CHAPTER 1

CRYSTAL STRUCTURE AND SYMMETRY

1-1 Introduction

Many solids around us are crystalline. Obvious examples are diamonds and other precious stones which have an outward crystalline appearance. Many metals are also crystalline. However, they are usually composed of numerous small crystals fused together so that their outward appearance is *not* crystalline. In this book, we will consider only crystalline solids.

A *crystal* is a solid in which all the atoms are arranged in a periodic manner. As a simple example, consider the cubic arrangement of atoms shown in Fig. 1-1. We show only a portion of the crystal. We imagine that it extends out in all directions to infinity. Real crystals, of course, have finite dimensions, but, for now, we consider the crystal to be infinitely large with no surfaces.

The atoms in the crystal shown in Fig. 1-1 are in **equivalent positions**. If we sit on one of the atoms, we cannot tell where we are by looking at the neighboring atoms. All atoms have exactly the same surroundings. (This, of course, is only strictly true in an *infinite* crystal.) If we move the entire crystal in some direction so that each atom is now at a position where some other atom used to be, the crystal looks the same as before. We cannot tell that it has been moved. This is called **translational symmetry**. We may now state the definition of a crystal more precisely. A **crystal** is a solid which has translational symmetry.
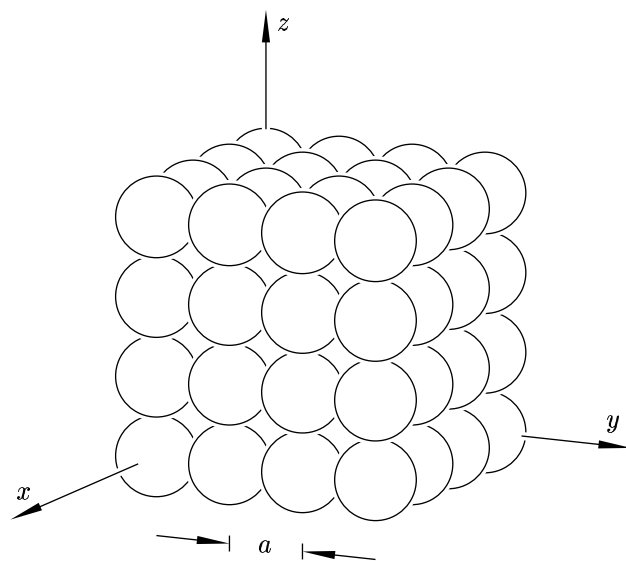

Fig. 1-1. Simple cubic arrangement of atoms.

1-2 Lattices

In order to quantitatively describe a crystal, we introduce a group of geometric points called the crystal **lattice** which defines the positions of the atoms. As an example, consider the two-dimensional square lattice shown in Fig. 1-2. This lattice is a set of geometric points on a plane. If we were to place an atom at each point, then we would have a two-dimensional crystal. All lattice points in the figure are equivalent. This lattice has translational symmetry in two dimensions.
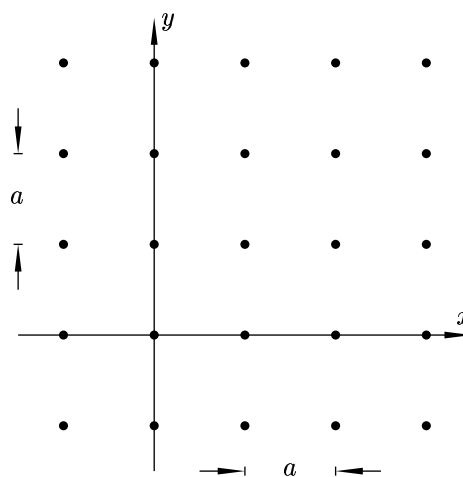

Fig. 1-2. The two-dimensional square lattice.

1-3 Basis Vectors

A **lattice vector** is a vector which takes us from one lattice point to any other lattice point. Obviously, all lattice vectors $\mathbf{R}$ in the two-dimensional square lattice (Fig. 1-2) have the form

$$\mathbf{R} = n_1 a\hat{\mathbf{i}} + n_2 a\hat{\mathbf{j}}, \qquad (1\text{-}1)$$

where n_1 and n_2 are integers (including negative values and zero), and a is the distance between adjacent lattice points in the x or y directions, as shown in Fig. 1-2. $\hat{\mathbf{i}}$ and $\hat{\mathbf{j}}$ are unit vectors in the x and y directions, respectively. If we define two vectors (see Fig. 1-3),

$$\mathbf{a}_1 = a\hat{\mathbf{i}},$$
$$\mathbf{a}_2 = a\hat{\mathbf{j}}, \qquad (1\text{-}2)$$

then we can write $\mathbf{R}$ as

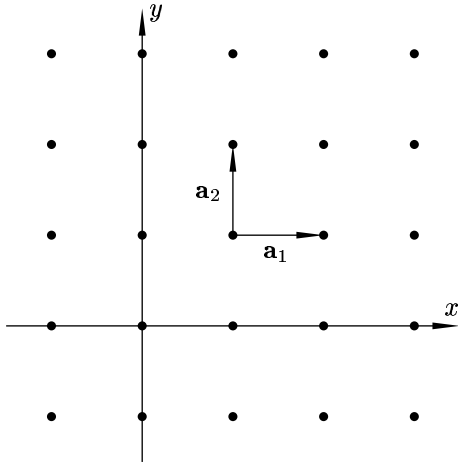$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2. \qquad (1\text{-}3)$$
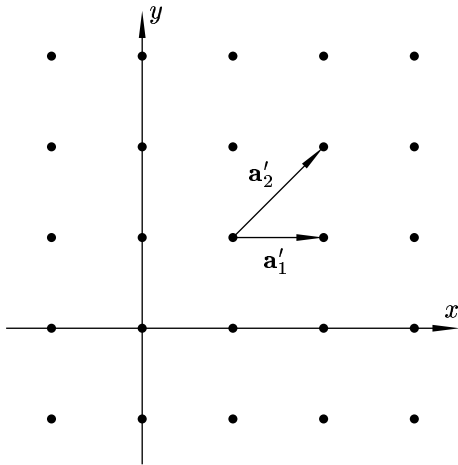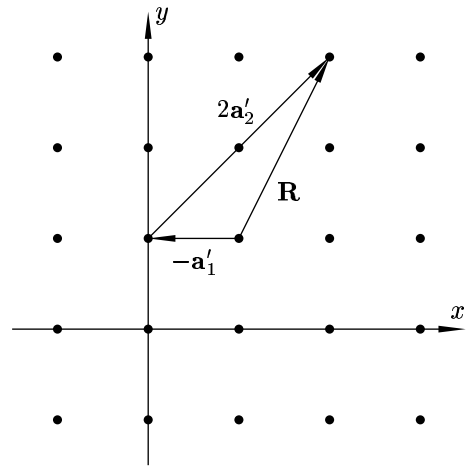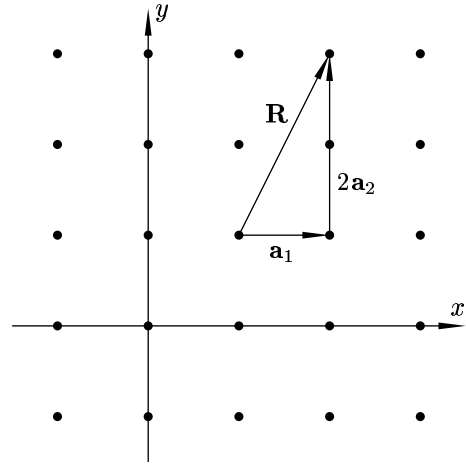
Fig. 1-3. Basis vectors for the square lattice.

Fig. 1-4. An alternate choice of basis vectors for the square lattice.

Thus, *any* lattice vector $\mathbf{R}$ can be written as a linear combination of $\mathbf{a}_1$ and $\mathbf{a}_2$ (using integers, n_1 and n_2). Conversely, it is also true that any linear combination of $\mathbf{a}_1$ and $\mathbf{a}_2$ (using integers, n_1 and n_2) is a lattice vector $\mathbf{R}$. Such vectors, $\mathbf{a}_1$ and $\mathbf{a}_2$, are called **basis vectors** of the lattice.

The choice of basis vectors, $\mathbf{a}_1$ and $\mathbf{a}_2$, is not unique. We could just as well choose (see Fig. 1-4)

$$\mathbf{a}_1' = a\hat{\mathbf{i}},$$
$$\mathbf{a}_2' = a\hat{\mathbf{i}} + a\hat{\mathbf{j}}. \tag{1-4}$$

For example, consider the lattice vector $\mathbf{R} = a\hat{\mathbf{i}} + 2a\hat{\mathbf{j}}$. This can be written as $\mathbf{R} = \mathbf{a}_1 + 2\mathbf{a}_2$ or as $\mathbf{R} = -\mathbf{a}_1' + 2\mathbf{a}_2'$ as shown in Fig. 1-5. There are an infinite number of ways to choose basis vectors for a given lattice. There is, however, usually a **conventional** choice of basis vectors. For example, the conventional

Fig. 1-5. Lattice vector $\mathbf{R}$ expressed as a linear combination of the basis vectors, $\mathbf{a}_1$ and $\mathbf{a}_2$, and also as a linear combination of the basis vectors, $\mathbf{a}_1'$ and $\mathbf{a}_2'$.

basis vectors for the square lattice are those given in Eq. (1-2). Basis vectors can be found for any lattice of *equivalent* points.

1-4 Simple Cubic Lattice

The extension to three dimensions is straightforward. The lattice which underlies the crystal structure in Fig. 1-1 has basis vectors given by

$$\mathbf{a}_1 = a\hat{\mathbf{i}},$$
$$\mathbf{a}_2 = a\hat{\mathbf{j}}, \tag{1-5}$$
$$\mathbf{a}_3 = a\hat{\mathbf{k}},$$

and the lattice vector is given by

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3. \tag{1-6}$$

This lattice is called **simple cubic** (sc).

1-5 Unit Cells

A crystal can always be divided into "building blocks" called **unit cells**. Each unit cell has the same shape, the same volume, and the same contents. For the sc lattice, we may choose the unit cell to be a cube of side a (see Fig. 1-6). The choice of position of the lattice point within the unit cell is arbitrary. We may arrange the cubes so that each cube contains one lattice point at its center (see Fig. 1-7a). Alternately, we may arrange the cubes so that the lattice points are at the corners of the cube (see Fig. 1-7b). The second choice is the **conventional unit cell**.

Each of these unit cells contains one lattice point. This is obviously true for the unit cell in Fig. 1-7a which contains one lattice point in the center. But the conventional unit cell in Fig. 1-7b appears to contain *eight* lattice points, one at each corner. Actually, each of those lattice points is shared by eight neighboring unit cells that adjoin at the corner so that each unit cell contains "$\frac{1}{8}$ lattice point" at the corner. Eight such lattice points give us a total of one lattice point in the unit cell.

Just as the choice of basis vectors for a lattice is not unique, the choice of unit cells is also not unique. For example, we could just as well choose the unit cell shown in Fig. 1-8. We only require that the unit cells be identical to each other and fill all space. There are an infinite number of ways to choose the unit cell. However, the *conventional* unit cell for the sc lattice is the cube shown in Fig. 1-7b. The distance a between adjacent lattice points in the x, y, or z direction is called the **lattice parameter**.
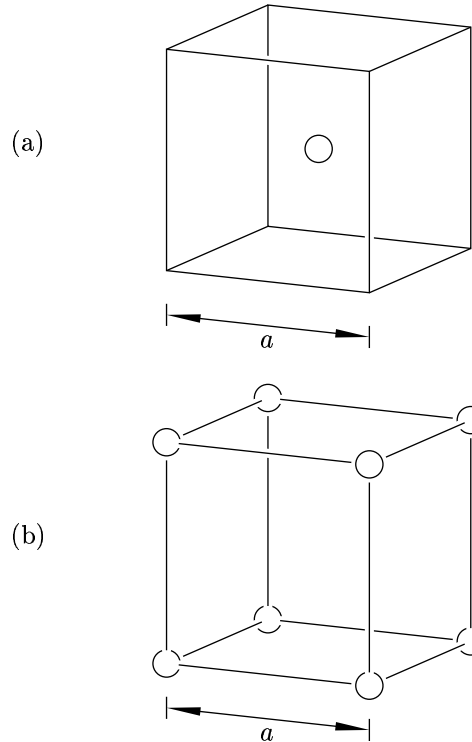
(a)

(b)

Fig. 1-7. The unit cell for the sc lattice (a) with a lattice point at the center and (b) with a lattice point at each corner (conventional unit cell).
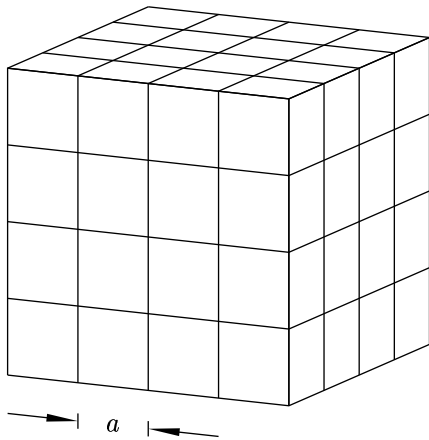

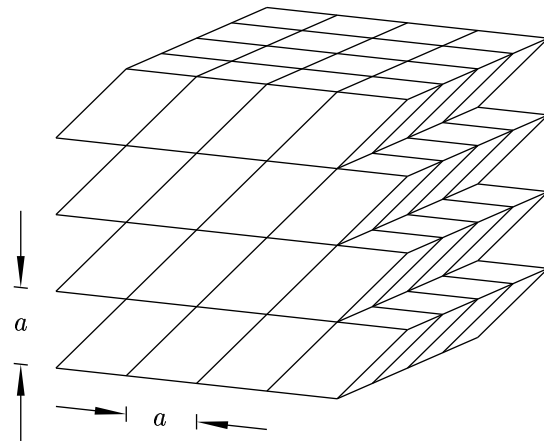Fig. 1-6. Unit cells of the sc lattice

Fig. 1-8. An alternate choice of unit cell for the sc lattice.

