

SOLID STATE PHYSICAL ELECTRONICS SERIES

Nick Holonyak, Jr.,

Editor

ALDERT van der ZIEL

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Solid State Physical Electronics

Third Edition

Aldert van der Ziel

*Department of Electrical Engineering
University of Minnesota*

*Department of Electrical Engineering
University of Florida*

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Preface

For the third edition of *Solid State Physical Electronics* to keep up with the rapidly changing field, a major revision and extension of the second edition was necessary. As a consequence the part of dielectric, piezoelectric and magnetic devices had to be eliminated.

This edition consists of three parts: I. Introductory chapters (1-6), dealing with wave mechanics, atomic physics, statistics, the theory of solid state materials in general, and of semiconductors in particular; II. Electron emission and conduction devices (Chapters 7-13), dealing with thermionic emission, field emission, photoemission, secondary electron emission, photoconduction, luminescence, and the application of these principles to electron devices; III. Semiconductor devices (Chapters 14-20), dealing with metal-semiconductor diodes, p - n junction diodes, bipolar transistors, field effect transistors, junction luminescence, p - n junction lasers, avalanche oscillators, Gunn oscillators, space-charge-limited devices, Hall devices, thermoelectric devices, amorphous semiconductor devices, and their applications.

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A. VAN DER ZIEL

Minneapolis, Minnesota

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Structure of the Solid State

In some solids, such as glass, the atoms or atom groups are arranged in an irregular, more or less random fashion like the atoms or molecules in a liquid; such solids are called *noncrystalline* or *amorphous*. In other solids the atoms or atom groups are arranged in a regular order; such solids are called *crystalline*. If the regular order extends over a whole piece of material, the material is said to be a *single crystal*; if the regularity extends over only a small part of the material, so that it consists of an agglomerate of smaller or larger crystallites, the material is said to be *polycrystalline*. If the crystallites are very small, the crystalline character of the solid may manifest itself only in x-ray or electron-diffraction experiments; such techniques may in fact be used to determine the size of the crystallites.

1.1. CRYSTAL SYSTEMS AND NOMENCLATURE

Since the atoms or atom groups of a crystal are arranged in a regular order, it is possible to move the crystal in certain directions over certain distances such that each atom again coincides with an atom of the same kind. Thus we can define *three fundamental translation vectors* \mathbf{a} , \mathbf{b} , and \mathbf{c} , such that the most general movement that makes each atom coincide with one of the same kind is a movement in the direction of and over the length of a vector \mathbf{v} ,

$$\mathbf{v} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c} \quad (1.1)$$

where n_1 , n_2 , and n_3 are arbitrary integers. The points in space defined by Eq. (1.1) are called *lattice points*; the assembly of lattice points defined by (1.1) is called a *space lattice*; the parallelepiped defined by the vectors \mathbf{a} , \mathbf{b} , and \mathbf{c} is called a *primitive cell*. An infinite number of primitive cells can be defined for a given crystal; usually the one with the highest symmetry is chosen. The space lattice is a geometrical structure that has the same symmetry as the crystal, but that has nothing to do with the crystal otherwise. In particularly simple cases we can assign an atom or atom group to each lattice point.

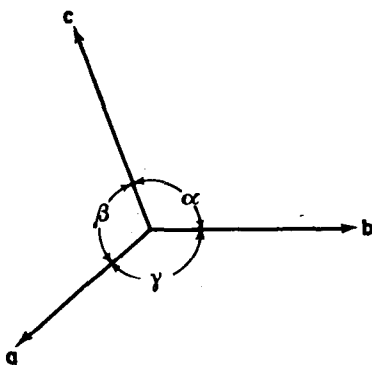


Fig. 1.1. Arbitrary primitive cell $a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90^\circ$.

A primitive cell has lattice points only at the corners. It is sometimes more convenient to draw *unit cells*, which are somewhat larger than the primitive cells and which have lattice points not only at the corners but also at the centers of certain faces or at the center of volume of the unit cell. This is done so that the symmetry of the unit cell comes closer to the symmetry of the crystal itself.

