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Chapter 6

Defects in Solids

Extended crystalline solids are not perfect repeating structures. All real materials possess defects or imperfections in the regular repeat pattern of the crystal. Defects may be atoms or ions that are missing from the structure, out of position, or replaced by impurity atoms or ions, for example. Defects can exert tremendous influence over the physical and chemical properties of a material. There is, in fact, an old saying among solid-state scientists: “Solids are like people. It is their defects that make them interesting.”

In this chapter we present examples of the effects of defects on the behavior and properties of solids. These examples are particularly easy to demonstrate, principally those involving mechanical properties of metals and optical properties of salts. In other sections, defects that lead to the remarkable electronic properties of semiconductors (Chapter 8) and superconductors (Chapter 9) are discussed.

Why should a chemist be interested in defects? As has already been mentioned in Chapter 1, materials science is an interdisciplinary field, and its challenges are increasingly being met by teams whose members have backgrounds that span the scientific and engineering disciplines. One of the primary skills that a chemist brings to such a group is an understanding of synthesis. As scientists seek to control the arrangement of matter on a smaller and smaller scale (as evidenced by the direction of developments in microelectronic circuitry in the past half century), the synthetic control on the scale of individual atoms and molecules that chemists bring to the table will play a crucial role in the creation of new materials and devices.

At present a great deal of research is directed toward what are called nanostructured materials *(1)*. These are particles, layers, or filaments with sizes on the order of 1–100 nm (1 nm = 10^{-9} m). The reduction in size to nanostructured materials has resulted in dramatic changes in properties. In many cases this change results because a significant portion of the solid

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now consists of interparticle and intraparticle interfaces, which are normally considered to be types of defects in crystals. Thus, the solutions to many problems in materials science will involve an understanding of synthesis (arrangement of atoms), the control of defects, and the relationship between structure and properties. This chapter will provide a foundation for such an understanding.

Defects in Metals

Metals can be processed by a number of means (e.g., alloying, cold working, heat treating) to give them high strength or other desirable properties. Such treatments typically produce defects within the metals. These defects range in dimensions from a few nanometers to tens or hundreds of micrometers (1 μm $=10^{-6}$ m), and thus are referred to as microstructures. Microstructures play a critical role in determining the mechanical properties of a material.

A useful context for an initial discussion of defects is provided by comparing the macroscopic mechanical properties of metals with those of salts and extended covalent solids. Application of a mechanical stress (such as stretching) to a metal crystal causes the bonds between planes of atoms to stretch and distort. If the displacement of each atom is small (less than halfway to the next equivalent location in the crystal), the strain is elastic, and the planes relax back to their original positions when the stress is removed. The crystal will deform under the influence of the stress and then return to its original shape when the stress is removed (rather like the behavior of a rubber band). If the stress is large enough, the planes of atoms slide (slip) with respect to each other, giving the atoms new neighbors, and the crystal becomes permanently deformed. This deformation that results from the sliding of planes of atoms is known as plastic deformation; it generally does not reverse itself when the stress is removed.

The ductility of metals, particularly those with face-centered cubic structures, markedly differentiates them from ionic and covalent solids. When a mechanical stress is applied to an ionic solid in certain directions, like-charged ions are forced into proximity with one another, as illustrated in Figure 6.1, and the repulsive electrostatic forces lead to fracturing. In covalent solids, mechanical stress breaks highly directional covalent bonds, again causing fracturing.

Two rows of atoms in a metal sliding past one another pass through a series of energetically stable positions, as shown in Figure 6.2. The plane along which sliding occurs is called a slip plane. Sliding is easiest when one close-packed plane (Chapter 5) slides over another, because the distortion required for the atoms to move from one stable position to another is smallest between close-packed planes (*see* Figure 6.3). Fcc [also called cubic close-packed (ccp), *see* Chapter 5] metals have four sets of close-packed planes in a unit cell (*see* Figure 5.9). As a consequence, fcc metals such as Cu, Al, Au, Pb, Ni, and Pt are relatively easily deformed.

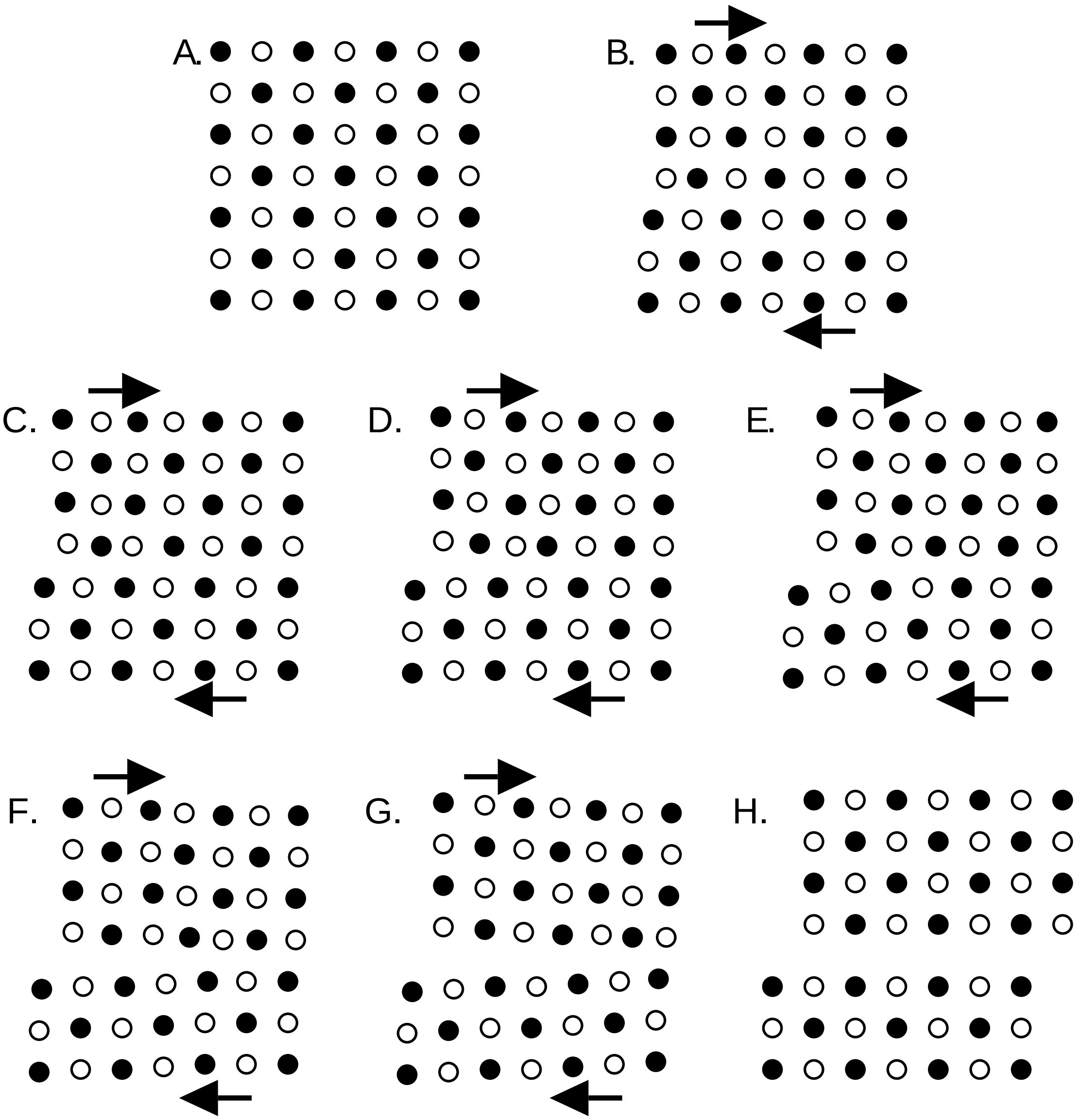

Figure 6.1. The effect of mechanical stress on an ionic crystal; filled and open circles correspond to cations and anions, respectively (or vice-versa). As a shearing force (displaced opposing forces indicated by the arrows) is applied, part of the crystal begins to slide. This sliding brings like charges into close contact, and the repulsion causes the layers to begin to separate. This separation of layers generates cracks and ultimately results in fracture of the crystal. (Compare Figure 6.8, which shows the effect of mechanical stress on a metallic crystal.)

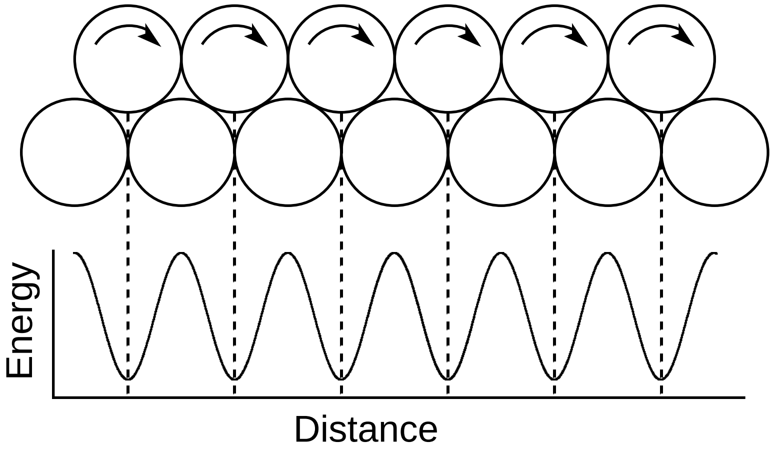

Figure 6.2. Potential energy diagram for sliding one row of spheres (the top row) across another row.

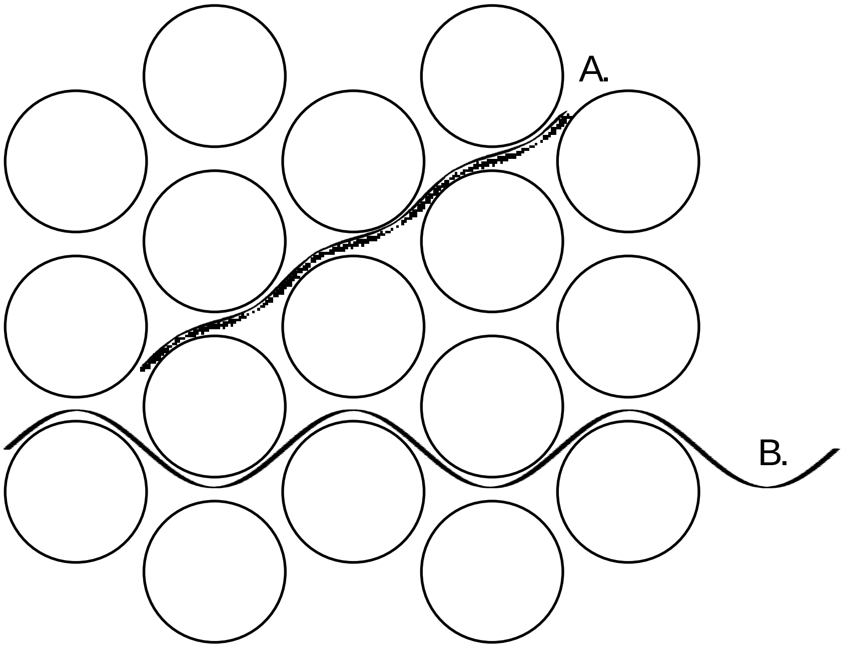

Figure 6.3. Slip plane motion between (A) close-packed planes and (B) non-close-packed planes. Distortion is much greater in the latter case.