1-6 Crystal Directions and Planes

Directions in crystals are usually represented in shorthand by three integers inside a set of square brackets. The direction $\mathbf{R} = n_1 a\hat{\imath} + n_2 a\hat{\jmath} + n_3 a\hat{\mathbf{k}}$ in a cubic crystal, for example, is written as $[n_1, n_2, n_3]$. The integers are usually chosen to be as small as possible. Three common directions in cubic crystals with which we will deal are (see Fig. 1-9)

$$\begin{aligned}
\mathbf{R} &= a\hat{\imath} & &\text{or} \quad [100], \\
\mathbf{R} &= a\hat{\imath} + a\hat{\jmath} & &\text{or} \quad [110], \qquad (1\text{-}7) \\
\mathbf{R} &= a\hat{\imath} + a\hat{\jmath} + a\hat{\mathbf{k}} & &\text{or} \quad [111].
\end{aligned}$$

Consider a hypothetical crystal which has one atom at each lattice point of an sc lattice with $a = 5.00$ Å. (No naturally occurring element forms an sc lattice.) Starting from an atom at the origin, we see that along the [100] direction, there are atoms at $a\hat{\imath}$, $2a\hat{\imath}$, $3a\hat{\imath}$, etc. The distance between adjacent atoms along the [100] direction is $a = 5.00$ Å, which is the length of the vector $\mathbf{a}_1 = a\hat{\imath}$.

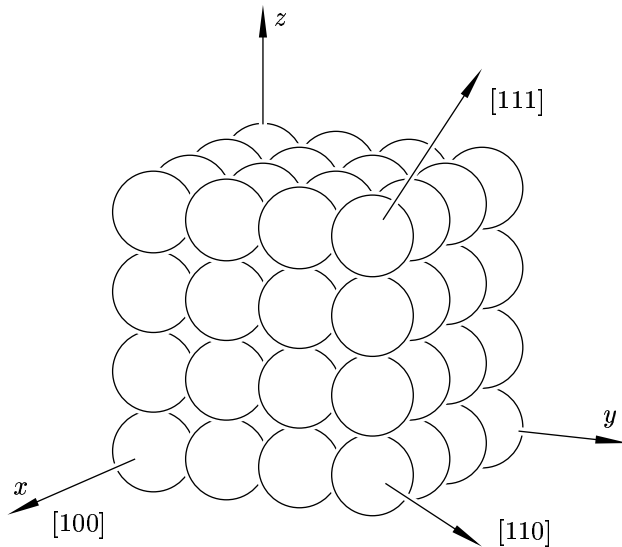Fig. 1-9. Three common directions in cubic crystals.

If we go along the [110] direction from the atom at the origin, we find atoms at $a\hat{\imath} + a\hat{\jmath}$, $2a\hat{\imath} + 2a\hat{\jmath}$, $3a\hat{\imath} + 3a\hat{\jmath}$, etc., and the distance between adjacent atoms is the length of the vector $a\hat{\imath} + a\hat{\jmath}$, which is $\sqrt{2}a = 7.07$ Å. Similarly, along the [111] direction, atoms are at $a\hat{\imath} + a\hat{\jmath} + a\hat{\mathbf{k}}$, $2a\hat{\imath} + 2a\hat{\jmath} + 2a\hat{\mathbf{k}}$, $3a\hat{\imath} + 3a\hat{\jmath} + 3a\hat{\mathbf{k}}$, etc., and the distance between adjacent atoms is the length of the vector $a\hat{\imath} + a\hat{\jmath} + a\hat{\mathbf{k}}$, which is $\sqrt{3}a = 8.66$ Å.

We would find, in general, that along any given direction in a crystal, atoms are evenly spaced. The distance between adjacent atoms is smallest along the [100] direction. These atoms are **nearest neighbors** to each other. If we imagine the atoms to be "hard" spheres such as those shown in Fig. 1-1, then we see that the nearest neighbors "touch" each other, and the distance between the centers of nearest-neighbor atoms is the diameter of the atoms. Thus, in this hypothetical crystal, the diameter of the atoms is 5.00 Å.

Planes of atoms in a crystal are usually represented in shorthand by three integers inside a set of *parentheses*. In cubic crystals, a plane denoted by (n_1, n_2, n_3) is perpendicular to the direction $[n_1, n_2, n_3]$. These three integers n_1, n_2, n_3, when re-
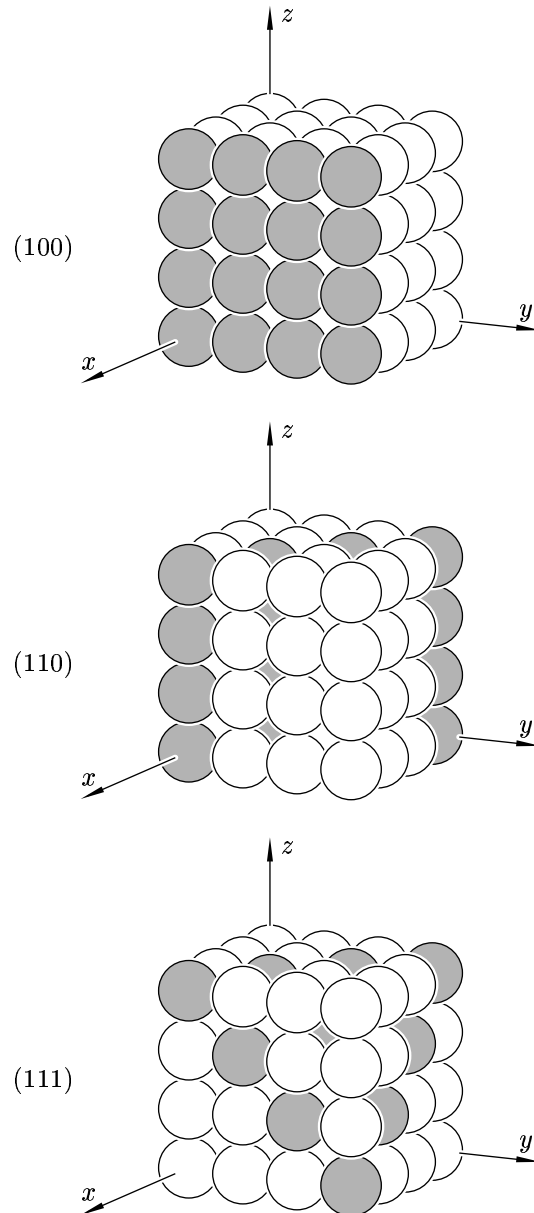

Fig 1-10. Some typical planes of atoms in a cubic crystal. The atoms forming the planes are shaded.

ferring to crystal planes, are called **Miller indices**. (In non-cubic crystals, the meaning of Miller indices is more complicated.) In Fig. 1-10 are shown some typical planes in a cubic crystal. Distances between adjacent planes of atoms can be computed by inspection for the simpler cases. For example, from Fig. 1-11, we see that the distance between adjacent (100) planes is a and between adjacent (110) planes is $a/\sqrt{2}$. For our hypothetical crystal of $a = 5.00$ Å, these distances are 5.00 Å and 3.54 Å, respectively.

The atomic density n of a crystal (in units of atoms/unit volume) is easily obtained by considering a single unit cell. For our hypothetical crystal, there is one atom per unit cell, and the volume of the unit cell is a^3. Thus, $n = a^{-3}$. For $a = 5.00$ Å, we have $n = 8.00 \times 10^{21}$ atoms/cm^3. To obtain the *mass* density ρ (in units of g/cm^3, for example), we only need to know the mass of each atom. We will illustrate this later for the case of an actual crystal.

1-7 Body-Centered Cubic Lattice

We can form a new lattice which is different from the sc lattice by placing an additional lattice point at the center of the unit cell of Fig. 1-7b. The resulting lattice
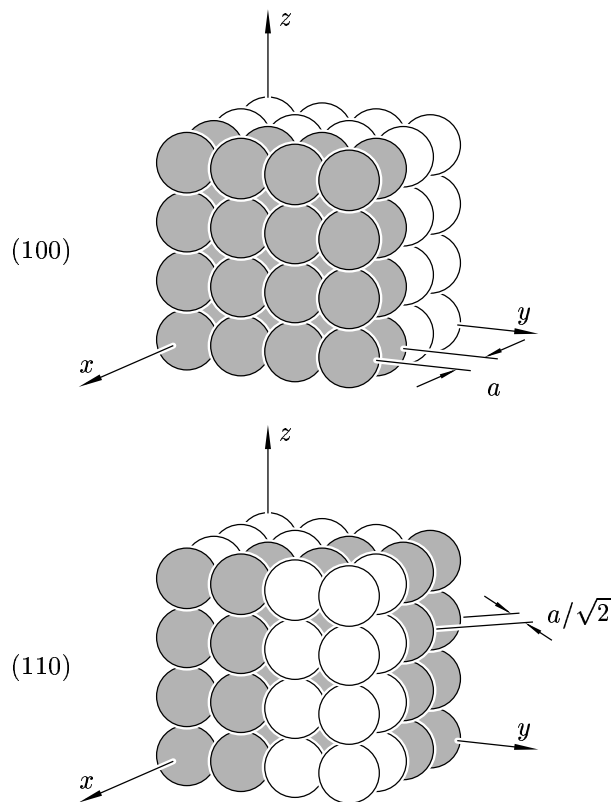
is called body-centered cubic (bcc) and is shown in Fig. 1-12. Note that every lattice point is equivalent to every other lattice point. Each of the original sc lattice points is also in the body-centered position of eight of the new lattice points.

The conventional unit cell for the bcc lattice is a cube of side a as shown in Fig. 1-13. We see that there are two lattice points in this unit cell: a lattice point in the center and $\frac{1}{8}$ lattice point at each of the eight corners. This is *not* the smallest possible unit cell which can be constructed for the bcc lattice. The smallest possible unit cell, called the **primitive unit cell**, contains only *one* lattice point. Its volume is *half* the volume of the conventional unit cell shown in Fig. 1-13.

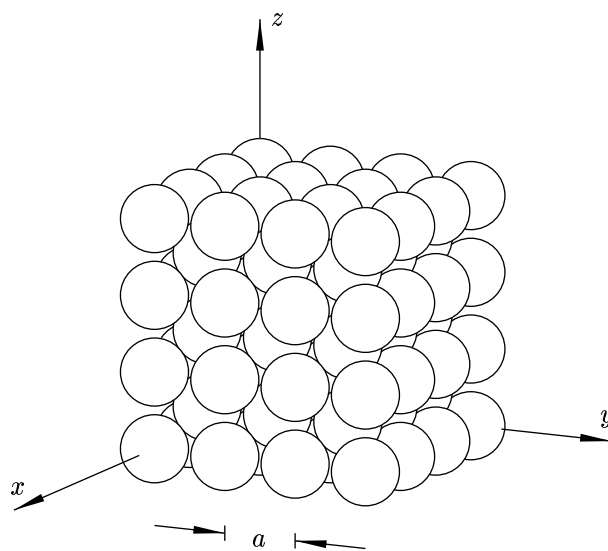Fig. 1-12. Body-centered cubic arrangement of atoms.

(100)

(110)

Fig 1-11. Distances between adjacent planes of atoms for two cases in a cubic crystal. The adjacent planes of atoms are shaded.
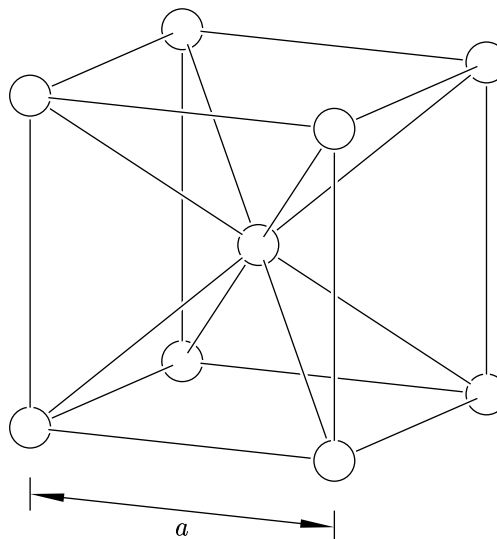

Fig. 1-13. The conventional unit cell of the bcc lattice.

