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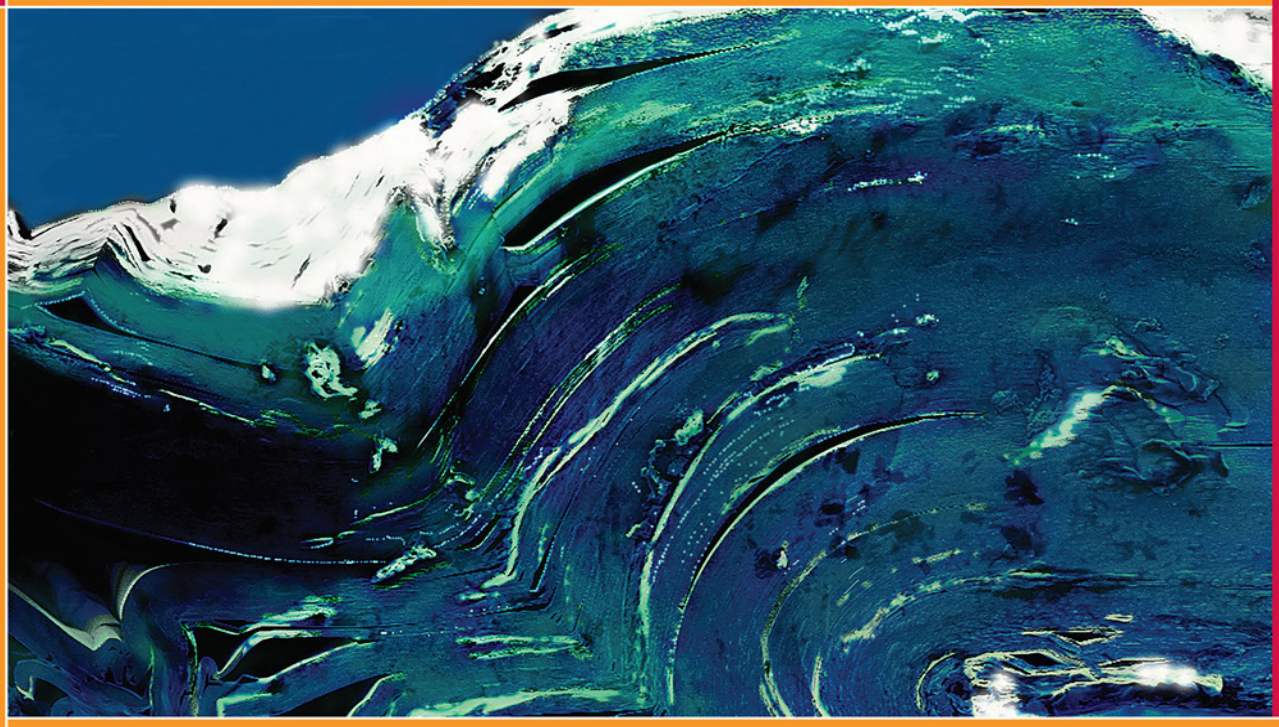

FUNDAMENTALS OF CERAMICS

Second Edition

Michel W. Barsoum

CRC Press
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Fundamentals of Ceramics

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Fundamentals of Ceramics, Second Edition
Michel W. Barsoum

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With abiding love and deep gratitude to my treasured and unusual family, Patricia, Michael, Kate, Eric and, last but not least, Quinn.

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SERIES PREFACE

The series publishes cutting edge monographs and foundational textbooks for interdisciplinary materials science and engineering.

Its purpose is to address the connections between properties, structure, synthesis, processing, characterization and performance of materials. The subject matter of individual volumes spans fundamental theory, computational modeling and experimental methods used for design, modeling and practical applications. The series encompasses thin films, surfaces and interfaces, and the full spectrum of material types, including biomaterials, energy materials, metals, semiconductors, optoelectronic materials, ceramics, magnetic materials, superconductors, nanomaterials, composites and polymers.

It is aimed at undergraduate and graduate level students, as well as practicing scientists and engineers.

PREFACE TO THE SECOND EDITION

McGraw Hill first printed this book in 1996. The Institute of Physics (acquired by Taylor and Francis) printed the second printing in 2003. The major differences between the two were the many less typos in the latter. Since 2003, I found about 200 more typos—entropy is a powerful force—that have been eliminated in this second edition. This is not to say that the second edition is perfect, but it at least should have a few less typos. The figures have also been spruced and now, most, include red.

The world is changing quite rapidly indeed and we have to change with it. Fortuitously, for me, the fundamentals have not changed. It follows that writing this second edition was not as long and protracted as the first that was written over 11 years. To bring this edition to the 21st century, at the ends of each chapter I added one or more sections that I labeled Case Histories and/or Computational Materials Science.

If a picture is worth a thousand words, then a one-minute video probably contains as many words as are in this book. In today's world videos are ubiquitous. When combined with computational materials science we can now not only imagine what is happening at the atomic scale, but actually simulate it.

The Case History sections were added to highlight some of the new developments and exciting directions the field, broadly defined as ceramics, is embarking on. This includes the advent of nanotechnology in general and the two dimensional materials revolution in particular. In these sections I did not restrict myself to the future, but also looked back to highlight some tremendous achievements in the field, again broadly defined as ceramics.

Two dimensional solids, including MXenes, are briefly described in Chap. 3. In Chap. 7, I discuss solid oxide fuel cells and the kinetics of alumina forming materials that are key to most high temperature applications in air. In Chap. 9, the focus is on glass-ceramics, that are not new, but have been commercially quite successful. A much more recent development that has been phenomenally successful is the manufacturing of very strong and thin glasses that, among other applications, cover all our cell phones. Electric field assisted and microwave sintering are described in Chap. 10. In Chap. 11, I introduce wear resistant ceramics, strong and tough ceramics and how crack deflection enhances the toughness. In Chap. 12, I highlight the incredible strengths and environmental stability of glass fibers—that are routinely manufactured today by the millions of kilometers and without which the internet would slow to a crawl. These fibers are not only incredibly strong, but are also of such high purity as to possess unparalleled transparency. I also overview ceramic matrix composites that are currently used in jet engines. Talking of the latter, a ceramic-based technology that allows jet engines to run significantly hotter and hence more efficiently are thermal barrier coatings discussed in Chap. 13. Also in Chap. 13, I describe the space shuttle tile, not new, but still noteworthy. In Chap. 14, I overview electrochemical impedance spectroscopy. Cobalites, manganites and colossal magnetoresistance are reviewed in Chap. 15. In the last chapter I discuss optical fibers and how point defects can lead to color.

The Computational Materials Science sections reflect the tremendous progress made and continuing to be made in computational materials science. In Chap. 2, density functional theory, DFT, and molecular dynamics are introduced. Chapter 4 deals with elastic tensor properties and surface energies, two of the

more challenging physical properties to measure. How DFT can be used to determine the phonon distributions—another physical property that is non-trivial to measure experimentally—in solids is presented. The energies needed to form point defects are another facet of the solid state that is not easy to measure and where DFT calculations have come to the rescue. This is outlined in Chap. 6.

Our world is currently facing unprecedented problems. Amongst the most challenging is how to power an ever more energy hungry world without generating greenhouse gases that are acidifying our oceans, melting our polar caps and resulting in more extreme weather. How do we insure that every human being has access to clean water and enough food.

In some way or other, I am convinced that new materials will allow us to solve, or at least ameliorate, some of these problems. It is my sincere hope that this textbook will in some small way inspire some young and creative minds to this quest. I, for one, would prefer to live in a world that is not self-destructing. One of my favorite sayings is: There is no hope, but I could be wrong.

I would be remiss if I did not acknowledge and thank all the students I have interacted with and learned from over the years. So thank you to my PhD students, in chronological order, D. Brodkin, T. El-Raghy, M. Radovic, P. Finkel, A. Murugaiah, T. Zhen, A. Ganguly, S. Gupta, E. Hoffman, S. Basu, A. Zhou, S. Amini, A. R. Sakulich, T. Scabarozi, A. Moseson, N. Lane, M. Naguib, B. Anasori, J. Griggs, D. Tallman, J. Halim, M. Ghidiu, S. Kota, V. Natu, M. Carey, H. Badr and T. El-Melegy. I would like to thank the visiting scientists and post-docs, L. Verger, M. Sokol, C. Hu, G. Ying, C. Li and D. Zhao. The list would not be complete without thanking my MSc students, I. Albaryak, S. Chakraborty, J. Spencer, I. Salama and A. Procopio.

I would also like to thank V. Natu and M. Sokol for helping with some of the figures. Finally I would like to thank my wife and son for their help with many of the figures and also for putting up with me for all the time I spent on this book.

PREFACE TO FIRST EDITION

It is a mystery to me why, in a field as interesting, rich and important as ceramics, a basic fundamental text does not exist. My decision to write this text was made almost simultaneously with my having to teach my first introductory graduate class in ceramics at Drexel a decade ago. Naturally, I assigned Kingery, Bowen and Uhlmann's *Introduction to Ceramics* as the textbook for the course. A few weeks into the quarter, however, it became apparent that KBU's book was difficult to teach from and more importantly to learn from. Looking at it from the student's point of view it was easy to appreciate why—few equations are derived from first principles. Simply writing down a relationship, in my opinion, does not constitute learning; true understanding only comes when the trail that goes back to first principles is made clear. However, to say that this book was influenced by KBU's book would be an understatement—the better word would be inspired by it, and for good reason—it remains an authoritative, albeit slightly dated, text in the field.

In writing this book I had a few guiding principles. First, nearly all equations are derived, usually from first principles, with the emphasis being on the physics of the problem, sometimes at the expense of mathematical rigor. However, whenever that trade-off is made, which is not often, it is clearly noted in the text. I have kept the math quite simple, nothing more complicated than differentiation and integration. The aim in every case was to cover enough of the fundamentals, up to a level deep enough to allow the reader to continue his or her education by delving, without too much difficulty, into the most recent literature. In today's fast-paced world, it is more important than ever to understand the fundamentals.