Demonstration 6.1. Ductility and Fracturing

Materials

A piece of 10-gauge Cu wire (house wiring from a hardware store)
Solid surface on which to hammer
Wafer or chunk of silicon
Rock salt, sold for water softeners, etc. (or transparent NaCl crystal) (*see* Supplier Information)
Paddle spatula or razor blade
Hammer
Overhead projector and screen
Bubble raft
Goggles and gloves

Procedure

- Flatten a piece of copper wire with a hammer. For viewing by a classroom audience, the change in shape can be seen by comparing the initial and final outlines of the sample when it is placed on an overhead projector.
- Model the deformation using the bubble raft *(2)* (Chapter 5): gently squeeze part of the raft against a wall of the Plexiglas tray by use of the slider. This squeezing will cause it to deform, as shown in Figure 6.4A. Alternatively, use two sliders or glass slides to provide a shearing motion, as shown in Figure 6.4B, which will also deform the packing arrangement.
- While wearing goggles and gloves, flex or hammer a piece of silicon, which will cause it to shatter. **Caution: Silicon wafers, like glass, can shatter and form sharp edges when broken.**
- Fracture a sodium chloride crystal in such a way that natural cleavage planes are revealed: While wearing goggles, place the transparent crystal on an overhead projector and drive a razor blade or a paddle spatula into the plate by striking it with a pencil, screwdriver handle or similar instrument. If the blade is oriented parallel to a face of the NaCl cubic unit cell, a clean fracture occurs; if not, jagged edges are observed *(3, 4)*.

Types of Defects

The mechanism for plastic deformation shown in Figure 6.2 is an oversimplification. When scientists first began to understand that plastic deformation involves the sliding of atomic planes past one another, they assumed that the sliding occurs all at once. Only later did it become apparent that this is not the case. Reliable theoretical calculations showed that if all the bonds between two atomic planes were distorted at the same time, the stress required would be high, roughly 10^6 psi (~10^7 kPa; ~10^5

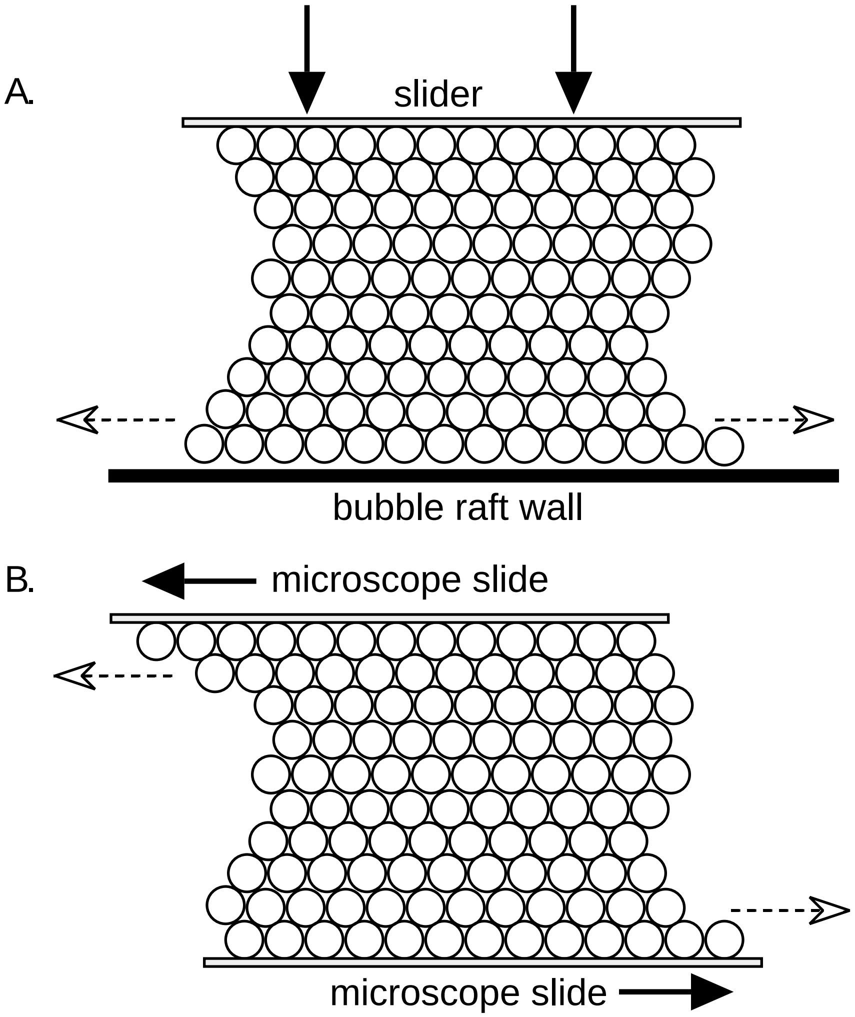

Figure 6.4. Deformations using the bubble raft (A) by squeezing the bubbles against the wall of the tray using the slider or (B) by using the shearing motion of two glass slides.

atm) for high-purity iron *(5)*. These calculations presented a direct conflict with experimental evidence, which showed that the stress required to deform pure metals is actually much lower, on the order of a few tens or hundreds of pounds per square inch. The explanation for the discrepancy lies in a type of one-dimensional crystal defect, the dislocation, first postulated in the 1930s *(6)*.

Defects in crystals are imperfections in the regular repeat pattern of the crystal and may be classified in terms of their dimensionality. A point defect is a defect that occurs at some point in a crystal and involves only one atom or interstitial site in the crystal. Examples include vacancies (atoms missing from the regular array of atoms that forms the crystal) and substitutional impurities (impurity atoms that occupy atom sites in the crystal). Interstitials are also point defects in which atoms occupy the voids between the normal atomic positions. Figure 6.5A illustrates these three types of point defects. Point defects are effectively zero-dimensional defects because they do not extend through the crystal. The concentration of vacancies is governed by chemical equilibria, as illustrated in Chapter 9.

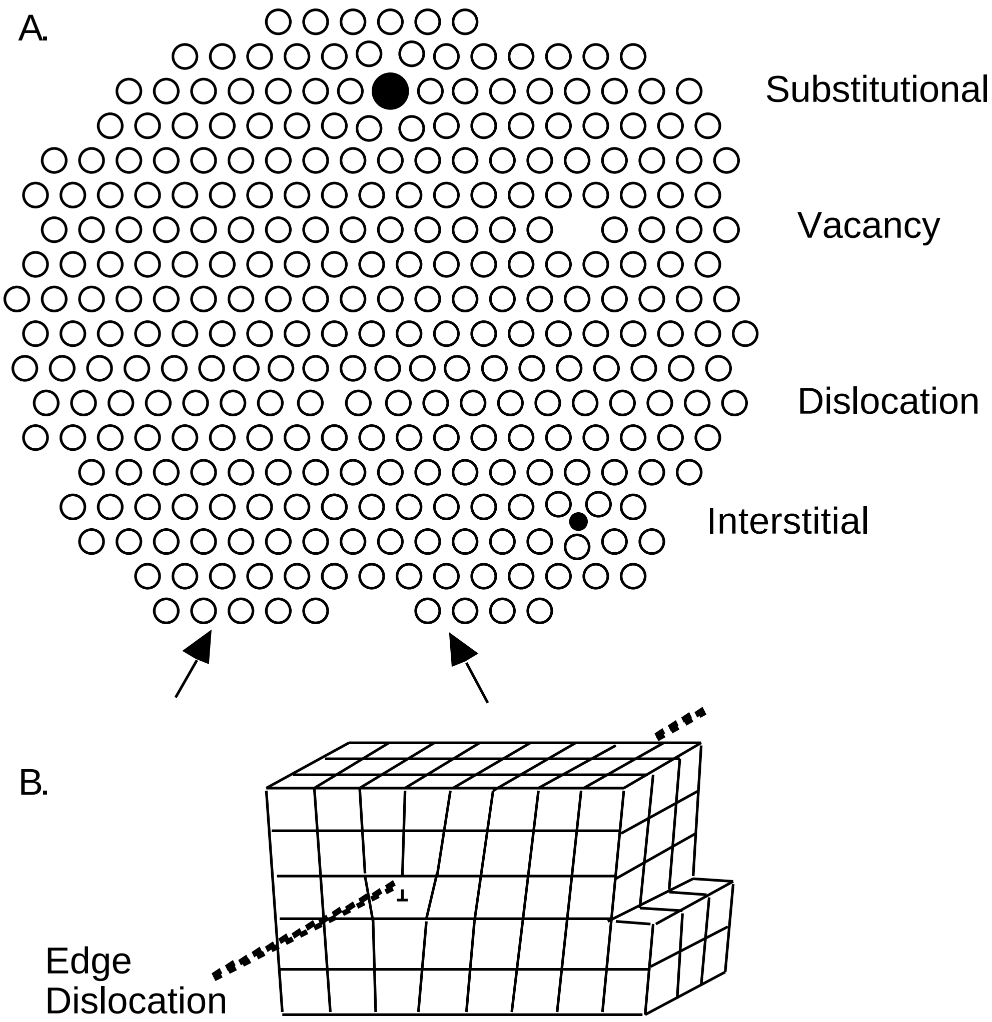

Figure 6.5. A: Crystalline defects include point defects such as the vacancy, interstitial impurities, and substitutional impurities; and extended imperfections such as dislocations. (To more easily see the dislocation, sight along the arrows while viewing from an oblique angle to the page.) B: A schematic representation of a three-dimensional crystal containing an edge dislocation, emphasizing the dislocation as a line defect. designates the core of the dislocation.

