VI. THE STRUCTURE OF SOLIDS

6-1 MOTIVATION

We have come a great distance in the past weeks. If everything is going according to plan, you are beginning to picture engineering as the design of energy distribution and storage systems. (If I had told you that on the first day of class, you would have thought me nuts, and maybe you still do.) Of course, these systems are constrained by the two great laws of Nature. The first tells us that energy is conserved and is stored only in the motion of atoms, called heat, or in the arrangement of atoms, called work. The second tells us that Nature prefers to distribute energy in a particular fashion, which is mathematically expressed in the form of the Boltzmann distribution.

In our labs and readings, we have found that some materials are able to store energy as work more successfully than others. In particular, tough materials can store a great deal of energy through the rearrangement of atoms to produce what we call deformation. On the other hand, the atoms of brittle materials do not easily undergo rearrangement.

We don't yet know, however, what about the arrangement of atoms in tough material allows for the storage of energy as work, and how this arrangement differs from that of atoms in a brittle material. We will now turn our attention to this puzzle. As you proceed through labs and the reading, put yourself in the position of the scientists and engineers of the early 1900s who were wrestling with this same question. They found the puzzle's solution; see if you can do the same.

6-2 CRYSTALS

The structure of solids can be broadly classified as crystalline or amorphous. By way of analogy, an amorphous material is to a crystal as a forest is to a Christmas tree farm. It is very hard to become lost in a Christmas tree farm because there are obvious directions. If you were dropped into a large Christmas tree farm, just walk along the furrows and eventually you will emerge. But in a forest, there are no obvious direction, which is why people get lost and end up walking in circles. On the other hand, while it is fun to "go for a walk in the forest" a walk through a Christmas tree farm is boring. The Christmas tree farm looks the same no matter where you are, while every point in a forest is subtly different. In a similar way, crystalline materials are marked by aligned repeating patterns. An amorphous material does not possess aligned repeating units. Window glass is an example of an amorphous material, but by and large, most engineering materials are crystalline. And an important consideration from our perspective is that the atoms comprising the

perfect crystal have their lowest possible potential energy. Hence, energy cannot be extracted from a flawless crystal only added.[1]

6-2 TWO DIMENSIONAL CRYSTALS

We will begin by looking at crystals with 2-dimensional examples since a number of conceptual advantages exist in this dimension—not the least of which is that it is much easier to draw and visualize in 2-D. After we have mastered the basics, we will move on to 3-D crystals.

There is a specific vocabulary used to describe crystals. There are volumes and volumes of books—and in these days websites and software—devoted to nothing more than categorizing crystal structures. If you have some combination of elements and want to know how these elements are arranged, more than likely that structure is recorded somewhere. And when found, the information will be conveyed in a tabular form consisting of two parts: information about the crystal **lattice,** and the **motif** or **basis** associated with this lattice.

A lattice is a purely mathematical construct. It is nothing more than an infinite collection of coordinates called **lattice points**. In 2-D these coordinates are constructed from two non-collinear **lattice vectors**, which we will denote as $\vec{a}$ and $\vec{b}$. We could specify these lattice vectors in a number of ways, say with respect to some Cartesian coordinate system. However, the most general way to describe them is in terms of their lengths and the angle between them.

We can build the lattice by picking an arbitrary starting point p_0. Then an infinite array of lattice points, p_{nm}, is generated through the relationship $p_{nm} = p_0 + n\,\vec{a} + m\,\vec{b}$ where n and m are integers. Another way to say this is that if you are standing at any point in a crystal lattice and you walk some integral number of $\vec{a}$ vectors followed by some integral number of $\vec{b}$ vectors, you will find yourself at a place where the arrangement of points indistinguishable from your starting point. Remember this is an idealized infinite lattice and hence there are no edges.
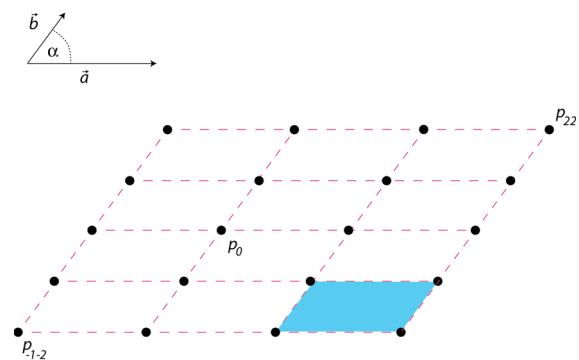

