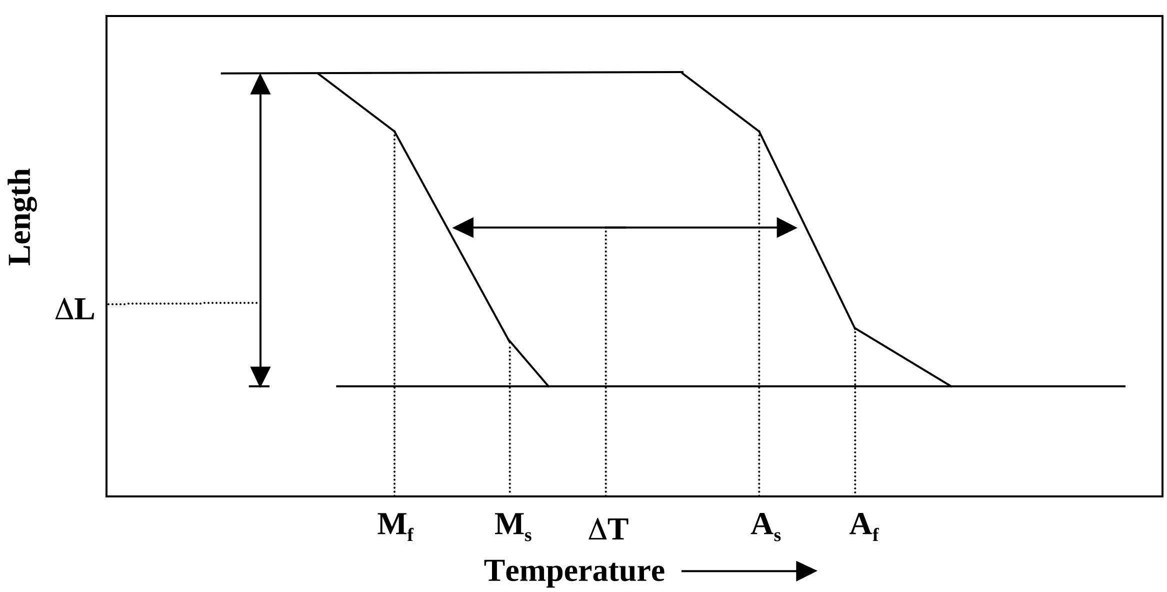


Figure 4: From "Shape Memory Effect" at
http://www.aem.umn.edu/people/others/hane/shape.memory.html

EXPERIMENT 1

PROBLEM

Determine the Transformation Temperature (TTR) for your sample of shape memory metal.

PROCEDURE

Think about the investigations you have worked on in this unit and use what you have learned to devise your own procedure. There are many ways of doing this. You should consider the scientific method as you proceed to help you formulate your thoughts. **Be sure that your procedure has been approved by your instructor before you begin.**

DATA

Dependent upon procedure.

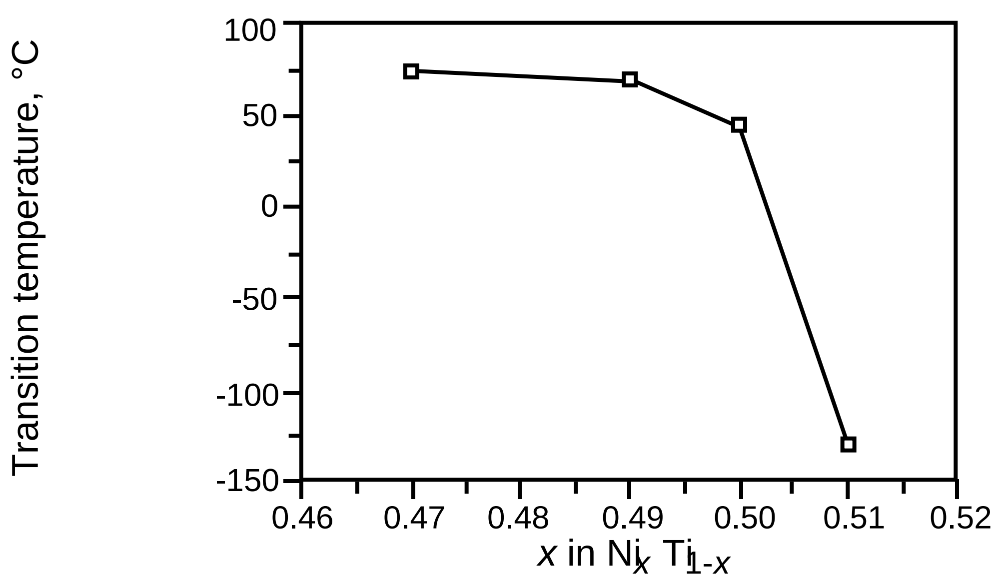
ANALYSIS

CONCLUSION

TTR

EXTENSIONS

Based upon the graph below, estimate the composition of your sample.