A dislocation is a line defect; it runs somewhat like a string through a crystal. A two-dimensional representation of a dislocation is shown in Figure 6.5A in which a crystal is represented by a two-dimensional array of circles similar to the bubble raft. When viewed at an oblique angle along the directions indicated by the arrows, extra lines of atoms are seen in the top half of the figure. These lines of atoms correspond to extra planes of atoms in a three-dimensional crystal. Although the dislocation is recognizable from what appears to be an extra half-plane of atoms inserted into the structure, the line that terminates this extra half-plane is important. This terminating line is located in the core of the edge dislocation; that is, in the highly distorted region at the intersection of the directions indicated by the two arrows at the bottom of Figure 6.5A. The linelike character of a dislocation in a three-dimensional crystal is indicated by the dashed line in Figure 6.5B. Dislocations that define a spiral shape (screw dislocations) also occur (Figure 6.6) and are important in crystal growth mechanisms.

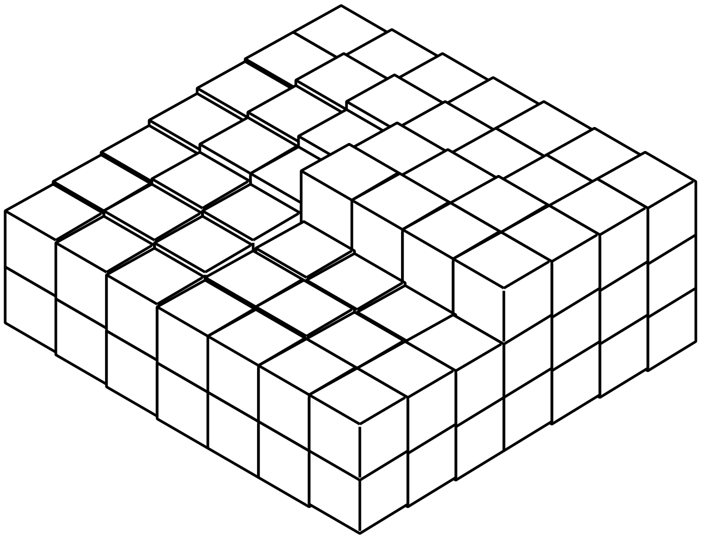

Figure 6.6. A screw dislocation (the blocks represent atoms).

An ear of corn can exhibit edge dislocations. Normally the kernels of corn grow in parallel rows on the ear. On some ears, however, an extra partial row of kernels is inserted between two rows. This defect is illustrated in Figure 6.7.

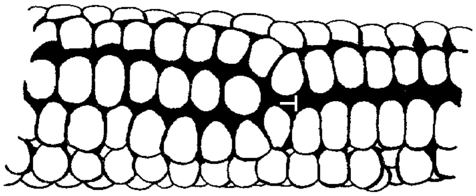

Figure 6.7. A dislocation in an ear of corn. designates the core of the dislocation. (From reference 7.)

The presence of a dislocation relaxes the requirement that entire planes of interatomic bonds must distort and break simultaneously for plastic deformation to occur. Instead, plastic deformation can accompany the motion of a dislocation through a crystal. The motion of a dislocation from left to right through a crystal is illustrated in Figure 6.8.

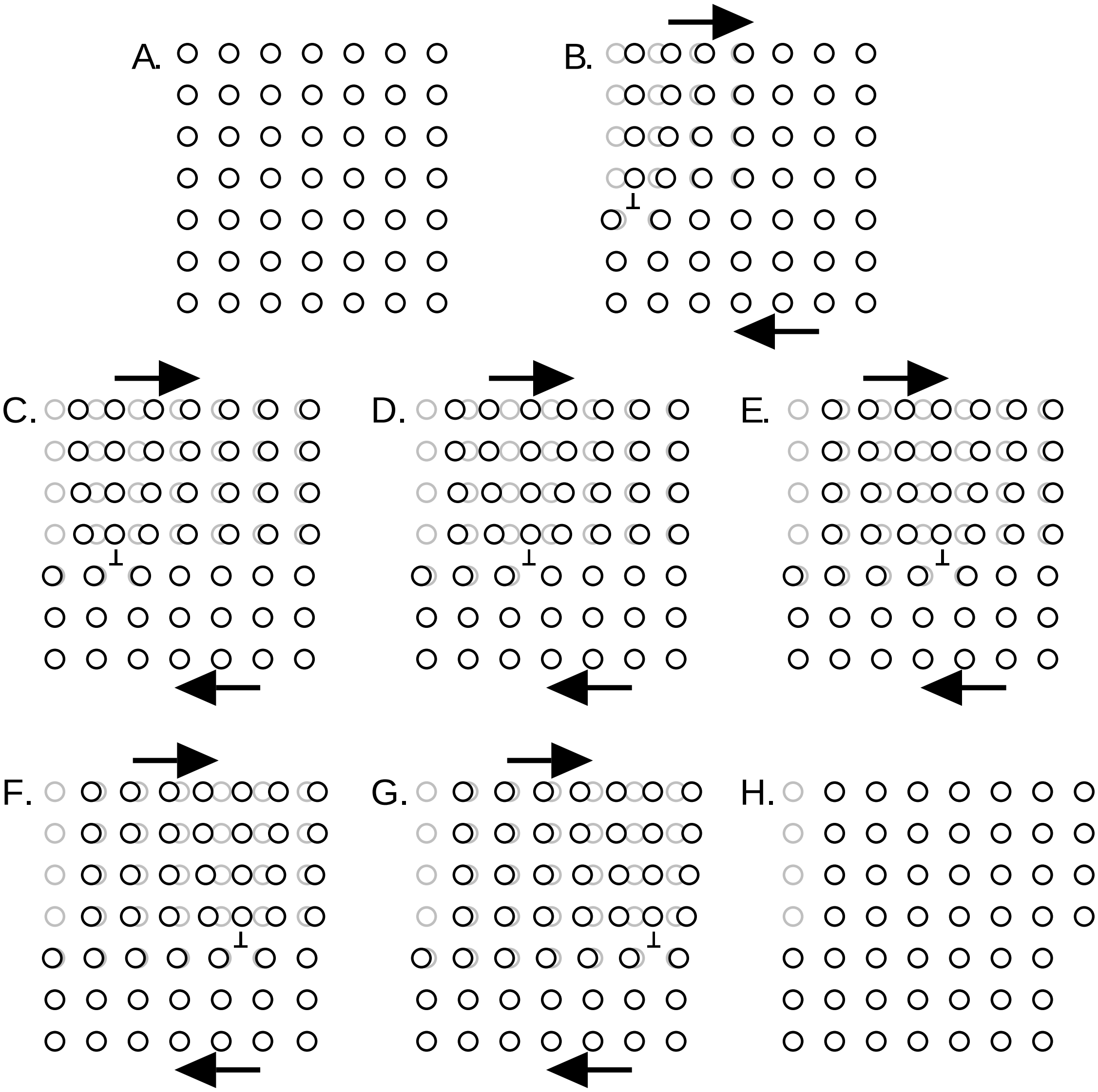

Figure 6.8. When a crystal is subjected to a shearing force (represented by bold arrows), dislocations move along crystallographic slip planes. Atoms above the slip planes shear away from their original neighbors below the slip plane, then bond with a new set of neighbors to restore the internal structure of the crystal. designates the core of the dislocation. As the core moves through the crystal, the identity of the "extra" half plane of atoms changes. Each circle in this figure represents a line of atoms going into the page. Light circles represent the original positions of atoms.

As the dislocation moves and becomes associated with new half-planes, bonds on one side of the dislocation are broken and bonds on the other side are formed. As a consequence of the motion of the dislocation, the top half of the crystal slips to the right by one plane of atoms, yet the entire set of bonds between the planes that slip need not be broken simultaneously. Thus the motion of dislocations provides a low-energy mechanism for plastic deformation that is based on sequential shifts in atomic position. Shifts in atomic positions can occur at the speed of sound in the solid; a demonstration of this effect is described later.

Metals, like other crystalline solids, are usually polycrystalline: they are composed of many small crystals called grains (Figure 6.9). The grains within a metal usually have random orientations with respect to one another and are separated by grain boundaries, which can be regarded as two-dimensional or planar defects. (The surface of a crystal would be another example of a two-dimensional defect.) Every grain boundary is an array of dislocations. Along a grain boundary, the atomic packing is imperfect and the energies of atoms at a grain boundary are higher than those of atoms within the grains. In addition, atoms at grain boundaries are more reactive than those within grains. As a consequence, grain boundaries can often be seen using a microscope to view a polished, then chemically etched, flat metal surface. Etching with an acid removes material from grain boundaries more rapidly because of the higher energy of these sites. The patchy appearance of brass doorknobs is due to this effect, as the acids in perspiration can etch away atoms at the grain boundaries.

Laboratory. An experiment that makes use of the reactivity of alpha-particle-generated defects in polymers to detect radon gas in the home is presented in Experiment 6.

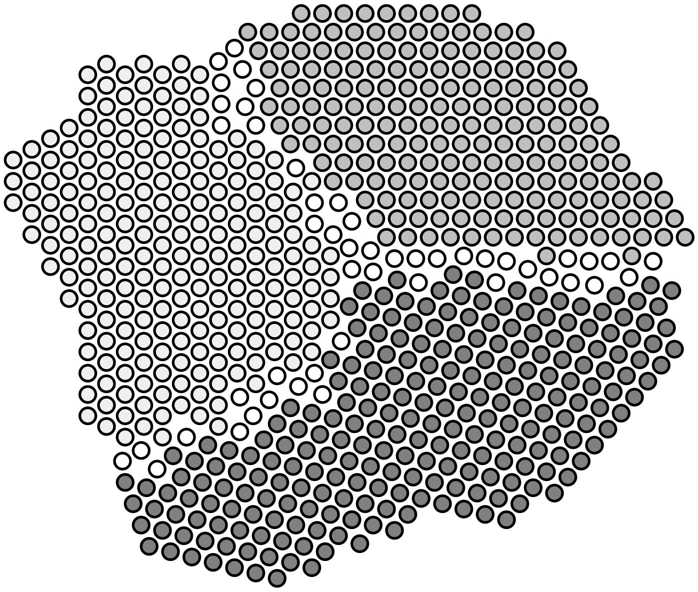

Figure 6.9. A two-dimensional representation of grains in a polycrystalline material; different shading is used for atoms in different grains. Grain boundaries are higher in energy than the interiors of the grains because of less efficient packing.

Plastic or irreversible deformation of crystalline substances occurs primarily by the movement of dislocations within grains. Dislocations are the carriers of deformation, because the passage of a dislocation through a crystal results in the relative motion of one part of a crystal past the other. Mechanical stress can cause dislocations to move through the grain until they are trapped or annihilated. Unlike vacancies, the concentrations of dislocations are not governed by chemical equilibria.

