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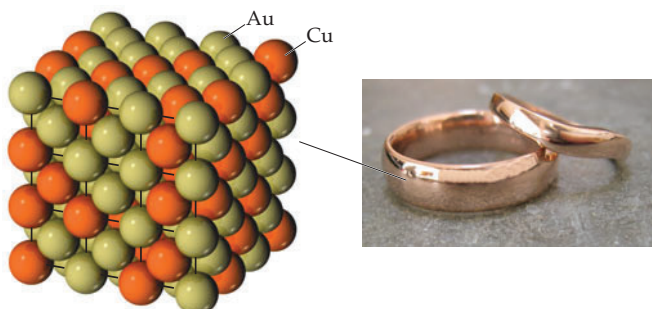
## 12.4 METALLIC BONDING

Consider the structures of elements of the third period (Na–Ar). Argon with eight valence electrons has a complete octet; as a result it does not form any bonds. Chlorine, sulfur, and phosphorus form molecules ( $\text{Cl}_2$ ,  $\text{S}_8$ , and  $\text{P}_4$ ) in which the atoms make one, two, and three bonds, respectively (► **FIGURE 12.20**). Silicon forms an extended network solid in which each atom is bonded to four equidistant neighbors. Each of these elements forms  $8 - N$  bonds, where  $N$  is the number of valence electrons. This behavior can easily be understood through application of the octet rule.

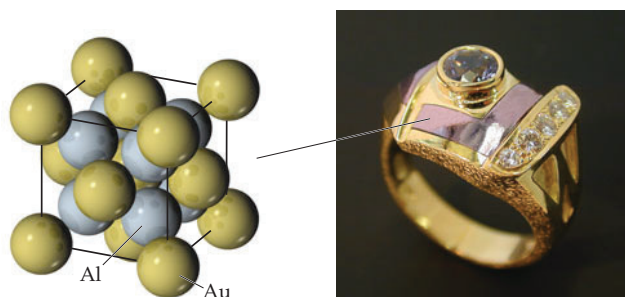
If the  $8 - N$  trend continued as we move left across the periodic table, we would expect aluminum (three valence electrons) to form five bonds. Like many other metals, however, aluminum adopts a close-packed structure with 12 near neighbors. Magnesium and sodium also adopt metallic structures. What is responsible for this abrupt change in the preferred bonding mechanism? The answer is that, as noted earlier, metals do not have enough valence-shell electrons to satisfy their bonding requirements by forming localized electron-pair bonds. In response to this deficiency, the valence electrons are collectively shared. A structure in which the atoms are close-packed facilitates this delocalized sharing of electrons.

## GO FIGURE

In which of these alloys are the gold atoms and the other atoms (Cu or Al) arranged randomly?