Fig 6-1

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[1] *This is actually a rough statement of the third law of thermodynamics*

By way of illustration, shown in Figure 6-1 are the lattice vectors $\vec{a}$ and $\vec{b}$ and the angle α between them. These vectors together with the point p_0 define a lattice. Note that this collection of points is just that, a collection of points; they have no physicality. The lattice vectors also have no physicality. Thus, the lattice is **not** the lines and the dots.

The shaded region shown in the Figure 6-1 is known as a **unit cell**. It is the parallelogram defined by the lattice vectors. Think of the unit cell as one of an infinite number of identical regions that could be used to tile a floor of infinite extent.

Now, we transform the lattice into a crystal by associating with each lattice point a motif or basis. In our case, the motif will be made up of atoms, but it could be anything. A wallpaper designer might associate some floral design with each point. I like to think of lattice points as the places where Maxwell's Demon can hang atoms as if decorating a Christmas tree, which is why I chose red and green "atoms" for Figure 6-2. Here Maxwell's demon has "hung" from each lattice point a red and a green atom to pr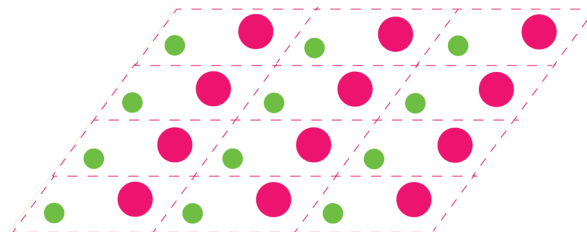oduce the crystal. Note that he did not place an atom directly on each point but hung a pair of atoms some distance from each point. The hanger he used

Fig 6-2

caused the atoms to be displaced from the lattice point. Even though you will hear this in future classes, remember, **a lattice point is not an atom**.

The periodicity of a crystal is easy to describe exactly. One simply needs to specify the length of the two basis vectors and the angle between them and then the motif that will be associated with each lattice point. Pretty neat.

Yet there is one more step in simplification. All 2D unit cells are parallelograms, but special parallelograms also exist. In the case of 2-D lattices, in addition to the general parallelogram, four special parallelograms arise where there are particular relationships between $\vec{a}$, $\vec{b}$ and α. The general parallelogram 2D lattice exists when $|\vec{a}| \neq |\vec{b}|$ and α≠ 90°, and is called an oblique lattice as in Figure 6-1. The other four special parallelograms are the rectangular lattice ($|\vec{a}| \neq |\vec{b}|$ and α= 90°), square ($|\vec{a}| = |\vec{b}|$ and α= 90°), hexagonal ($|\vec{a}| = |\vec{b}|$ and α= 120°), and centered rectangular ($|\vec{a}| = |\vec{b}|$ and α≠ 90° or 60°). The general parallelogram plus the four special parallelograms form the five 2D crystal classes.
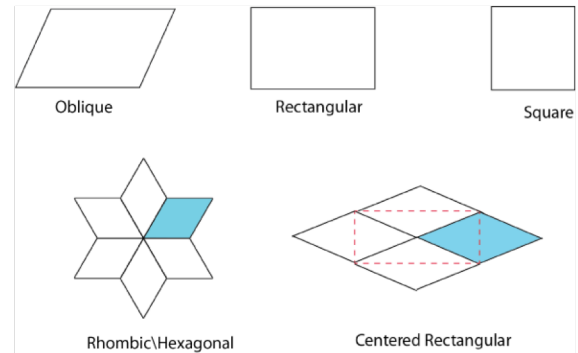
Notice that the hexagonal and centered rectangular lattices take their names from the way the unit cells pack together to give additional symmetry. Recognize the unit cell of the hexagonal lattice is **not** a hexagon and the unit cell of the centered rectangle is not a rectangle.