Demonstration 6.2. Dislocations and Other Defects

Materials

Bubble raft setup (*see* Chapter 5)

Procedure

- Prepare a bubble raft as described earlier.
- Pop individual bubbles with a dry finger or pencil tip to make vacancies.
- Stress the bubble raft by compressing or expanding it. Push the slider gently toward one end of the tray to compress the bubble raft, and pull the slider gently in the opposite direction to stretch it. Be careful not to the scratch the bottom of the tray.
- The bubble raft illustrates a variety of dynamic processes. As the bubble raft is forming, it undergoes reconstruction: Grains form, grow, and disappear. Point defects, dislocations, and grain boundaries can all be easily observed in a two-dimensional bubble raft model. However, because the bubble raft is a two-dimensional model, the dislocation looks more like a point (zero-dimensional) defect, and the grain boundary looks like a line (one-dimensional) defect. Many parts of the raft have a very regular hexagonal arrangement of bubbles. However, there are always a number of imperfections. When the raft is stressed, dislocations zip through the grains, moving to the grain boundaries and causing plastic deformation. As the raft is repeatedly expanded and compressed, dislocations are created and annihilated. Vacancies present in the bubble raft do not move as the raft is deformed. Vacancies are frequently annihilated, however, when they interact with dislocations that pass nearby.
- A static model illustrating many of the same concepts of structure and microstructure can be made with a sealed plastic tray of metal BB pellets. A description of the construction of this BB board is currently in press and will be available from ICE Publications, Department of Chemistry, University of Wisconsin—Madison, Madison, WI 53706.

In some metals, the motion of atoms during plastic deformation occurs at the speed of sound in the solid, which is typically on the order of several thousand meters per second or about an order of magnitude faster than the speed of sound in air. Three metals, zinc, indium, and tin, exhibit a snapping sound when rods of the metals are bent at room temperature, due to the dislocation-assisted motion of their atoms. Because the rate at which the atoms move exceeds the speed of sound in air (“Mach 1”), an audible click results.

Demonstration 6.3. Hearing Atoms Move: Breaking the Sound Barrier *(8)*

Materials

Zinc, tin or indium rods (Aldrich, 6-mm diameter; 100 mm long)
Microphone (for large audiences)

Procedure

- Bend any of the rods. A snapping or cracking sound will be heard. The sound can be made audible in a lecture room by placing a microphone near the rod as it is being bent and bringing the microphone's sensitivity to the optimum level (this should be tried in advance).

Variations

- If only short pieces of metal are available, the ends may be placed in metal or rigid plastic tubes to provide the extra leverage needed to bend them.
- Because the ability to move planes of atoms depends on the defects in the solid, which eventually become tangled, and thereby hinder atomic motion (*see* the description of work hardening, later), the experiment cannot be repeated indefinitely. Of the three metals, the zinc rods can be bent the most times without fracture and still produce the snapping sound. (For example, more than 200 students have bent a zinc rod and the sound was still audible.) Both the tin and the indium rods can be heated to about 130 °C for 24 hours in an oven to anneal the samples (*see* later), which will restore the acoustical response to bending.

Work Hardening and Annealing

The movement of dislocations is the key to plastic deformation; therefore, strengthening a metal, that is, increasing its resistance to deformation, requires either eliminating dislocations or preventing them from moving. In practice, removing all of the dislocations from a crystal or growing a crystal without dislocations is practically impossible except for very small crystals. Therefore, metallurgists go to great lengths to find clever ways of pinning dislocations (preventing the motion of dislocations) in order to strengthen metals. Dislocations are often pinned by other defects in the crystal. New dislocations are created during deformation and become pinned by the initial dislocations. The effect cascades as the material is repeatedly deformed, and dislocations collect in tangles in the metal.[1] This buildup of pinned dislocations leads to the hardening of the metal in a process known as work hardening.

An analogy for picturing dislocations and how they produce work hardening is to think of moving a heavy rug across a floor: The rug represents a plane of atoms that is to be moved relative to another plane of atoms, the floor. If the rug were to be lifted slightly at one end and dragged, a great deal of energy would be required for the movement, analogous to the aforementioned calculation of the substantial energy cost associated with breaking all of the bonds between planes of atoms simultaneously in order to move one plane of atoms past the other.

On the other hand, if a wrinkle is present in the rug (Figure 6.10A), it serves as a kind of dislocation in facilitating the movement of the rug: The wrinkle can be pushed to the edge, resulting in a net movement of the entire rug. However, at any given time only a small portion of the rug actually moves; and, consequently, relatively little energy cost is associated with the motion.

Extending the analogy, work hardening is akin to having multiple tangled wrinkles in the rug. As Figure 6.10B shows and experience verifies, if multiple wrinkles meet at various angles, it is difficult to eliminate them: The movement of one wrinkle is “pinned” by another, preventing movement of the rug. Similarly, tangled dislocations make it difficult to move atoms in a metal by creating a kind of “atomic gridlock” and effectively hardening the metal.

A work-hardened metal can be softened again by annealing (heating) at high temperatures, generally at temperatures above one-half of the melting point on the absolute temperature scale. As a piece of metal is heated, the increased thermal vibrations allow atoms to rearrange and go to lower energy states by diffusion, thereby reducing the number of dislocations present.

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[1] The density of dislocations stored in a work-hardened metal can become huge, on the order of 10^6 km of line dislocations per cubic centimeter of material.

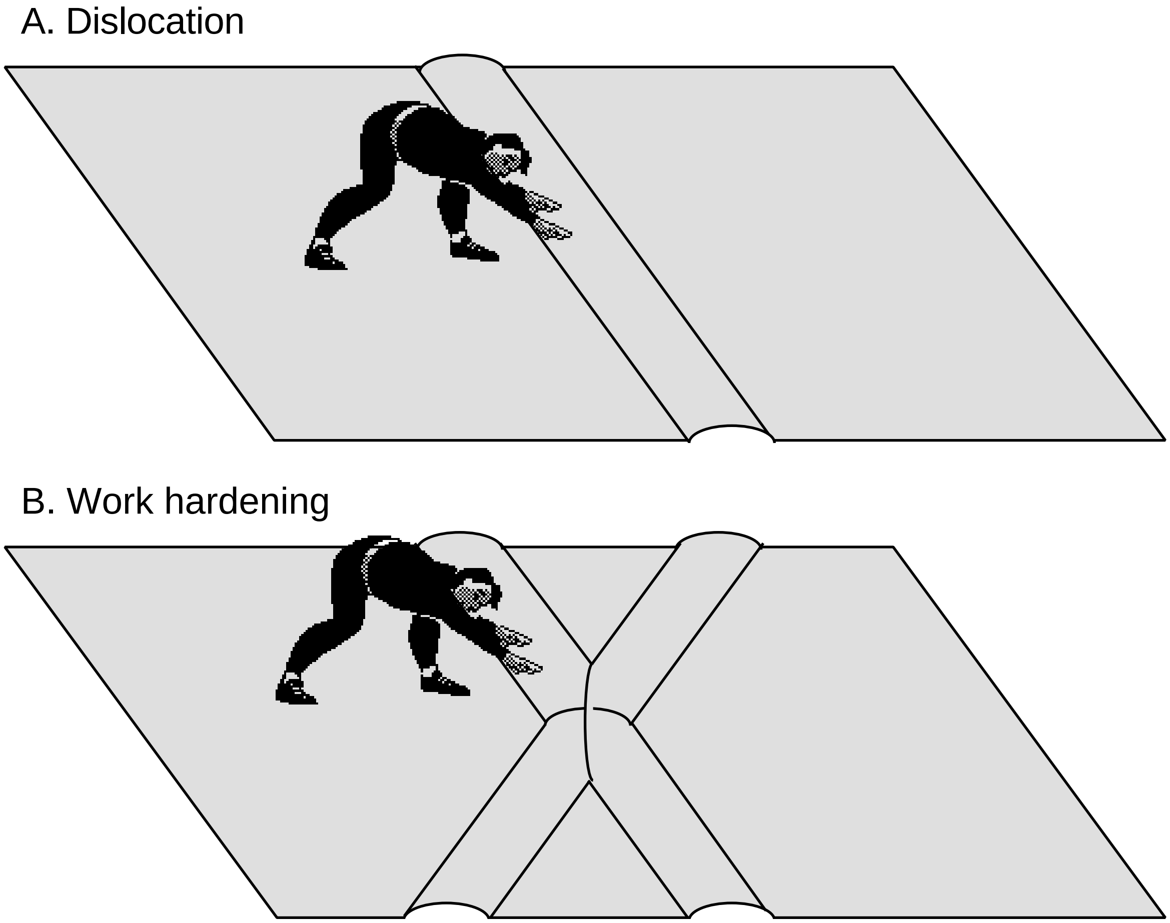

Figure 6.10. A rug as a model for movement and pinning of dislocations in a metal. A: If a wrinkle is present in a rug, the wrinkle may be pushed through it so that the rug moves across the floor. In this way the rug can move across the floor without requiring that the entire rug move at once; this is similar to the movement of a plane of atoms with respect to a second plane in the plastic deformation of a metal. B: If two or more wrinkles in the rug meet, it is more difficult to move them. The presence of one “pins” the other. The collection of pinned dislocations leads to the hardening of a metal in a process known as work hardening.

Demonstration 6.4. Work Hardening *(9, 10)*

Materials

Solid copper wire (10 gauge or thicker, used for 120-V house wiring and available at a hardware store)
Weight (~700 g works well. If a hole is drilled into the handle of a hammer, it can serve as the weight.)
Meker burner or torch
Tongs
Ring stand
18-gauge copper wire (optional)

Procedure

- Bend the wire. The more you bend it, the more difficult it will be to bend.
- Heat a piece of the wire red hot by holding it with tongs in the flame of a Meker burner. Let it cool slowly on the iron plate of a ring stand. The heat-treated (annealed) piece will be easy to bend at first, although continued bending will again work-harden the copper.

Variation 1

- Prepare a 9-inch-long piece of 10-gauge copper wire by heating the wire red hot in the flame of a Bunsen burner (annealing) while holding it with tongs and letting it cool slowly on the iron plate of a ring stand.
- Hold one end of the cool wire.
- Hang a ~700-g weight on the other end of the wire. The annealed wire should bend under the applied weight.
- Work-harden the wire by grasping it at its two ends and bending it many times. Show that the wire now supports the weight without bending.
- If time permits, anneal the wire by heating as described above to show that hanging the weight on its end again causes the wire to sag.