The sides of the unit cell define *fundamental translation vectors* \mathbf{a} , \mathbf{b} , and \mathbf{c} . We obtain *seven crystal systems* characterized by these vectors—that is, by their lengths a , b , and c , and their angles α , β , and γ (Fig. 1.1):

<i>Triclinic:</i>	$\alpha \neq 90^\circ, \beta \neq 90^\circ, \gamma \neq 90^\circ$	$c \leq a \leq b$
<i>Monoclinic:</i>	$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$	$c \leq a; b$ arbitrary
<i>Orthorhombic:</i>	$\alpha = \beta = \gamma = 90^\circ$	$c < a < b$
<i>Tetragonal:</i>	$\alpha = \beta = \gamma = 90^\circ$	$a = b \neq c$
<i>Hexagonal:</i>	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	$a = b; c$ arbitrary
<i>Cubic:</i>	$\alpha = \beta = \gamma = 90^\circ$	$a = b = c$
<i>Rhombohedral:</i>	$\alpha = \beta = \gamma \neq 90^\circ$	$a = b = c$

The unit cells form together the *space lattice*. A space lattice is called *simple* if the unit cell has lattice points only in the corners, *base-centered* if it also has lattice points at the center of two opposite faces, *face-centered* if it also has lattice points at the center of all faces, and *body-centered* if it has a lattice point at the center of volume (Fig. 1.2). This does not yield 4×7 possible arrangements, since not all these possibilities are actually needed. In some cases the unit cell can be replaced by an elementary cell of the same symmetry, in other cases the extra lattice points would destroy the symmetry

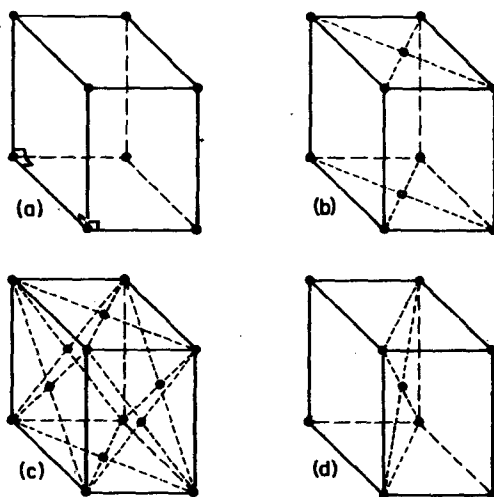


Fig. 1.2. Orthorhombic unit cells. (a) Simple; (b) base-centered; (c) face-centered; (d) body-centered.

of the unit cell, and so on. It can be shown by geometrical arguments that only the following *fourteen space lattices occur*:

1. Triclinic: simple
2. Monoclinic: simple, body-centered
3. Orthorhombic: simple, base-centered, body-centered, face-centered
4. Tetragonal: simple, body-centered
5. Hexagonal: simple
6. Cubic: simple, face-centered, body-centered
7. Rhombohedral: simple

It is common practice to specify the orientation of a crystal plane by its *Miller indices*. These are defined as follows:

1. Let the plane intercept the basis axis of the crystal at the points n_1a , n_2b , and n_3c , where a , b , and c are the side lengths of the unit cell. The plane can thus be characterized by the set of numbers (n_1, n_2, n_3) .
2. The Miller indices (h, k, l) are now defined as the smallest set of integers m/n_1 , m/n_2 , m/n_3 , with m being the lowest integer for which all three numbers m/n_1 , m/n_2 , and m/n_3 are integral. Examples are given in Fig. 1.3.

If the atoms that constitute the crystal can be considered hard spheres, there are three possible ways of packing the spheres densely.

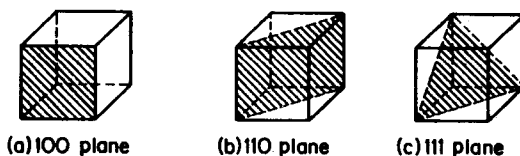


Fig. 1.3. Location of the crystal planes described by the Miller indices (100), (110), and (111).