You may be wondering what is gained by distinguishing the special parallelograms from the general. Be reassured, a very good reason exists for this. Imagine that we were to cut a specimen from the crystal shown in Figure 6-2 and measure its strength and modulus (stiffness) while applying stress in the $\vec{a}$ direction and then again in $\vec{b}$ direction. Would you expect that we would get the same result for both measurements? Obviously not. However, if we were to make the same set of measurements on a crystal with a square lattice, we would get the same answers. The point is that a crystal's properties are intimately tied to the symmetry of the lattice. The square lattice possesses a symmetry that the oblique lattice lacks. Its structure is indistinguishable when rotated 90°. While perhaps not immediately apparent, this symmetry means that the modulus of the crystal will be the same in all directions—not just when pulling along the $\vec{a}$ and $\vec{b}$ directions but when pulling in any direction. This is an example of an isotropic property, i.e., one that is the same in all directions. Materials with isotropic properties are desirable for many engineering applications. In turn, these properties are often a consequence of crystal structure.

Above, we discussed a perfect crystal. These structures are in their ground state arrangement—its lowest potential energy. Yet, if energy is to be stored in a crystal as work, it must be possible to "slightly" rearrange the crystal's atoms. So, many structures of higher energy exist in which the crystalline structure is interrupted by defects. And such defects are responsible for many materials properties. (You should be on the lookout for the defect responsible for toughness). As a result, much of materials science is concerned with developing processes to control defects.

There are four types of defects classified by extent (shape and size): point defects, line defects, surface and boundary defects, and bulk defects.

Though there are several different types of point defects, in lab you may observe a type called a vacancy. Vacancies are produced when an atom is missing from the position it should occupy—leaving an empty space or a hole in the crystal. Point defects play an important role in determining electronic and optical properties of materials.

Also in lab, you may observe grain boundaries. These boundary defects mark a change in the orientation of lattice vectors. In 2D, grain boundaries appear as lines, but in real 3D crystals, they are surface defects that surround individual single crystals called grains. Most, though not all, technologically interesting crystalline materials are polycrystalline with the size of the grains being important in determining mechanical properties.

In lab, you may observe dislocations. Dislocations are examples of line defects. These are a very important class of defect as they move in response to a force and allow whole planes of atoms to shift positions.

Finally, there is a class of defects called bulk defects. In these regions, an entirely different structure extends over significant distances. Voids are a common bulk defect that significantly impacts the strength of a material.