Variation 2

- Take a long piece of copper wire (about 2 feet of 18-gauge wire) and pull it two or three times over a nail or other small diameter object, as if the wire were like the rope of a pulley. The wire will bend much more easily on the first pass than on the third pass.
- Heat a section of the strained wire red hot in a Bunsen burner, and let it cool slowly. The treated wire will again bend easily at first.

Hardening of Alloys: Steel

To work-harden a metal by deformation is one way to strengthen it. However, metallurgists often rely on more sophisticated means of hardening and take advantage of the many solid phases—both equilibrium and metastable—present in binary and multicomponent alloys. The fact that the metallic bond is not particularly selective allows metal atoms of different kinds to intermingle and form alloys over wide ranges of composition. Changing the composition on an atomic scale can also increase the strength of a metal.

The presence of dissolved impurities in a metal makes it more difficult for dislocations to move, especially if the sizes of the atoms of the impurity and host metal differ significantly. (Recall from Chapter 3 that if the atomic radii of two elements differ by more than ~15% the solubility of a substitutional impurity element in a host metal is very low.) The resulting hardening of the metal is called solid solution hardening (*see* Figure 6.11). For example, dissolution of tin in copper produces bronze, which is harder than either pure copper or pure tin. The difference in the size of the atoms roughens the slip plane on the atomic scale, making it harder for dislocations to move.

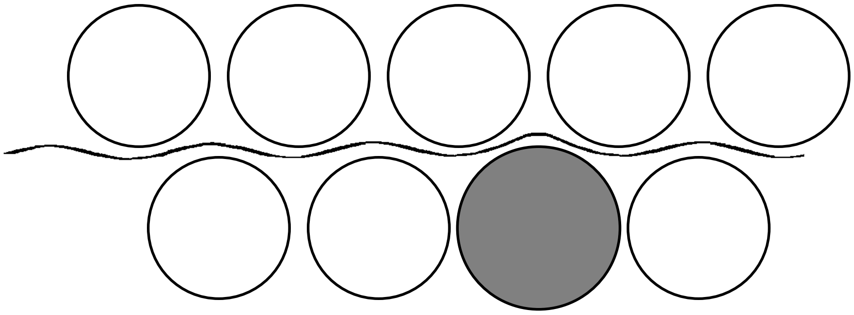

Figure 6.11. The addition of impurity atoms (shaded circle) causes slip planes (wavy line) to roughen and thereby increases the hardness of the alloy relative to the pure metal.

Precipitation hardening occurs when the room-temperature solubility of an impurity is exceeded, and a fine-grained precipitate forms throughout the metal. For example, Cu dissolves in Al at high temperatures, but its lower solubility as the solid solution cools results in precipitation of grains of $CuAl_2$. Second phases can precipitate at the grain boundaries, where the imperfect nature of the atomic packing can accommodate them more easily.

Two demonstrations that will be described provide striking illustrations of how phase transformations (also discussed in Chapter 9) and the solubility of carbon are used for strengthening in carbon steels *(11)*. Pure iron melts at 1538 °C. Between room temperature and the melting point, however, iron undergoes several allotropic phase transformations, from a body-centered cubic (bcc) phase, called α–iron or ferrite, at room temperature, to a face-centered cubic (fcc) phase, called γ–iron or austenite, at temperatures between about 900 and 1400 °C (Table 6.1). At temperatures above 1400 °C, iron transforms to a bcc structural type that is generally not an important feature in the heat treatment of steels.

Austenite, the fcc structure of iron, has the ability to dissolve much more carbon than ferrite, the bcc structure of iron. [The maximum solubility of carbon in austenite is 2.11 wt % at about 1148 °C, compared to the maximum solubility of carbon in ferrite of only 0.02 wt % at 727 °C *(11)*.]: Although the structure of ferrite is more open in terms of the total volume of interstices or voids between iron atoms, the structure of austenite contains fewer but larger interstitial sites and is able to dissolve larger amounts of carbon as an interstitial defect in the crystal.[2] The carbon atoms do not dissolve well in ferrite, because the carbon atom is too big to fit in the interstices.

Table 6.1 Phases of Iron Important in Steel

Phase	Structure	Stable Temp. Range	Carbon Solubility
α-Iron (ferrite)	bcc	under 900 °C	0.02 wt % at 727 °C
γ-Iron (austenite)	fcc	900–1400 °C	2.11 wt % at 1148 °C

Many of the important heat treatments of steels involve phase transformations across the austenite–ferrite phase boundary. When steel, such as the type used to make piano wire (containing about 1 wt % carbon), is slowly cooled below the austenite–ferrite phase-transition temperature, the excess carbon, which is no longer soluble in ferrite, precipitates as iron carbide (Fe_3C).[3] This process requires the carbon to diffuse moderate distances (~ 0.1–1 µm) through the austenite. The presence of iron carbide precipitates serves to strengthen the steel by pinning dislocations. The more carbon there is in the steel, the more iron carbide there will be, and generally, the stronger the steel will be (but it will also be more brittle).

The kinetics of the phase transformation depend strongly on temperature, a fact that allows careful tailoring of the size distributions

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[2] Recall from Chapter 5 that a body-centered cubic structure has a packing efficiency of 68%, and a face-centered cubic structure has a packing efficiency of 74%. The fcc structure has octahedral holes that can contain a sphere of size $0.414r$ (r is the radius of the atoms forming the face-centered cube) and tetrahedral holes with radius $0.225r$. The bcc structure, on the other hand, contains a distorted octahedral hole formed by the four atoms on the face of a cube, and the two centered atoms in the unit cells that share that face. Though the distance from the center of this hole to an atom on the face is $0.633r$, the distance from the center of the hole to the atoms in the centers of the unit cell is $0.154r$. Consequently, only very small spheres will fit here. Also, slightly enlarged tetrahedral holes in the bcc structure have radii of $0.291r$. Thus, the fcc structure has larger void spaces because of the octahedral holes, even through it is a more densely packed structure. *See also* reference 12.

[3] Iron carbide (Fe_3C) is a metastable phase, meaning that it is unstable with respect to decomposition to pure iron and graphite. However, in most alloys, this decomposition is so sluggish that it is unimportant. In certain cast irons the carbon is present as graphite, and in these alloys, the formation of graphite has been catalyzed with the addition of an element like silicon.

and types of second phase precipitates within steels. If the steel is quenched from high temperature by rapid cooling in a water bath, the driving force for the austenite–ferrite phase transformation becomes very large. However, at the same time, the steel is cooled so quickly that the carbon has insufficient time to concentrate by diffusion into the Fe_3C precipitates. The result is a new phase, called martensite, which is essentially a distorted form of the bcc ferrite structure, distorted because it contains large amounts of carbon trapped during the transformation.

Martensite, when it contains large amounts of carbon, is a very hard material, but the large distortions of the crystal lattice that occur during the phase transformation produce high internal stresses that promote fracture. Therefore, martensite can be very brittle and can shatter like glass when dropped if it has not been treated by a process called tempering. In tempering, the sample is gently heated after it has been quenched by the sudden cooling. Tempering the steel allows the carbon to diffuse short distances and allows some of the internal stresses to relax, yielding a greater resistance to fracture.

Demonstration 6.5. Annealing, Hardening, and Tempering of Bobby Pins *(13)*

Materials

Four bobby pins
Tongs
Bunsen burner or torch
Iron ring stand (or other heat-proof surface)
Medium-sized beaker of water

Procedure

- Obtain four bobby pins; one pin will be left untreated for reference.
- Holding the ends of a bobby pin with crucible tongs, heat the bend of the pin red hot in a Bunsen burner flame (annealing), then allow it to cool slowly on a heat-proof surface such as the iron plate of a ring stand. This bobby pin loses its springiness and stays open when stretched.
- Heat the bend of another bobby pin red hot, but drop it into cold water to cool quickly. This bobby pin is quite brittle and snaps into pieces when bent.
- Heat a third bobby pin red hot, and drop it into cold water. Hold the now-cool pin above a flame and gently heat (tempering) until an iridescent blue coating forms and then let the pin cool slowly. This bobby pin will be as springy as the original.

A more elaborate experiment using steel piano wire can also be done as a lecture demonstration. The ostensible objective of the demonstration is to make a useful spring from a piece of piano wire.

Demonstration 6.6. Annealing, Hardening, and Tempering of Piano Wire

Materials

Two (2–foot) strands of 16.5-gauge, single-strand piano treble wire
(Available in music stores or see Supplier Information)
A 1-foot length of 1-inch-diameter wooden dowel
Variable-voltage transformer (Variac)
Power cord with two large, insulated alligator clips
Bucket of water

Procedure

- Wrap the piano wire around the wooden dowel as though trying to shape it into a coiled spring. As received, the piano wire is very resistant to bending and will not retain this shape, making it unsuitable for serving as a spring.
- Connect a variable-voltage transformer (maximum current 10 A) to a heavy power cord that terminates with two large, insulated alligator clips. This device will be used to pass a current through the steel piano
- Connect one alligator clip to each end of the steel piano wire. Set the variable-voltage transformer for 20–30 V and maintain the current flow just until the wire turns red hot. **Disconnect** the wire from the variable-voltage transformer, wait about 30 seconds, and cool the wire by immersing it in a bucket of water. **CAUTION: Avoid touching the bare wire while the variable-voltage transformer is on and current is passing through the wire! And do not immerse the wire in the water unless the variable-voltage transformer is disconnected!**
- Again, wrap the piano wire around the wooden dowel, trying to shape the wire into a coiled spring. Do not cross the strands of wire as you wind the wire around the dowel. This time, the wire retains the shape of a spring when the wooden dowel is removed.
- Test the springiness of the now-coiled wire by pulling gently on one end and observing the resulting behavior. The wire retains the shape of a spring, but the spring is not very elastic.
- To harden the spring, connect the alligator clips to it, one clip on each end, and again heat the wire until it turns red hot, using the variable-voltage transformer setting of 20–30 V. Try not to let adjacent coils touch each other during this heating process. Disconnect the variable-voltage transformer from the wire, and *immediately* quench the wire in a bucket of cold water.

- Remove the alligator clips and test the springiness by pulling on one end of the coiled spring. The wire should break under a minimum of force.
- Heat a second piece of wire, anneal it, shape it into a spring and harden it as described. After the spring has been quenched, remove it from the water and connect the alligator clips to each end. Starting with the variable-voltage transformer set to less than 10 V, heat the wire gently (tempering). Avoid heating the wire to the point where it turns red hot. Turn the variable-voltage transformer off, wait about 30 seconds, and then cool the spring by immersing it in water.
- Remove the alligator clips. After tempering, the coiled spring has more elasticity than the untreated spring and loses much of the brittleness of the hardened spring. If the spring is neither brittle nor elastic, the temperature reached during tempering was probably too high.