The choice of primitive unit cell is not unique. There are an infinite number of possible ways to choose it. However, in physics, we usually use the primitive unit cell called the **Wigner-Seitz cell**. This cell contains one lattice point at its center and contains the region of space that is closer to that point than to any other lattice point. This is best explained by example. The Wigner-Seitz cell for a two-dimensional square lattice is shown in Fig. 1-14. For the two-dimensional centered-rectangular lattice shown in Fig. 1-15, the result is more complicated. Note that each line segment which forms a cell boundary is a perpendicular bisector of a line joining two lattice points.

In three dimensions, the case of the sc lattice is simple. The Wigner-Seitz cell is the cube we already showed in Fig. 1-7a. For the bcc lattice, the Wigner-Seitz cell is a "truncated octahedron" as shown in Fig. 1-16. Its volume is $\frac{1}{2}a^3$. These cells nest together and fill all space.

The basis vectors of a bcc lattice are *not* those given in Eq. (1-5) for the sc lattice. No linear combination of those vectors (using integers) can take us

(a)

(b)

Fig. 1-16. (a) The Wigner-Seitz cell for the bcc lattice. (b) These cells fit together to fill all space.
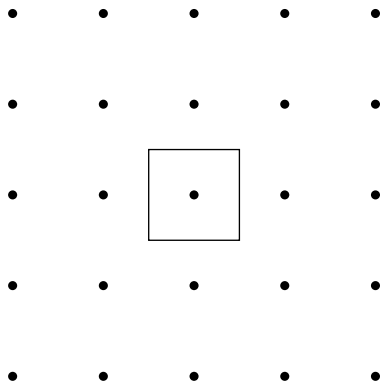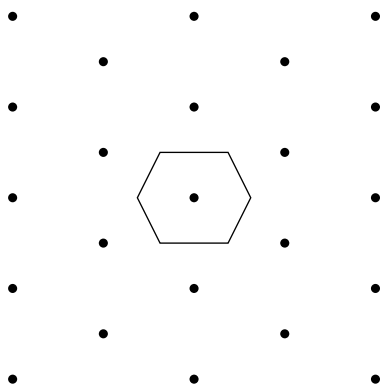
Fig. 1-14. The Wigner-Seitz cell for a two-dimensional square lattice.

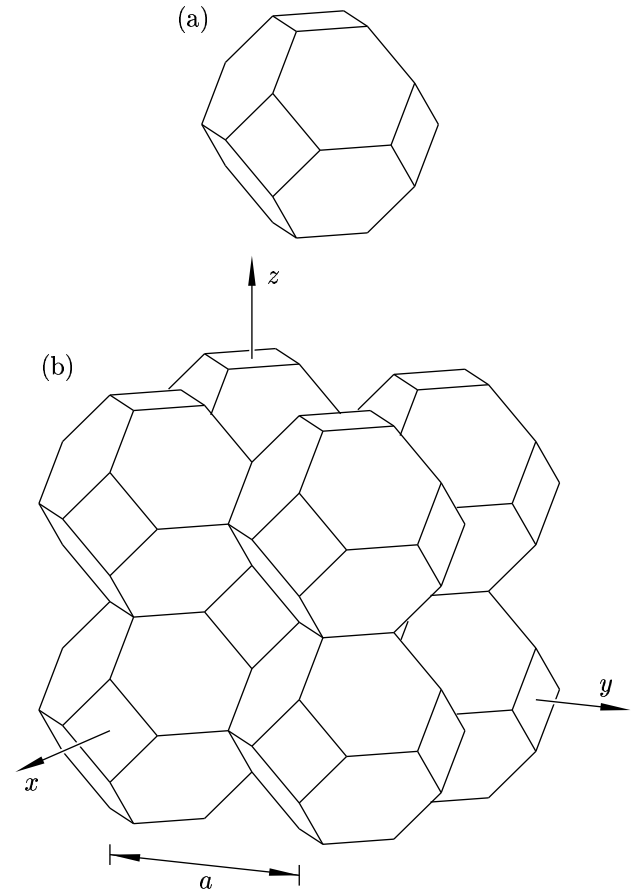Fig. 1-15. Wigner-Seitz cell for the two-dimensional centered-rectangular lattice.

to any of the body-centered lattice points such as $\mathbf{R} = \frac{1}{2}a\hat{\mathbf{i}} + \frac{1}{2}a\hat{\mathbf{j}} + \frac{1}{2}a\hat{\mathbf{k}}$. There is no unique way to choose the basis vectors of a bcc lattice, but a very common choice is

$$\mathbf{a}_1 = -\tfrac{1}{2}a\hat{\mathbf{i}} + \tfrac{1}{2}a\hat{\mathbf{j}} + \tfrac{1}{2}a\hat{\mathbf{k}},$$
$$\mathbf{a}_2 = \tfrac{1}{2}a\hat{\mathbf{i}} - \tfrac{1}{2}a\hat{\mathbf{j}} + \tfrac{1}{2}a\hat{\mathbf{k}}, \qquad (1\text{-}8)$$
$$\mathbf{a}_3 = \tfrac{1}{2}a\hat{\mathbf{i}} + \tfrac{1}{2}a\hat{\mathbf{j}} - \tfrac{1}{2}a\hat{\mathbf{k}}.$$

All lattice points can be expressed in the form $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$. For example, $\frac{1}{2}a\hat{\mathbf{i}} + \frac{1}{2}a\hat{\mathbf{j}} + \frac{1}{2}a\hat{\mathbf{k}} = \mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3$. Also, as another example, $a\hat{\mathbf{i}} = \mathbf{a}_2 + \mathbf{a}_3$.

Directions and planes in a bcc crystal are *not* labeled in reference to these new basis vectors, but are labeled according to the convention we introduced for the sc lattice. Thus, directions $[n_1, n_2, n_3]$ and planes (n_1, n_2, n_3) have the same meaning with respect to the x, y, and z axes as in the sc lattice shown in Figs. 1-9 and 1-10. In the bcc lattice, points along the [111] direction are nearest neighbors. The distance between them is the length of the vector $\mathbf{R} = \frac{1}{2}a\hat{\mathbf{i}} + \frac{1}{2}a\hat{\mathbf{j}} + \frac{1}{2}a\hat{\mathbf{k}}$ which is $\frac{1}{2}a\sqrt{3} = 0.866a$.

Examples of elements which form bcc crystals are given in Appendix 6. For example, iron (Fe) forms a bcc crystal with $a = 2.86$ Å. The distance between nearest-neighbor atoms is $0.866a = 2.48$ Å. One can think of this as the "diameter" of the Fe atom. The easiest way to compute the atomic density n of Fe is to use the conventional unit cell of Fig. 1-13. It contains two atoms and has a volume of a^3. Thus, $n = 2a^{-3} = 8.55 \times 10^{22}$ atoms/cm^3. To obtain the mass density ρ, we need to know the mass of a single Fe atom. The **atomic mass** given in Appendix 2 is the mass in units of atomic mass units. From Appendix 2, we find the mass of one Fe atom is 55.85 u or 9.27×10^{-23} g. Thus, the mass density of Fe is $\rho = (8.55 \times 10^{22}$ atoms/cm$^3) \times (9.27 \times 10^{-23}$ g/atom$) = 7.93$ g/cm^3.

Problem 1-1. Consider a crystal of iron (Fe). Find the distance between adjacent atoms in the [100] direction. Repeat for the [110] and [111] directions. Find the distance between the (100) planes. Repeat for the (110) planes. Answer: 2.86 Å, 4.04 Å, 2.48 Å, 1.43 Å, 2.02 Å.

Problem 1-2. Using the data in Appendix 6, find the atomic diameter of lithium (Li). Repeat for sodium (Na), potassium (K), rubidium (Rb), and cesium (Cs). (Consider the atoms to be spheres which touch each other.) Answer: 3.03 Å, 3.72 Å, 4.50 Å, 4.84 Å, 5.63 Å.

Problem 1-3. Using data in Appendix 6, find the volume of a primitive unit cell in a crystal of chromium (Cr). Answer: 11.8 Å^3.

1-8 Face-Centered Cubic Lattice

Yet another lattice can be formed from the sc lattice by placing a lattice point at the center of each *face* of the unit cell shown in Fig. 1-7b. The resulting lattice is called face-centered cubic (fcc) and is shown in Fig. 1-17. As with the bcc lattice, every lattice point in the fcc lattice is equivalent. The *conventional* unit cell for the fcc lattice is a cube of side a as shown in Fig. 1-18. Let us count the number of lattice points in this unit cell. There are eight corners (each containing $\frac{1}{8}$ lattice point) and six faces (each containing $\frac{1}{2}$ lattice point) which gives us a total of four lattice points. This, of course, is *not* a primitive unit cell for the fcc lattice. The Wigner-Seitz primitive unit cell for the fcc lattice is a rhombic dodecahedron and is shown in Fig. 1-19. It contains one lattice point, and thus its volume is $\frac{1}{4}a^3$.
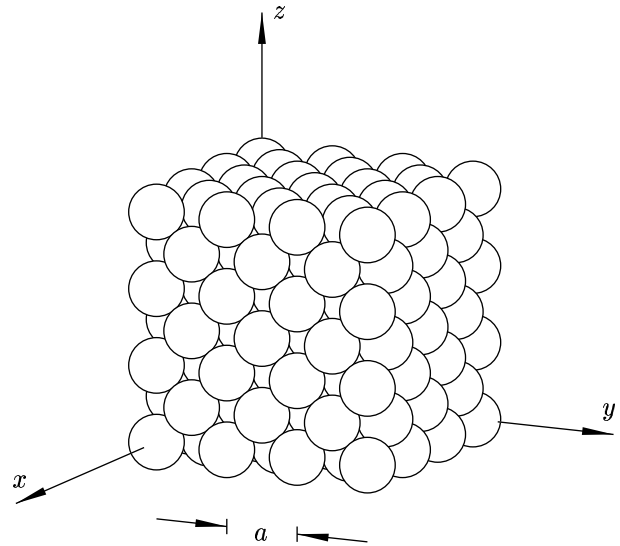
Fig. 1-17. Face-centered cubic arrangement of atoms.
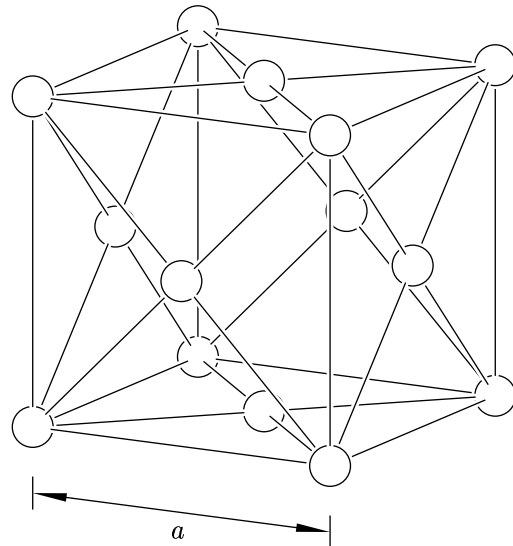
Fig. 1-18. The conventional unit cell of the fcc lattice.

A common choice for basis vectors of the fcc lattice is the following:

$$\mathbf{a}_1 = \tfrac{1}{2}a\hat{\mathbf{j}} + \tfrac{1}{2}a\hat{\mathbf{k}},$$
$$\mathbf{a}_2 = \tfrac{1}{2}a\hat{\mathbf{i}} + \tfrac{1}{2}a\hat{\mathbf{k}}, \qquad (1\text{-}9)$$
$$\mathbf{a}_3 = \tfrac{1}{2}a\hat{\mathbf{i}} + \tfrac{1}{2}a\hat{\mathbf{j}}.$$

Lattice points along the [110] direction are nearest neighbors. The distance between them is the length of the vector $\frac{1}{2}a\hat{\mathbf{i}} + \frac{1}{2}a\hat{\mathbf{j}}$ which is $\frac{1}{2}a\sqrt{2} = 0.707a$. Examples of elements which form fcc crystals are given in Appendix 6.

(a)

(b)

Fig. 1-19. (a) The Wigner-Seitz cell for the fcc lattice. (b) These cells fit together to fill all space.