14-karat red gold, a substitutional alloy marked with a red dot in Figure 12.18



Purple gold, the intermetallic compound  $\text{AuAl}_2$

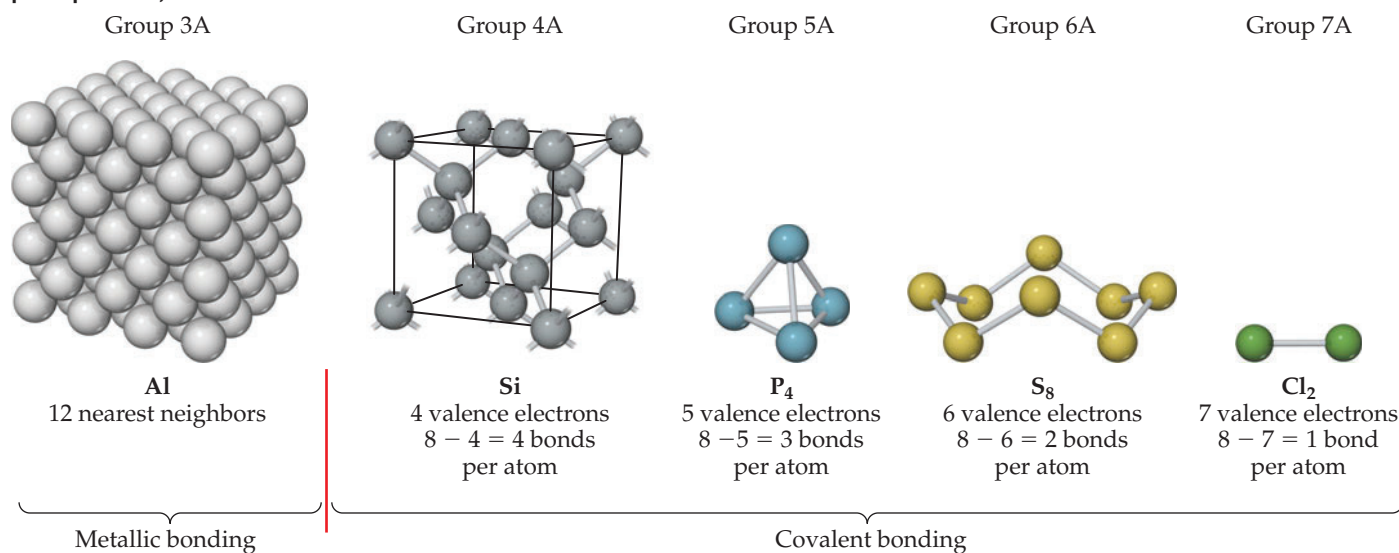
Gold can also be alloyed with many other metals. White gold is generally obtained by alloying either nickel or palladium with gold. Although Ni-Au alloys are cheaper, they are generally considered inferior because they are harder to work and because many people suffer an allergic reaction to nickel. All of these alloys are substitutional alloys, but gold also forms some interesting intermetallic compounds. Reacting gold and aluminum in a 1:2 mole ratio produces the intermetallic compound  $\text{AuAl}_2$ , which is known as purple gold for its unusual color. If the aluminum is replaced with indium to form  $\text{AuIn}_2$  the color changes to blue. Because they are intermetallic compounds, purple and blue gold are brittle, which makes it very difficult to form them into rings and other jewelry pieces. They can be used as gemstones or inlays, however, as in the ring shown in Figure 12.19.

RELATED EXERCISES: 12.41, 12.42, 12.110

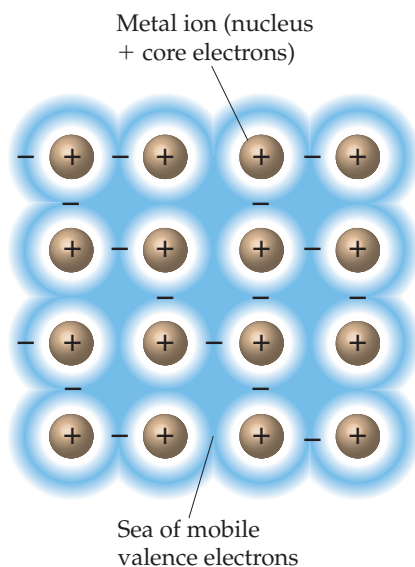
▲ FIGURE 12.19 Red and purple gold at the macroscopic and microscopic levels.

## GO FIGURE

How many nonbonding electron pairs are there per atom in chlorine, sulfur, phosphorus, and silicon?



▲ FIGURE 12.20 Bonding in period 3 elements.



▲ **FIGURE 12.21** **Electron-sea model of metallic bonding.** The valence electrons delocalize to form a sea of mobile electrons that surrounds and binds together an extended array of metal ions.

## Electron-Sea Model

A simple model that accounts for some of the most important characteristics of metals is the **electron-sea model**, which pictures the metal as an array of metal cations in a “sea” of valence electrons (◀ **FIGURE 12.21**). The electrons are confined to the metal by electrostatic attractions to the cations, and they are uniformly distributed throughout the structure. The electrons are mobile, however, and no individual electron is confined to any particular metal ion. When a voltage is applied to a metal wire, the electrons, being negatively charged, flow through the metal toward the positively charged end of the wire.

The high thermal conductivity of metals is also accounted for by the presence of mobile electrons. The movement of electrons in response to temperature gradients permits ready transfer of kinetic energy throughout the solid.

The ability of metals to deform (their malleability and ductility) can be explained by the fact that metal atoms form bonds to many neighbors. Changes in the positions of the atoms brought about in reshaping the metal are partly accommodated by a redistribution of electrons.

