

Chapter 1

Introduction

A Introduction

Every active field of scientific investigation has a central, fundamental question that motivates continued research. One way to phrase the motivating question in materials research is: how can elements be combined to produce a solid with specified properties? This is, of course, a complicated question, and it is appropriate to break it up into at least three separate issues. First, when any given elements are combined under some controlled conditions, will they be immiscible, will they dissolve in one another, or will they react to form a compound and, if so, in what atomic ratio? Second, what structure will the product of this combination have and how is it influenced by the processing conditions? While this book deals almost exclusively with the atomic structure of the crystals, it is equally important to be able to specify the defect structure, the microstructure, and the mesoscale structure. Third, given the product phase or phases and the structure (at each length scale), what are the properties of this material? Addressing these fundamental questions in a systematic way requires familiarity with established principles of thermodynamics, kinetics, chemistry, physics, and crystallography. The present book is intended to provide a set of necessary (but not sufficient) skills to conduct materials research. Specifically, the scope of the course encompasses the description of the structure of crystalline matter, the experimental interrogation of crystalline structure, the origin of the cohesive forces that stabilize crystalline structures, and how these cohesive forces vary with the elements in the solid.

In this introductory chapter, the primary goal is to review the elementary ideas that are used to understand the links between chemical bonding, crystal structures, and physical properties. The secondary goal is to motivate the study of more advanced models throughout the remainder of the book by exploring the limitations of the elementary concepts. We begin this chapter by describing the periodic chart and the principles of its arrangement.

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Table 1.1. *A comparison of properties predicted by Mendeleev (1871) with those currently accepted for germanium [1]*

Property	Predicted	Current
Color	dark gray	grayish-white
Atomic weight	72	72.59
Density (g cm ⁻³)	5.5	5.35
Atomic volume (cm ³ g-atom ⁻¹)	13	13.5
Specific heat (cal g ⁻¹ °C ⁻¹)	0.073	0.074
Oxide stoichiometry	XO ₂	GeO ₂
Oxide density (g cm ⁻³)	4.7	4.703
Chloride stoichiometry	XCl ₄	GeCl ₄
Chloride boiling point	<100 °C	86 °C
Chloride density (g cm ⁻³)	1.9	1.844

B Periodic trends in atomic properties

i. *The importance of the periodic table: Mendeleev predicts Ge in 1871*

Over a century ago, Mendeleev demonstrated how useful it is to understand the periodic trends in atomic mass, size, ionization energies, and electronegativity. According to the periodic law that he formulated in 1869, ‘the chemical properties of the elements are not arbitrary, but vary in a systematic way according to atomic mass.’ In 1913, Henry Mosely discovered that it was actually atomic number (the number of protons and, thus, the number of electrons in the neutral atom), rather than atomic mass, that underpins the periodic law. The periodic law allowed Mendeleev to make a number of interesting predictions. For example, although element 32 (Ge) was not yet known, he successfully predicted many of its properties, as shown in Table 1.1. This example demonstrates the useful predictive power that comes with an understanding of periodicity. In the following subsections, the periodic trends in metallicity, electronegativity, and size are discussed.

ii. *Metallicity*

The property of *metallicity* can be defined as the tendency of an atom to donate electrons to metallic or ionic bonds. Metallicity increases from top to bottom and from right to left on the periodic chart. The metallicity trend can be understood

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according to the following line of reasoning. Metallicity increases as an atom binds its valence electrons with diminished strength. As you descend in a group on the periodic chart, the valence electron–nuclear separation is greater, and the binding force is diminished. The decrease in the binding force is a result both of the increased electron–nuclear distance and the screening of the nuclear charge by core electrons. On the other hand, as you go from right to left on the chart, the valence electron–nuclear separation is nearly the same (the electrons occupy the same principal levels), but the nuclear charge decreases. The decrease in nuclear charge is accompanied by a decrease in the electron binding force and an increase in the metallicity.