Suggest some possible uses of shape memory metals; don't just list those that you know already exist, but also think about some that may not yet exist, but would be really useful if they did.

Do TTR's change if the sample is repeatedly deformed. If so, how? Why?

How quickly does the shape change as a function of temperature?

Memory Metal Review Questions

1. One of the problems with syringes used in some chemistry experiments is that the metal plunger can bend, making the expensive syringe useless. To eliminate this problem, a company has recently produced a syringe whose plunger is made from memory metal, NiTi. Recall the equilibrium for this material:

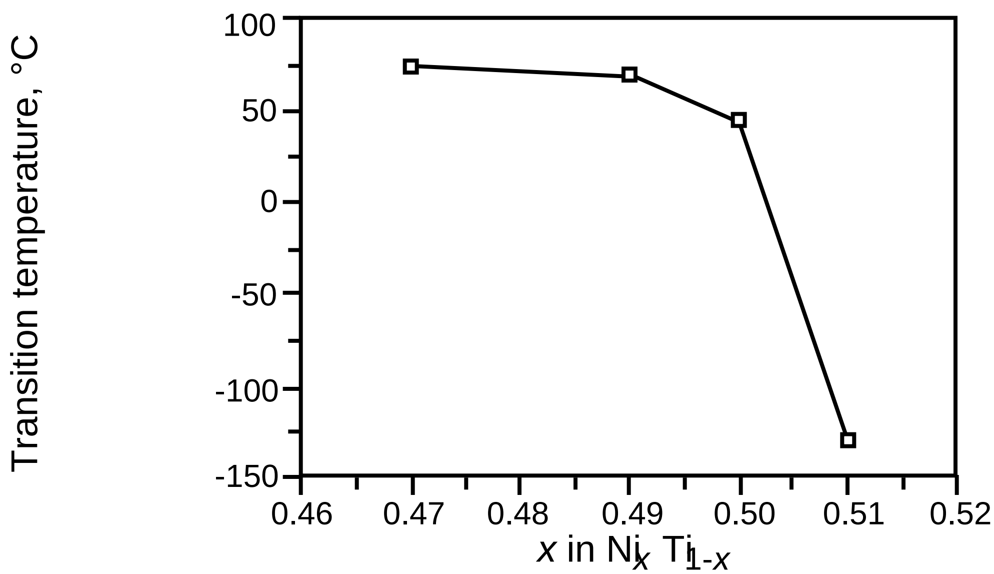
   heat + NiTi martensite ⇐⇒ NiTi austenite
   more dense — less dense

   Based on temperature and/or pressure effects associated with this equilibrium, design such a plunger: Specifically, how is its operation connected to the equilibrium, and what instructions, if any, would you need to give the purchaser?

   The plunger should be in the high temperature phase (austenite) because you want the plunger to be rigid and hard so that it doesn't bend when pressure is applied to it. As you apply pressure the equilibrium may shift towards the denser martensite phase. If it does bend under applied pressure, you can straighten it out by heating it up.

2. Sarah Mason's recently published mystery thriller, "Dying Breath," describes a knife that could be fashioned from memory metal. The following graph shows the transition temperature of the phase change of memory metal as a function of its composition, i.e., x in the formula Ni_xTi_{1-x}.

The Effect of Ni Concentration on the Transition Temperature



This figure was adapted from *Teaching General Chemistry: A Material Science Companion*. It is a compilation of data by several researchers, who measured the composition and transition temperatures by different methods.

a. If the villain desires the knife to be in the low-temperature phase at room temperature (about 25°C), select a value of x that will produce this result and explain your choice.