## Molecular-Orbital Model

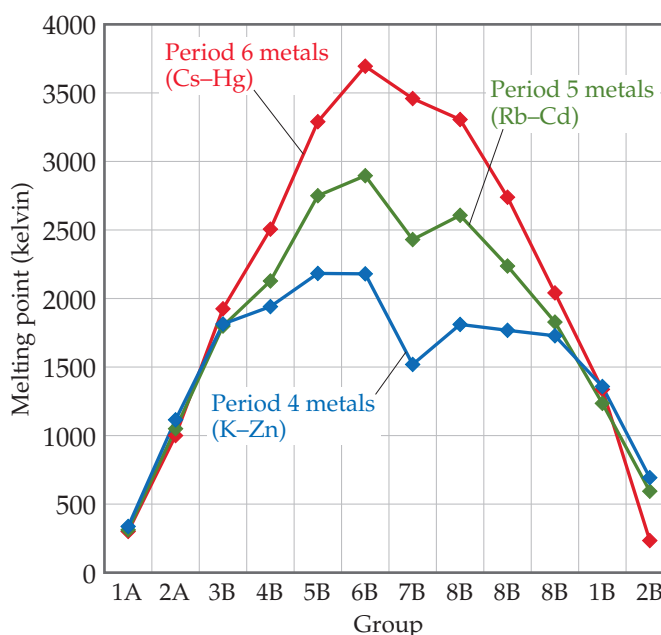
Although the electron-sea model works surprisingly well given its simplicity, it does not adequately explain many properties of metals. According to the model, for example, the strength of bonding between metal atoms should steadily increase as the number of valence electrons increases, resulting in a corresponding increase in the melting points. However, elements near the middle of the transition metal series, rather than those at the end, have the highest melting points in their respective periods (▼ **FIGURE 12.22**). This trend implies that the strength of metallic bonding first increases with increasing number of electrons and then decreases. Similar trends are seen in other physical properties of the metals, such as the boiling point, heat of fusion, and hardness.

To obtain a more accurate picture of the bonding in metals, we must turn to molecular-orbital theory. In Sections 9.7 and 9.8 we learned how molecular orbitals are created from the overlap of atomic orbitals. Let’s briefly review some of the rules of molecular-orbital theory:



### GO FIGURE

Which element in each period has the highest melting point? In each case, is the element you named at the beginning, middle, or end of its period?

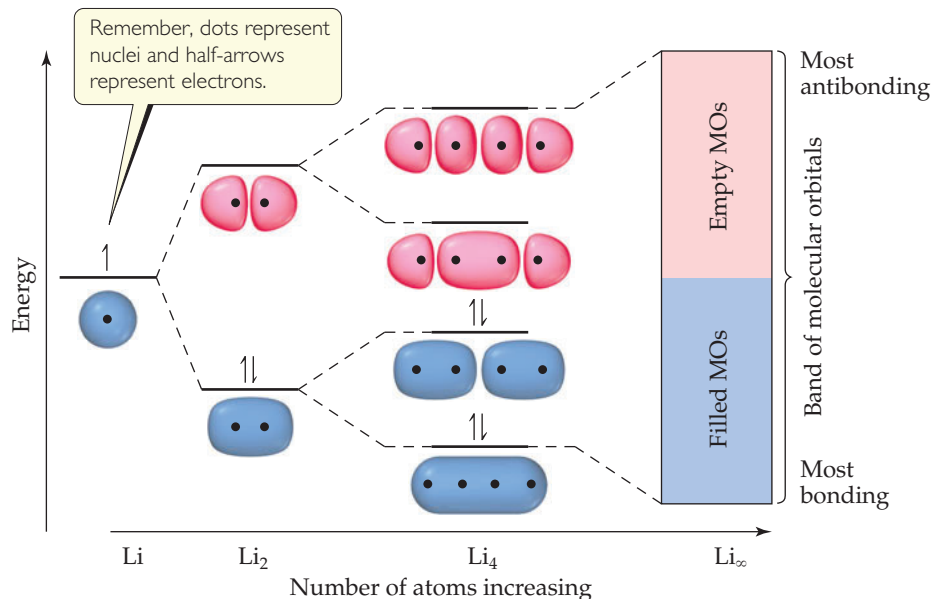


▲ **FIGURE 12.22** The melting points of metals from periods 4, 5, and 6.