So far, we have talked only about patterns in two dimensions. What we are really interested in, however, are patterns of atoms in three dimensions. First, it is clear that a three-dimensional crystal will have three primitive vectors, $\vec{a}$, $\vec{b}$, and $\vec{c}$, whose orientation relative to each other may be specified by three angle as shown in Figure 6-4. The resulting three-dimensional primitive unit cell will form a parallelepiped. Just as with the 2D crystals, where there are special parallelograms, in 3D crystals there are special parallelepipeds. The most general parallelepiped is characterized by three primitive vectors ($\vec{a}$, $\vec{b}$, and $\vec{c}$) of different lengths and inclined to each other at three different angles. The resulting lattice is called triclinic. When all the basis vectors are of the same length we have a trigonal lattice. If one of the primitive vectors, say $\vec{c}$, is at right angles to the other two, we get a monoclinic unit cell. The hexagonal lattice is produced when, in addition to being perpendicular to $\vec{c}$, $\vec{a}$ and $\vec{b}$ are of equal length and the angle between them is 60°. Finally, we have the orthorhombic lattices that result when the all three lattice vectors are orthogonal to each other. When, in addition, two or three of the lattice vectors are of equal length, the result is a tetragonal or cubic lattice respectively. That is it; these cells represent all the special parallelepipeds and give rises to the seven classes of crystal lattices.
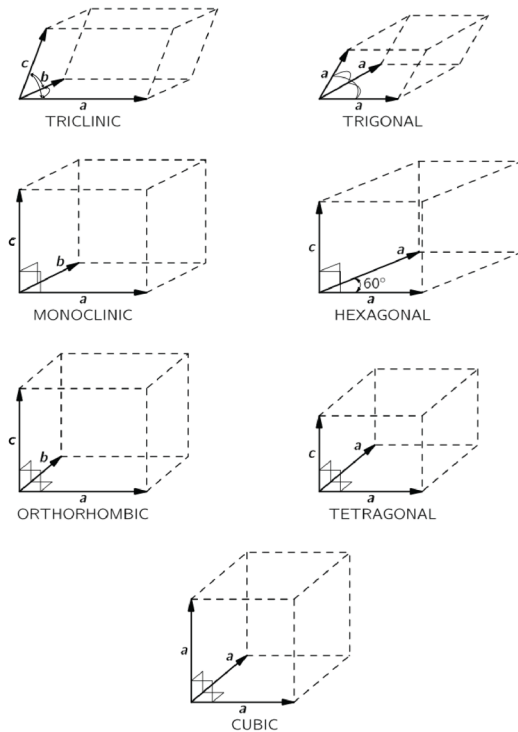

Fig. 6-4. The seven classes of crystal lattices

6-5 CUBIC LATTICES

Just as there are two primitive rectangular lattices (rectangular and centered rectangular), there are different primitive unit cells comprising some of the crystal classes. We are particularly interested in the unit cells that comprise the cubic crystal class, of which there are three: simple cubic (SC), body-centered cubic (BCC) and face-centered cubic (FCC).
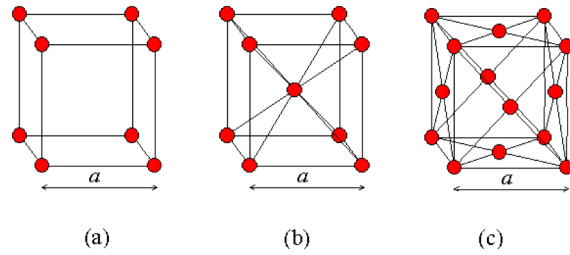

(a)   (b)   (c)

Fig. 6-5. The cubic lattices: a) simple cubic, b) body-centered cubic and c) face-centered cubic

While a primitive unit cell for each of these structures exists, more commonly they are represented in terms of their conventional, or cubic unit, cells as shown in Figure 6-5.

The SC cell can also be identified as a primitive unit cell. The BCC conventional unit cell has an additional lattice point in what is called the cube's *body center*. The FCC conventional unit cell contains additional lattice points in the cube faces.

The BCC and FCC lattices are of particular interest because many engineering materials are commonly composed of these lattice structures. Iron, the principal component of steel, is BCC, and so is the very hard and dense metal tungsten. The ductile metals of copper, silver, gold and aluminum, which may be drawn easily into wires or hammered into sheets, share the FCC lattice. Collectively when we refer to these metals as BCC or FCC, by convention we assume that a single atom sits on each lattice point. However, this is not always the case. Silicon, which is an important component of almost all electronics, has an FCC crystal structure with a two-atom motif.

6-6 THE HEXAGONAL CLOSE PACKED STRUCTURE

Another technologically important crystal is the hexagonal close packed (HCP) structure. Metals like zinc and magnesium share this structure. The HCP structure is built from a hexagonal lattice with a two-atom motif as pictured in Figure 6-6. Note that the primitive cell

Fig. 6-6: left) The HCP primitive unit cell, right) Several primitive cells showing hexagonal symmetry

is not a hexagonal prism. The hexagonal symmetry results from the packing of three primitive cells.