Problem 1-4. Consider a crystal of copper (Cu). Find the distance between adjacent atoms in the [100] direction. Repeat for the [110] and [111] directions. Find the distance between the (100) planes. Repeat for the (110) planes. Answer: 3.61 Å, 2.55 Å, 6.25 Å, 1.81 Å, 1.28 Å.
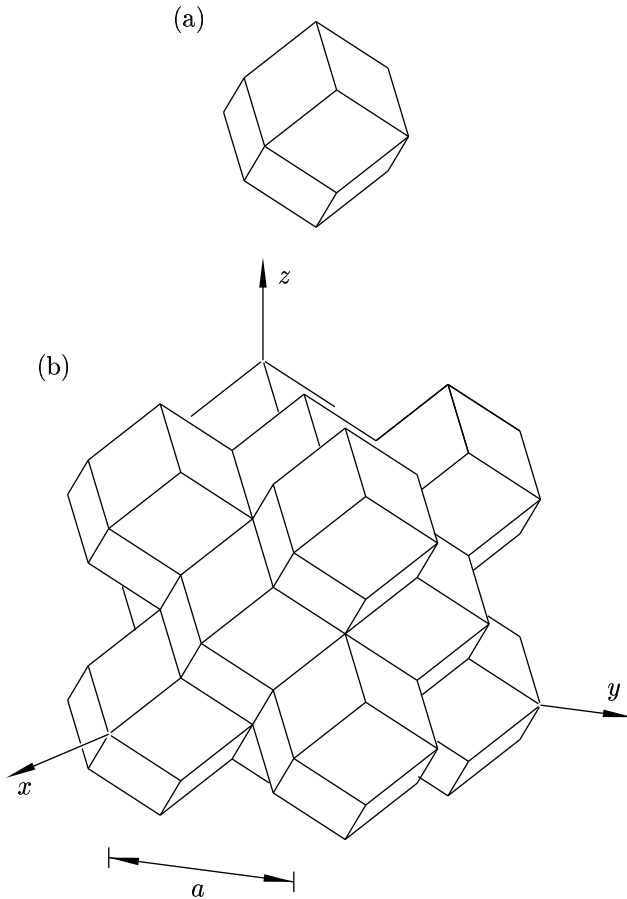
Problem 1-5. Using the data in Appendix 6, find the atomic diameter of copper (Cu). Repeat for silver (Ag) and gold (Au). (Consider the atoms to be spheres which touch each other.) Answer: 2.55 Å, 2.88 Å, 2.88 Å.

Problem 1-6. Using data in Appendices 2 and 6, find the density (in g/cm^3) of aluminum (Al). Answer: 2.72 g/cm^3.

Problem 1-7. The structure of iron is found to be bcc below 910°C and fcc above 910°C. The density of iron increases by 1.0% as it goes through the transition from bcc to fcc at 910°C. By what percentage does the nearest-neighbor distance between iron atoms change? Answer: 2.5%.

Problem 1-8. Using data in Appendix 6, find the volume of a primitive unit cell in a crystal of nickel (Ni). Answer: 10.9 $Å^3$.

Problem 1-9. $\mathbf{R} = a\hat{i}$ is a lattice vector of the fcc lattice. Write this vector in the form $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$, using the basis vectors in Eq. (1-9).

Problem 1-10. Consider a box of volume 1.00 m^3 filled with balls of diameter 1.00 mm. (a) If we pack the balls in an sc lattice, how many can we get into the box? (b) Repeat for bcc lattice. (c) Repeat for fcc lattice. Answer: 1.00×10^9, 1.30×10^9, 1.41×10^9.

1-9 Sodium Chloride Structure

Next, let us consider the structure of NaCl (sodium chloride, common table salt). In Fig. 1-20, we see that the Na and Cl atoms occupy the lattice points of an sc lattice. However, since some lattice points are occupied by Na atoms and others by Cl atoms, not all lattice points are *equivalent*. We can tell the difference between the two kinds of sites because the atoms there are different.

If we look carefully at Fig. 1-20, we can see that the Na sites form a set of lattice points which *are* equivalent. We cannot tell the difference between Na atoms. They are each in identical surroundings. Such a set of lattice points which are equivalent to each other is called a **Bravais lattice**. The Bravais lattice of NaCl corresponds to the set of Na sites and is fcc as we can see in Fig. 1-20. Actually, the absolute location of the lattice points is arbitrary, and we could just as well
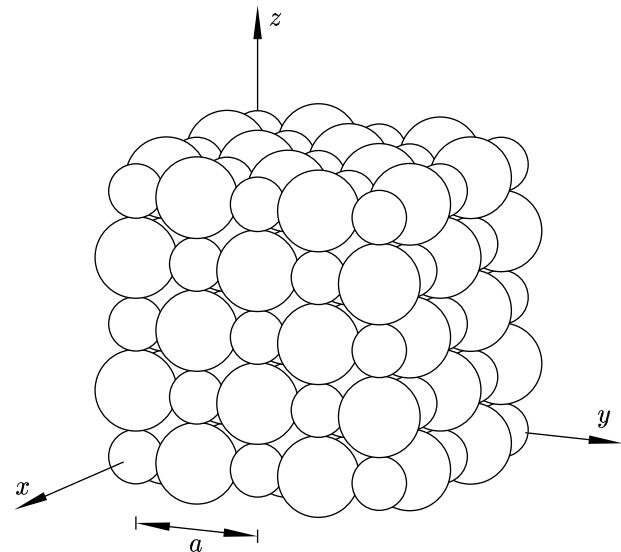
Fig. 1-20. The sodium chloride structure. The small spheres represent Na atoms, and the large spheres represent Cl atoms.

put the lattice points at the Cl sites, which are also equivalent to each other, or we could put the lattice points between Na and Cl atoms. The choice of origin for the lattice is arbitrary. For any given origin $\mathbf{R}_0$ for the lattice, all points $\mathbf{R}_0 + n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$ (where $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ are basis vectors for the fcc Bravais lattice) are at equivalent positions in the crystal.

Associated with each lattice point are two atoms, Na and Cl. These two atoms are called the **basis**. (Do not confuse this usage of the word *basis* with that in *basis vector*.) The lattice is a set of geometric points. The basis is a set of one or more real atoms associated with each lattice point. A *crystal* is a basis combined with a lattice.

The conventional unit cell for the NaCl structure is the same as that for its fcc Bravais lattice and is shown in Fig. 1-21. This unit cell contains four Na atoms and four Cl atoms. We can obtain this result by actually counting them as we did for the bcc and fcc lattices, but the result is more easily obtained by remembering that the conventional unit cell of the fcc lattice contains four lattice points. Since the basis for the NaCl structure is one Na atom and one Cl atom, then the conventional unit cell must contain four of these bases, or four Na and four Cl atoms. The Wigner-Seitz primitive unit cell for the NaCl structure is that of its Bravais fcc lattice, the rhombic dodecahedron in Fig. 1-19, and, of course, contains one Na atom and one Cl atom. Examples of crystals with the NaCl structure are given in Appendix 6.
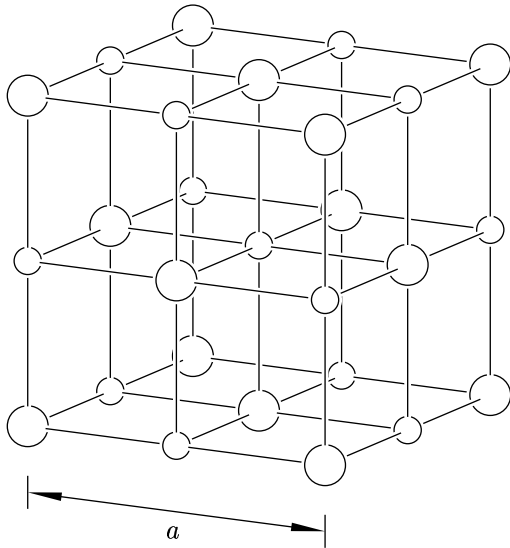
Problem 1-11. Find the distance between nearest-neighbor atoms in sodium chloride (NaCl). Answer: 2.82 Å.

Problem 1-12. The density of sodium chloride (NaCl) is 2.165 g/cm^3. Using the atomic masses in Appendix 2, calculate the lattice parameter a and compare with the value given in Appendix 6.

Problem 1-13. Using data in Appendix 6, find the volume of a primitive unit cell in a crystal of potassium chloride (KCl). Answer: 61.6 Å^3.

Problem 1-14. Consider the two-dimensional crystal shown in Fig. 1-22. The ○ and ● symbols represent two different kinds of atoms. Are all ○ atoms in equivalent positions? Are all ● atoms in equivalent positions? Draw a "conventional" unit cell which is rectangular in shape and has a ○ atom on each corner. How many ○ atoms are in this unit cell? How many ● atoms? Draw a Wigner-Seitz primitive unit cell centered on a ○ atom. Warning: draw carefully!

Problem 1-15. Consider the two-dimensional crystal in Fig. 1-23. There is only one kind of atom in the crystal, represented by the symbol ● in the figure. Are all atoms in equivalent positions? Draw a primitive unit cell. (It does not necessarily need to be a Wigner-Seitz cell.) How many atoms are in this cell?

Fig. 1-21. The conventional unit cell for the sodium chloride structure. The large and small spheres represent two different types of atoms.
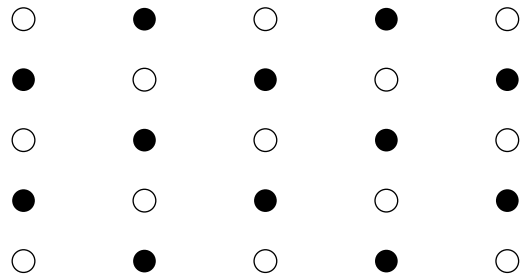
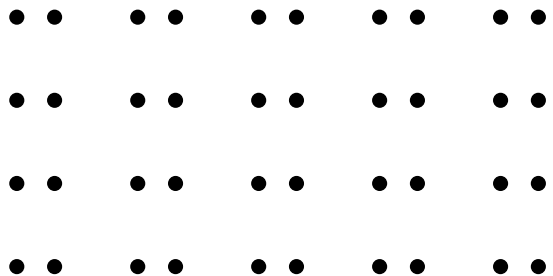

Fig. 1-22. Two-dimensional crystal for Problem 1-14.

Fig. 1-23. Two-dimensional crystal for Problem 1-15.

1-10 Cesium Chloride Structure

Another rather common structure is that of CsCl (cesium chloride, see Fig. 1-24). The Cs and Cl atoms sit at the lattice points of a bcc lattice, but, as with NaCl, since the sites are occupied by different atoms and are not equivalent, the Bravais lattice is given by the set of lattice points just occupied by the Cs atoms and is therefore sc. The basis associated with each lattice point is one Cs atom and one Cl atom. The conventional unit cell of CsCl is the same as that of its sc Bravais lattice (see Fig. 1-25) and contains one Cs atom and one Cl atom. Examples of crystals with the CsCl structure are given in Appendix 6.

Problem 1-16. Using data in Appendix 6, find the volume of a primitive unit cell in a crystal of cesium chloride (CsCl). Answer: 69.4 $Å^3$.