Second, I wanted to write a book that more or less "stood alone" in the sense that it did not assume much prior knowledge of the subject from the reader. Basic chemistry, physics, mathematics and an introductory course in materials science or engineering are the only prerequisites. In that respect, I believe this book will appeal to, and could be used as a textbook in, other than material science and engineering departments, such as chemistry or physics.

Pedagogically I have found that students in general understand concepts and ideas best if they are given concrete examples rather than generalized treatments. Thus maybe, at the expense of elegance and brevity, I have opted for that approach. It is hoped that once the concepts are well understood, for at least one system, the reader will be able to follow more advanced and generalized treatments that can be found in many of the references that I have included at the end of every chapter.

Successive drafts of this book have been described by some reviewers as being arid, a criticism that I believe has some validity and that I have tried to address. Unfortunately, it was simply impossible to cover the range of topics, at the depth I wanted to, and be flowery and descriptive at the same time (the book is already over 650 pages long).

Another area where I think this book falls short is in its lack of what I would term a healthy skepticism (à la Feynman lectures, for instance). Nature is too complicated, and ceramics in particular, to be neatly packaged into monosize dispersed spheres and their corresponding models, for example.

I thus sincerely hope that these two gaps will be filled in by the reader and especially the instructor. First, a little bit of "fat" should make the book much more appetizing—examples from the literature or the

instructor's own experience would be just what is required. Second, a dose of skepticism concerning some of the models and their limitation is required. Being an experimentalist, I facetiously tell my students that when theory and experiment converge one of them is probably wrong.

This book is aimed at junior, senior and first-year graduate students in any materials science and engineering program. The sequence of chapters makes it easy to select material for a one-semester course. This might include much of the material in Chaps. 1–8, with additional topics from later chapters. The book is also ideally suited to a two-quarter sequence, and I believe there may even be enough material for a two-semester sequence.

The book can be roughly divided into two parts. The first nine chapters deal with bonding, structure and the physical and chemical properties that are influenced mostly by the type of bonding rather than the microstructure, such as defect structure and the atomic and electronic transport in ceramics. The coverage of the second part, Chaps. 11–16, deals with properties that are more microstructure dependent, such as fracture toughness, optical, magnetic and dielectric properties. In between the two parts lies Chap. 10, which deals with the science of sintering and microstructural development. The technological aspects of processing have been deliberately omitted for two reasons. The first is that there are a number of good undergraduate texts that deal with the topic. Second, it is simply not possible to discuss that topic and do it justice in a section of a chapter.

Chapter 8 on phase diagrams was deliberately pushed back until the notions of defects and nonstoichiometry (Chap. 6) and atom mobility (Chap. 7) were introduced. The chapter on glasses (Chap. 9) follows Chap. 8 since once again the notions introduced in Chaps. 6, 7 and 8 had to be developed in order to explain crystallization.

And while this is clearly not a ceramics handbook, I have included many important properties of binary and ternary ceramics collected over 10 years from numerous sources. In most chapters I also include, in addition to a number of well-tested problem sets with their numerical answers, worked examples to help the student through some of the trickier concepts. Whenever a property or phenomenon is introduced, a section clearly labeled experimental details has been included. It has been my experience that many students lacked knowledge of how certain physical properties or phenomena are measured experimentally, which needless to say makes it rather fruitless to even try to attempt to explain them. These sections are not intended, by any stretch of the imagination, to be laboratory guides or procedures.

Finally, it should also be pointed out that Chaps. 2, 5 and 8 are by no means intended to be comprehensive—but are rather included for the sake of completion, and to highlight aspects that are referred to later in the book as well as to refresh the reader's memory. It is simply impossible to cover inorganic chemistry, thermodynamics and phase equilibria in three chapters. It is in these chapters that a certain amount of prior knowledge by the reader is assumed.

I would like to thank Dr. Joachim Maier for hosting me, and the Max-Planck Institute fur Festkorperforchung in Stuttgart for its financial support during my sabbatical year, when considerable progress was made on the text. The critical readings of some of the chapters by C. Schwandt, H. Naefe, N. Nicoloso and G. Schaefer is also gratefully acknowledged. I would especially like to thank Dr. Rowland M. Cannon for helping me sort out, with the right spirit I may add, Chaps. 10 through 12—his insight, as usual, was invaluable.

I would also like to thank my colleagues in the Department of Materials Engineering and Drexel University for their continual support during the many years it took to finish this work. I am especially indebted to Profs. Roger Doherty and Antonious Zavaliangos with whom I had many fruitful and illuminating discussions. Finally I would like to take this opportunity to thank all those who have, over the many years I was a student, first at the American University in Cairo, Egypt, followed by the ones at the University of Missouri-Rolla and, last but not least, MIT, taught and inspired me. One has only to leaf through the book to appreciate the influence Profs. H. Anderson, R. Coble, D. Kingery, N. Kreidl, H. Tuller, D. Uhlmann, B. Wuench and many others had on this book.

Comments, criticisms, suggestions and corrections, from all readers, especially students, for whom this book was written, are most welcome. Please send them to me at the Department of Materials Engineering, Drexel University, Philadelphia, PA 19104, or by e-mail at Barsoumw@drexel.edu.

Finally, I would like to thank my friends and family, who have been a continuous source of encouragement and support.

Michel W. Barsoum

AUTHOR

Prof. Michel W. Barsoum is Distinguished Professor in the Department of Materials Science and Engineering at Drexel University. As the author of two entries on the MAX phases in the *Encyclopedia of Materials Science*, and the book *MAX Phases* published in 2013, he is an internationally recognized leader in the area of MAX phases. In 2011, he and colleagues at Drexel, selectively etched the A-group layers from the MAX phases to produce an entirely new family of 2D solids that they labeled MXenes, that have sparked global interest because of their potential in a multitude of applications. He has authored the book *MAX Phases: Properties of Machinable Carbides and Nitrides*, published by Wiley VCH in 2013. He has published over 450 refereed papers, including ones in top-tier journals such as *Nature* and *Science*. According to Google Scholar his h-index is >100 with over 44,000 citations. He made ISI's most cited researchers list in 2018 and 2019. He is a foreign member of the Royal Swedish Academy of Engineering Sciences, a fellow of the American Ceramic Society and the World Academy of Ceramics. The latter awarded him the quadrennial International Ceramics Prize 2020, one of the highest honors in the field. In 2000, he was awarded a Humboldt-Max Planck Research Award for Senior US Research Scientists and spent a sabbatical year at the Max Planck Institute in Stuttgart, Germany. In 2008, he spent a sabbatical at the Los Alamos National Laboratory as the prestigious Wheatly Scholar. He has been a visiting professor at Linkoping University in Sweden since 2008. In 2017, he received a Chair of Excellence from the Nanoscience Foundation in Grenoble, France. He is co-editor of Materials Research Letters, published by Taylor & Francis.

1

INTRODUCTION

All that is, at all
Lasts ever, past recall,
Earth changes,
But thy soul and God stand sure,
Time's wheel runs back or stops:
Potter and clay endure.

Robert Browning

1.1 INTRODUCTION

The universe is made up of elements, which in turn consist of neutrons, protons and electrons. There are roughly 100 elements, each possessing a unique electronic configuration determined by their atomic number, Z, and the spatial distribution and energies of their electrons. What determines the latter requires some understanding of quantum mechanics and is discussed in greater detail in the next chapter.

One of the major triumphs of quantum theory was a rational explanation of the **periodic table** (see inside front cover) of the elements that had been determined from experimental observation long before the advent of quantum mechanics. The periodic table places the elements in horizontal rows of increasing atomic number and vertical columns or groups, so that all elements in a group display similar chemical properties. For instance, all elements of group 17, known as halides, exist as diatomic gases characterized

by very high reactivity. Conversely, the elements of group 18, the noble gases, are monoatomic and are chemically extremely inert.

A large fraction of the elements are solids at room temperature, and because they are shiny, ductile, and good electrical and thermal conductors, they are considered *metals*. A fraction of the elements—most notably, N, O, H, the halides and the noble gases—are gases at room temperature. The remaining elements are predominantly covalently bonded solids that, at room temperature, are either insulators (B, P, S, C[1]) or semiconductors (Si, Ge). These elements, are typically referred to as metalloids.

Few elements are used in their pure form; most often they are alloyed with other elements to create engineering materials. The latter can be broadly classified as metals, polymers, semiconductors or ceramics, with each class having distinctive properties that reflect the differences in the nature of their bonding.

In metals, the bonding is predominantly metallic, where delocalized electrons provide the "glue" that holds the positive ion cores together. This delocalization of the bonding electrons has far-reaching ramifications since it is responsible for properties most associated with metals: ductility, thermal and electrical conductivity, reflectivity and other distinctive properties.

Polymers consist of very long, for the most part, C-based chains, to which other organic atoms (for example, C, H, N, Cl, F) and molecules are attached. The bonding within the chains is strong, directional and covalent, while the bonding between chains is relatively weak. Thus, the properties of polymers, as a class, are dictated by the weaker bonds, and consequently they possess lower melting points, have higher thermal expansion coefficients and are less stiff than most metals or ceramics.

Semiconductors are covalently bonded solids that, in addition to Si and Ge, already mentioned, include GaAs, CdTe and InP, among many others. The usually strong covalent bonds holding semiconductors together render their mechanical properties similar to those of ceramics (i.e., brittle and hard).

Now that these distinctions have been made, it is possible to answer the nontrivial question: What is a ceramic?

1.2 DEFINITION OF CERAMICS

Ceramics can be defined as *solid compounds that are formed by the application of heat, and sometimes heat and pressure, comprising at least two elements provided one of them is a non-metal or a metalloid. The other element(s) may be a metal(s) or another metalloid(s).* A somewhat simpler definition was given by Kingery, who defined ceramics as "the art and science of making and using solid articles, which have, as their essential component, and are composed in large part of inorganic, nonmetallic materials". In other words, what is neither a metal, a semiconductor or a polymer is a ceramic.

To illustrate, consider the following examples: Magnesia,[2] or MgO, is a ceramic since it is a solid compound of a metal, Mg, bonded to the nonmetal, oxygen, O. Silica is also a ceramic since it combines a

[1] In the form of diamond. It is worth noting that although graphite is a good electrical conductor, it is not considered a metal since it is neither shiny nor ductile.