Now let's see how energy is stored in metals during deformation. Most of the familiar metals are considered tough because one layer of the crystal easily slides over the next. Suppose we look at two layers of a crystal subjected to a shear force, as shown in the diagram of Figure 6-7 (a). You might at first think the whole layer would resist motion until the force was big enough to push the whole layer "over the hump," so that it shifted one notch to the left. Although slipping does occur along a plane, it doesn't happen that way. What happens is more like one atom going at a time; first the atom on the left makes its jump, then the next, and so on, as indicated in Figure 6-7 (b). In effect, the vacant space between two atoms quickly travels to the right, with the net result that the whole second layer
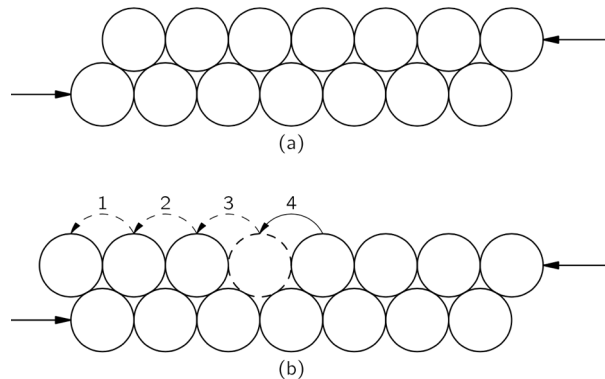
Fig 6-7 Slippage o0f crystal planes

has moved over one atomic spacing. The slipping goes this way because much less energy is required to lift one atom at a time over the hump than to lift a whole row. Once enough stress is applied to start the process, the rest of movement occurs very fast. The stress at which the slip begins is the yield stress we discussed in the last chapter.

It turns out that in a real crystal, slipping will occur repeatedly at one plane, stop, and then start again at some other plane. The details of why it starts and stops are quite mysterious. It is, in fact, quite strange that successive regions of slip are often fairly evenly spaced. Figure 6-8 shows a photograph of a tiny thin copper crystal that has been stretched. You can see the various planes where slipping has occurred. These are called slip planes.

Fig. 6-8 Slip bands in a copper wire

The sudden slipping of individual crystal planes is quite apparent if you take a piece of tin wire and stretch it while holding it next to your ear. You can hear a rush of "ticks" as the planes snap to their new positions, one after the other.

The problem of having a "missing" atom in one row is somewhat more difficult than it might appear from Figure 6-7. When there are more layers, the situation must be something like that shown in Figure 6-9. Such an imperfection in a crystal is called a *dislocatio*n. This defect is generated when a metal is subjected to stresses greater than the yield stress. The work of deformation is thus stored in these dislocations. Once dislocations are produced, they can move relatively freely through the crystal. Moreover, the gross deformation results from the production of many of such dislocations.
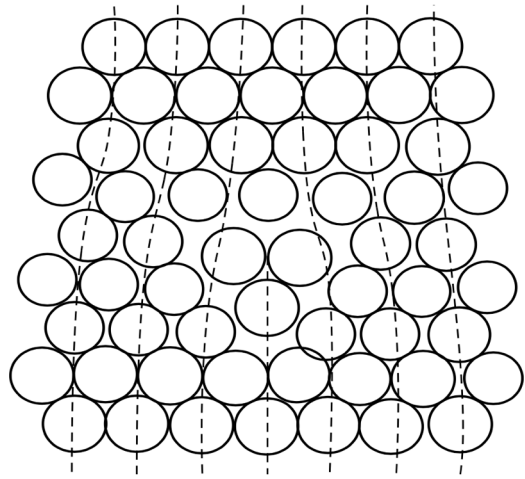

Fig 6-9 Across section through a dislocation

Dislocations can move freely—that is, they require little extra energy to move—so long as the rest of the crystal has a perfect lattice. But they may get "stuck" if they encounter some other kind of crystalline defect such as a grain boundary. If it takes a lot of energy for a dislocation to pass the imperfection, they will stop and instead transfer that energy to make another dislocation nearby. This is one of the ways we can increase the yield strength of a metal using a process called alloying. Pure FCC, BCC, or HCP metals are quite soft—dislocations are created and move easily--but a small concentration of impurity atoms may block the dislocations. These immobilized dislocations require more force to start moving and hence yielding begins at larger stresses.