1-11 Zincblende Structure

Next, let us examine the structure of ZnS (zinc sulfide or "zincblende"). This structure is more difficult to visualize than those which we already discussed. The conventional unit cell is shown in Fig. 1-26. The Zn atoms (large spheres) sit at fcc lattice points. If we imagine this unit cell to be divided into eight smaller cubes, then the S atoms (small spheres) sit at the centers of four of these cubes, as shown in Fig. 1-26. Another way of describing the positions of the S atoms is to say that each S atom is displaced from a Zn atom by a vector $\frac{1}{4}a\hat{\mathbf{i}} + \frac{1}{4}a\hat{\mathbf{j}} + \frac{1}{4}a\hat{\mathbf{k}}$. The Bravais lattice of the
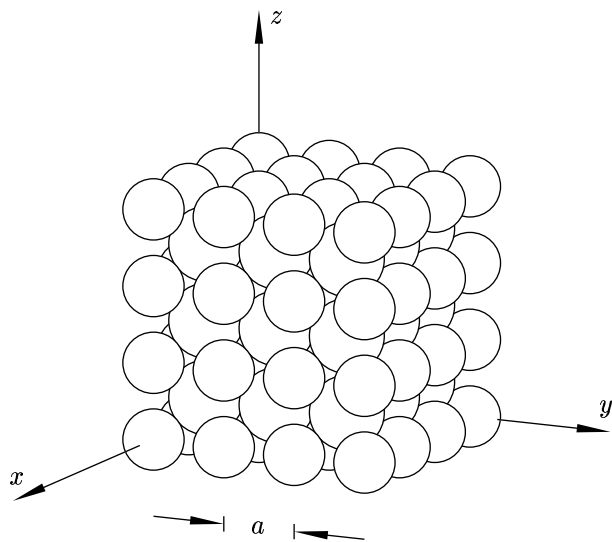
Fig. 1-24. The cesium chloride structure. The small spheres represent the Cs atoms and the large spheres represent the Cl atoms.
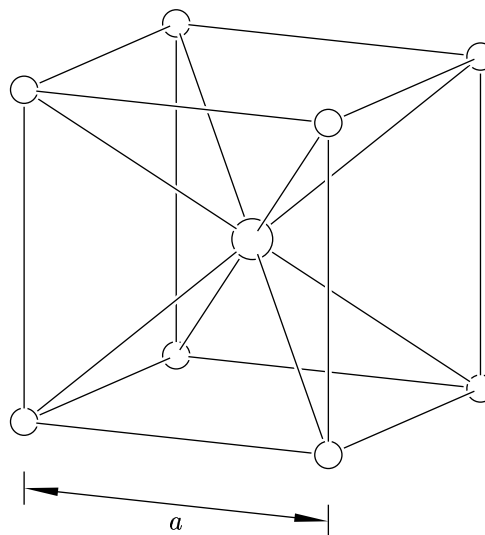
Fig. 1-25. The conventional unit cell of the cesium chloride structure. The large and small spheres represent two different types of atoms.
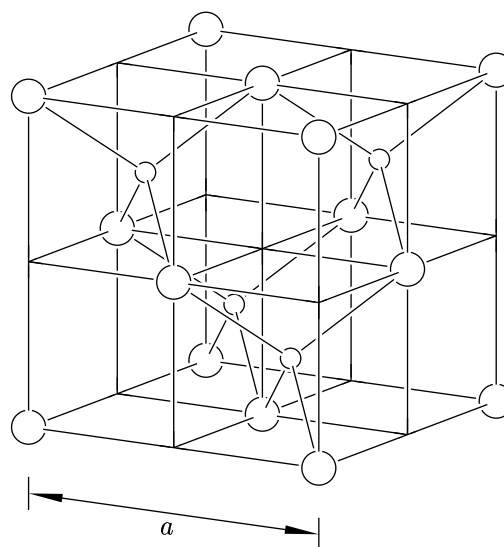
Fig. 1-26. The conventional unit cell for the zincblende structure. The large and small spheres represent two different types of atoms.

ZnS structure is, of course, fcc. The conventional unit cell is the same as that of its fcc Bravais lattice and contains four lattice points (see Fig. 1-26). Thus the conventional unit cell contains four Zn atoms and four S atoms. The Wigner-Seitz primitive unit cell is that of its fcc Bravais lattice, the rhombic dodecahedron in Fig. 1-19, and, of course, contains one Zn atom and one S atom. Examples of crystals with the zincblende structure are given in Appendix 6.

Problem 1-17. Using data in Appendix 6, find the volume of a primitive unit cell in a crystal of gallium arsenide (GaAs). Answer: 44.9 Å^3.

1-12 Diamond Structure

The structure of diamond (carbon crystal) is almost identical to that of ZnS. If we change each Zn atom to a C atom and each S atom to a C atom, we obtain the diamond structure. The conventional unit cell is shown in Fig. 1-27. You might expect here that since all the atoms are of the same type, all atoms are now at equivalent positions, and we have a new Bravais lattice. Such is *not* the case. The sites formerly occupied by Zn and S atoms are *not* equivalent, even though they are now both occupied by C atoms. The environment of each kind of site is not identical. Note that in the ZnS structure of Fig. 1-26, all "small" atoms have four nearest neighbors arranged like that of Fig. 1-28a, while all "large" atoms have four nearest neighbors arranged like that of Fig. 1-28b. These two arrangements are different. Thus, even though all atoms in the diamond structure are the same type, we can still tell the difference between these two kinds of sites by looking at the arrangement of nearest neighbors. The Bravais lattice of diamond is therefore fcc, the same as for ZnS. The conventional unit cell contains eight C atoms, and the primitive unit cell contains *two* C atoms. Examples of crystals with the diamond structure are given in Appendix 6.
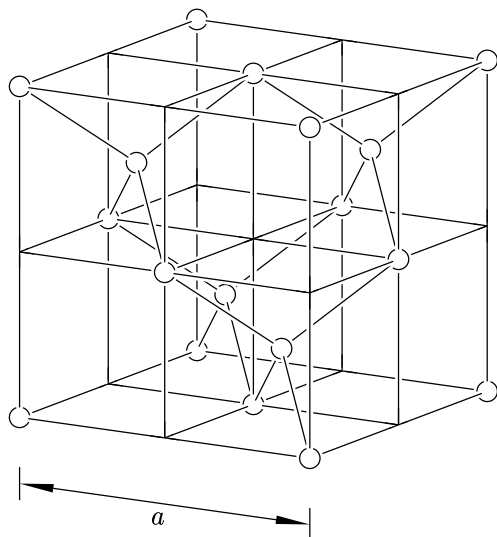

Fig. 1-27. The conventional unit cell of the diamond structure. All atoms are identical.
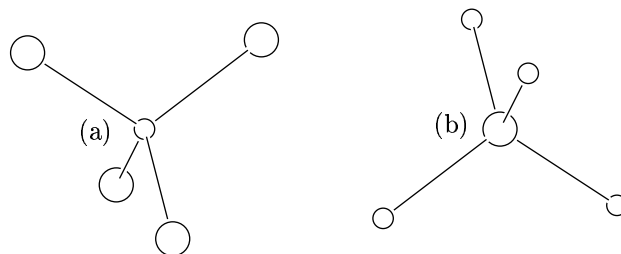

Fig. 1-28. Arrangement of nearest neighbors to (a) "small" atoms and (b) "large" atoms in the ZnS structure of Fig. 1-26.

Problem 1-18. Using the data in Appendices 2 and 6, find the density of diamond (carbon crystal) in g/cm^3. Answer: 3.54 g/cm^3.

Problem 1-19. Using data in Appendix 6, find the volume of a primitive unit cell in a crystal of silicon (Si). Answer: 39.8 Å^3.

Problem 1-20. Using the data in Appendix 6, find the atomic diameter of carbon (C). Repeat for silicon (Si) and germanium (Ge). (Consider the atoms to be spheres that touch each other.) Answer: 1.54 Å, 2.35 Å, 2.44 Å.

1-13 Point Operators

A **symmetry operator** of a crystal is something we can do to the crystal such that the crystal looks identical to what it looked like before we did it. For example, a translation of the crystal by a lattice vector **R** is a symmetry operator. There is also another class of symmetry operators called **point operators**. Point operators always leave some *point* in the crystal fixed.

As an example, let us consider the point operators which are symmetry operators of a crystal with the simple-cubic structure, like that shown in Fig. 1-1. One such point operator is a rotation of the crystal by 180° about the x axis. All of the points on the axis remain fixed in this operation. We call the x axis a two-fold rotation axis, since *two* successive 180° rotations bring the crystal back to where it started again. We label this point operator C_{2x}. Similarly, the y and z axes are also two-fold rotation axes in this crystal, and C_{2y} and C_{2z} are symmetry operators. In addition, there are six other two-fold rotation axes, located along the face-diagonals ([110], [1$\bar{1}$0], [101], etc.). These point operators are labeled C_{2a}, C_{2b}, C_{2c}, etc. The convention for labeling these point operators is given in Appendix 3.

Another symmetry operator for the simple-cubic crystal is a 90° rotation about the x axis. The x axis

is thus a four-fold rotation axis, as well as a two-fold rotation axis. The symmetry operator is labeled C_{4x}^+. The superscript "+" in the symbol means that the rotation is in the "positive" direction. (A positive rotation is in a counter-clockwise direction if the axis of rotation is pointed towards you.) The symmetry operator which rotates the crystal by $-90°$ about the x axis is labeled C_{4x}^-. Similarly, the y and z axes are also four-fold rotation axes in this crystal, and $C_{4y}^\pm$ and $C_{4z}^\pm$ are symmetry operators.

The simple-cubic crystal also has a three-fold rotation axis in the [111] direction. The angles of rotation are $\pm 120°$, and the corresponding symmetry operators are C_{31}^+ and C_{31}^-. Similarly, there are also three-fold rotation axes along the $[11\bar{1}]$, $[\bar{1}11]$, and $[1\bar{1}1]$ directions, and these symmetry operators are labeled $C_{32}^\pm$, $C_{33}^\pm$, and $C_{34}^\pm$, respectively.

At this point, we should note the symmetry operator E, called the **identity operator**. It does *nothing* to the crystal and is thus a symmetry operator for *any* crystal. It is added to the list of symmetry operators for completeness.

Another symmetry operator of the simple-cubic crystal is the **inversion operator** I which takes every point x, y, z into $\bar{x}, \bar{y}, \bar{z}$. This point operator leaves only the point at the origin fixed.

The (100), (010), and (001) planes in the simple-cubic crystal are mirror planes. Reflections through those planes are symmetry operators of that crystal. They are labeled σ_x, σ_y, and σ_z, respectively. The subscript x, y, or z refers to the direction perpendicular to the mirror plane. Similarly, the (110), $(1\bar{1}0)$, (101),... planes are mirror planes. Reflections through those planes are the symmetry operators σ_{da}, σ_{db}, σ_{dc}... The subscript d refers to the face-*diagonal* directions of these planes.

Another symmetry operator of the simple cubic crystal is a $90°$ rotation about the [100] direction followed by a reflection through the (100) plane. This is called a $90°$ rotation-reflection and is labeled S_{4x}^+. Similarly, there are symmetry operators S_{4x}^-, $S_{4y}^\pm$, and $S_{4z}^\pm$. Yet another symmetry operator is a $60°$ rotation about the [111] direction followed by a reflection through the (111) plane. This rotation-reflection is labeled S_{61}^+. Note that a $60°$ rotation about the [111] direction by itself is not a symmetry operator of the simple-cubic crystal, and a reflection through the (111) plane by itself is not a symmetry operator. But together they are indeed a symmetry operator of the crystal. Similarly, we also have S_{61}^-, $S_{62}^\pm$, $S_{63}^\pm$, and $S_{64}^\pm$. All together, there are 48 point operators which are symmetry operators of the simple-cubic crystal in Fig. 1-1.

Let us now consider the action of a point operator on some point x, y, z in the crystal. For example,

a $180°$ rotation about the z axis takes x into $-x$ and y into $-y$ and leaves z unaffected so that x, y, z becomes $\bar{x}, \bar{y}, z$. We say that C_{2z} operates on x, y, z and the result is $\bar{x}, \bar{y}, z$. As another example, a reflection through the (001) plane takes z into $-z$ and leaves x and y unaffected so that x, y, z becomes $x, y, \bar{z}$.

Let us look at a more difficult example, C_{4z}^+. In Fig. 1-29a, we show a point (7,3,2) projected onto the xy plane. When we rotate the crystal by $90°$ (counter-clockwise) about the z axis (out of the page), the point becomes $(-3, 7, 2)$, as shown in Fig. 1-29b. The x coordinate of the point is now equal in value to the negative of its original y coordinate. The y coordinate of the point is now equal in value to its original x coordinate. The z coordinate remains unaffected. Thus, C_{4z}^+ takes x, y, z into $\bar{y}, x, z$. The x, y, z notation for each of the point operators is given in Appendix 3.
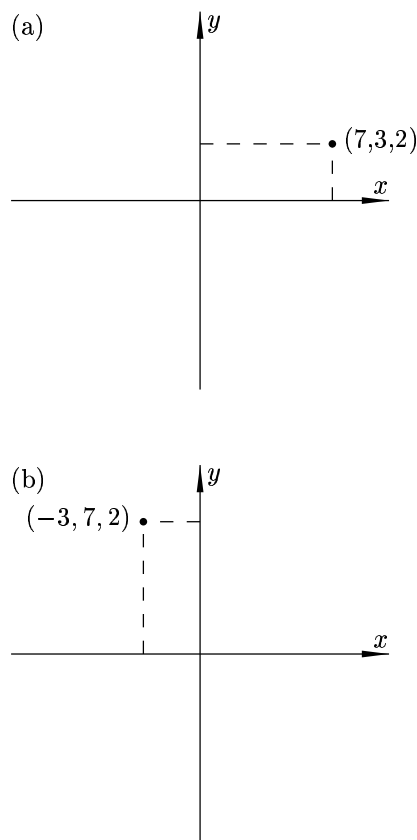

Fig. 1-29. (a) Projection of the point (7,3,2) onto the xy plane. (b) After a $90°$ rotation about the z axis, the point becomes $(-3, 7, 2)$.

1-14 Bravais Lattices

A **lattice translation** is a symmetry operator on a crystal. This operator moves every point in the crystal by a vector **R**, which is one of the lattice vectors. Altogether, there are 14 different Bravais lattices. Three of these are cubic (sc, bcc, fcc). The conventional unit cells for each of the 14 Bravais lattices are shown in Appendix 4. The basis vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ shown in the figure are called the **conventional basis vectors** of the lattice. (These basis vectors are more commonly labeled **a,b,c** by other authors.) In the centered lattices, they are not the true basis vectors since they do not take us to any of the centered points. However, as we will see, they are more convenient to use for many purposes.