iii. Electronegativity

Metallicity is a good property to begin with because most people have a fairly clear idea of the difference between metals and nonmetals. However, it is far more common to describe the properties of atoms in terms of their *electronegativity*, which is the opposite of the metallicity. The electronegativity can be defined as the tendency of an atom to attract an electron. Based on this definition and the reasoning applied in the previous paragraph, you can see that the electronegativity trend is opposite to the metallicity trend. Numerous electronegativity scales have been proposed, but the most commonly used is the one originally devised by Pauling [2]. Because Pauling was an academic, he graded electronegativities on a 0 to 4.0 scale, with fluorine having the highest electronegativity of 4.0 and cesium having the lowest with 0.7. The Pauling electronegativities are shown in Fig. 1.1, and throughout this book we will use these values. In Chapter 7, more recent efforts to determine improved values will be described and alternative values will be presented.

iv. Size and mass

The periodic trends in *size* are the same as those for metallicity for the same reasons. Descending or moving from right to left on the chart, the atomic size increases. It is also worth remembering that cations (positive ions) are smaller than neutral atoms, while anions (negative ions) are larger. Ions always shrink with increasing positive charge and expand with increasing negative charge. *Mass*, of course, increases with atomic number.

As a closing note, it should be recognized that the periodic trends are not absolute. For example, when moving from left to right, the electronegativity does not increase continuously for every element. Note for example, that the electronegativity actually decreases to the immediate right of the noble metals (group IB). The fact that the mass of tellurium is actually greater than the mass of iodine illustrates that even the masses are not perfectly ordered. Despite these

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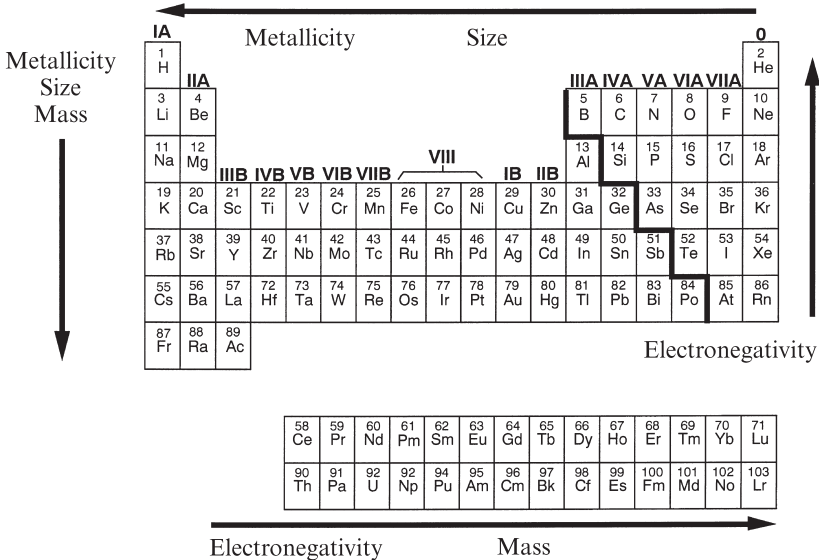


Figure 1.2. Summary of the periodic trends in atomic properties [1]. Arrows indicate the direction of increase in the property values.

metallically bonded solids. Second, nonmetallic elements and nonmetal–nonmetal combinations are covalently bonded. Third, bonds between metals and nonmetals are either ionic or covalent, depending on the electronegativity difference.

These rules are fairly clear, except for the third which requires some critical electronegativity difference to separate ionic bonds from covalent bonds. We get this critical electronegativity difference from Pauling's expression for the ionic fraction of a bond (f) [2], where

$$f = 1 - e^{-\frac{1}{4}(x_{\text{nm}} - x_{\text{m}})^2} \quad (1.1)$$

and x_{nm} is the electronegativity of the nonmetallic element and x_{m} is the electronegativity of the metallic element. We will assume that when $f > 0.5$ ($\Delta x > 1.7$), the bonds are ionic and that when $f \leq 0.5$ ($\Delta x \leq 1.7$), the bonds are covalent. In ternary or more complex compounds, the fractional ionicity can be determined by using stoichiometrically weighted averages for the values of x_{m} and/or x_{nm} in Eqn. 1.1.