Any x value that corresponds to a transition temperature above 25°C. If you want the knife to be in the low-temperature, more flexible phase at 25°C, then the transition temperature must be above room temperature. A value for x less than or equal to 0.50 would work.

b. The villain has designed the knife's initial shape to leave an unusual imprint when it is used for the crime. The knife is subsequently to be bent into a different shape at room temperature, so that it appears that the knife could not have caused the imprint. Would hot water (50°C) or candle flame temperature (500°C) have been required to give the knife its initial, unusual shape and does this temperature correspond to a phase change of the Ni and Ti atoms; or to movement of defects in the alloy and why?

Candle flame temperature (500°C) is required to give the knife its initial, unusual shape, because it needs to be at a temperature high enough to move the defects in the alloy. If the defects are not changed, the knife will not remember its new shape.

c. If you were the investigator assigned to the case, how would you change the temperature to cause the knife to recover its initial, unusual shape, and does this temperature correspond to a phase change of the Ni and Ti atoms; or to movement of defects in the alloy and why?

The investigator would use hot water or a heat gun (hair dryer) to cause the knife to recover its unusual shape. This temperature corresponds to a phase change of the Ni and Ti atoms. If the defects are changed, the knife will not return to its original shape, and it would not match up

with the wound.

3. When a NiTi rod is heated into its symmetric high temperature se from the less
symmetric structure of its low temperature phase which of the owing is true?

a. it becomes more flexible and thuds when dropped
b. it becomes more flexible and rings when dropped
c. it becomes more rigid and thuds when dropped
d. it becomes more rigid and rings when dropped

4. A sculpture made of memory metal is found to change its shape when electricity is
passed through it because

a. it is cooled into the low-temperature martensite phase
b. it is heated into the high-temperature austenite phase
c. passing electricity through the structure changes its atomic composition
d. passing electricity through the structure removes electrons from the structure

5. Which of the following phase changes will release heat?

a. melting an alloy
b. transforming NiTi memory metal from the phase that thuds to the phase that rings when dropped
c. subliming dry ice into the gas phase
d. condensing gaseous water into liquid water

Memory Metal Review Questions

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   heat + NiTi martensite ←→ NiTi austenite
   more dense less dense

   Based on temperature and/or pressure effects associated with this equilibrium, design such a plunger: Specifically, how is its operation connected to the equilibrium, and what instructions, if any, would you need to give the purchaser?

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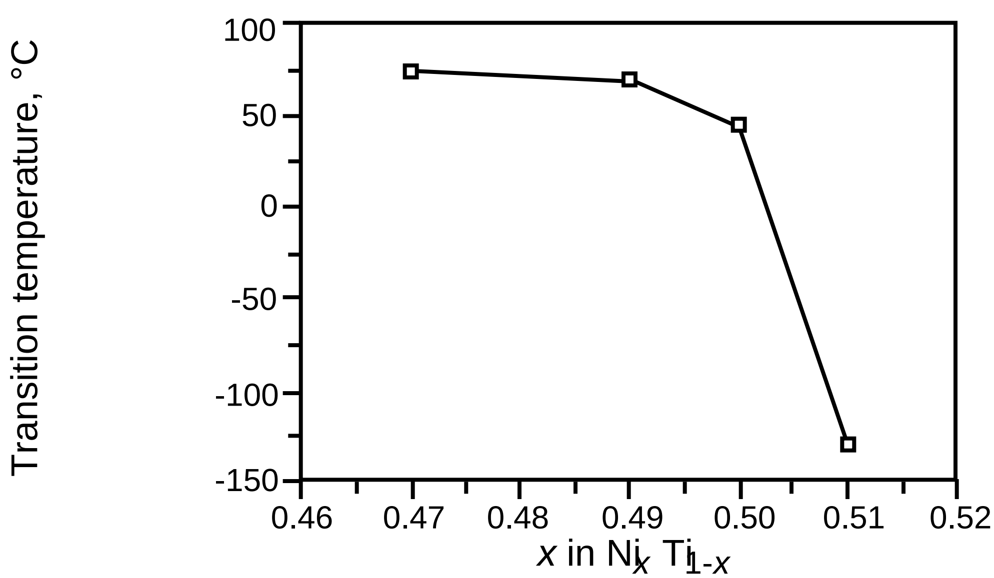

This figure was adapted from *Teaching General Chemistry: A Material Science Companion*. It is a compilation of data by several researchers, who measured the composition and transition temperatures by different methods.

a. If the villain desires the knife to be in the low-temperature phase at room temperature (about 25°C), select a value of x that will produce this result and explain your choice.