Positions of points in the conventional unit cell are usually denoted by three dimensionless numbers (x, y, z), such that the point is at

$$\mathbf{r} = x\mathbf{a}_1 + y\mathbf{a}_2 + z\mathbf{a}_3. \qquad (1\text{-}10)$$

The values of x, y, z are considered to be inside the unit cell if

$$0 \le x < 1, \qquad 0 \le y < 1, \qquad 0 \le z < 1. \qquad (1\text{-}11)$$

For example, in CsCl (see Fig. 1-25), there are two atoms in the unit cell. The Cs atom is at (0,0,0), and the Cl atom is at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

Problem 1-21. (a) List the x, y, z coordinates for the atoms in the unit cell of NaCl. Indicate which ones are Na atoms and which ones are Cl atoms. (b) Repeat for diamond.

The lattices are grouped into six **crystal systems**: triclinic, monoclinic, orthorhombic, tetragonal, hexagonal, and cubic. The Bravais lattice is denoted by its crystal system followed by a letter indicating the type of centering (see Appendix 4). Some Bravais lattices are also known by other common names. For example, the cubic P lattice is known as simple cubic (sc), the cubic F lattice is known as face-centered cubic (fcc), and the cubic I lattice is known as body-centered cubic (bcc). The hexagonal R lattice is also known as trigonal or rhombohedral.

You may notice that only certain types of centering are listed for each crystal system. For example, there is only one kind of centered monoclinic lattice: monoclinic B. A monoclinic A lattice is the same as a monoclinic B lattice with the labels of $\mathbf{a}_1$ and $\mathbf{a}_2$ interchanged. Since changing labels does not produce a

physically different arrangement of lattice points, the two lattices are the same, and we only give one of them in the list of 14 *different* Bravais lattices.

Similarly, a monoclinic C lattice becomes a monoclinic P lattice if we define new basis vectors, $\mathbf{a}'_1 = \frac{1}{2}\mathbf{a}_1 + \frac{1}{2}\mathbf{a}_2$ and $\mathbf{a}'_2 = -\frac{1}{2}\mathbf{a}_1 + \frac{1}{2}\mathbf{a}_2$ (see Fig. 1-30). In this case, we cannot simply interchange the labels of $\mathbf{a}_2$ and $\mathbf{a}_3$, since $\mathbf{a}_3$ must be perpendicular to both $\mathbf{a}_1$ and $\mathbf{a}_2$ in this crystal system, and the new $\mathbf{a}_3$ (the old $\mathbf{a}_2$) would not be perpendicular to $\mathbf{a}_1$.
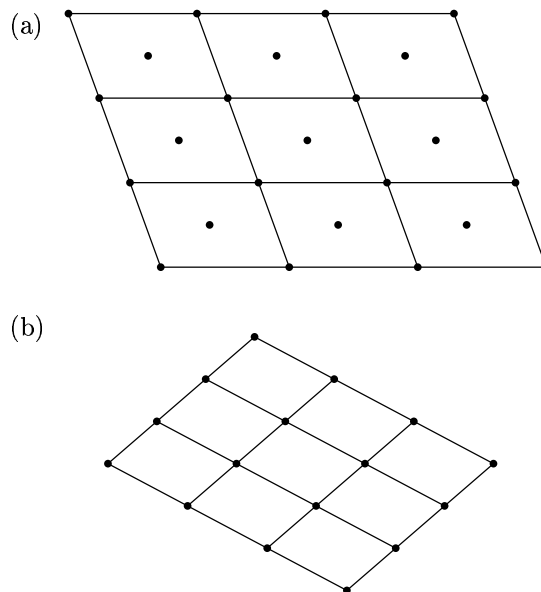
Fig. 1-30. (a) The xy plane of a monoclinic C lattice showing the unit cells. (b) The same lattice but with a rearrangement of unit cells so that the lattice now appears to be monoclinic P.

Problem 1-22. (a) Consider a monoclinic I lattice. Is this a monoclinic B or monoclinic P lattice? Find new basis vectors $\mathbf{a}'_1, \mathbf{a}'_2, \mathbf{a}'_3$ in terms of the old basis vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ such that the lattice will appear as one of those two types. (Remember that the two-fold rotation axis along $\mathbf{a}_3$ must remain along $\mathbf{a}'_3$. Also, $\mathbf{a}'_1$ and $\mathbf{a}'_2$ must be perpendicular to $\mathbf{a}'_3$. A drawing of this lattice projected onto the xy plane may be helpful.) (b) Repeat for a monoclinic F lattice.

Problem 1-23. Consider a crystal with a monoclinic lattice such that the angle between $\mathbf{a}_1$ and $\mathbf{a}_2$ is γ. Find the volume of the the the primitive unit cell if (a) the lattice is P type and (b) if the lattice is B type. Give the answer in terms of the magnitudes of $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ and the angle γ.

There is a relationship between the crystal system and the point operators which are symmetry operators of the crystal. When we apply a symmetry operator to a lattice vector, it must produce another lattice vector. Since the crystal appears identical both before and after the action of the point operator, the lattice point to which $\mathbf{R}$ points must still be a lattice point, and therefore the new vector $\mathbf{R}$ must still be a lattice vector. This means that the relationships between the basis vectors in a lattice may restrict which point operators may be symmetry operators of the crystal.

In the triclinic lattice, for example, the basis vectors each have arbitrary lengths and directions, so only the point operators, E and I, may be symmetry operators of a crystal with this lattice. (The inversion I changes $\mathbf{R}$ to $-\mathbf{R}$, which is always another lattice vector.) Conversely, if the symmetry operators of a crystal only include the point operators E and I and no others, then the lattice *must* be triclinic. Note that a crystal with a triclinic lattice may possibly not even have the inversion I as one of its symmetry operators. Even though I may be a symmetry operator of the *lattice*, the atoms associated with each lattice point may be arranged so that I is not a symmetry operator of the *crystal*.

Suppose there exists a single two-fold rotation axis in a crystal. Let us choose the direction of the z axis to be along that two-fold rotation axis. The point operator C_{2z} is a symmetry operator of the crystal. Let us choose an arbitrary lattice vector $\mathbf{R}$ which is not pointing along the two-fold rotation axis. $C_{2z}\mathbf{R}$ is also a lattice vector since C_{2z} is a symmetry operator. A vector sum of any two lattice vectors is also a lattice vector. Therefore, $\mathbf{R} - C_{2z}\mathbf{R}$ is a lattice vector. It is also perpendicular to the two-fold rotation axis. (Draw a picture to see this.) Let us choose this vector to be the basis vector $\mathbf{a}_1$. In a similar manner, we can start with another lattice vector $\mathbf{R}$ and construct another vector $\mathbf{R} - C_{2z}\mathbf{R}$ perpendicular to the two-fold rotation axis. We choose this vector to be $\mathbf{a}_2$. Lastly, starting with a lattice vector $\mathbf{R}$ *not* perpendicular to the two-fold rotation axis, we can construct a lattice vector $\mathbf{R} + C_{2z}\mathbf{R}$. This vector is in the *same* direction as the two-fold rotation axis, and we choose it to be $\mathbf{a}_3$.

As can be seen, starting only with the fact that the crystal has a two-fold rotation axis, we can construct the basis vectors of a monoclinic lattice: $\mathbf{a}_1$ and $\mathbf{a}_2$ are both perpendicular to $\mathbf{a}_3$. Depending on what lattice vectors $\mathbf{R}$ we used to construct the basis vectors, the resulting unit cell may or may not be centered in some way. However, we can always choose the basis vectors so that we finally have a conventional unit cell of either a monoclinic P or monoclinic B lattice. What we have shown here is that a single two-fold rotation axis

is a sufficient condition for a crystal to be monoclinic. Similarly, we could show that a single mirror plane is also a sufficient condition for a crystal to be monoclinic. A monoclinic crystal may also contain both a two-fold rotation axis and a mirror plane, if the two-fold rotation axis is perpendicular to the mirror plane. In that case, the intersection of the two-fold rotation axis with the mirror plane is a point of inversion, and I will also be a symmetry operator of the crystal.

If a crystal contains two two-fold rotation axes, perpendicular to each other, then it can be shown that a third two-fold rotation axis must also exist, perpendicular to the other two. The presence of these three two-fold rotation axes makes it possible for us to construct three mutually perpendicular lattice vectors, and therefore the crystal is orthorhombic. Similarly, if a crystal contains two mirror planes, perpendicular to each other, then the intersection of those planes will be a two-fold rotation axis, and the crystal is likewise orthorhombic.

There is a strong relationship between the crystal system and the point operators which are symmetry operators of the crystal. If a crystal contains more than one two-fold rotation axis or more than one mirror plane, then it cannot be monoclinic. On the other hand, if a crystal contains only one two-fold rotation axis and/or only one mirror plane, it cannot be orthorhombic, because the basis vectors $\mathbf{a}_1,\mathbf{a}_2$ cannot be chosen to be perpendicular to each other. Even if a measurement shows that they are perpendicular to within experimental uncertainty, we know that they cannot be *exactly* perpendicular to each other because of the symmetry of the crystal.

We can find the conditions on the other crystal systems in a similar way. A single four-fold rotation axis and/or four-fold rotation-reflection axis is a sufficient condition for a tetragonal lattice. A single three-fold rotation axis and/or a six-fold rotation-reflection axis is a sufficient condition for a hexagonal lattice. Note that the hexagonal R lattice does not have a six-fold rotation axis or a three-fold rotation-reflection axis, whereas the hexagonal P lattice does. For this reason, the hexagonal R lattice is often considered to belong to a separate crystal system, called the trigonal crystal system.

Two three-fold rotation axes and/or two six-fold rotation-reflection axes are a sufficient condition for a cubic lattice. Note that a cubic crystal does not need to have any four-fold rotation axes. The three-fold rotation axes are sufficient to guarantee that the basis vectors are the same length and mutually perpendicular to each other. The arrangement of atoms in the unit cell may in fact not allow the cubic crystal to have a four-fold rotation axis.

The different combinations of point operators which may be symmetry operators of a crystal are called **point groups**. All crystals with the same point group belong to the same **crystal class**. There are 32 crystal classes in all. They are listed in Appendix 5. Note that for some crystal classes, two different combinations of point operators are listed. Only the number of each type of point operator (four-fold rotation, reflection, etc.) and their relationship to each other distinguishes one crystal class from another.

The action of the different point operators on x, y, z are given in Appendix 3. This table is divided into two lists, one for non-hexagonal lattices and one for hexagonal lattices. The list for non-hexagonal lattices uses cartesian coordinates. For this reason, the operator C_{4z}^+ would not produce $(\bar{y}, x, z)$ in a monoclinic lattice if x, y, z are defined by Eq. (1-10), since $\mathbf{a}_1$ and $\mathbf{a}_2$ are not perpendicular to each other. However, this does not matter, since C_{4z}^+ is never a symmetry operator of a monoclinic crystal. Each of the x, y, z operations listed in Appendix 3 is correct whenever that point operator is a symmetry operator of a crystal.

The hexagonal lattices require special treatment. In these lattices, the angle between $\mathbf{a}_1$ and $\mathbf{a}_2$ is 120°, and a hexagonal coordinate system must be used. As an example, let us consider the point operator C_3^+. We see from Fig. 1-31 that after the rotation, $\mathbf{a}_1$ is in direction of the original $\mathbf{a}_2$, and $\mathbf{a}_2$ is in the direction of the original $-\mathbf{a}_1 - \mathbf{a}_2$. Thus a point (x, y, z) becomes

$$x\mathbf{a}_1 + y\mathbf{a}_2 + z\mathbf{a}_3 \rightarrow x\mathbf{a}_2 + y(-\mathbf{a}_1 - \mathbf{a}_2) + z\mathbf{a}_3$$
$$= -y\mathbf{a}_1 + (x - y)\mathbf{a}_2 + z\mathbf{a}_3,$$
$$(1\text{-}12)$$

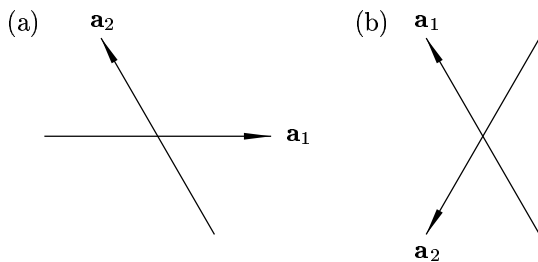and the operation of C_3^+ on x, y, z results in $\bar{y}, x - y, z$, as shown in Appendix 3.

1-15 Directions and Planes Revisited

A direction $\mathbf{r}$ in a crystal is written in terms of components of the conventional basis vectors:

$$\mathbf{r} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3. \qquad (1\text{-}13)$$

This direction is denoted by the symbol $[n_1 n_2 n_3]$. If a line along this direction passes through at least two lattice points, then the coefficients n_1, n_2, n_3 can always be chosen to be integers.