[2] A note on nomenclature: The addition of the letter a to the end of an element name implies one is referring to its oxide. For example, while silicon refers to the element, silica is SiO_2 or the oxide of silicon. Similarly, alumina is the oxide of aluminum or Al_2O_3; magnesium, magnesia; etc.

metalloid, Si, with a nonmetal. Similarly, TiC and ZrB_2 are ceramics since they combine metals (Ti, Zr) and a metalloid (C, B). SiC is a ceramic because it combines two metalloids. Ceramics are not limited to binary compounds: $BaTiO_3$, $YBa_2Cu_3O_3$, and Ti_3SiC_2 are all perfectly respectable class members.

It follows that the oxides, nitrides, borides, carbides, and silicides (not to be confused with silicates) of all metals and metalloids are ceramics; which, needless to say, leads to a large number of compounds. This number becomes even more daunting when it is appreciated that the silicates are also, by definition, ceramics. Because of the abundance of oxygen and silicon in nature, silicates are ubiquitous; rocks, dust, clay, mud, mountains, sand, in short, the vast majority of the earth's crust is composed of silicate-based minerals. When it is also appreciated that cement, bricks, and concrete are essentially silicates, a case could be made that we live in a ceramic world.

In addition to their ubiquitousness, silicates were singled out above for another reason, namely, as the distinguishing chemistry between traditional and modern ceramics. Before that distinction is made, however, it is important to briefly explore how atoms are arranged in three dimensions.

1.2.1 CRYSTALLINE VERSUS AMORPHOUS SOLIDS

The arrangement of atoms in solids, in general, and ceramics, in particular, will exhibit **long-range order**, only **short-range order**, or a combination of both.[3] Solids that exhibit long-range order[4] are referred to as **crystalline**, while those in which that periodicity is lacking are known as **amorphous**, **glassy** or **noncrystalline solids.**

The difference between the two is illustrated schematically in Fig. 1.1. From the figure, it is obvious that a solid possesses long-range order when the atoms repeat with a periodicity that is much greater than the bond lengths or the distance between the atoms. Most metals and ceramics, with the exception of glasses and glass-ceramics (see Chap. 9), are crystalline.

Since, as discussed throughout this book, the details of the lattice patterns can strongly influence the macroscopic properties of ceramics, it is imperative to understand the rudiments of crystallography.

1.3 ELEMENTARY CRYSTALLOGRAPHY

As noted above, long-range order requires that atoms be arrayed in a three-dimensional (3D) pattern that repeats. The simplest way to describe a pattern is to describe a **unit cell** within that pattern. A *unit cell* is defined as the smallest region in space that, when repeated, completely describes the 3D pattern of atoms in a crystal. Geometrically, it can be shown that there are only seven unit cell *shapes*, or **crystal systems**, that can be stacked together to fill three-dimensional space. The seven systems, shown in Fig. 1.2, are cubic, tetragonal, orthorhombic, rhombohedral, hexagonal, monoclinic and triclinic. These systems are

[3] Strictly speaking, only solids in which grain boundaries are absent, i.e., single crystals, can be considered to possess only long-range order. As discussed below, the vast majority of crystalline solids possess grain boundaries that are areas in which the long-range order breaks down, and thus should be considered as a combination of amorphous and crystalline areas. However, given that in most cases the volume fraction of the grain boundary regions is much less than 0.01, it is customary to describe polycrystalline materials as possessing only long-range order.

[4] Any solid that exhibits long-range order must also exhibit short-range order, but not vice versa.

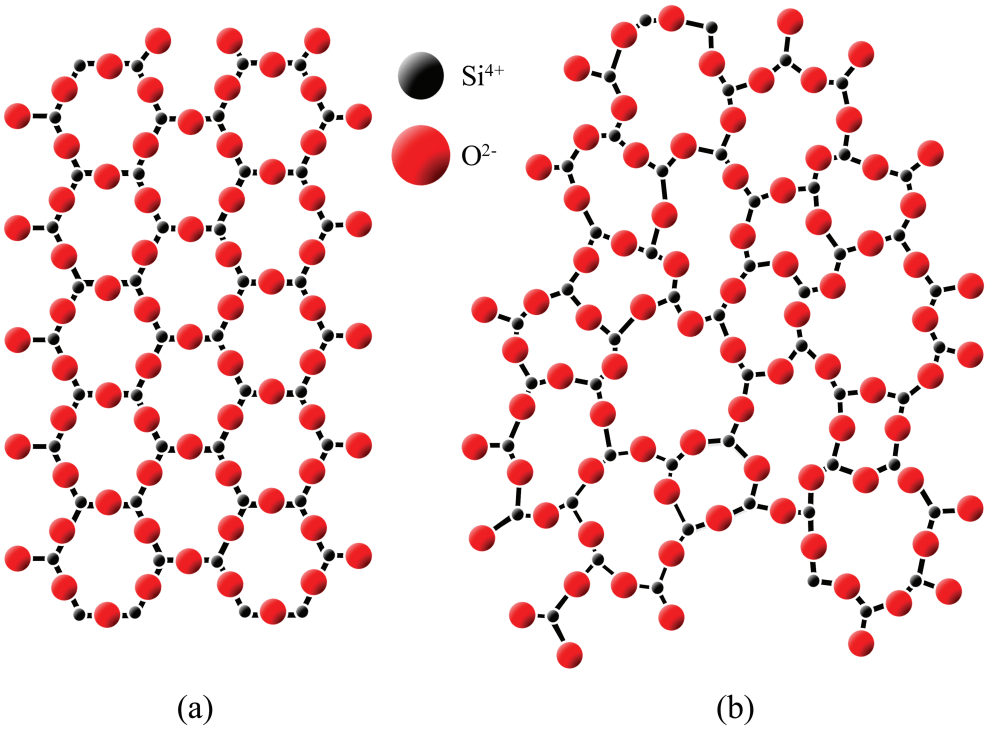

FIGURE 1.1 (*a*) Long-range order; (*b*) short-range order in silica.

distinguished from one another by the lengths of the unit cell edges and the angles between the edges, collectively known as the **lattice parameters** or **lattice constants** (a, b, c, α, β and γ in Fig. 1.2).

It is useful to think of a given crystal system as a "brick" of a certain shape. For example, the bricks can be cubes, hexagons, parallelepipeds, etc. And while the shape of the bricks is an important descriptor of a crystal structure, it is insufficient. In addition to the brick shape, it is important to know the *symmetry* of the lattice pattern within each brick, as well as the actual location of the atoms on these lattice sites. Only then would the description be complete.

It turns out that if one considers only the symmetry within each unit cell, the number of possible permutations is limited to 14. The 14 arrangements, shown in Fig. 1.2, are also known as the **Bravais lattices**. A **lattice** can be defined as an indefinitely extending arrangement of points, each of which is surrounded by an identical grouping of neighboring points. To carry the brick analogy a little further, the Bravais lattice represents the *symmetry* of the *pattern* found on the bricks.

Finally, to describe the atomic arrangement, one must describe the symmetry of the *basis*, defined as the atom or grouping of atoms located at each lattice site. When the basis is added to the lattices, the total number of possibilities increases to 32 *point groups*.[5]

[5] For more information, see, for example, A. Kelly and G. W. Groves, *Crystallography and Crystal Defects*, Longmans, London, 1970.

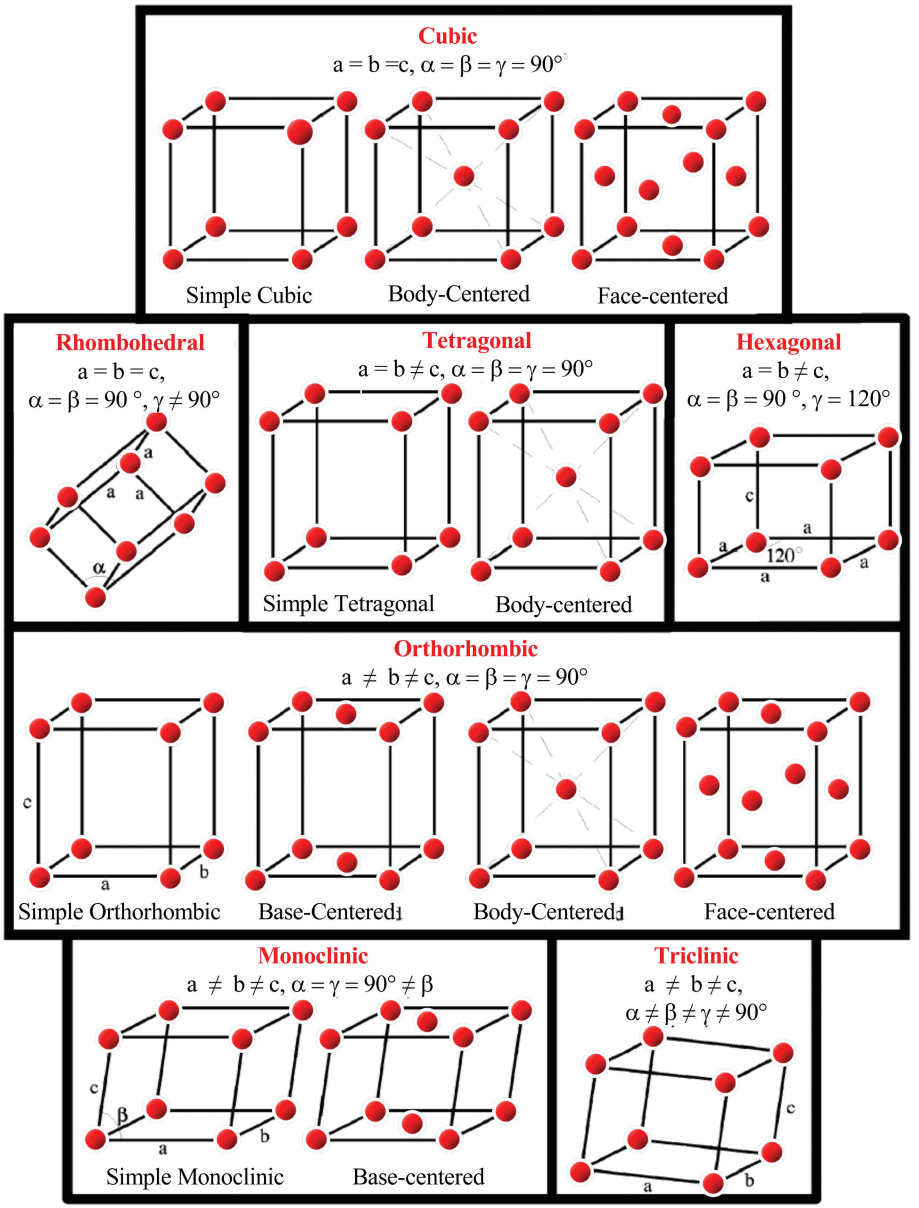

FIGURE 1.2 Geometric characteristics of 7 crystal systems and 14 Bravais lattices.