b. The villain has designed the knife's initial shape to leave an unusual imprint when it is used for the crime. The knife is subsequently to be bent into a different shape at room temperature, so that it appears that the knife could not have caused the imprint. Would hot water (50°C) or candle flame temperature (500°C) have been required to give the knife its initial, unusual shape and does this temperature correspond to a phase change of the Ni and Ti atoms; or to movement of defects in the alloy and why?

c. If you were the investigator assigned to the case, how would you change the temperature to cause the knife to recover its initial, unusual shape, and does this temperature correspond to a phase change of the Ni and Ti atoms; or to movement of defects in the alloy and why?

3. When a NiTi rod is heated into its symmetric high temperature ›e from the less
symmetric structure of its low temperature phase which of the ›wing is true?

a. it becomes more flexible and thuds when dropped
b. it becomes more flexible and rings when dropped
c. it becomes more rigid and thuds when dropped
d. it becomes more rigid and rings when dropped

4. A sculpture made of memory metal is found to change its shape when electricity is passed through it because

a. it is cooled into the low-temperature martensite phase
b. it is heated into the high-temperature austenite phase
c. passing electricity through the structure changes its atomic composition
d. passing electricity through the structure removes electrons from the structure

5. Which of the following phase changes will release heat?

a. melting an alloy
b. transforming NiTi memory metal from the phase that thuds to the phase that rings when dropped
c. subliming dry ice into the gas phase
d. condensing gaseous water into liquid water

Memory Metal Assessment

Teacher's Guide

Name ___________________

Date __________ Hour _____

Matching

Match the word with the best definition.

__**G**__	1. austenite	a. a pattern that can be shifted repeatedly to create the entire structure of atoms in a crystal
__**H**__	2. martensite	b. a solid solution composed of two or more metals
__**I**__	3. transition temperature	c. alloy containing nearly equal amounts of nickel and titanium
__**C**__	4. Nitinol	d. a physical state of matter
__**B**__	5. alloy	e. a type of unit cell
__**F**__	6. smart material	f. a substance that can respond to stimuli in its environment
__**J**__	7. density	g. high temperature phase
__**A**__	8. unit cell	h. low temperature phase
__**K**__	9. coordination number	i. the temperature at which a phase transformation occurs
__**E**__	10. body-centered cubic	j. mass per unit volume
__**D**__	11. phase	k. number of nearest neighbors
__**L**__	12. LeChatelier's Principle	l. when a system at equilibrium experiences a stress, the equilibrium shifts partially to relieve that stress partially
		m. the temperature at which martensite melts

Multiple Choice

Choose the best answer.

__**D**___ 13. In the high-temperature phase of NiTi, the coordination numbers of the Ni and Ti are
a. 6 for Ni and 6 for Ti
b. 6 for Ni and 8 for Ti
c. 8 for Ni and 6 for Ti
d. 8 for Ni and 8 for Ti

__**D**___ 14. What technique lets us determine the atomic positions in NiTi memory metal both before and after the solid has undergone its phase change?
a. spectroscopy with visible light
b. measurement of specific heat
c. electrical resistivity
d. x-ray diffraction

__**B**___ 15. Austenite exhibits which characteristic?
a. less symmetrical than martensite
b. more rigid than martensite
c. more flexible than martensite
d. both a and c

__**B**___ 16. At room temperature Nitinol can exist in either of two structures, which are dependent upon
a. the mass of the sample.
b. the exact ratio of Ni to Ti.
c. the length of the sample.
d. the diameter of the rod.

__**A**___ 17. In some phase changes like that of ice and water, there is a noticeable change; however, there is no visible phase change between austenite and martensite because
a. it only occurs at the atomic level.
b. only two atoms exchange places.
c. the structures are the same
d. the temperature is too high
e. no phase change occurs.

Problems

18. Using figure 9.10, what compositions of Ni_xTi_{1-x} would you choose so as to have two samples, one of which is in the low-temperature phase at 0 °C, with the other in the high temperature phase at this same temperature. How could you tell them apart without chemical analysis?

From the figure, at 0 °C, a sample of Ni_xTi_{1-x} with x = 0.51 would be in the high-temperature phase, whereas a sample with x = 0.49 would be in the low-temperature phase. They could be distinguished by their flexibility, sound, etc.