## GO FIGURE

How does the energy spacing between molecular orbitals change as the number of atoms in the chain increases?



▲ **FIGURE 12.23** Discrete energy levels in individual molecules become continuous energy bands in a solid. Occupied orbitals are shaded blue, and empty orbitals red.

1. Atomic orbitals combine to make molecular orbitals that can extend over the entire molecule.
2. A molecular orbital can contain zero, one, or two electrons.
3. The number of molecular orbitals in a molecule equals the number of atomic orbitals that combine to form molecular orbitals.

The electronic structures of crystalline solids and small molecules have similarities as well as differences. To illustrate, consider how the molecular-orbital diagram for a chain of lithium atoms changes as we increase the length of the chain (▲ **FIGURE 12.23**). Each lithium atom contains a half-filled  $2s$  orbital in its valence shell. The molecular-orbital diagram for  $\text{Li}_2$  is analogous to that of an  $\text{H}_2$  molecule: one filled bonding molecular orbital and one empty antibonding molecular orbital with a nodal plane between the atoms. (Section 9.7) For  $\text{Li}_4$ , there are four molecular orbitals, ranging from the lowest-energy orbital, where the orbital interactions are completely bonding (0 nodal planes), to the highest-energy orbital, where all interactions are antibonding (3 nodal planes).

As the length of the chain increases, the number of molecular orbitals increases. Regardless of chain length, the lowest-energy orbitals are always the most bonding and the highest-energy orbitals always the most antibonding. Furthermore, because each lithium atom has only one valence shell atomic orbital, the number of molecular orbitals is equal to the number of lithium atoms in the chain. Because each lithium atom has one valence electron, half of the molecular orbitals are fully occupied and the other half are empty, regardless of chain length.\*

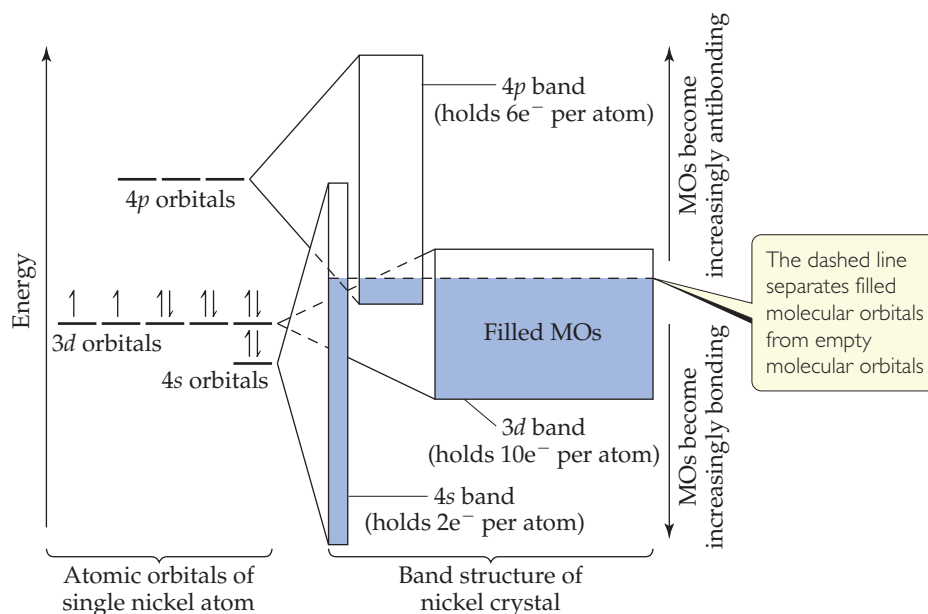
If the chain becomes very long, there are so many molecular orbitals that the energy separation between them becomes vanishingly small. As the chain length goes to infinity, the allowed energy states become a continuous **band**. For a crystal large enough to see with the eye (or even an optical microscope), the number of atoms is extremely large. Consequently, the electronic structure of the crystal is like that of the infinite chain, consisting of bands, as shown on the right-hand side of Figure 12.23.