1. If the layers of spheres are arranged so that each sphere has *four nearest neighbors*, the spheres of the second layer fit into the holes of the first layer, the spheres of the third layer fit into the holes of the second layer, and so on. It is easy to see that the spheres of the third layer are right above the spheres of the first layer and that the arrangement forms a *body-centered cubic lattice*. In this case the atoms *touch along the body diagonals* of the unit cell.

2. If the layers of spheres are arranged so that each sphere has *six closest neighbors*, the spheres of the second layer fit into the holes of the first layer and the spheres of the third layer fit into the holes of the second layer. The latter can happen in two ways:

(a) The spheres of the third layer are placed directly over the spheres of the first layer, so that the arrangement has a hexagonal symmetry; this is the *hexagonal close-packed structure* (Fig. 1.4a).

(b) The spheres of the third layer are placed directly over those holes of the first layer that are not occupied by the second layer. We can see by inspection that this leads to a *face-centered cubic structure* (*cubic close-packed structure*) (Fig. 1.4b). Both close-packed structures have equal density; their density is slightly greater than for the body-centered cubic structure, since the packing is closer.

In both structures there are two types of holes between the spheres. Between four spheres packed in a tetrahedron there are *tetrahedral holes*, and between six spheres packed in an octahedron there are *octahedral holes*. The octahedral holes are somewhat larger than the tetrahedral ones. By drawing a unit cell and inspecting it closely (Fig. 1.5), the reader can verify for himself that the eight tetrahedral holes are in the eight corners of the unit cell. One octahedral hole is wholly inside the cell. The cell also contains parts of twelve octahedral holes. Each of these octahedral holes is shared by four neighboring cells; we thus have in total $1 + \frac{12}{4} = 4$ octahedral holes per unit cell.

This arrangement has an important bearing on the crystal structure of ionic crystals (Sec. 1.2a). Often the large negative ions form a close-packed structure and the small positive ions are located in the holes. Small ions are

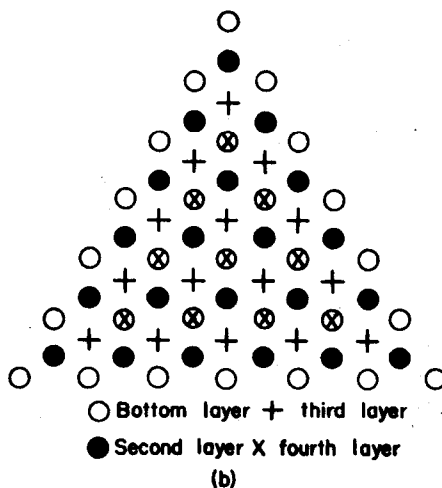
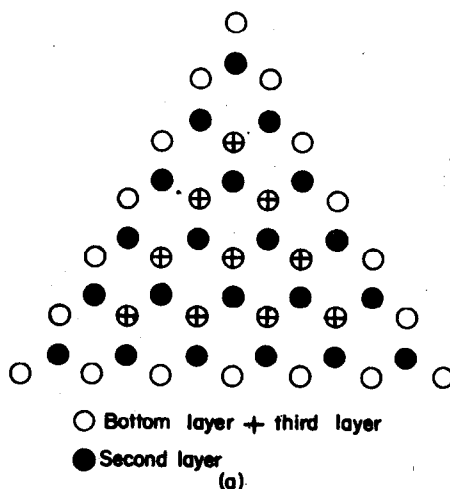


Fig. 1.4. Dense packing of hard spheres (hexagonal and cubic). A common feature of both structures is that one can designate crystal planes in which each atom is surrounded symmetrically by six neighbors so that the atoms of the next plane fit into the holes of the previous one. In the hexagonal structure these are the 100 planes, in the cubic structure the 111 planes.