19. Design a sculpture made of memory metal that will change its shape using electricity. Why can this be done?

Any drawing of a sculpture that has moved will do; show both pictures.

Electricity can be used to heat the sculpture resistively, thereby transforming the memory metal from its low-temperature to its high-temperature shape.

20. When a thin straight wire of NiTi memory metal in the low-temperature phase is bent and placed in a concentrated solution of bromine in wet methanol, it straightens out as it dissolves. Why?

This must be an exothermic reaction, the heat from which can be used to drive the martensite-to-austenite conversion of the unreacted NiTi.

Depending upon when you add this material to your curriculum, you may want to ask students to speculate on the products. Using redox chemistry and knowing that Ni likes to be divalent, Ti tetravalent, and Br diatomic, the formula and balanced reaction is

$$NiTi + 3\ Br_2 \longrightarrow NiBr_2 + TiBr_4$$

The $TiBr_4$ is an assumed product.

21. Since NiTi memory metal is biocompatible, it has been proposed that it could be inserted into arteries to help unclog them. Given that the metal is to be coiled like a spring in one phase and straight in the other, how is the experiment carried out?

A sample could be prepared that is coiled or spring-shaped in the high-temperature form and linear in the low-temperature form. Insert the cold linear sample into the artery, and when it warms to body temperature, it assumes the coiled shape that can help keep the artery open.

22. Why do purely solid-state phase changes like that exhibited by NiTi memory metal often involve enthalpies of only a few kilojoules of energy per mole compared to values like 40 kJ to vaporize a mole of water?

Vaporization of water requires the disruption of strong intermolecular forces (hydrogen bonding) and therefore requires a great deal of energy in order to convert the condensed, liquid phase to the disordered gaseaous phase. A solid-state phase change like that exhibited by NiTi involves only slight shifts in atomic positions and thus much less energy.

Memory Metal Assessment

Name ___________________
Date __________ Hour _____

Matching

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_____	5. alloy	e. a type of unit cell
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		m. the temperature at which martensite melts

Multiple Choice

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APPENDIX A

UNIT CELLS

Crystallography is the study of the structure of crystals; it includes the ways of describing the structure of a crystal, the principles that govern the different types of structures possible, the structures of crystals of specific substances, and the methods by which structures are determined.

A knowledge of crystallography is important in numerous scientific fields, including metallurgy, materials science, ceramics, physics and chemistry. Although each of these fields has its own special requirements, there is a basic core of knowledge common to them all. This consists of the description of the structure in terms of the smallest unit that can be used to represent it and the three-dimensional lattice with which the atom sites may be associated, and (2) the accepted method for determining planes and directions in crystal structures. It is (1) that will be further addressed here.

All crystal structures are periodic arrays of atoms, ions, or molecules, for which an imaginary box, the unit cell, may be constructed. The unit cell is the basic unit of the crystal structure. Consider the array shown in Figure 1 in which circles have been used to represent atoms, ions, or molecules. Three valid unit cells have been outlined that can be used to represent the array. The criterion for a valid unit cell is that if any of the three unit cells is moved along any of its edges by the length of the edge, the entire pattern is reproduced. Note that each unit cell contains one complete circle and that only the shaded portion of the circle lies within the unit cell.

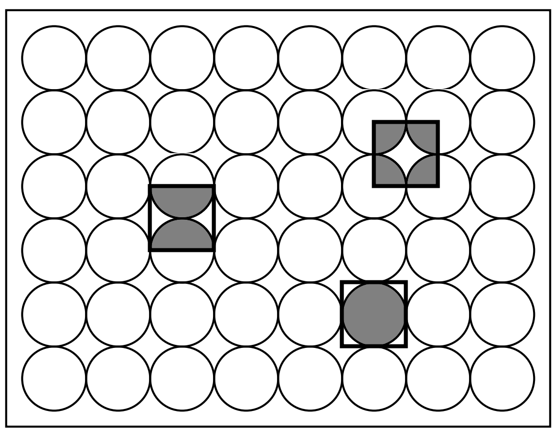


Figure 1: *A Cartesian array of circles with three valid unit cells, each containing a total of one circle.*

There are four properties of unit cells that may be generalized from the figure above.