1.4 CERAMIC MICROSTRUCTURES

Crystalline solids exist as either single crystals or polycrystalline solids. A **single crystal** is a solid in which the periodic and repeated arrangement of atoms is perfect and extends throughout the entirety of the specimen without interruption. A **polycrystalline solid**, Fig. 1.3, is comprised of a collection of many single crystals, termed **grains**, separated from one another by areas of disorder known as **grain boundaries** (see Chap. 6 for more details).

Typically, in ceramics the grains are in the range of 1 to 50 μm and are visible only under a microscope. The shape and size of the grains, together with the presence of porosity, second phases, etc., and their distribution describe what is termed the **microstructure**. As discussed in later chapters, many of the properties of ceramics are microstructure-dependent.

1.5 TRADITIONAL VERSUS ADVANCED CERAMICS

Many people associate the word *ceramics* with pottery, sculpture, sanitary ware, tiles, etc. And whereas this view is not incorrect, it is incomplete because it considers only the traditional, or silicate-based, ceramics. Today the field of ceramic science and engineering encompasses much more than silicates and can be divided into traditional and modern ceramics. Before the distinction is made, however, it is worthwhile to trace the history of ceramics and people's association with them.

It has long been appreciated by our ancestors that some muds, when wet, were easily moldable into shapes that upon heating became rigid. The formation of useful articles from fired mud must constitute one of the oldest and more fascinating of human endeavors. Fired-clay articles have been traced to the dawn of civilization. The usefulness of these new materials, however, was limited by the fact that when fired, they

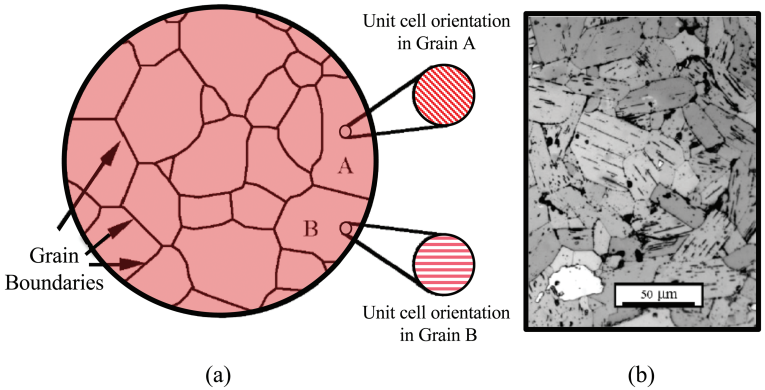

FIGURE 1.3 (*a*) Schematic of a polycrystalline sample. A polycrystal is made up of many grains separated from one another by regions of disorder known as grain boundaries. (*b*) Typical microstructure as seen through an optical microscope.

were porous and thus could not be used to carry or store liquids. Later the serendipitous discovery was made that when heated and slowly cooled, some sands tended to form a transparent, water-impervious solid, known today as glass. From that point on, it was simply a matter of time before glazes were developed that rendered clay objects not only watertight, but also quite beautiful.

With the advent of the industrial revolution, structural clay products such as bricks and heat-resistant refractory materials for the large-scale smelting of metals were developed. And with the discovery of electricity and the need to distribute it, a market was developed for electrically insulating, silicate-based ceramics.

Traditional ceramics are characterized by mostly silicate-based, porous microstructures that are quite coarse, nonuniform and multiphase. They are typically formed by mixing clays and feldspars, followed by forming either by slip casting or on a potter's wheel, firing in a kiln to sinter them and finally glazing.

In a much later stage of development, other ceramics that were not clay- or silicate-based depended on much more sophisticated raw materials, such as binary oxides, carbides, perovskites and even completely synthetic materials for which there are no natural equivalents. The microstructures of these modern ceramics were at least an order of magnitude finer, more homogeneous and much less porous than those of their traditional counterparts. It is the latter—the **modern** or **technical ceramics**—with which this book is mainly concerned.

1.6 GENERAL CHARACTERISTICS OF CERAMICS

As a class, ceramics are hard, wear-resistant, nonmachinable, brittle, prone to thermal shock, refractory, electrically and thermally insulative, intrinsically transparent, nonmagnetic, chemically stable and oxidation-resistant. As with all generalizations, there will be exceptions; some ceramics are electrically and thermally quite conductive, while others are even superconducting. An entire industry is based on the fact that some ceramics are magnetic.

One of the main goals of this book is to answer the question of why ceramics exhibit the properties they do. And while this goal will have to wait until later chapters, at this point it is worthwhile to list some of the applications for which ceramics have been, or are being, developed.

1.7 APPLICATIONS

Traditional ceramics are quite common, from sanitary ware to fine chinas and porcelains to glass products. Currently ceramics are being considered for uses that a few decades ago were inconceivable; applications ranging from ceramic engines to optical communications, from electrooptic applications to laser materials and from substrates in electronic circuits to electrodes in photoelectrochemical devices. Some of the recent applications for which ceramics are used and/or are prime candidates are listed in Table 1.1.

Historically, ceramics were mostly exploited for their electrical insulative properties, for which electrical porcelains and aluminas are prime examples. Today, the so-called electrical and electronic ceramics still play a pivotal role in any modern technological society. For example, their insulative properties together

TABLE 1.1 Properties and applications of advanced ceramics

Property	Applications (Examples)
Thermal	
Insulation	High-temperature furnace linings for insulation (oxide fibers such as SiO_2, Al_2O_3 and ZrO_2)
Refractoriness	High-temperature furnace linings for insulation and containment of molten metals and slags
Thermal conductivity	Heat sinks for electronic packages (AlN)
Electrical and dielectric	
Conductivity	Heating elements for furnaces (SiC, ZrO_2, $MoSi_2$)
Ferroelectricity	Capacitors (Ba-titanate-based materials)
Low-voltage insulators	Ceramic insulation (porcelain, steatite, forsterite)
Insulators in electronic circuits	Substrates for electronic packaging and electrical insulators in general (Al_2O_3, AlN)
Insulators in harsh environments	Spark plugs (Al_2O_3)
Ion-conducting	Sensor and fuel cells (ZrO_2, Al_2O_3, etc.)
Semiconducting	Thermistors and heating elements (oxides of Fe, Co, Mn)
Nonlinear I-V characteristics	Current surge protectors (bi-doped ZnO, SiC)
Gas-sensitive conductors	Gas sensors (SnO_2, ZnO)
Magnetic and superconductive	
Hard magnets	Ferrite magnets [$(Ba, Sr)O{\cdot}6Fe_2O_3$]
Soft magnets	Transformer cores [$(Zn, M)Fe_2O_3$, with M = Mn, Co, Mg]; magnetic tapes (rare-earth garnets)
Superconductivity	Wires and SQUID magnetometers ($YBa_2Cu_3O_7$)
Optical	
Transparency	Windows (soda-lime glasses), cables for optical communication (ultrapure silica)
Translucency and chemical inertness	Heat- and corrosion-resistant materials, usually for Na lamps (Al_2O_3MgO)
Nonlinearity	Switching devices for optical computing ($LiNbO_3$)
IR transparency	Infrared laser windows (CaF_2, SrF_2, NaCl)
Nuclear applications	
Fission	Nuclear fuel (UO_2, UC), fuel cladding (C, SiC) and neutron moderators (C, BeO)
Fusion	Tritium breeder materials (zirconates and silicates of Li, Li_2O); fusion reactor lining (C, SiC, Si_3N_4)
Chemical	
Catalysis	Filters (zeolites); purification of exhaust gases
Anticorrosion	Heat exchangers (SiC), chemical equipment in corrosive environments
Biocompatibility	Artificial joint prostheses (Al_2O_3)
Mechanical	
Hardness	Cutting tools (SiC whisker-reinforced Al_2O_3, Si_3N_4)
High-temperature strength retention	Stators and turbine blades, ceramic engines (Si_3N_4)
Wear resistance	Bearings (Si_3N_4)

with their low loss factors and excellent thermal and environmental stability make them the materials of choice for substrate materials in electronic packages. The development of the perovskite family, with exceedingly large dielectric constants (Chap. 15) holds a significant market share of capacitors produced worldwide. Similarly, the development of magnetic ceramics based on the spinel ferrites is today a mature technology. Other electronic/electrical properties of ceramics that are being commercially exploited include piezoelectric ceramics for sensors and actuators, nonlinear *I-V* characteristics for circuit protection and ionically conducting ceramics for use as solid electrolytes in high-temperature fuel cells, batteries and as chemical sensors.

Mechanical applications of ceramics at room temperature usually exploit their hardness, wear and corrosion resistance. The applications include cutting tools, nozzles, valves and ball bearings in aggressive environments. However, it is the refractoriness of ceramics and their ability to sustain high loads at high temperatures, together with their low densities, that has created the most interest. Applications in that area include ceramic engines for transportation and turbines for energy production.

1.8 THE FUTURE

Paradoxically, because interest in modern ceramics came later than interest in metals and polymers, ceramics are simultaneously mankind's oldest and newest solids. Consequently, working in the field of ceramics can be quite rewarding and exciting. There are a multitude of compounds that have never been synthesized, let alone characterized. Amazing discoveries are always around the corner, as the following examples illustrate.