\*This is strictly true only for chains with an even number of atoms.



## GO FIGURE

If the metal were potassium rather than nickel, which bands— $4s$ ,  $4p$ , and/or  $3d$ —would be partially occupied?



▲ FIGURE 12.24 The electronic band structure of nickel.

The electronic structures of most metals are more complicated than shown in Figure 12.23 because we have to consider more than one type of atomic orbital on each atom. Because each type of orbital can give rise to its own band, the electronic structure of a solid usually consists of a series of bands. The electronic structure of a bulk solid is referred to as a **band structure**.

The band structure for a typical metal is shown schematically in ▲ FIGURE 12.24. The electron filling depicted corresponds to nickel metal, but the basic features of other metals are similar. The electron configuration of a nickel atom is  $[\text{Ar}]3d^84s^2$ , as shown on the left side of the figure. The energy bands that form from each of these orbitals are shown on the right side. The  $4s$ ,  $4p$ , and  $3d$  orbitals are treated independently, each giving rise to a band of molecular orbitals. In practice, these overlapping bands are not completely independent of each other, but for our purposes this simplification is reasonable.

The  $4s$ ,  $4p$ , and  $3d$  bands differ from one another in the energy range they span (represented by the heights of the rectangles on the right side of Figure 12.24) and in the number of electrons they can hold (represented by the area of the rectangles). The  $4s$ ,  $4p$ , and  $3d$  bands can hold 2, 6, and 10 electrons per atom, respectively, two per orbital, as dictated by the Pauli exclusion principle. ∞ (Section 6.7) The energy range spanned by the  $3d$  band is smaller than the range spanned by the  $4s$  and  $4p$  bands because the  $3d$  orbitals are smaller and, therefore, overlap with orbitals on neighboring atoms less effectively. This reduces the strength of the bonding interactions, which dominate the bottom of the band, as well as the antibonding interactions, which dominate the top of the band. As a result, the  $3d$  band spans a narrower range of energy than the  $4s$  and  $4p$  bands.

Many properties of metals can be understood from Figure 12.24. We can think of the energy band as a partially filled container for electrons. The incomplete filling of the energy band gives rise to characteristic metallic properties. The electrons in orbitals near the top of the occupied levels require very little energy input to be “promoted” to higher-energy orbitals that are unoccupied. Under the influence of any source of excitation, such as an applied electrical potential or an input of thermal energy, electrons move into previously vacant levels and are thus freed to move through the lattice, giving rise to electrical and thermal conductivity.

Without the overlap of energy bands, the periodic properties of metals could not be explained. In the absence of the  $d$ - and  $p$ -bands, we would expect the  $s$ -band to be half-filled for the alkali metals (group 1A) and completely filled for the alkaline-earth metals (group 2A). If that were true, metals like magnesium, calcium, and strontium would not be good electrical and thermal conductors, in disagreement with experimental observations.

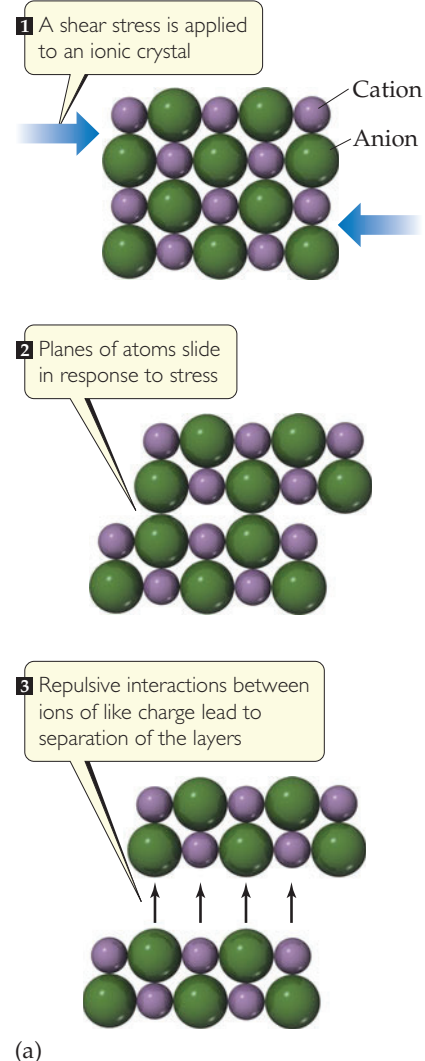
While the conductivity of metals can be qualitatively understood using either the electron-sea model or the molecular-orbital model, many physical properties of transition metals, such as the melting points plotted in Figure 12.22, can be explained only with the latter model. The molecular-orbital model predicts that bonding first becomes stronger as the number of valence electrons increases and the bonding orbitals are populated. Upon moving past the middle elements of the transition metal series, the bonds grow weaker as we fill the antibonding orbitals. Strong bonds between atoms lead to metals with higher melting and boiling points, higher heats of fusion, higher hardness, and so forth.