The figure shows a projection of the subsequent close-packed atomic layers upon the bottom layer. (a) Hexagonal close-packed structure. The third atomic layer is above the first layer, giving the structure a hexagonal symmetry; the hexagonal axis is perpendicular to the bottom layer. (b) Cubic close-packed structure. The fourth atomic layer is above the first layer. The body diagonal of the cubic structure is perpendicular to the bottom layer.

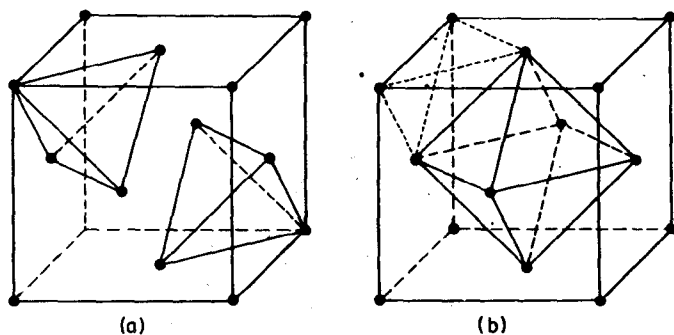


Fig. 1.5. Location of the tetrahedral and octahedral holes in a close-packed cubic structure. (a) The tetrahedral holes are formed between one corner sphere and its three adjacent spheres in the face centers. Two of these tetrahedrons are drawn. (b) One full octahedral hole is formed by the six spheres in the face centers. Twelve additional octahedral holes, having one of the sides of the cube as body diagonal, are shared by four neighboring unit cells. One of them is partly shown by two full-drawn lines and four dotted lines.

preferably located in the tetrahedral holes; if they are too big for the tetrahedral holes, they are located in the octahedral ones.

For example, the Cl ions in the *NaCl* structure form a cubic close-packed structure, and the Na ions are so big that they fit only into the octahedral holes (Fig. 1.6a). In *CsCl*, however, the Cs ions are too big to fit even into the octahedral holes; as a consequence a new type of crystal structure appears, the *CsCl* structure (Fig. 1.6b), in which the Cl ions form a simple cubic lattice and the Cs ions are located in the center of volume of the unit cells.

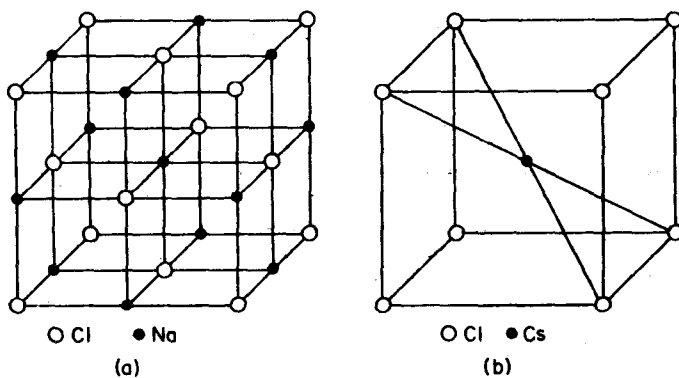


Fig. 1.6. (a) *NaCl* structure. The Cl ions form a cubic close-packed structure, the Na ions occupy the octahedral holes and are located in the middle of the body diagonals of the octahedron. (b) *CsCl* structure.

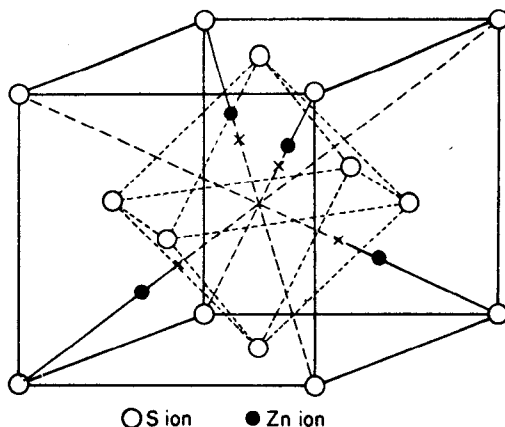


Fig. 1.7. Cubic ZnS (zincblende structure). The S ions form a close-packed structure; the Zn ions are located in the center of the tetrahedral holes, half of which are filled.