In 1986, the highest temperature at which any material became superconducting, i.e., the ability to conduct electricity with virtually no loss, was around –250°C, or 23 K. In that year a breakthrough came when Bednorz and Muller[6] shattered the record by demonstrating that a layered lanthanum, strontium copper oxide became superconducting at the relatively balmy temperature of 46 K. This discovery provoked a worldwide frenzy in the subject, and a few months later the record was again almost doubled, to about 90 K. The record today is in excess of 120 K.

Toward the end of 1995, we identified a new class of solids best described as machinable, thermodynamically stable polycrystalline nanolaminates[7,8] (Fig. 1.4*a*). These solids are ternary layered hexagonal early transition metal carbides and nitrides with the general formula $M_{n+1}AX_n$, where n = 1 to 3, M is an early transition metal, A is an A-group element (mostly IIIA and IVA) and X is C and/or N. Today this family numbers over 150, with more being still discovered on a routine basis.

Thermally, elastically, chemically and electrically these so-called MAX phases share many of the advantageous attributes of their respective stoichiometric binary transition metal carbides or nitrides: they are electrically and thermally conductive and chemically stable. Mechanically they cannot be more different. When deformed or fractured the basal planes readily kink, bend and delaminate, not unlike how wood

[6] T. G. Bednorz and K. A. Muller, *Z. Phys. B*, 64, 189 (1986).
[7] M. W. Barsoum, *MAX Phases: Properties of Machinable Carbides and Nitrides*, Wiley VCH GmbH & Co., Weinheim, 2013.
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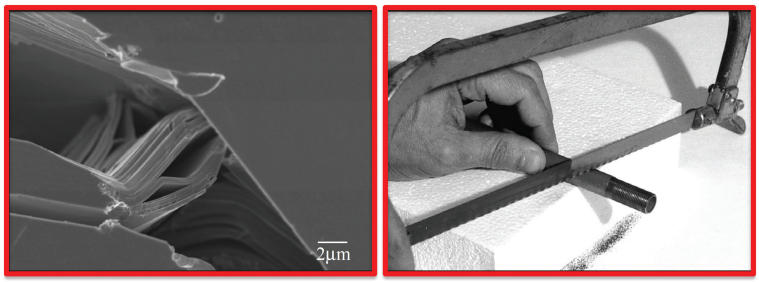

FIGURE 1.4 (*a*) Example of delaminations possible in Ti_3SiC_2. (*b*) Despite being quite stiff and lightweight, Ti_3SiC_2 is still most readily machinable. (M. W. Barsoum, MAX Phases, VCH-Wiley, 2013.)

would deform (Fig. 1.4*a*). These processes occur at room and elevated temperatures. It is this ability to delaminate, almost at will, that led us to describe them as thermodynamically stable nanolaminates. The MAX phases are also relatively soft and are most readily machinable (Fig. 1.4*b*).

Furthermore, some of these compounds (e.g., Ti_3SiC_2) combine many of the best attributes of metals and ceramics. Like metals, they are excellent electrical and thermal conductors, are *not* susceptible to thermal shock and behave plastically at higher temperatures. Like ceramics, they possess high specific stiffness values (Ti_3SiC_2 is roughly three times as stiff as Ti metal, with the same density) and yet as noted above are machinable with nothing more sophisticated than a manual hack-saw (Fig. 1.4*b*). Some also have good creep and fatigue properties; Ti_2AlC is exceptionally oxidation resistant.

My third example is also related to the MAX phases. In 2011, we wanted to use the MAX phases as anodes for Li ions to replace graphite, the current anode of choice for Li batteries. The one problem we faced was that the Li refused to enter the MAX phase structure. After roughly 9 months of trying several approaches, however, we figured out that all we had to do was immerse an Al-containing MAX phase in a solution containing F anions, such as HF or HCl and LiF. The latter selectively etched the Al layers replacing them with O, OH and F terminations. Once the Al layers are etched away it is not difficult to disperse the two-dimensional (2D) flakes in water to form an aqueous colloidal suspension. Once a colloid suspension is created, the possibilities are endless. I labeled these material MXenes for two reasons; the first is to indicate the removal of the A-layers from MAX and the second is to make the connection to graphene and other 2D materials. The name has stuck and today MXenes are bona fide members of the 2D family of materials that have generated tremendous interest. What renders them quite attractive for myriad applications is their unique combination of good electrical conductivity and hydrophilicity. MXenes can be described in a variety of ways such as 2D metals, conductive clays or hydrophilic graphene.

Traditional ceramics have served humanity well for at least the past ten millennia. However, the nature of modern technology, with its ever-mounting demands on materials, has prompted researchers to take a second look at these stone-age materials, and it now is clear that this oldest class of materials are shaping up to be truly the material of the future. It is my sincerest hope that this book will inspire a new generation of talented and dedicated researchers to embark on a voyage of discovery in this most exciting of fields.

PROBLEMS

1.1. (*a*) According to the definition of a ceramic given in the text, would you consider Si_3N_4 a ceramic? How about CCl_4, $SiCl_4$ or SiF_4? Explain.
(*b*) Would you consider $TiAl_3$ a ceramic? How about Al_3C_4, BN, CN or SiB_6? Explain.

1.2. (*a*) How many crystal systems would you expect in two dimensions? Draw and characterize them by their lattice parameters.
Answer: 4
How many Bravais lattices are there in two dimensions? Draw them.
Answer: 5

ADDITIONAL READING

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2

BONDING IN CERAMICS

All things are Atoms: Earth and Water, Air And Fire, all,
Democritus foretold. Swiss Paracelsus, in's alchemic lair,
Saw Sulfur, Salt, and Mercury unfold Amid Millennial
hopes of faking Gold. Lavoisier dethroned
Phlogiston; then Molecular Analysis made bold
Forays into the gases: Hydrogen
Stood naked in the dazzled sight of Learned Men.

John Updike; *The Dance of the Solids**

2.1 INTRODUCTION

The properties of a solid and the way its atoms are arranged in 3D are determined primarily by the nature and directionality of the bonds holding the atoms together. Consequently, to understand variations in properties, it is imperative to appreciate how and why a solid is "glued" together.

This glue can be strong, which gives rise to *primary bonds*, which can be ionic, covalent or metallic. Usually van der Waals and hydrogen bonds are referred to as secondary bonds and are weaker. *In all cases, however, it is the attractive electrostatic interaction between the positive charges of the nuclei and the negative charges of the electrons that is responsible for the cohesion of solids.*

Very broadly speaking, ceramics can be classified as being either ionically or covalently bonded and, for the sake of simplicity, this notion is maintained throughout this chapter. However, that this simple view

* J. Updike, *Midpoint and Other Poems*, A. Knopf, Inc., New York, 1969. Reprinted with permission.

needs some modification will become apparent in Chap. 4; bonding in ceramics is neither purely covalent nor purely ionic, but a mixture of both. Interestingly, in some ceramics, such as the MAX phases and transition metal carbides and nitrides, the bonding is a combination of metallic and covalent.

Before the intricacies of bonding are described, a brief review of the shape of atomic orbitals is presented in Sec. 2.2. The concept of electronegativity and how it determines the nature of bonding in a ceramic is introduced in Sec. 2.3. In Secs. 2.4 and 2.5, respectively, the ionic bond is treated by a simple electrostatic model, and how such bonds lead to the formation of ionic solids is discussed.

The more complex covalent bond, which occurs by the overlap of electronic wave functions, is discussed in Secs. 2.6 and 2.7. In Sec. 2.8, how the interaction of wave functions of more than one atom results in the formation of energy bands in crystalline solids is elucidated.

It is important to point out, at the outset, that much of this chapter is only intended as review of what the reader is assumed to be familiar with from basic chemistry. Most of the material in this chapter is covered in college-level chemistry textbooks.

2.2 STRUCTURE OF ATOMS

Before bonding between atoms is discussed, it is essential to appreciate the energetics and shapes of single atoms. Furthermore, since bonding involves electrons that obey the laws of quantum mechanics, it is crucial to review the following major conclusions of quantum theory as they apply to bonding.

1. The confinement of a particle results in the quantization of its energy levels. Said otherwise, whenever a particle is attracted to, or confined in space to a certain region, its energy levels are necessarily quantized. As discussed shortly, this follows directly from *Schrödinger's wave equation*.
2. A given quantum level cannot accept more than two electrons, which is *Pauli's exclusion principle*.
3. It is impossible to simultaneously know with certainty both the momentum and the position of a moving particle, which is the *Heisenberg uncertainty principle*.

The first conclusion explains the shape of orbitals and their energies; the second why higher-energy orbitals are stable and populated; and the third elucidates, among other things, why an electron does not spiral continually and fall into the nucleus.

In principle, the procedure for determining the shape of an atomic or molecular orbital is quite simple and involves solving Schrödinger's equation—with the appropriate boundary conditions—from which one obtains the all-important electronic wave function. The latter in turn, allows us to calculate the probability of finding an electron in a given volume. To illustrate, consider the simplest possible case, that of the hydrogen atom, which consists of a proton and an electron.

2.2.1 THE HYDROGEN ATOM

Schrödinger's time-independent equation in one dimension is given by:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m_e}{h^2}(E_{tot} - E_{pot})\psi = 0 \tag{2.1}$$

where m_e is the mass of the electron, 9.11×10^{-31} kg; h is Planck's constant, 6.625×10^{-34} J·s; and E_{tot} is the total (kinetic + potential) energy of the electron. The potential energy of the electron E_{pot} is nothing but the Coulombic attraction between an electron and a proton,[9] given by:

$$E_{pot} = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 r} = -\frac{e^2}{4\pi\varepsilon_0 r} \tag{2.2}$$

where z_1 and z_2 are the charges on the electron and nucleus, –1 and +1, respectively; e is the elementary electronic charge, 1.6×10^{-19} C; ε_0 is the permittivity of free space, 8.85×10^{-12} C²/(J•m) or F/m; r is the distance between the electron and the nucleus.