It is valuable to summarize the processes discussed so far and to emphasize that although the details may vary for a given metal or alloy, the microscopic phenomena are universal. Specifically, the movement of dislocations in a metal causes plastic deformation. Bending a piece of copper wire leads to the creation of new dislocations, which become pinned and then pin other dislocations in a process known as work hardening. Bobby pins and piano wire are examples of materials that have been heavily work-hardened. Precipitates, as are found in steel and almost all other alloys, are used as hardening agents because they pin dislocations. To a lesser degree, solid solution impurities also pin dislocations and strengthen metals. Heat treatments are used to tailor the mechanical properties of a metal, but how a heat treatment affects the properties depends on the particular alloy system as well as the details of how the heat treatment is performed. For example, when the work-hardened copper was heated, dislocations were removed, which resulted in a net softening effect. In the steels described herein, the various heat treatments take advantage of the phase chemistry and the transformation kinetics of the steel; a variety of phases and a range of mechanical properties are seen.

Defects in Ionic Compounds

Ionic compounds also have defects. Like metals, ionic crystals exhibit grain boundaries and dislocations. However, ionic compounds differ from metals in that cations and anions are present, and their presence introduces some new possibilities for defects. Several types of defects particularly important to the physical properties of ionic compounds (such as ionic conduction) will be discussed here.

Schottky defects are most common in the alkali halides and involve pairs of vacant cation and anion sites. It has been estimated that at room temperature only one in 10^{15} pairs of cations and anions is vacant in sodium chloride. This means that a 1-mg grain of salt still has about 10,000 Schottky defects *(14)*.

A Frenkel defect is one in which a cation (or anion) is located in an interstitial site that is normally empty. In AgCl, which has the sodium chloride structure, some of the silver ions may be located in interstitial tetrahedral holes, rather than the usual octahedral sites. Because electrical neutrality must be maintained in the crystal, there will be an equal number of vacant Ag^+ octahedral sites as well. Figure 6.12 illustrates Frenkel and Schottky defects for a general ionic compound with the formula MX.

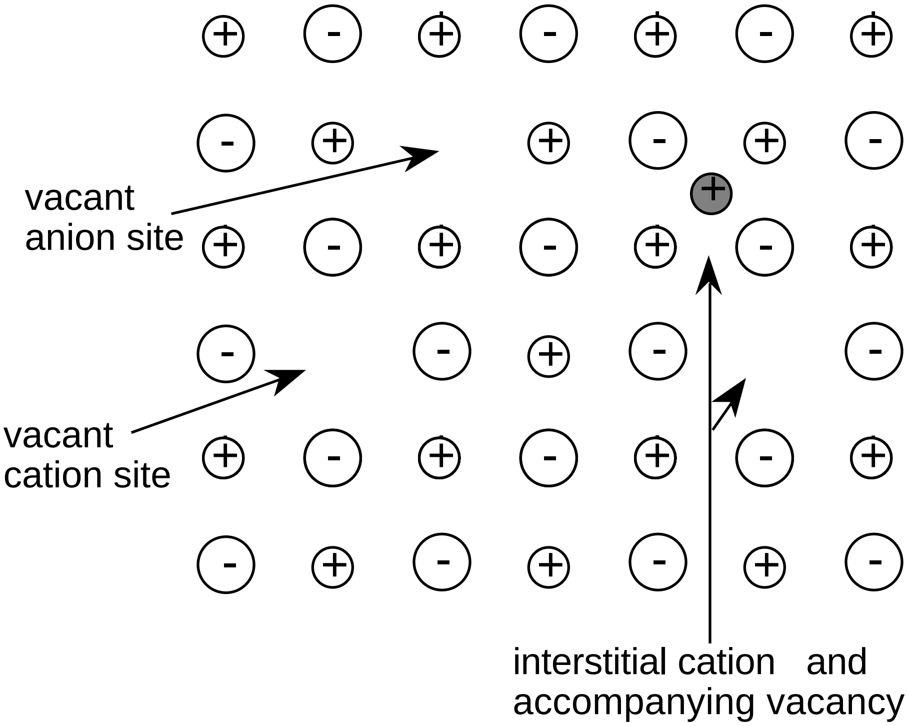

Figure 6.12. Defects in ionic compounds. Schottky defects are pairs of cation–anion vacancies and are represented by the empty sites in crystal positions normally occupied by a cation and an anion. A Frenkel defect is illustrated by the shaded atom in an interstitial site while a normally occupied site is vacant as a consequence.

Another type of defect involves substitution for some of the ions in the crystal. In sodium chloride, for example, impurity atoms such as potassium may substitute for the sodium and bromide may substitute for the chloride. [In general, if the substituting atoms are about the same size, the overall packing arrangement is maintained and a solid solution may form (*see* Chapter 3).] A different effect, however, is observed when a divalent cation such as calcium is substituted for the sodium. Such substitutions require charge compensation to maintain the overall electrical neutrality of the crystal. One way to accomplish charge compensation is that for each calcium substitution in the lattice, a second sodium is also removed from the crystal. This means that doping with calcium should serve to increase the number of Na^+ vacancies in the crystal. (This type of defect is intentionally introduced in a solid-state oxygen sensor that operates in catalytic converters. *See* Chapter 8 for details.)

Ionic compounds in the solid state are generally considered to be electrically non-conducting. However, in certain cases ionic solids act as conductors and are receiving consideration as battery electrolytes and oxygen sensors. Even sodium chloride and other classical ionic compounds conduct electricity at temperatures below their melting points. Unlike metals, which show conductivity by motion of electrons, ionic compounds are thought to be conductive due to ion mobility mediated by crystal defects. (In some cases the compounds have channels through which ions can move.)

Ionic conduction often involves the motion of the cations, presumably because of their smaller size, and can occur by a process in which a cation moves from an occupied site into a vacancy. This kind of cation motion will always leave behind a vacancy, and a second cation can move into the newly created vacancy, a third cation can move into the vacancy created by motion of the second, and so on. This process is believed to be the mechanism of conduction in sodium chloride (*see* Figure 6.13), which has predominantly Schottky defects. Substitution of a divalent cation for pairs of monovalent cations in the crystal should also serve to increase the conductivity by this mechanism, because the number of cation vacancies would be increased.

F-Centers in Salts: Spectroscopy of Defects

Certain types of point defects are readily created in alkali halides by ionizing radiation. The best understood of these point defects is the F-center, after *farbe,* the German word for color *(15–17).* The nature of the F-center has been elucidated by various spectroscopic techniques and is described as an electron that is trapped at a halide vacancy in the crystal. This state is shown pictorially in Figure 6.14 for KCl. The absorption spectrum of the trapped electron gives rise to a deep coloration of the crystal, a beautiful deep purple in KCl. The color observed is due to the absorption of a photon by the trapped electron and excitation from the ground state of the F-center to an excited state. A related defect is also responsible for the colors of smoky quartz and amethyst. [These minerals

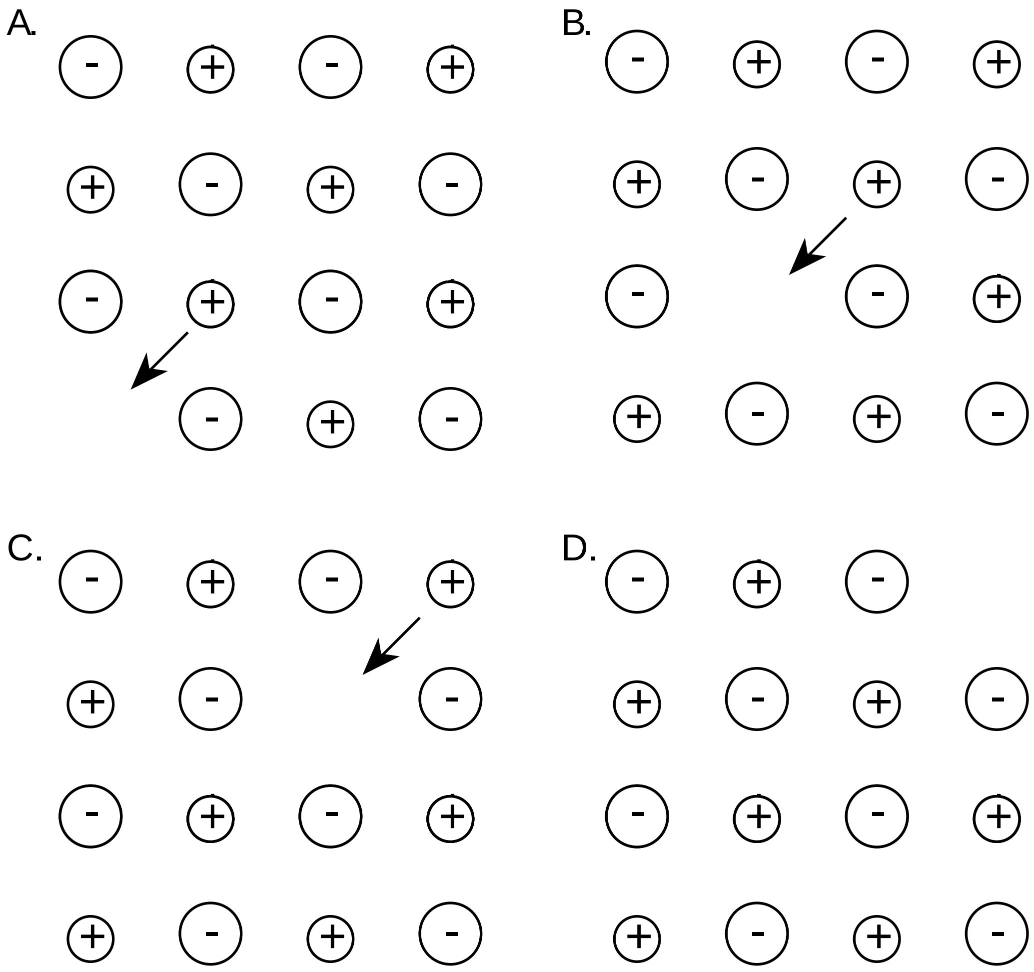

Figure 6.13. Conductivity in an ionic crystal. The sequence A–D shows how cation migration can occur by a series of movements of cations into crystal vacancies.

are predominantly SiO_2. However, the substitution of very small amounts of Al^{3+} (smoky quartz) and Fe^{3+} (amethyst) for Si^{4+} (about one substitution for every 10,000 Si atoms) in the crystal coupled with ionization of an electron from an oxygen produces the color center. As noted in Chapter 5, substitution of a trivalent cation for silicon requires the presence of one more unit of positive charge in order to maintain electrical neutrality. This unit is generally thought to be a proton located in an interstitial site *(15)*.]