1. The opposite sides of a unit cell are parallel.

2. Each unit cell contains an integer number of structural units (circles, atoms, ions, etc.)- in this case, one.

3. The unit cells fit together so as to fill space completely and they are identical to one another.

4. The corners of the unit cell can be anywhere.

Figure 2 below contains an oblique array of circles with a valid unit cell. Note that the unit cell selected possesses all four properties of a valid unit cell listed above.

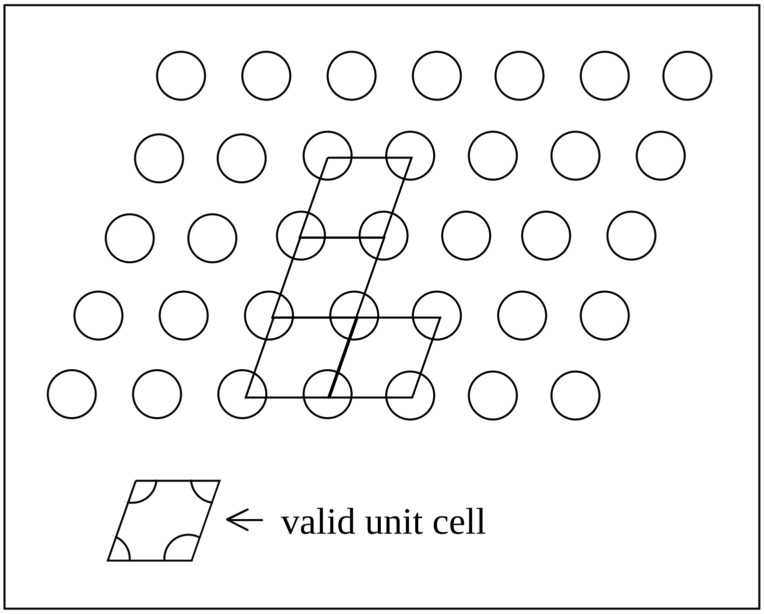


Figure 2: *An oblique array of circles with a valid unit cell.*

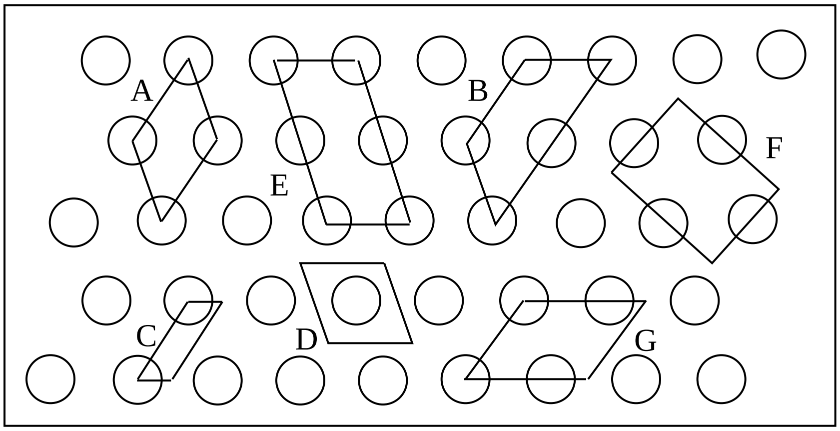


Figure 3. *An oblique array of circles with some valid and invalid unit cells.*

Note that in Figure 3 above, B, C, and G are not valid unit cells. B does not have parallel sides. C does not contain at least one complete structural unit (circle). Neither B, C, nor G fill space completely when shifted while still retaining the same arrangement of circles in each unit cell.