It must be emphasized that the change from metallic to nonmetallic character is continuous and complex, so much so that many authors would refute the

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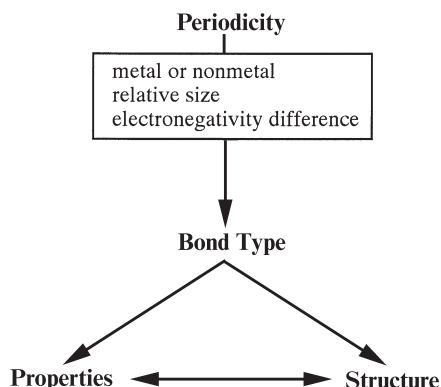


Figure 1.3. Knowledge of periodicity allows one to distinguish elements as metals or nonmetals and to gauge relative electronegativities and sizes. Based on this, it is possible to assign a bonding type. From knowledge of the bond type, characteristic structures and properties can be inferred.

apparently arbitrary binary categorization defined above. It is more common to define a third class of elements, the metalloids, which straddle the metal–nonmetal boundary (for example: B, Si, Ge, As, Te, and Sb). However, with such criticism noted, a binary classification is nevertheless implemented because it has the practical advantage of leading to a simple set of rules to determine bond types. Once the bond type is defined, the type of atomic structure and properties that the solid might have can also be inferred. This relationship, upon which the following sections elaborate, is illustrated schematically in Fig. 1.3.

ii. *Simple bonding models and typical properties*

The simplest *metallic bonding model* assumes that positively charged ion cores are arranged periodically in a ‘sea’ of free electrons (formed by valence electrons which leave the sphere of influence of the atom). Metals include those elements from group IA and IIA where the s levels are filled (the alkali and alkaline earth metals), the B-group or transition metal series where the d levels are filled, and the lanthanide and actinide series where the f levels are filled. A number of post-transition metals are also found in the region of the chart where the p levels are filled. Materials that we would classify as metals include elemental substances such as Cu, Ag, Au, Al, Fe, Pb, intermetallic compounds such as Ni_3Al , NiAl , CuZn , CuZn_3 , and random solid solutions or alloys, A_xB_{1-x} , where both A and B are metallic elements. Typical properties of metals include high reflectivity (when polished), high electronic and thermal conductivity, low to intermediate melting temperatures, and high ductility at temperatures less than half of their melting points. As exceptions, we should note that many intermetallic compounds and refractory metals have very high melting points and little ductility at room temperature.

The simplest model for the *ionic bond* assumes that charge is transferred from

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the more metallic (low electronegativity) atom to the less metallic (high electronegativity) atom forming oppositely charged species, the cation (+) and anion (−). The electrostatic interaction between the two ions, F_{12} , increases with increasing charge (q_1 and q_2) and decreases with increasing separation, r_{12} , according to Coulomb's law:

$$F_{12} = \frac{kq_1q_2}{r_{12}^2}. \quad (1.2)$$

Crystals that we consider to be ionically bound include salts (such as NaCl and CaCl₂) and ceramics (such as MgO, ZrO₂, TiO₂). In each case, the electronegativity difference between the two atoms is greater than 1.7. Ionically bound materials are typically transparent and colorless, electronically and thermally insulating, have intermediate to high melting temperatures, are brittle at ambient temperatures, and are soluble in polar solvents or acids. Although these generalizations are well accepted, there are numerous exceptions, especially to the optical, electrical, and solubility descriptions. For example, we can compare TiO and CaO, both of which have the same crystal structure (rock salt) and, according to our definition, would be considered ionically bonded ceramics. However, while CaO is a transparent, colorless insulator, TiO is a reflective, metallic conductor that superconducts at sufficiently low (near absolute zero) temperatures.