The points (x, y, z) that lie on a plane satisfy the equation

$$hx + ky + lz = A, \qquad (1\text{-}14)$$

where A is some constant. [Note that x, y, z are components of the conventional basis vectors, as in Eq. (1-10), so the coordinate system in Eq. (1-14) is not necessarily cartesian.] This plane described by Eq. (1-14) is denoted by (hkl). The numbers (hkl) are called **Miller indices**. If the plane contains at least three non-collinear lattice points, then the Miller indices can always be chosen to be integers. Note that A/h, A/k, A/l are the intercepts of the plane with the $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ axes, respectively. In cubic crystals, the $[hkl]$ direction is perpendicular to the (hkl) plane, but this is not generally true for any of the other crystal systems. In hexagonal crystals, *four* Miller indices $(hkil)$ are often given. In this case, A/i is the intercept of the plane with the $(-\mathbf{a}_1 - \mathbf{a}_2)$ axis.

Fig. 1-31. A 120° rotation about the z axis. (a) Before the rotation. (b) After the rotation.

APPENDIX 3

POINT OPERATORS

Non-Hexagonal Lattices:

E	x, y, z	identity
C_{2x}	$x, \bar{y}, \bar{z}$	180° rotation about $\mathbf{a}_1$
C_{2y}	$\bar{x}, y, \bar{z}$	180° rotation about $\mathbf{a}_2$
C_{2z}	$\bar{x}, \bar{y}, z$	180° rotation about $\mathbf{a}_3$
C_{2a}	$y, x, \bar{z}$	180° rotation about $\mathbf{a}_1 + \mathbf{a}_2$
C_{2b}	$\bar{y}, \bar{x}, \bar{z}$	180° rotation about $\mathbf{a}_1 - \mathbf{a}_2$
C_{2c}	$z, \bar{y}, x$	180° rotation about $\mathbf{a}_1 + \mathbf{a}_3$
C_{2d}	$\bar{x}, z, y$	180° rotation about $\mathbf{a}_2 + \mathbf{a}_3$
C_{2e}	$\bar{z}, \bar{y}, \bar{x}$	180° rotation about $\mathbf{a}_1 - \mathbf{a}_3$
C_{2f}	$\bar{x}, \bar{z}, \bar{y}$	180° rotation about $\mathbf{a}_2 - \mathbf{a}_3$
C_{31}^+	z, x, y	120° rotation about $\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3$
C_{32}^+	$\bar{z}, x, \bar{y}$	120° rotation about $-\mathbf{a}_1 - \mathbf{a}_2 + \mathbf{a}_3$
C_{33}^+	$\bar{z}, \bar{x}, y$	120° rotation about $\mathbf{a}_1 - \mathbf{a}_2 - \mathbf{a}_3$
C_{34}^+	$z, \bar{x}, \bar{y}$	120° rotation about $-\mathbf{a}_1 + \mathbf{a}_2 - \mathbf{a}_3$
C_{31}^-	y, z, x	240° rotation about $\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3$
C_{32}^-	$y, \bar{z}, \bar{x}$	240° rotation about $-\mathbf{a}_1 - \mathbf{a}_2 + \mathbf{a}_3$
C_{33}^-	$\bar{y}, z, \bar{x}$	240° rotation about $\mathbf{a}_1 - \mathbf{a}_2 - \mathbf{a}_3$
C_{34}^-	$\bar{y}, \bar{z}, x$	240° rotation about $-\mathbf{a}_1 + \mathbf{a}_2 - \mathbf{a}_3$
C_{4x}^+	$x, \bar{z}, y$	90° rotation about $\mathbf{a}_1$
C_{4y}^+	$z, y, \bar{x}$	90° rotation about $\mathbf{a}_2$
C_{4z}^+	$\bar{y}, x, z$	90° rotation about $\mathbf{a}_3$
C_{4x}^-	$x, z, \bar{y}$	270° rotation about $\mathbf{a}_1$
C_{4y}^-	$\bar{z}, y, x$	270° rotation about $\mathbf{a}_2$
C_{4z}^-	$y, \bar{x}, z$	270° rotation about $\mathbf{a}_3$
I	$\bar{x}, \bar{y}, \bar{z}$	inversion
σ_x	$\bar{x}, y, z$	reflection in plane $\perp$ to $\mathbf{a}_1$
σ_y	$x, \bar{y}, z$	reflection in plane $\perp$ to $\mathbf{a}_2$
σ_z	$x, y, \bar{z}$	reflection in plane $\perp$ to $\mathbf{a}_3$
σ_{da}	$\bar{y}, \bar{x}, z$	reflection in plane $\perp$ to $\mathbf{a}_1 + \mathbf{a}_2$
σ_{db}	y, x, z	reflection in plane $\perp$ to $\mathbf{a}_1 - \mathbf{a}_2$
σ_{dc}	$\bar{z}, y, \bar{x}$	reflection in plane $\perp$ to $\mathbf{a}_1 + \mathbf{a}_3$
σ_{dd}	$x, \bar{z}, \bar{y}$	reflection in plane $\perp$ to $\mathbf{a}_2 + \mathbf{a}_3$
σ_{de}	z, y, x	reflection in plane $\perp$ to $\mathbf{a}_1 - \mathbf{a}_3$
σ_{df}	x, z, y	reflection in plane $\perp$ to $\mathbf{a}_2 - \mathbf{a}_3$

S_{61}^+ $\bar{y}, \bar{z}, \bar{x}$ 60° rotation about $\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3$ followed by reflection in plane $\perp$ to that axis

S_{62}^+ $\bar{y}, z, x$ 60° rotation about $-\mathbf{a}_1 - \mathbf{a}_2 + \mathbf{a}_3$ followed by reflection in plane $\perp$ to that axis

S_{63}^+ $y, \bar{z}, x$ 60° rotation about $\mathbf{a}_1 - \mathbf{a}_2 - \mathbf{a}_3$ followed by reflection in plane $\perp$ to that axis

S_{64}^+ $y, z, \bar{x}$ 60° rotation about $-\mathbf{a}_1 + \mathbf{a}_2 - \mathbf{a}_3$ followed by reflection in plane $\perp$ to that axis

S_{61}^- $\bar{z}, \bar{x}, \bar{y}$ 300° rotation about $\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3$ followed by reflection in plane $\perp$ to that axis

S_{62}^- $z, \bar{x}, y$ 300° rotation about $-\mathbf{a}_1 - \mathbf{a}_2 + \mathbf{a}_3$ followed by reflection in plane $\perp$ to that axis

S_{63}^- $z, x, \bar{y}$ 300° rotation about $\mathbf{a}_1 - \mathbf{a}_2 - \mathbf{a}_3$ followed by reflection in plane $\perp$ to that axis

S_{64}^- $\bar{z}, x, y$ 300° rotation about $-\mathbf{a}_1 + \mathbf{a}_2 - \mathbf{a}_3$ followed by reflection in plane $\perp$ to that axis

S_{4x}^+ $\bar{x}, \bar{z}, y$ 90° rotation about $\mathbf{a}_1$ followed by reflection in plane $\perp$ to that axis

S_{4y}^+ $z, \bar{y}, \bar{x}$ 90° rotation about $\mathbf{a}_2$ followed by reflection in plane $\perp$ to that axis

S_{4z}^+ $\bar{y}, x, \bar{z}$ 90° rotation about $\mathbf{a}_3$ followed by reflection in plane $\perp$ to that axis

S_{4x}^- $\bar{x}, z, \bar{y}$ 270° rotation about $\mathbf{a}_1$ followed by reflection in plane $\perp$ to that axis

S_{4y}^- $\bar{z}, \bar{y}, x$ 270° rotation about $\mathbf{a}_2$ followed by reflection in plane $\perp$ to that axis

S_{4z}^- $y, \bar{x}, \bar{z}$ 270° rotation about $\mathbf{a}_3$ followed by reflection in plane $\perp$ to that axis

Hexagonal Lattices

E x, y, z identity

C_2 $\bar{x}, \bar{y}, z$ 180° rotation about $\mathbf{a}_3$

C_3^+ $\bar{y}, x - y, z$ 120° rotation about $\mathbf{a}_3$

C_3^- $y - x, \bar{x}, z$ 240° rotation about $\mathbf{a}_3$

C_6^+ $x - y, x, z$ 60° rotation about $\mathbf{a}_3$

C_6^- $y, y - x, z$ 300° rotation about $\mathbf{a}_3$

C_{21}' $y - x, y, \bar{z}$ 180° rotation about $\mathbf{a}_1 + 2\mathbf{a}_2$

C_{22}' $x, x - y, \bar{z}$ 180° rotation about $2\mathbf{a}_1 + \mathbf{a}_2$

C_{23}' $\bar{y}, \bar{x}, \bar{z}$ 180° rotation about $\mathbf{a}_1 - \mathbf{a}_2$

C_{21}'' $x - y, \bar{y}, \bar{z}$ 180° rotation about $\mathbf{a}_1$

C_{22}'' $\bar{x}, y - x, \bar{z}$ 180° rotation about $\mathbf{a}_2$

C_{23}'' $y, x, \bar{z}$ 180° rotation about $\mathbf{a}_1 + \mathbf{a}_2$

I $\bar{x}, \bar{y}, \bar{z}$ inversion

σ_h $x, y, \bar{z}$ reflection in plane $\perp$ to $\mathbf{a}_3$

S_3^+ $\bar{y}, x - y, \bar{z}$ 120° rotation about $\mathbf{a}_3$ followed by reflection in plane $\perp$ to that axis

S_3^- $y - x, \bar{x}, \bar{z}$ 240° rotation about $\mathbf{a}_3$ followed by reflection in plane $\perp$ to that axis

S_6^+ $x - y, x, \bar{z}$ 60° rotation about $\mathbf{a}_3$ followed by reflection in plane $\perp$ to that axis

S_6^- $y, y - x, \bar{z}$ 300° rotation about $\mathbf{a}_3$ followed by reflection in plane $\perp$ to that axis

σ_{d1} $x - y, \bar{y}, z$ reflection in plane $\perp$ to $\mathbf{a}_1 + 2\mathbf{a}_2$

σ_{d2} $\bar{x}, y - x, z$ reflection in plane $\perp$ to $2\mathbf{a}_1 + \mathbf{a}_2$

σ_{d3} y, x, z reflection in plane $\perp$ to $\mathbf{a}_1 - \mathbf{a}_2$

σ_{v1} $y - x, y, z$ reflection in plane $\perp$ to $\mathbf{a}_1$

σ_{v2} $x, x - y, z$ reflection in plane $\perp$ to $\mathbf{a}_2$

σ_{v3} $\bar{y}, \bar{x}, z$ reflection in plane $\perp$ to $\mathbf{a}_1 + \mathbf{a}_2$

APPENDIX 4

BRAVAIS LATTICES

Conditions on the Basis Vectors:

a_1, a_2, a_3 are the magnitudes of the basis vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$, respectively.

α is the angle between $\mathbf{a}_2$ and $\mathbf{a}_3$.

β is the angle between $\mathbf{a}_3$ and $\mathbf{a}_1$.

γ is the angle between $\mathbf{a}_1$ and $\mathbf{a}_2$.