The exact mechanism for F-center formation is not known; however, various models have been postulated *(18)*. One model is that high energy radiation (for example, X–rays or gamma rays) interacts with the alkali halide, causing a halide ion to lose an electron, producing a halogen atom. The electron released in the process moves freely throughout the crystal until it encounters a halide vacancy. Strong electrostatic forces trap the electron at this site, as the electron is surrounded by six positively charged alkali metal ions. Also, a halogen atom can interact with an adjacent halide ion to form a molecular-type defect such as Cl_2^-, which is the electron-deficient complement to the F-center.

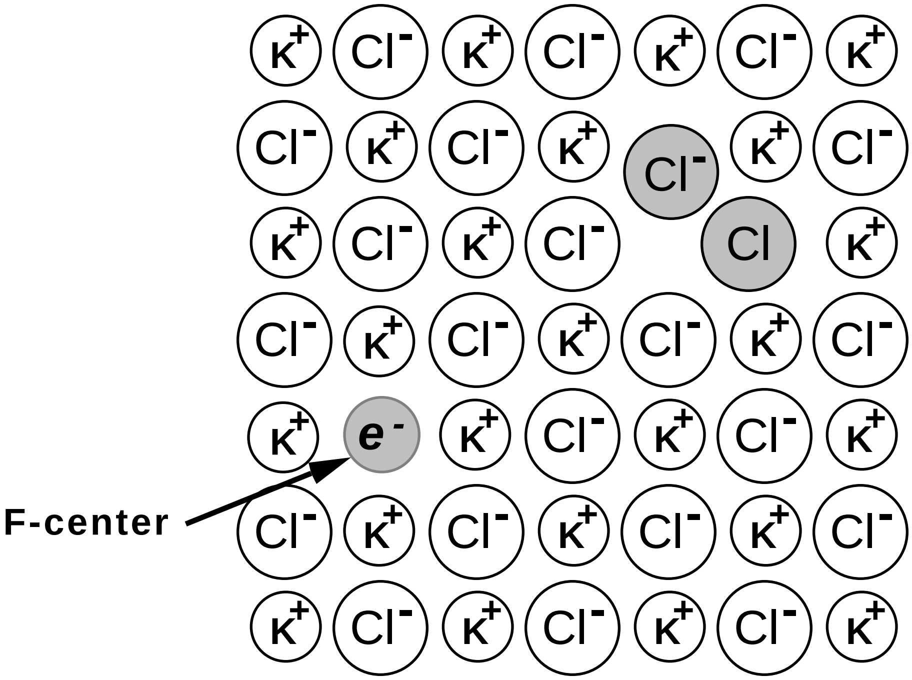

Figure 6.14. An F-center is an electron trapped in a halide vacancy. Other defects such as the formation of Cl_2^- species (indicated by the shaded pair of spheres) occur for charge balance.

F-centers can also be produced by heating the alkali halide in alkali metal vapor. In this case, the alkali metal ionizes, producing a cation, which diffuses into the crystal, and a free electron, which is trapped at a halide vacancy. The color observed in the crystal is characteristic of the crystal and does not depend on the alkali metal vapor used. Thus, potassium chloride crystals become purple whether they are heated in the presence of potassium vapor or sodium vapor.

The observation of F-centers in alkali halides arises from stoichiometric deviations on the order of one electron for every 10,000 halide ions. Thus, the effect on the optical properties of even a very small deviation from the ideal stoichiometry can be very large. F-centers can be readily prepared in alkali halides by excitation with a Tesla coil, commonly used to detect leaks in glass vacuum lines.

Demonstration 6.7. F-Centers *(19)*

Materials

Crystals of KCl, NaCl, RbCl, or KBr (Optical grade random crystal

cuttings of NaCl, KCl, and KBr can be obtained at an economical price. *See* Supplier Information.)
Small side-arm flask and stopper
Vacuum pump or oil diffusion pump
Tesla coil

Procedure

- Evacuate a small flask containing KCl or other alkali halide crystals using a good mechanical vacuum pump (10^{-3} mm Hg) or, better yet, by using a high-vacuum line with an attached oil diffusion pump (10^{-5} mm Hg or better). **CAUTION: Make sure that the flask has no defects. Small cracks may cause it to shatter under vacuum. Conduct the evacuation behind an explosion shield.**
- Direct the discharge from a Tesla coil at the KCl through the wall of the flask for several minutes, until the salt turns a bright purple (*see* Figure 6.15). This technique also yields an orange-brown coloration in NaCl, and a light blue coloration in RbCl or KBr, which persists for hours to days depending on the salt.

Variations

- If the crystals are sealed in a glass container under high vacuum, the vacuum will persist and the color can be regenerated when needed by the discharge of a Tesla coil. This demonstration works on both powdered salts or large crystals. However, one advantage of using large, optical grade crystals is that the absorption spectra of the F-centers can be readily measured with a standard spectrometer.

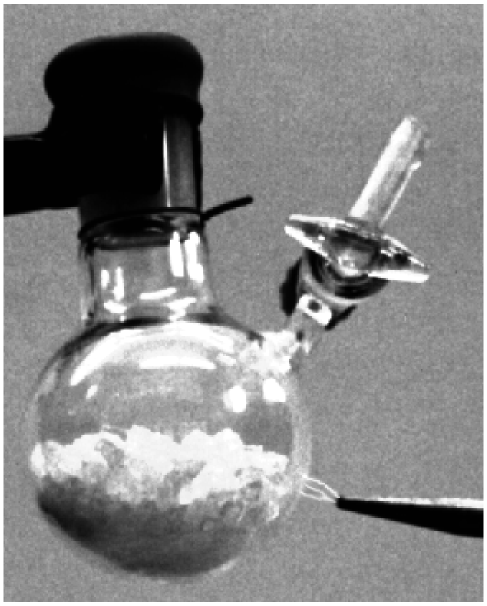

Figure 6.15. F-center production in an evacuated flask by a tesla coil.

Spectroscopy

After coloration of a large crystal, the absorption spectrum of the F-center can be obtained via transmission in a UV–visible spectrometer. The absorption spectra obtained from color centers in NaCl, KCl, and KBr are shown in Figure 6.16. The peaks are generally broad, but exhibit a clear trend in the variation of the band maximum (λ_{max}) with the size of the halide vacancy (as estimated by the lattice parameter, the length of an edge of the cubic unit cell): As the size of the vacancy increases, λ_{max} increases. This trend holds for color centers that have been observed in all of the alkali halides *(20)*.

Figure 6.17 is a plot of the F-center absorption energy versus the lattice parameters of the salts, which have cubic unit cells. The maximum absorption energy, E, is inversely related to the size of the vacancy, modeled as a cubic box:

$$E \sim a^{-1.8}$$

where a is the cubic lattice parameter (the length of the edge of the cubic unit cell) for a given salt.[4]

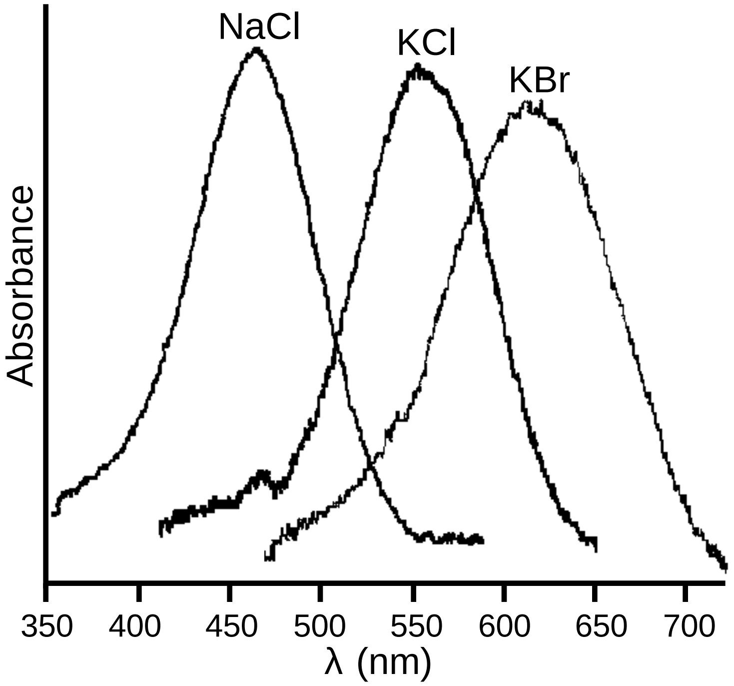

Figure 6.16. Absorption spectra from F-centers in NaCl, KCl, and KBr at 298 K. These spectra were obtained in air.

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[4] This result is similar to the result of the particle-in-a-box problem in which the energy is inversely related to the square of the length of the box.

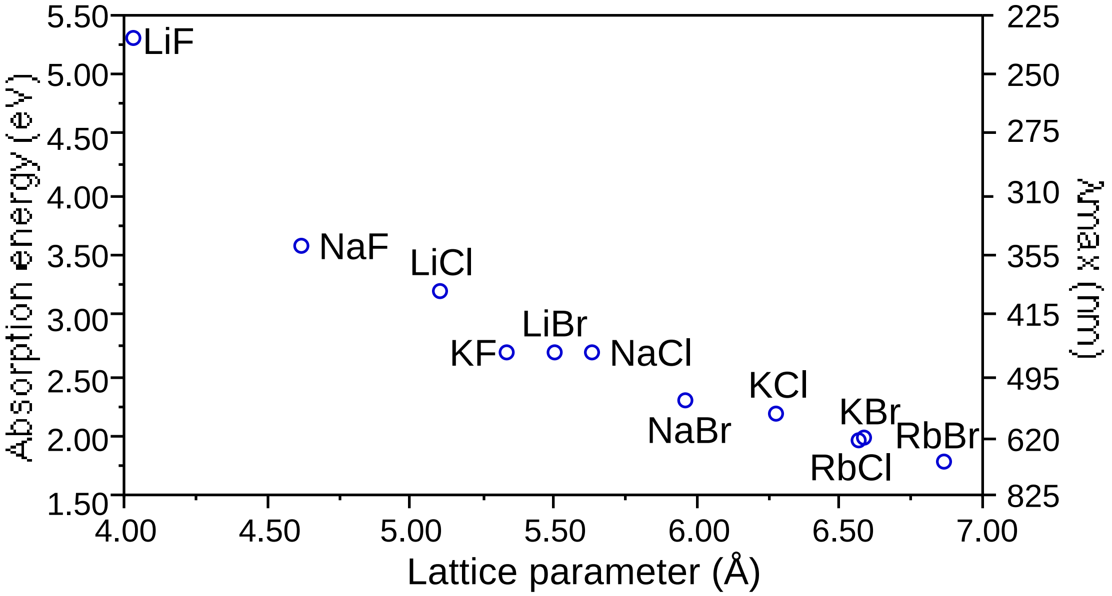

Figure 6.17. Plot of color F-center absorption maxima as a function of the lattice parameter at 298 K.