The simple model for *covalent bonding* assumes that electrons are shared between atoms and that electron charge density accumulates between relatively positive atomic cores. Before going further, we must make an important distinction between the two types of solids that contain covalent bonds. The first type includes three-dimensional covalent networks such as Si, SiC, GaAs, and BN. These crystals are composed of individual atoms, all linked by covalent bonds. In other words, there is a covalently bonded path between any two atoms in the solid. The second type includes molecular solids or polymeric solids. In these crystals, atoms within each molecule are linked by covalent bonds, but the molecules that make up the crystal are held together only by the weak interactions known collectively as intermolecular forces or secondary bonds (including van der Waals, dipolar, and hydrogen bonds). In such solids, not all atoms are connected by a path of strong covalent bonds. The difference between these two types of solids is illustrated schematically in Fig. 1.4. Examples of molecular solids include crystalline N₂, O₂, H₂O, C₆₀, and even macromolecular materials such as polyethylene. While it is easy to decide when a material will bond covalently, it is difficult to decide if it will form a three dimensional covalent network or a molecular solid. If more than two thirds of the components in a covalently bonded compound are H, C, O, N, or a

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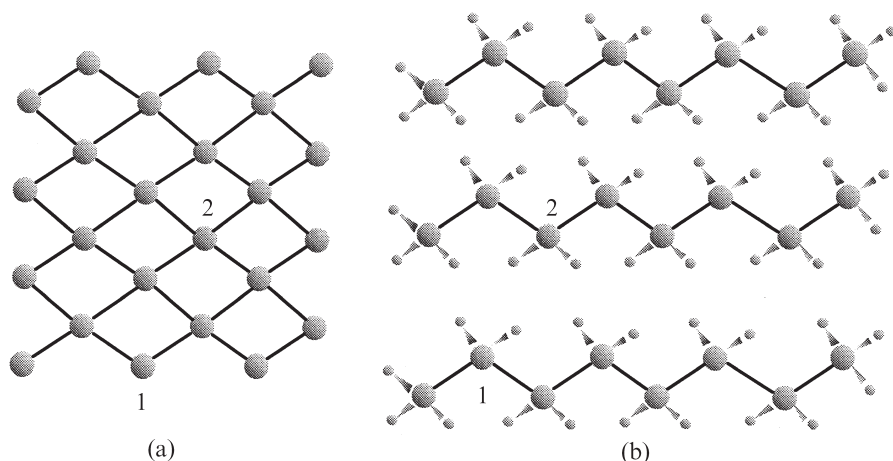


Figure 1.4. Comparison of (a) a covalently bonded three-dimensional network and (b) a molecular solid. The molecular solid has covalent bonds (dark lines) only within individual molecules. Thus, there is no covalently bonded path between the atom labeled 1 and the atom labeled 2; the molecules are bonded to one another only by weak secondary forces. In the covalently bonded network, however, there is a covalently bonded path between any two atoms.

halogen, then it is likely to be a molecular solid. However, diamond is a noteworthy example illustrating that this guideline should be applied with caution.

Covalently bonded networks typically have high melting points and are non-reflective, insulating, and brittle. On the other hand, molecular solids held together by secondary forces have low melting temperatures and are transparent, insulating, soft, and soluble. Perhaps one of the most obvious inadequacies of the simple models proposed here for assigning bond types is the inability to distinguish between these two types of solids.

iii. *Ketelaar's triangle*

Based on our discussion above, we can identify three types of primary bonds: metallic, ionic, and covalent; we will classify the weaker intermolecular forces as secondary. For simplicity, a set of rules has been defined that allow all substances to be placed in one of these three categories. However, one of the important objectives of this book is to establish the idea that these three types of bonding are limiting cases and that very few substances are well described by such an insensitive classification system. Most substances exhibit characteristics associated with more than one type of bonding and must be classified by a comparison to the limiting cases. In other words, when all of the possibilities are