Now ψ is the wave function of the electron and by itself has no physical meaning, but $|\psi(x,y,z;t)|^2$ gives the probability of finding an electron in a volume element dxdydz. The higher ψ^2 is in some volume in space, the more likely the electron is to be found there.

For the simplest possible case of the hydrogen atom, the orbital is spherically symmetric; and so it is easier to work in spherical coordinates. Thus instead of Eq. (2.1), the differential equation to solve is

$$\frac{h^2}{8\pi^2 m_e}\left(\frac{\partial^2\psi}{\partial r^2} + \frac{2}{r}\frac{\partial\psi}{\partial r}\right) + \left(E_{tot} + \frac{e^2}{4\pi\varepsilon_0 r}\right)\psi = 0 \tag{2.3}$$

where E_{pot} was replaced by the value given in Eq. (2.2). The solution of this equation yields the functional dependence of ψ on r, and it can be shown that (see Prob. 2.1)

$$\psi = \exp(-c_0 r) \tag{2.4}$$

satisfies Eq. (2.3), but *only* provided the energy of the electron is given by

$$E_{tot} = -\frac{m_e e^4}{8\varepsilon_0^2 h^2} \tag{2.5}$$

and

$$c_0 = \frac{\pi m_e e^2}{\varepsilon_0 h^2} \tag{2.6}$$

As noted above, ψ by itself has no physical significance, but ψ^2 is the probability of finding an electron in a given volume element. It follows that the probability distribution function, W, of finding the electron in a thin spherical shell between r and r + dr is obtained by multiplying $|\psi|^2$ by the volume of that shell (see hatched area in Fig. 2.1*a*), or

$$W = 4\pi r^2 |\psi|^2 dr \tag{2.7}$$

[9] For the hydrogen atom z_1 and z_2 are both unity. In general, however, the attraction between an electron and a nucleus has to reflect the total nuclear charge, viz. an element's atomic number.

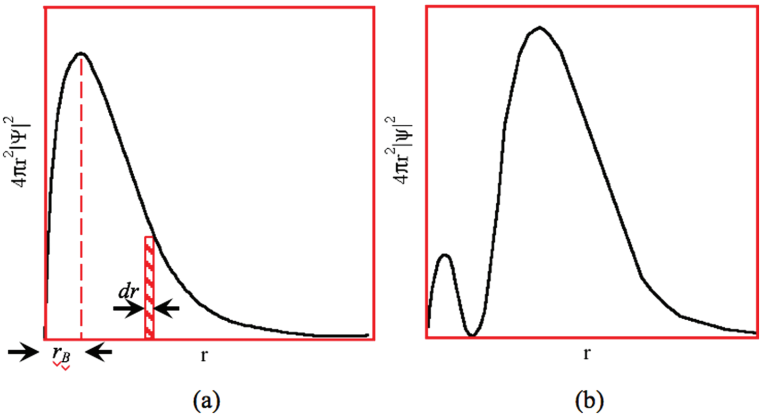

FIGURE 2.1 (*a*) Radial distribution function of 1s state electron. The crosshatched strip has a volume $4\pi r^2 dr$, which, when multiplied by $|\psi|^2$, gives the probability of finding the electron between r and r + dr. The probability of finding the electron very near or very far from the nucleus approaches zero. The most probable position for the electron is at a distance $r_B = 1/c_o$. (*b*) Radial distribution function of a 2s electron, whose energy is one-fourth that of the 1s state.

In other words, the y-axis is simply a measure of the probability of finding the electron at any distance r.

Figure 2.1*a* shows that the probability of finding an electron at the nucleus, or very far from the nucleus, is negligible, but that somewhere in between that probability is at a maximum. This distance is known as the **Bohr radius**, r_B (see Fig. 2.1*a*). The importance of this result lies in appreciating that (1) while the electron spends most of its time at a distance r_B, its spatial extent is clearly not limited to that value and (2) the best one can hope for when discussing the location of an electron is to talk about the probability of finding it in some volume. It is worth noting here that by combining Eqs. (2.4) to (2.7) and finding the location of the maximum, it can be shown that $r_B = 1/c_o$.

Worked Example 2.1

Calculate the ground-state energy level of the electron in the hydrogen atom, and compare the result with the experimentally derived value of –13.6 eV.

ANSWER[10]

Using Eq. (2.5) gives

$$E_{tot} = -\frac{me^4}{8\varepsilon_0^2 h^2} = -\frac{(9.1\times10^{-31})(1.6\times10^{-19})^4}{8(8.85\times10^{-12})^2(6.63\times10^{-34})^2} \tag{2.8}$$

$$= -2.165\times10^{-18}\,\text{J} = -13.6\ \text{eV}$$

[10] In all problems and throughout this book, SI units are used almost exclusively.

This value is the lowest energy level of a hydrogen electron, a fact that was experimentally known well before the advent of quantum mechanics. This result was one of the first and greatest successes of quantum theory. It is important to note that since this energy is negative, it follows that the electron energy, in the vicinity of the proton, is lower than at an infinite distance away (which corresponds to zero energy).[11]

Equation (2.4) is but one of many possible solutions. For example, it can also be shown that

$$\psi(r) = A(1 + c_1 r)\exp\left(-\frac{rc_0}{2}\right) \tag{2.9}$$

is another perfectly legitimate solution to Eq. (2.3), provided that Eq. (2.5) is divided by 4. The corresponding radial distribution function is plotted in Fig. 2.1*b*. It follows that the energy of this electron is –13.6/4 and it will spend most of its time at a distance given by the second maximum in Fig. 2.1*b*.

To generalize, for a spherically symmetric wave function, the solution (given here without proof) is

$$\psi_n(r) = e^{-c_n r} L_n(r)$$

where L_n is a polynomial. The corresponding energies are given by

$$E_{tot} = \frac{-me^4}{8n^2\varepsilon_0^2 h^2} = -\frac{13.6eV}{n^2} \tag{2.10}$$

where n is known as the *principal quantum number*. As n increases, the energy of the electron increases (i.e., becomes less negative) and its spatial extent increases.

2.2.2 ORBITAL SHAPE AND QUANTUM NUMBERS

Equations (2.4) and (2.9) were restricted to spherical symmetry. An even more generalized solution is

$$\psi_{n,I,m} = R_{nl}(r)Y_l^m(\theta,\pi)$$

where Y_l depends on θ and π. Consequently, the size and shape of an orbital will depend on the specific solution considered. It can be shown that each orbital will have associated with it three characteristic

[11] A thorny question that had troubled physicists as they were developing the theories of quantum mechanics was: What prevented an electron from continually losing energy, spiraling into the nucleus and releasing an infinite amount of energy? Originally, the classical explanation was that the angular momentum of the electron gives rise to the apparent repulsion—this explanation is invalid here, because s electrons have *no* angular momentum (see Chap. 15). The actual reason is related to the Heisenberg uncertainty principle and goes something like this: As an electron is confined to a smaller and smaller volume, the uncertainty in its position Δx decreases. But since $\Delta x \Delta p = h$ is a constant, it follows that its momentum p, or, equivalently, its kinetic energy, will have to increase as Δx decreases. Given that the kinetic energy scales with $1/r^2$, but the potential energy scales only as $1/r$, an energy minimum has to be established at a given equilibrium distance.

interrelated quantum numbers, labeled n, l and m_l, known as the *principal*, *angular* and *magnetic quantum numbers*, respectively.

The **principal quantum number**, **n**, determines the *spatial extent* and *energy* of the orbital.

The **angular momentum quantum number**,[12] **l**, determines the *shape* of the orbital for any given value of n and can only assume the values 0,1,2,3, . . . n – 1. For example, for n = 3, the possible values of l are 0, 1 and 2.

The **magnetic quantum number**, $\mathbf{m_l}$, is related to the *orientation* of the orbital in space. For a given value of l, m_l can take on values from –l to +l. For example, for l = 2, m_l can be +2, +1, 0, –1 or –2. Thus for any value of l there are 2l + 1 values of m_l.

All orbitals with l = 0 are called **s *orbitals*** and are spherically symmetric (Fig. 2.1). When l = 1, the orbital is called a **p *orbital***, and there are three of these (Fig. 2.2*a*), each corresponding to a different value of m_l associated with l = 1, that is, $m_l = -1, 0, +1$. These three orbitals are labeled p_x, p_y and p_z because their lobes of maximum probability lie along the x, y and z axes, respectively. Note the electron spins in the two lobes are opposite to each other. This is why the orbitals are colored red and gray. It is worth noting that although each of the p orbitals is nonspherically symmetric, their sum gives a spherically symmetric distribution of ψ^2.

When l = 2, there are five possible m_l values corresponding to the **d *orbitals***, shown schematically in Fig. 2.2*b*. These orbitals are labeled, d_{xy}, d_{xz}, d_{yz}, d_{z^2} and $d_{x^2-y^2}$. The latter two are oriented along the main axes, while the former three plot lobes between the axes. Here again the different colors denote different spins. Table 2.1 summarizes orbital notation up to n = 3. The physical significance of l and m_l and their relationships to an atom's angular momenta are discussed in greater detail in Chap. 15.

One final note: The conclusions arrived at so far tend to indicate that all sublevels with the same n have exactly the same energy, when in reality they have slightly different energies. Also, a fourth quantum number, the **spin quantum number**, $\mathbf{m_s}$, which denotes the direction of electron spin, was not mentioned. Both of these omissions are a direct result of ignoring relativistic effects which, when taken into account, are fully accounted for.

2.2.3 POLYELECTRONIC ATOMS AND THE PERIODIC TABLE

Up to now the discussion has been limited to the simplest possible case, namely, that of the hydrogen atom—the only case for which an exact solution to Schrödinger's equation exists. The solution for a polyelectronic atom is similar to that of the hydrogen atom except that the former is inexact and is much more difficult to obtain. Fortunately, the basic shapes of the orbitals do *not* change, the concept of quantum numbers remains useful, and, with some modifications, the hydrogen-like orbitals can account for the electronic structure of atoms having many electrons.