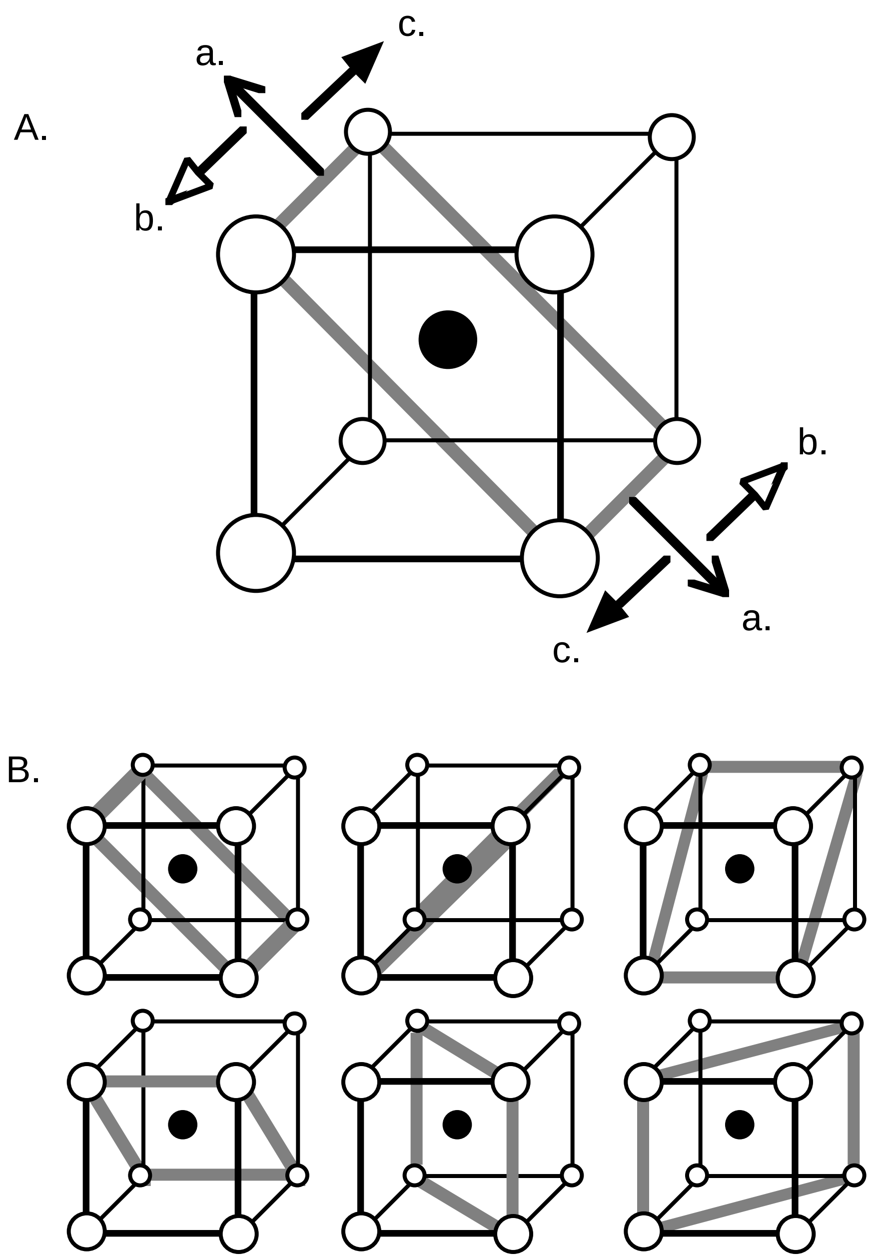
SUGGESTIONS

In order for students to identify a unit cell in the three-dimensional models that they are to construct, a presentation of the material above during the class session prior to Investigation 2 is probably necessary. Making overheads of the enlarged images contained here is also a good idea.

APPENDIX B

As was mentioned in Investigation 2, the flexibility of the martensite phase of NiTi can be explained by the existence of “variants” in the structure and the ability of these variants to shift to relieve the applied stress during deformation. This relaxation of stress by the reorientation of the variants gives this phase of NiTi a property we call flexibility.

The nature of these variants, however, is not obvious. Hopefully the figure below will help to clarify how these variants originate.



During the transition from austenite to martensite the overall movement of atoms in the structure is both a sliding motion and a shearing one. These are relatively sinple movements, but there are 24 different ways in which they may be carried out. Figure **A** above illustrates the two types of shearing that occur. The planes can slide relative to one another in each of two directions (arrows **a**) parallel to the face diagonal. Because this is a sliding motion the atoms are displaced without changing the 90° angles of the plane. The planes can also shear through the simultaneous motion in two directions parallel to the cell edges(either pair of arrows **b** or **c).** Because this is a shearing motion; the plane is being pulled in opposite directions at the top and bottom; the 90° angles of the plane are destroyed. The result from **A** alone is a total of four martensite variants for each plane that passes through a face diagonal in the CsCl structure. A shift up; a shift down; a shear in which the top goes left and the bottom, right; and a shear in which the top goes right and the bottom, left.

Figure **B** shows six equivalent planes that pass through face diagonals in the CsCl structure. Therefore, a total of 6 x 4 = 24 different variants may grow from the planes.