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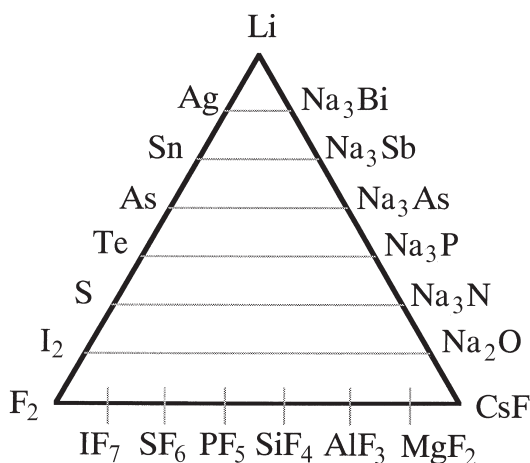


Figure 1.5. Ketelaar's triangle illustrates that there is a continuum of bonding types between the three limiting cases [3].

considered, we can say that there is a continuous transition from one type of bonding to another and that most materials are in the transition region rather than at the limits.

Ketelaar [3] expressed this idea in the simple diagram shown in Fig. 1.5. Taking the substance with the most nearly ideal metallic bond to be Li, and taking CsF and F₂ to have the most nearly ideal ionic and covalent bonds, respectively, these three substances form the vertices of the Ketelaar's triangle. All other substances fall at intermediate points; their proximity to the vertices corresponds to how well any of the three limiting cases will describe the bonding. The substances listed on the lateral edges of the triangle are merely examples chosen based on periodicity; all materials can be located on this triangle. So, when trying to understand the bonding and properties of any particular chemical compound, it is more useful to think about where it lies on Ketelaar's triangle than to try to associate it with one of the three limiting cases. In the next section, we cite some examples of how bonding is related to the properties of some real materials.

iv. *Examples of trends in bonding*

When the metal/nonmetal boundary on the periodic chart is crossed, the properties of the elements in group IV change dramatically, as is illustrated in Table 1.2. The properties of diamond are representative of a covalently bonded material and the properties of Pb are representative of a metallic material. The properties of Si and Ge are intermediate between these two limits. Note the continuous change in the melting points of these solids. To a first approximation, we can gauge relative bond strengths by melting points.

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Table 1.2. *Properties of selected group IV elements.*

element	Electronic conductivity ($\Omega\text{-cm}$) ⁻¹	hardness	appearance	melting point/ boiling point T_m/T_b °C
C (diamond)	10^{-10}	10	transparent	3550/4827
Si	$>10^{-10}$		black	1410/2355
Ge	$<10^{-9}$		black	937/2830
Pb	10^9	2	reflective	327/1740

Table 1.3. *Properties of selected fourth row elements.*

element	electronic conductivity	appearance	T_m / T_b °C
Zn	conductive metal	reflective	420/907
Ga	conductive metal	reflective	30/2403
Ge	semiconductor	black	937/2830
As	insul./ photocond.	dull	817/(high press.)
Se	insul./ photocond.	dull	217/685
Br	insulator	diatomic gas	-7.2/59

The properties of elements in the fourth row of the periodic table (where the 4p shell is being filled) are shown in Table 1.3. Here, the metal–nonmetal boundary on the periodic chart is crossed in the horizontal direction. The series begins with a typical metal (Zn), goes to a three-dimensionally bonded covalent network (Ge), and finishes with a molecular solid (Br₂). Although the two atoms in a single diatomic bromine molecule are held together by a covalent bond, the molecules in the solid are held in place only by weak, secondary bonds. The difference between the melting points of solid Ge and Br₂ illustrates the difference between the properties of a three-dimensional covalent network and a molecular covalent solid.

To illustrate the changes that accompany the transition from covalent to ionic bonding, we examine the properties of isoelectronic compounds. As an example, we choose the oxides of group IV elements, which are given in Table 1.4. By examining these data, you can see that the bonding changes from ionic (ZrO₂) to a covalent network (SiO₂) and then to molecular covalent (CO₂). Note the profound difference between the behaviors of the isoelectronic compounds SiO₂ (a crystalline solid) and CO₂ (a molecular solid).