As you observed in laboratory, pure copper is very soft, but can be "work-hardened." This is done by hammering on it or bending it back and forth. In this case, many new dislocations of various kinds are made, which interfere with one another, cutting down their mobility. In the process, the copper was work-hardened and cannot easily be unbent. A work-hardened metal like copper can be made soft again by annealing at a high temperature. The thermal motion of the atoms takes them over the energy barrier transforming the metastable dislocation into the lower energy crystal.

1) For each pattern, outline the **primitive unit cell** and identify the **lattice type**. *If you find a centered rectangular lattice, indicate BOTH the primitive and the **conventional unit cell**.*
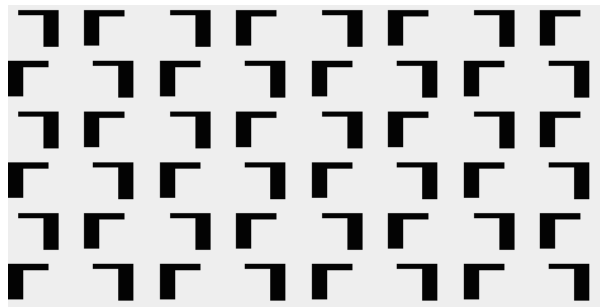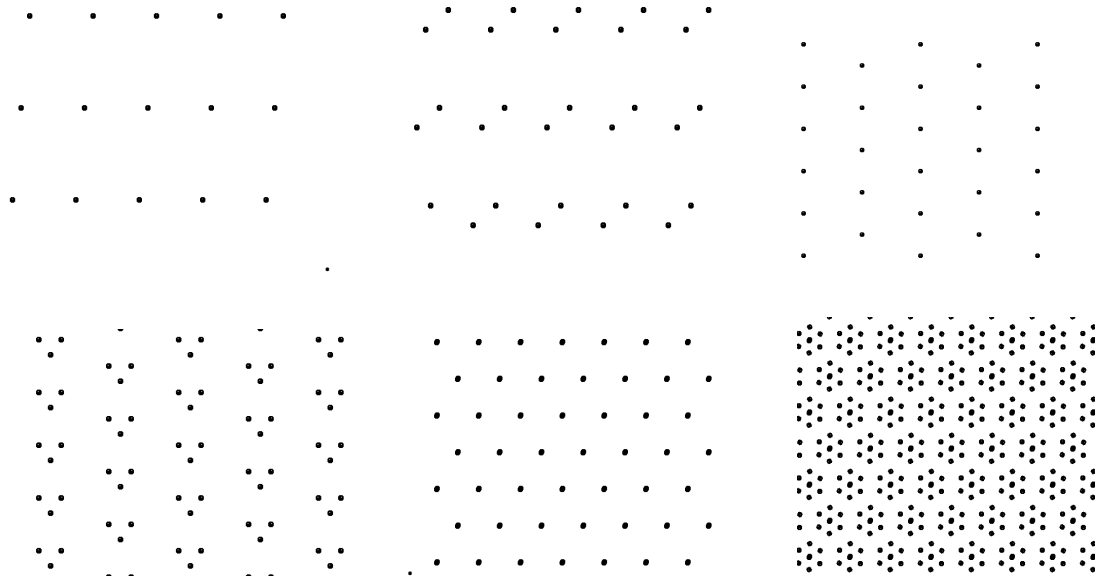
2) Among the 2D lattice types is the centered rectangular lattice, but there is no "centered square" lattice or "centered hexagonal" lattice. Why not?

3) For both the FCC and BCC structures, calculate the lattice constant of the conventional unit cell that will result from the packing of atoms of radius **r**.

4) **Journaling activity:**
   How do we know the crystal structures of materials? Who was the first person to determine a crystal structure? (Hint: this might be a good place to start. http://learn.crystallography.org.uk/learn-crystallography/history/.)