The effects of temperature and pressure on the size of the halide vacancy suggest that as the crystal is cooled or squeezed and the ions move closer together, the absorption peak should shift to higher energies. If a colored KCl crystal is cooled in liquid nitrogen, the purple color observed at room temperature changes to a deep pink color at 77 K. However, complex changes occur in the spectral distribution that have been attributed to an equilibrium between several different types of defect structures *(21)*. With increasing pressure, the absorption maxima of F-centers in NaCl and KCl shift to higher energies as the crystal contracts *(22)*.

Another method of changing the size of the halide vacancy is to prepare solid solutions (Chapter 3). Solid solutions of $K_{1-x}Rb_xCl$ can be prepared by heating a mixture of KCl and RbCl above the melting point and then cooling. F-centers produced in these mixed crystals have absorption maxima that lie between pure KCl and pure RbCl *(23)*.

The F-centers produced by the Tesla coil method bleach slowly at room temperature. The kinetics of this decay can be measured on a spectrophotometer by monitoring the absorption over a period of time. Figure 6.18 shows the decay of the F-center absorption in KBr over a period of 2 hours. This particular salt bleaches faster than either NaCl or KCl, allowing for the observation of a larger change in the absorption within a reasonable time frame. Analysis of the absorption-versus-time data does not fit a simple rate law. The decay probably occurs through several different pathways.

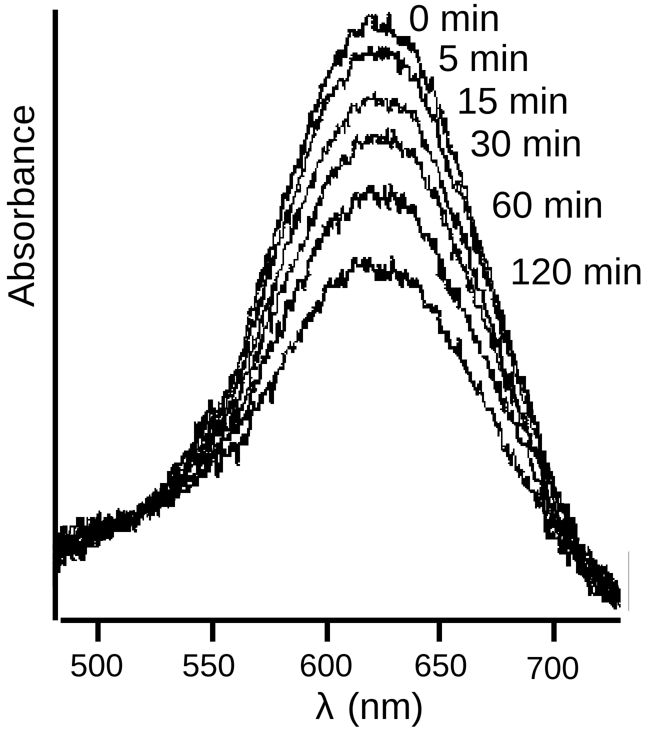

Figure 6.18. Plot showing the decay in F-center absorption of KBr at 298 K over a period of time.

F-Center Luminescence

The energy that is stored in the F-center can be released through thermoluminescence, the process of using heat to generate luminescence from a compound *(24)*. A demonstration of this phenomenon requires salt crystals with a much higher concentration of F-centers than those produced using a Tesla coil. Salts that have been irradiated with gamma rays are deeply colored as a result of a high concentration of F-centers. These samples have been irradiated but are not radioactive.

Demonstration 6.8. Thermoluminescence from F-Centers

Materials

Hot plate
Samples of irradiated, alkali halides containing high concentrations of F-centers. Irradiated NaCl, which has a brownish color, is commercially available. (*See* Supplier Information.)
Spatula

Procedure

- Turn a hot plate to the high setting (190 °C or higher).
- When the hot plate is sufficiently warm, darken the lights in the room and sprinkle a spatula full of irradiated NaCl on the hot plate. As the salt hits the hot plate, bright orange light can be seen emanating from the crystals at the surface of the hot plate.
- If samples of irradiated LiCl are sprinkled on the hot plate, the observed luminescence is bluish-white.
- When the room lights are turned back on, the salt on the hot plate is no longer colored, but has returned to its characteristic white color.

Recalling how the F-center was formed, the general phenomenon of thermoluminescence can be explained in the following way: *(25, 26)* The thermal energy provided by the hot plate allows the trapped electron of the F-center to be released from the halide vacancy trap and thereby recombine with the electron-deficient defects, such as Cl_2^- (*see* Figure 6.14), releasing part of the energy in the form of light. The thermoluminescence seen in this demonstration is in the visible region of the spectrum, but the energy required to form F-centers in NaCl and LiCl is much larger (*see* Band-Gap Energies for Ionic Solids, Chapter 7). Therefore, the emission observed is only part of the excess energy of the trapped electron. The remainder of the energy must be lost either in photons outside of the visible region or in nonradiative processes.

Finally, it is worth speculating on the reactivity of these defects. The dissolution of irradiated salt crystals in water may produce hydrated electrons that go on to react further in solution. A radiochemistry laboratory experiment described in the *Journal of Chemical Education (27)* investigates the chemical reactivity of F-centers upon dissolution in water and the exploitation of this reactivity to obtain quantitative information on the concentration of F-centers produced in irradiated NaCl.

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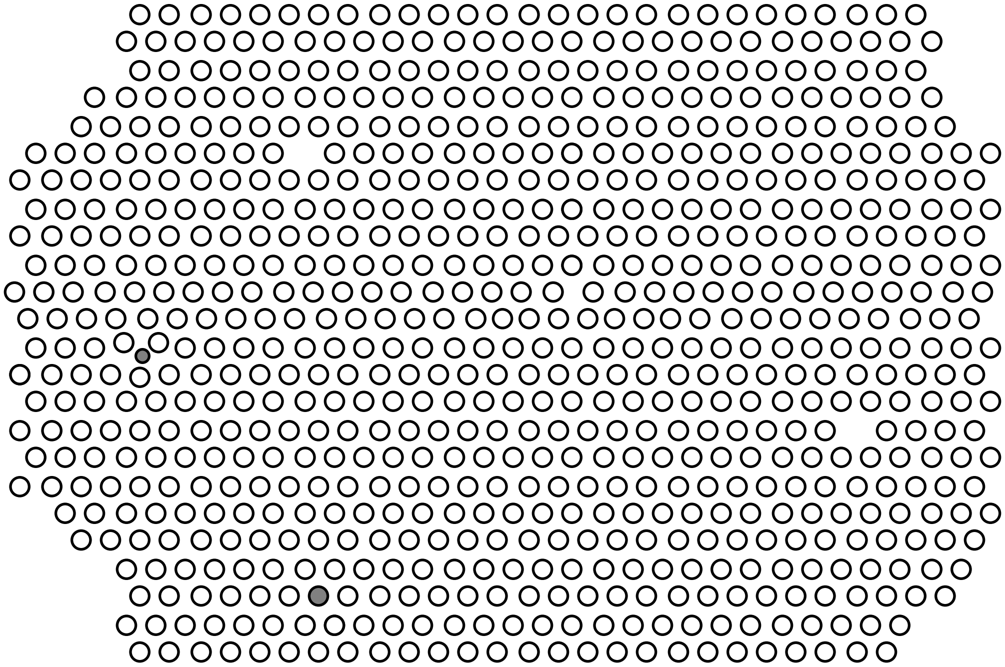
Exercises

1. An important difference between a vacancy and a dislocation is that if you sketch a regular polygon around the vacancy in Figure 6.5 by traveling along atoms, the polygon will close. The same polygon will not close around a dislocation. Try it, using a regular hexagon to encircle each defect.
2. Calculate the density of defect-free iron from the information in Appendix 5.6. What would the density be if 0.10% of the iron sites were vacant? How much would the mass of 1.000 cm^3 of defect-free iron differ from the mass of the iron with 0.10% vacancies?
3. Why might scanning tunneling microscopy give more information about the structure of defects in a metal than X-ray diffraction?
4. How many Schottky defects are present in a 1-mg crystal if 1 in 10^{15} pairs of cations and anions are missing? (Hints: NaCl has a fcc structure with a unit cell edge length of 5.64 Å and the density of NaCl is 2.16 g/cm^3.)
5. Assume that F-centers can be generated in the following compounds that have the NaCl structure. Using information in Figure 6.17 and Appendix 5.6 for unit cell dimensions, estimate the approximate wavelength at which each would absorb.
   a. NaI
   b. LiI

6. Find and label the types of defects in the representation of a plane of atoms shown below.



A two-dimensional array of atoms showing defects.

7. Choose the correct ending to the following statement. If 1% of the Na^+ ions in a crystal of NaCl are replaced with Mg^{2+} ions, the required overall electrical charge neutrality of the crystal can be maintained if
   a. another 1% of the Na^+ ions are replaced by Al^{3+} ions.
   b. another 1% of the Na^+ ions are replaced by Ca^{2+} ions.
   c. another 1% of the Na^+ ions are replaced by Li^+ ions.
   d. another 1% of the Na^+ ions are removed from the crystal and their positions left vacant.

8. How does the movement of a caterpillar involve a kind of dislocation?

9. Consider the seats in an auditorium or coliseum, in which the number of seats in a row increases radially as you go from the stage or playing field to the back of the room or field, respectively. Make a sketch that shows the problem of lining up seats in columns, one behind the other, in registry. How do aisles serve as dislocations to address this problem?

10. Estimate the edge length of the cubic unit cell (lattice parameter) and the absorption band maximum (wavelength in nm) for an F-center in a $K_{0.5}Rb_{0.5}Cl$ solid solution.

11. How would the absorption properties of a physical mixture of equal moles of powdered KCl and RbCl differ from those of a powdered solid solution of $K_{0.5}Rb_{0.5}Cl$ if F-centers are produced in both samples using a tesla coil?

12. Describe the close-packed slip planes in a sample of an hcp metal like Zn.