In ZnS, the *zincblende structure* occurs; the S ions form a cubic, close-packed structure and the very small Zn ions again fit into the tetrahedral holes (Fig. 1.7). Another modification of ZnS, the *wurtzite structure*, differs in that the S ions form a hexagonal close-packed structure, the Zn ions again being located in the tetrahedral holes.

1.2. TYPES OF CRYSTAL BINDING

The most important examples of crystal binding that concern us here are the ionic, the metallic, the covalent, and the hydrogen bonds.

1.2a. Ionic Bond

In the ionic bond the atoms are ionized so that the electron structure of each ion consists of closed shells. Examples are Na^+Cl^- and $\text{Mg}^{2+}\text{O}^{2-}$. Since each ion has a closed shell, and therefore has quantum numbers $L = 0$ and $S = 0$, the charge distribution has spherical symmetry (see Chapter 2). One would therefore expect crystals of high symmetry—for example, crystals of the cubic and the hexagonal type. In crystals in which the negative ions are atom complexes, the crystal structure may be determined by the structure of the negative ions.

The binding forces at larger distances are strong electrostatic forces; at very small distances the space-charge clouds start to penetrate, and a very strong repulsion occurs. As a consequence, the ions are drawn so closely together that the space-charge clouds just start to penetrate. This is the

explanation for the close-packed structure of the negative ions in many ionic crystals and for the large binding energy of those crystals.

1.2b. Metallic Bond

The metallic bond structure is formed by positively charged metal ions embedded in a sea of mobile free electrons. The negative charges are not fixed to atoms bound in fixed positions, as in the ionic bond, but are associated with the mobile free electrons that are distributed more or less uniformly through the crystal. This explains the large differences in the properties of metals and ionic crystals. The attractive force is electrostatic, and usually the binding is so strong that the metal ions form a close-packed structure of either the hexagonal or the cubic type. In the case of the alkali metals the atomic distance is relatively large and the body-centered cubic lattice is energetically more favorable; this^{*} explains the relatively small binding energy for these metals.

1.2c. Covalent Bond

With the covalent bond a strong bond between the atoms is obtained because of the mutual sharing (exchange) of electrons by adjacent atoms; bonds in which two atoms mutually share an *electron pair* are particularly stable and are called *covalent bonds*. The binding is electrostatic but of a form that cannot be explained on a classical basis; the interaction is a consequence of the wave character of the electron. It is known as *exchange interaction*.

A good example of such a bond is the structure of diamond, silicon, and germanium. Each of these atoms has four outer electrons and therefore can share an electron pair with four neighbors, which are arranged around it in a symmetrical fashion; hence the four neighbors form a regular tetrahedron with the atom itself in its center (Fig. 1.8). This gives rise to a cubic structure known as the *diamond structure*.

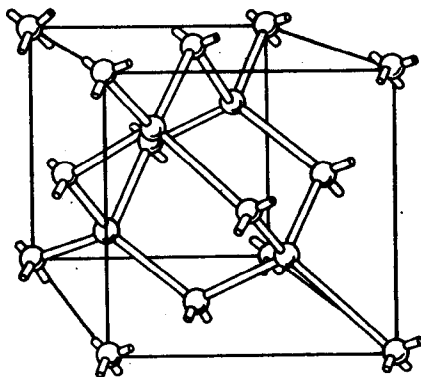


Fig. 1.8. Diamond structure (cubic). Each carbon atom is tetrahedrally surrounded by four neighbors. (Courtesy Bell System Technical Journal.)

Often the binding in a crystal is a mixture of two types of bonds. In some oxides the bond is a mixture of ionic and covalent bonds. In metals having an incomplete *d* shell ($l = 2$; see Chapter 2), the *d* electrons, which are relatively deep inside the atom,