### GIVE IT SOME THOUGHT

Which element, W or Au, has the greater number of electrons in antibonding orbitals? Which one would you expect to have the higher melting point?

### GO FIGURE

Why don't metals cleave in the way depicted here for ionic substances?



(b)

**▲ FIGURE 12.25 Brittleness and faceting in ionic crystals.** (a) When a shear stress is applied to an ionic solid, the crystal separates along a plane of atoms as shown here. (b) This property of ionic crystals is used to facet gemstones, such as rubies.



## CHAPTER SUMMARY AND KEY TERMS

**SECTION 12.4** The properties of metals can be accounted for in a qualitative way by the **electron-sea model**, in which the electrons are visualized as being free to move throughout the metal. In the molecular-orbital model the valence atomic orbitals of the metal atoms interact to form energy **bands** that are incompletely filled by valence electrons. Consequently, the electronic structure of a bulk solid is referred to as a **band structure**. The orbitals that constitute the energy band are delocalized over the atoms of the metal, and their energies are closely spaced. In a metal the valence shell *s*, *p*, and *d* orbitals form bands and these bands overlap resulting in one or more partially filled bands. Because the energy differences between orbitals *within a band* are extremely small, promoting electrons to higher-energy orbitals requires very little energy. This gives rise to high electrical and thermal conductivity, as well as other characteristic metallic properties.

## KEY SKILLS

- Use the molecular-orbital model to qualitatively predict the trends in melting point, boiling point, and hardness of metals. [Section 12.4]

## METALLIC BONDING (section 12.4)

- 12.43** Explain how the electron-sea model accounts for the high electrical and thermal conductivity of metals.
- 12.44** (a) Compare the electronic structures of atomic chromium and atomic selenium. In what respects are they similar, and in what respects do they differ? (b) Chromium is a metal, and selenium is a nonmetal. What factors are important in determining this difference in properties?
- 12.45** The molecular-orbital diagrams for two- and four-atom linear chains of lithium atoms are shown in Figure 12.23. Construct a molecular-orbital diagram for a chain containing six lithium atoms and use it to answer the following questions. (a) How many molecular orbitals are there in the diagram? (b) How many nodes are in the lowest-energy molecular orbital? (c) How many nodes are in the highest-energy molecular orbital? (d) How many nodes are in the highest-energy occupied molecular orbital (HOMO)? (e) How many nodes are in the lowest-energy unoccupied molecular orbital (LUMO)?
- 12.46** Repeat Exercise 12.45 for a linear chain of eight lithium atoms.
- 12.47** Which would you expect to be the more ductile element, (a) Ag or Mo, (b) Zn or Si? In each case explain your reasoning.
- 12.48** How do you account for the observation that the alkali metals, like sodium and potassium, are soft enough to be cut with a knife?
- 12.49** Explain this trend in melting points: Y 1522 °C, Zr 1852 °C, Nb 2468 °C, Mo 2617 °C.
- 12.50** For each of the following groups which metal would you expect to have the highest melting point; (a) gold (Au), rhenium (Re), or cesium (Cs); (b) rubidium (Rb), molybdenum (Mo), or indium (In); (c) ruthenium (Ru), strontium (Sr), or cadmium (Cd)?