The major modification involves the energy of the electrons. As the nuclear charge or atomic number, Z, increases, the potential energy of the electron has to decrease accordingly, since a large positive nuclear charge now attracts the electron more strongly. This can be accounted for, as a first and quite crude

[12] Sometimes l is referred to as the *orbital-shape quantum number*.

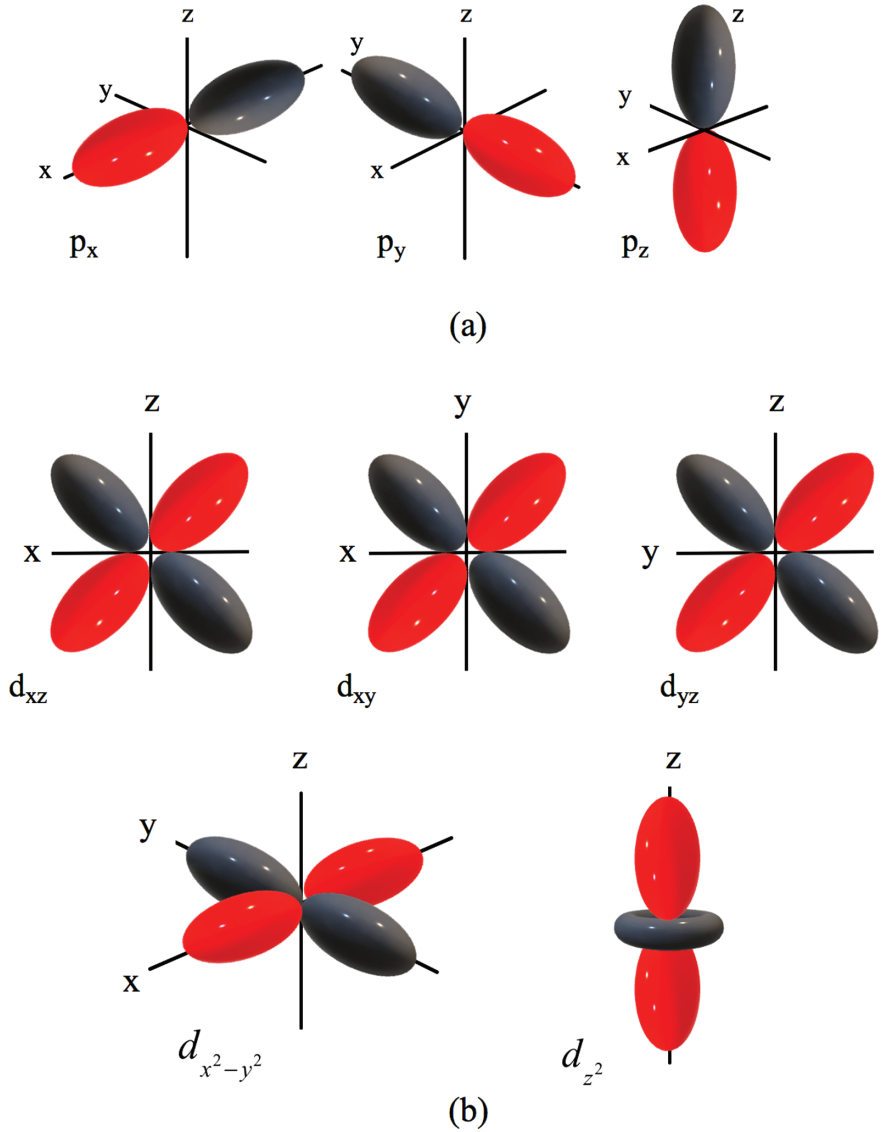

FIGURE 2.2 (*a*) Shape of p orbitals (top three) and (*b*) d orbitals (lower five). Note that the spin of the electrons in the red orbitals is opposite of that in the gray ones.

TABLE 2.1 Summary of orbitals and their notation

n	l	Orbital name	No. of m_l orbitals	Full designation of orbitals
1	0	1s	1	1s
2	0	2s	1	2s
	1	2p	3	$2p_x$, $2p_y$, $2p_z$
3	0	3s	1	3s
	1	3p	3	$3p_x$, $3p_y$, $3p_z$
	2	3d	5	$3d_{z^2}$, $3d_{x^2-y^2}$, $3d_{xy}$, $3d_{xz}$, $3d_{yz}$

approximation, by assuming that the electrons are noninteracting, in which case it can be shown that the energy of an electron is given by

$$E_n = -13.6\frac{Z^2}{n^2}\ \text{eV}$$

The actual situation is more complicated, however, due to electron–electron repulsions and electron screening—with both effects contributing to an increase in E_n. Conceptually this is taken into account by introducing the **effective nuclear charge**, $\mathbf{Z_{eff}}$, which takes into account the notion that the actual nuclear charge experienced by an electron is always less than, or equal to, the actual charge on the nucleus. This can be easily grasped by comparing the experimental first ionization energy, IE, of helium, viz. −24.59 eV (see Table 2.2), for which Z = 2 and n = 1, to what one would expect had there been no electron–electron interaction, or $-13.6 \times (2^2)/1^2$, or −54.4 eV. This simple example illustrates the dramatic effect of electron–electron interactions on the ionization energy of He and the importance of the concept of effective charge. Note that the measured second ionization energy for He listed in Table 2.2 is exactly 54.4 eV!

As the number of electrons increases, they are forced by virtue of Pauli's exclusion principle to occupy higher and higher-energy levels, i.e., higher n values. This in turn leads to the **aufbau principle**, the periodic table (see inside front cover) and a unique electronic configuration for each element. The electronic structures of the first 83 elements are summarized in Table 2.2.

Worked Example 2.2

(a) What are the electronic configurations of He, Li and F? (b) Identify the first transition metal series. What feature do these elements have in common?

ANSWER

(a) Helium (Z = 2) has two electrons, which can be accommodated in the 1s state as long as their spins are opposite. Hence the configuration is $1s^2$. Since this is a closed shell configuration, He is a very inert gas. Lithium (Z = 3) has three electrons; two are accommodated in the 1s shell and the third has to occupy a higher-energy state, namely, n = 2 and l = 0. The electronic configuration is thus: $1s^22s^1$. Similarly, the nine electrons of fluorine are distributed as follows: $1s^22s^22p^5$.

TABLE 2.2 Electronic configuration and first and second ionization energies of the elements

Z	Atom	Orbital electronic configuration	First IE, eV	Second IE, eV
1	H	$1s^1$	13.598	—
2	He	$1s^2$	24.587	54.416
3	Li	$(He)2s^1$	5.392	75.638
4	Be	$(He)\ 2s^2$	9.322	18.211
5	B	$(He)2s^22p^1$	8.298	25.154
6	C	$(He)2s^22p^2$	11.260	24.383
7	N	$(He)2s^22p^3$	14.534	29.601
8	O	$(He)2s^22p^4$	13.618	35.116
9	F	$(He)2s^22p^5$	17.422	34.970
10	Ne	$(He)2s^22p^6$	21.564	40.962
11	Na	$(Ne)3s^1$	5.139	47.286
12	Mg	$(Ne)3s^2$	7.646	15.035
13	Al	$(Ne)3s^23p^1$	5.986	18.828
14	Si	$(Ne)3s^23p^2$	8.151	16.345
15	P	$(Ne)3s^23p^3$	10.486	19.725
16	S	$(Ne)3s^23p^4$	10.360	23.330
17	Cl	$(Ne)3s^23p^5$	12.967	23.810
18	Ar	$(Ne)3s^23p^6$	15.759	27.630
19	K	$(Ar)4s^1$	4.340	31.625
20	Ca	$(Ar)4s^2$	6.113	11.871
21	Sc	$(Ar)4s^23d^1$	6.540	12.800
22	Ti	$(Ar)4s^23d^2$	6.820	13.580
23	V	$(Ar)4s^23d^3$	6.740	14.650
24	Cr	$(Ar)4s^13d^5$	6.766	16.500
25	Mn	$(Ar)4s^23d^5$	7.435	15.640
26	Fe	$(Ar)4s^23d^6$	7.870	16.180
27	Co	$(Ar)4s^23d^7$	7.860	17.060
28	Ni	$(Ar)4s^23d^8$	7.635	18.168
29	Cu	$(Ar)4s^13d^{10}$	7.726	20.292
30	Zn	$(Ar)4s^23d^{10}$	9.394	17.964
31	Ga	$(Ar)4s^23d^{10}4p^1$	5.999	20.510
32	Ge	$(Ar)4s^23d^{10}4p^2$	7.899	15.934
33	As	$(Ar)4s^23d^{10}4p^3$	9.810	18.633
34	Se	$(Ar)4s^23d^{10}4p^4$	9.752	21.190
35	Br	$(Ar)4s^23d^{10}4p^5$	11.814	21.800
36	Kr	$(Ar)4s^23d^{10}4p^6$	13.999	24.359
37	Rb	$(Kr)\ 5s^1$	4.177	27.280
38	Sr	$(Kr)\ 5s^2$	5.695	11.030
39	Y	$(Kr)\ 5s^24d^1$	6.380	12.240
40	Zr	$(Kr)\ 5s^24d^2$	6.840	13.130
41	Nb	$(Kr)\ 5s^14d^4$	6.880	14.320

(*Continued*)

TABLE 2.2 (CONTINUED) Electronic configuration and first and second ionization energies of the elements