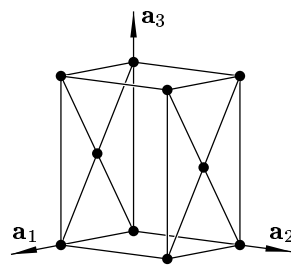| Crystal System	Conditions
Triclinic	none
Monoclinic	$\alpha = \beta = 90°$
Orthorhombic	$\alpha = \beta = \gamma = 90°$
Tetragonal	$a_1 = a_2, \quad \alpha = \beta = \gamma = 90°$
Hexagonal	$a_1 = a_2, \quad \alpha = \beta = 90°, \quad \gamma = 120°$
Cubic	$a_1 = a_2 = a_3, \quad \alpha = \beta = \gamma = 90°$

Centered Lattices:

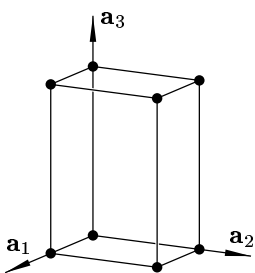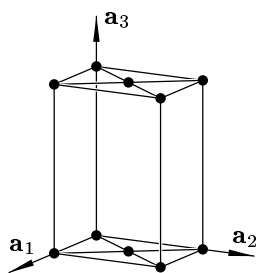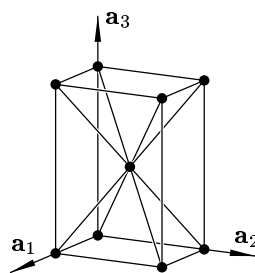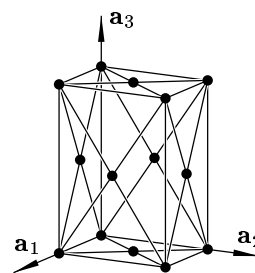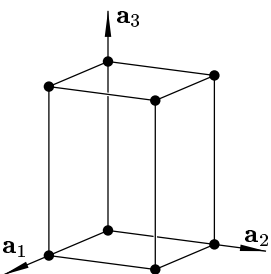| Type of Centering		Centered Points
Primitive	P	none
Base-centered	A	$\left(0, \frac{1}{2}, \frac{1}{2}\right)$
	B	$\left(\frac{1}{2}, 0, \frac{1}{2}\right)$
	C	$\left(\frac{1}{2}, \frac{1}{2}, 0\right)$
Face-centered	F	$\left(0, \frac{1}{2}, \frac{1}{2}\right), \left(\frac{1}{2}, 0, \frac{1}{2}\right), \left(\frac{1}{2}, \frac{1}{2}, 0\right)$
Body-centered	I	$\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$
Rhombohedral-centered	R	$\left(\frac{2}{3}, \frac{1}{3}, \frac{1}{3}\right), \left(\frac{1}{3}, \frac{2}{3}, \frac{2}{3}\right)$
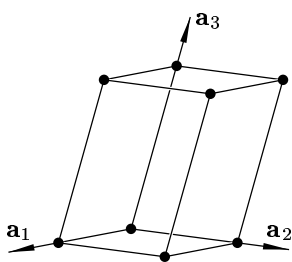
Triclinic P
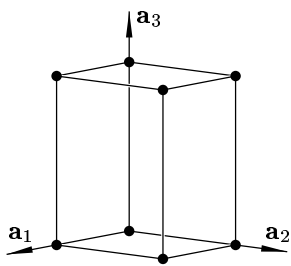
Monoclinic P
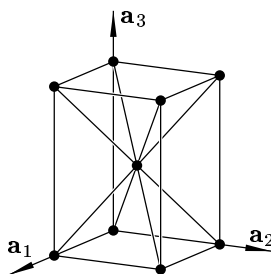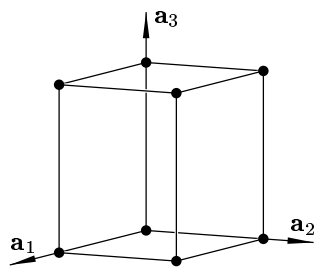
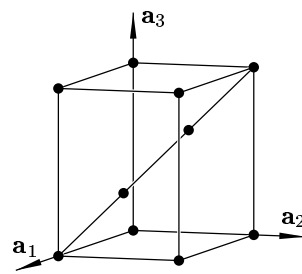Monoclinic B

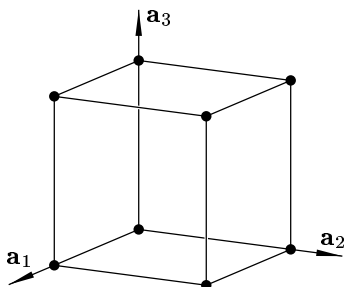Orthorhombic P

Orthorhombic C

Orthorhombic I

Orthorhombic F

Tetragonal P

Tetragonal I

Hexagonal P

Hexagonal R

Cubic P
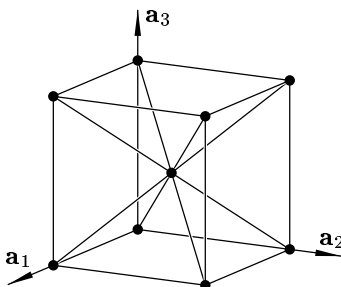
Cubic I
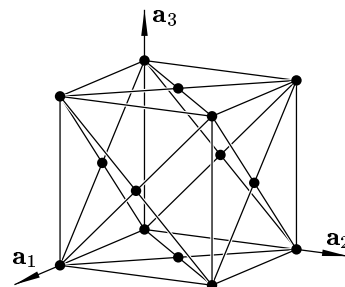
Cubic F

APPENDIX 5

SPACE GROUPS

Space Groups	Class	Point Operators
Triclinic		
1	1	E
2	$\bar{1}$	E, I
Monoclinic		
3–5	2	E, C_{2z}
6–9	m	E, σ_z
10–15	$2/m$	E, C_{2z}, I, σ_z
Orthorhombic		
16–24	222	$E, C_{2x}, C_{2y}, C_{2z}$
25–46	$mm2$	$E, C_{2z}, \sigma_x, \sigma_y$
47–74	mmm	$E, C_{2x}, C_{2y}, C_{2z}, I, \sigma_x, \sigma_y, \sigma_z$
Tetragonal		
75–80	4	$E, C_{4z}^{\pm}, C_{2z}$
81–82	$\bar{4}$	$E, S_{4z}^{\pm}, C_{2z}$
83–88	$4/m$	$E, C_{4z}^{\pm}, C_{2z}, I, S_{4z}^{\pm}, \sigma_z$
89–98	422	$E, C_{4z}^{\pm}, C_{2z}, C_{2x}, C_{2y}, C_{2a}, C_{2b}$
99–110	$4mm$	$E, C_{4z}^{\pm}, C_{2z}, \sigma_x, \sigma_y, \sigma_{da}, \sigma_{db}$
111–122	$\bar{4}2m$	(1) $E, S_{4z}^{\pm}, C_{2z}, C_{2x}, C_{2y}, \sigma_{da}, \sigma_{db}$
		(2) $E, S_{4z}^{\pm}, C_{2z}, C_{2a}, C_{2b}, \sigma_x, \sigma_y$
123–142	$4/mmm$	$E, C_{4z}^{\pm}, C_{2z}, C_{2x}, C_{2y}, C_{2a}, C_{2b}, I, S_{4z}^{\pm}, \sigma_z, \sigma_x, \sigma_y, \sigma_{da}, \sigma_{db}$

Space Groups	Class	Point Operators

Hexagonal

Space Groups	Class	Point Operators
143–146	3	$E, C_3^\pm$
147–148	$\bar{3}$	$E, C_3^\pm, I, S_6^\pm$
149–155	32	(1) $E, C_3^\pm, C'_{21}, C'_{22}, C'_{23}$
		(2) $E, C_3^\pm, C''_{21}, C''_{22}, C''_{23}$
156–161	$3m$	(1) $E, C_3^\pm, \sigma_{d1}, \sigma_{d2}, \sigma_{d3}$
		(2) $E, C_3^\pm, \sigma_{v1}, \sigma_{v2}, \sigma_{v3}$
162–176	$\bar{3}m$	(1) $E, C_3^\pm, C'_{21}, C'_{22}, C'_{23}, I, S_6^\pm, \sigma_{d1}, \sigma_{d2}, \sigma_{d3}$
		(2) $E, C_3^\pm, C''_{21}, C''_{22}, C''_{23}, I, S_6^\pm, \sigma_{v1}, \sigma_{v2}, \sigma_{v3}$
168–173	6	$E, C_6^\pm, C_3^\pm, C_2$
174	$\bar{6}$	$E, S_3^\pm, C_3^\pm, \sigma_h$
175–176	$6/m$	$E, C_6^\pm, C_3^\pm, C_2, I, S_3^\pm, S_6^\pm, \sigma_h$
177–182	622	$E, C_6^\pm, C_3^\pm, C_2, C'_{21}, C'_{22}, C'_{23}, C''_{21}, C''_{22}, C''_{23}$
183–186	$6mm$	$E, C_6^\pm, C_3^\pm, C_2, \sigma_{d1}, \sigma_{d2}, \sigma_{d3}, \sigma_{v1}, \sigma_{v2}, \sigma_{v3}$
187–190	$\bar{6}m2$	(1) $E, C_3^\pm, C'_{21}, C'_{22}, C'_{23}, \sigma_h, S_3^\pm, \sigma_{v1}, \sigma_{v2}, \sigma_{v3}$
		(2) $E, C_3^\pm, C''_{21}, C''_{22}, C''_{23}, \sigma_h, S_3^\pm, \sigma_{d1}, \sigma_{d2}, \sigma_{d3}$
191–194	$6/mmm$	$E, C_6^\pm, C_3^\pm, C_2, C'_{21}, C'_{22}, C'_{23}, C''_{21}, C''_{22}, C''_{23},$ $I, S_3^\pm, S_6^\pm, \sigma_h, \sigma_{d1}, \sigma_{d2}, \sigma_{d3}, \sigma_{v1}, \sigma_{v2}, \sigma_{v3}$

Cubic

Space Groups	Class	Point Operators
195–199	23	$E, C_{31}^\pm, C_{32}^\pm, C_{33}^\pm, C_{34}^\pm, C_{2x}, C_{2y}, C_{2z}$
200–206	$m\bar{3}$	$E, C_{31}^\pm, C_{32}^\pm, C_{33}^\pm, C_{34}^\pm, C_{2x}, C_{2y}, C_{2z},$ $I, S_{61}^\pm, S_{62}^\pm, S_{63}^\pm, S_{64}^\pm, \sigma_x, \sigma_y, \sigma_z$
207–214	432	$E, C_{31}^\pm, C_{32}^\pm, C_{33}^\pm, C_{34}^\pm, C_{2x}, C_{2y}, C_{2z},$ $C_{2a}, C_{2b}, C_{2c}, C_{2d}, C_{2e}, C_{2f}, C_{4x}^\pm, C_{4y}^\pm, C_{4z}^\pm$
215–220	$\bar{4}3m$	$E, C_{31}^\pm, C_{32}^\pm, C_{33}^\pm, C_{34}^\pm, C_{2x}, C_{2y}, C_{2z},$ $\sigma_{da}, \sigma_{db}, \sigma_{dc}, \sigma_{dd}, \sigma_{de}, \sigma_{df}, S_{4x}^\pm, S_{4y}^\pm, S_{4z}^\pm$
221–230	$m\bar{3}m$	$E, C_{31}^\pm, C_{32}^\pm, C_{33}^\pm, C_{34}^\pm, C_{2x}, C_{2y}, C_{2z}, C_{4x}^\pm, C_{4y}^\pm, C_{4z}^\pm,$ $C_{2a}, C_{2b}, C_{2c}, C_{2d}, C_{2e}, C_{2f}, I, S_{61}^\pm, S_{62}^\pm, S_{63}^\pm, S_{64}^\pm,$ $\sigma_x, \sigma_y, \sigma_z, \sigma_{da}, \sigma_{db}, \sigma_{dc}, \sigma_{dd}, \sigma_{de}, \sigma_{df}, S_{4x}^\pm, S_{4y}^\pm, S_{4z}^\pm$

APPENDIX 6

CRYSTAL STRUCTURES

Listed below are the crystal structures of various elements and compounds. The lattice parameters a in units of Å are also given.

Elements with a bcc lattice

Li	3.50	Ba	5.02	Mo	3.14
Na	4.30	V	3.04	W	3.15
K	5.20	Nb	3.30	Fe	2.86
Rb	5.59	Ta	3.32	Eu	4.58
Cs	6.50	Cr	2.87		

Elements with an fcc lattice

Ca	5.56	Pd	3.87	Al	4.04
Sr	6.08	Pt	3.90	Pb	4.93
Ac	5.31	Cu	3.61	Ce	5.12
Rh	3.80	Ag	4.07	Yb	5.48
Ir	3.82	Au	4.07	Th	5.08
Ni	3.52				

Elements with the diamond structure

C	3.56	Ge	5.65	Sn	6.46
Si	5.42				

Compounds with the cesium chloride structure

CsCl	4.11	TlI	4.18	CuPd	2.99
CsBr	4.28	TlSb	3.85	AgZn	3.16
CsI	4.56	TlBi	3.90	AuZn	3.15
TlCl	3.84	CuZn	2.95	AlNi	2.82
TlBr	3.97				

Compounds with the sodium chloride structure

LiF	4.02	RbI	7.32	BaTe	6.99
LiCl	5.14	CsF	6.00	MnO	4.43
LiBr	5.49	MgO	4.20	MnS	5.21
LiI	6.00	MgS	5.19	MnSe	5.45
NaF	4.61	MgSe	5.45	FeO	4.28
NaCl	5.63	CaO	4.80	CoO	4.25
NaBr	5.96	CaS	5.68	NiO	4.17
NaI	6.46	CaSe	5.91	AgF	4.92
KF	5.36	CaTe	6.34	AgCl	5.54
KCl	6.27	SrO	5.15	AgBr	5.76
KBr	6.58	SrS	6.01	CdO	4.70
KI	7.05	SrSe	6.23	SnTe	6.28
RbF	5.63	SrTe	6.65	PbS	5.93
RbCl	6.53	BaO	5.53	PbSe	6.14
RbBr	6.85	BaSe	6.59	PbTe	6.44

Compounds with the zincblende structure

BeS	4.86	ZnTe	6.09	GaP	5.44
CuCl	5.41	CdTe	6.46	GaAs	5.64
CuBr	5.68	AlP	5.45	GaSb	6.09
CuI	6.05	AlAs	5.63	InSb	6.45
ZnS	5.42	AlSb	6.10	SnSb	6.13
ZnSe	5.66				