Z	Atom	Orbital electronic configuration	First IE, eV	Second IE, eV
42	Mo	(Kr) $5s^1 4d^5$	7.099	16.150
43	Tc	(Kr)$5s^2 4d^5$	7.280	15.260
44	Ru	(Kr)$5s^1 4d^7$	7.370	16.760
45	Rh	(Kr)$5s^1 4d^8$	7.460	18.080
46	Pd	(Kr)$4d^{10}$	8.340	19.430
47	Ag	(Kr)$5s^1 4d^{10}$	7.576	21.490
48	Cd	(Kr)$5s^2 4d^{10}$	8.993	16.908
49	In	(Kr)$5s^2 4d^{10} 5p^1$	5.786	18.869
50	Sn	(Kr)$5s^2 4d^{10} 5p^2$	7.344	14.632
51	Sb	(Kr)$5s^2 4d^{10} 5p^3$	8.641	16.530
52	Te	(Kr)$5s^2 4d^{10} 5p^4$	9.009	18.600
53	I	(Kr)$5s^2 4d^{10} 5p^5$	10.451	19.131
54	Xe	(Kr)$5s^2 4d^{10} 5p^6$	12.130	21.210
55	Cs	(Xe)$6s^1$	3.894	25.100
56	Ba	(Xe)$6s^2$	5.212	10.004
57	La	(Xe)$6s^2 5d^1$	5.577	11.060
58	Ce	(Xe)$6s^2 4f^1 5d^1$	5.470	10.850
59	Pr	(Xe)$6s^2 4f^3$	5.420	10.560
60	Nd	(Xe)$6s^2 4f^4$	5.490	10.720
61	Pm	(Xe)$6s^2 4f^5$	5.550	10.900
62	Sm	(Xe)$6s^2 4f^6$	5.630	11.070
63	Eu	(Xe)$6s^2 4f^7$	5.670	11.250
64	Gd	(Xe)$6s^2 4f^7 5d^1$	5.426	13.900
65	Tb	(Xe)$6s^2 4f^9$	5.850	11.520
66	Dy	(Xe)$6s^2 4f^{10}$	5.930	11.670
67	Ho	(Xe)$6s^2 4f^{11}$	6.020	11.800
68	Er	(Xe)$6s^2 4f^{12}$	6.100	11.930
69	Tm	(Xe)$6s^2 4f^{13}$	6.180	12.050
70	Yb	(Xe)$6s^2 4f^{14}$	6.254	12.170
71	Lu	(Xe)$6s^2 4f^{14} 5d^1$	5.426	13.900
72	Hf	(Xe)$6s^2 4f^{14} 5d^2$	7.000	14.900
73	Ta	(Xe)$6s^2 4f^{14} 5d^3$	7.890	—
74	W	(Xe)$6s^2 4f^{14} 5d^4$	7.980	—
75	Re	(Xe)$6s^2 4f^{14} 5d^5$	7.880	—
76	Os	(Xe)$6s^2 4f^{14} 5d^6$	8.700	—
77	Ir	(Xe)$6s^2 4f^{14} 5d^7$	9.100	—
78	Pt	(Xe)$6s^1 4f^{14} 5d^9$	9.000	—
79	Au	(Xe)$6s^1 4f^{14} 5d^{10}$	9.225	—
80	Hg	(Xe)$6s^2 4f^{14} 5d^{10}$	10.437	18.756
81	Tl	(Xe)$6s^2 4f^{14} 5d^{10} 6p^1$	6.108	20.428
82	Pb	(Xe)$6s^2 4f^{14} 5d^{10} 6p^2$	7.416	15.032
83	Bi	(Xe)$6s^2 4f^{14} 5d^{10} 6p^3$	7.289	16.600

(b) The first series transition metals are Sc, Ti, V, Cr, Mn, Fe, Co and Ni. They all have partially filled d orbitals. Note that Cu and Zn, which have completely filled d orbitals, are sometimes also considered to be transition metals, although strictly speaking, they would not be since their d orbitals are totally filled (see Table 2.2).

2.3 IONIC VERSUS COVALENT BONDING

In the introduction to this chapter, it was stated that ceramics, very broadly speaking, can be considered to be either ionically or covalently bonded. The next logical question is: What determines the nature of a bond?

Ionic compounds generally form between quite active metallic elements and active nonmetals. For reasons that will become clear shortly, the requirements for an AB ionic bond to form are that A be able to lose electrons readily (i.e., with as little a penalty as possible) and B be able to accept electrons without too much energy input. This restricts ionic bonding to mostly metals from groups 1, 2 and 3, as well as some of the transition metals

For covalent bonding to occur, ionic bonding must be unfavorable. This is tantamount to saying that the energies of the bonding electrons of A and B must be comparable because if the electron energy on one of the atoms were much lower than that on the other, then electron transfer from one to the other would occur and ionic bonds would tend to form instead.

These qualitative requirements, while shedding some light on the problem, do not have much predictive capability as to the nature of the bond that will form. In an attempt to semi-quantify the answer, Pauling[13] established a scale of relative **electronegativity** or "electron greed" of atoms and defined electronegativity to be *the power of an atom to attract electrons to itself*. Pauling's electronegativity scale—listed in Table 2.3—was obtained by arbitrarily fixing the value of H at 2.2. With this scale, it becomes relatively simple to predict a bond's nature. If two elements forming a bond have similar electronegativities, they will tend to share the electrons between them and will form covalent bonds. However, if the electronegativity difference, ΔX, between them is large (indicating that one element is much greedier than the other), the electron will be attracted to the more electronegative element, forming ions which, in turn, attract each other. Needless to say, the transition between ionic and covalent bonding is far from sharp and, except for homopolar bonds that are purely covalent, all bonds will have both an ionic and a covalent character (see Prob. 2.16). However, as a quite rough guide, a bond is considered predominantly ionic when $\Delta X > 1.7$ and predominantly covalent if $\Delta X < 1.7$.

Each type of bond and how it leads to the formation of a solid is discussed separately below, starting with the simpler of the two, namely, the ionic bond.

2.4 IONIC BONDING

Ionically bonded solids are made up of charged particles—positively charged ions, called **cations**, and negatively charged ions, called **anions.** Their mutual attraction holds the solid together. Ionic bonds

[13] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, NY, 1960.

TABLE 2.3 Relative electronegativity scale of the elements

Element	Electronegativity	Element	Electronegativity
1. H	2.20	42. Mo(II)	2.16
2. He		Mo(III)	2.19
3. Li	0.98	43. Tc	1.90
4. Be	1.57	44. Ru	2.20
5. B	2.04	45. Rh	2.28
6. C	2.55	46. Pd	2.20
7. N	3.04	47. Ag	1.93
8. O	3.44	48. Cd	1.69
9. F	3.98	49. In	1.78
10. Ne		50. Sn(II)	1.80
11. Na	0.93	Sn(IV)	1.96
12. Mg	1.31	51. Sb	2.05
13. Al	1.61	52. Te	2.10
14. Si	1.90	53. I	2.66
15. P	2.19	54. Xe	2.60
16. S	2.58	55. Cs	0.79
17. Cl	3.16	56. Ba	0.89
18. Ar		57. La	1.10
19. K	0.82	58. Ce	1.12
20. Ca	1.00	59. Pr	1.13
21. Sc	1.36	60. Nd	1.14
22. Ti(II)	1.54	62. Sm	1.17
23. V(II)	1.63	64. Gd	1.20
24. Cr(II)	1.66	66. Dy	1.22
25. Mn(II)	1.55	67. Ho	1.23
26. Fe(II)	1.83	68. Er	1.24
Fe(III)	1.96	69. Tm	1.25
27. Co(II)	1.88	71. Lu	1.27
28. Ni(II)	1.91	72. Hf	1.30
29. Cu(I)	1.90	73. Ta	1.50
Cu(II)	2.00	74. W	2.36
30. Zn(II)	1.65	75. Re	1.90
31. Ga(III)	1.81	76. Os	2.20
32. Ge(IV)	2.01	77. Ir	2.20
33. As(III)	2.18	78. Pt	2.28
34. Se	2.55	79. Au	2.54
35. Br	2.96	80. Hg	2.00

(*Continued*)

TABLE 2.3 (CONTINUED) Relative electronegativity scale of the elements

Element	Electronegativity	Element	Electronegativity
36. Kr	2.90	81. Tl(I)	1.62
37. Rb	0.82	82. Pb(II)	1.87
38. Sr	0.95	83. Bi	2.02
39. Y	1.22	90. Th	1.30
40. Zr(II)	1.33	92. U	1.70
41. Nb	1.60		

Source: https://en.wikipedia.org/wiki/Electronegativity.

are omnidirectional. Ionic compounds are typically hard and brittle and are poor electrical and thermal conductors.

To illustrate the energetics of ionic bonding consider the bond formed between Na and Cl. The electronic configuration of Cl (atomic number Z = 17) is $[1s^2 2s^2 2p^6]3s^2 3p^5$, while that of Na (Z = 11) is $[1s^2 2s^2 2p^6]3s^1$. For reasons that will become evident in a moment, when Na and Cl atoms are brought into close proximity, a bond will form by the transfer of an electron from the Na atom to the Cl atom, as shown schematically in Fig. 2.3. The Na atom configuration becomes $[1s^2 2s^2 2p^6]$ and is now +1 positively charged; the Cl atom gains an electron, acquires a –1 negative charge, and its electronic structure becomes $[1s^2 2s^2 2p^6]3s^2 3p^6$. Note that after the charge transfer, the configuration of the Na and Cl ions correspond to those of the noble gases, Ne and Ar, respectively.

The work done to bring the ions from infinity to a distance r apart is once again given by Coulomb's law [Eq. (2.2)]:

$$E_{pot} = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 r} \tag{2.11}$$

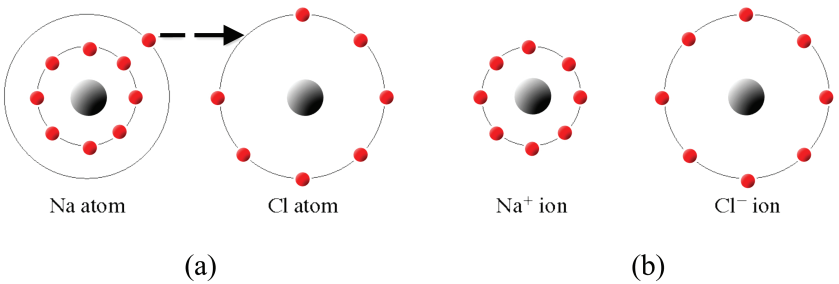

FIGURE 2.3 (*a*) Electron transfer from a Na atom to Cl atom results in the formation of, (*b*) a cation and an anion. Note that a cation is smaller than its atom and vice versa for the anion.

In this case, z_1 and z_2 are the *net* charges on the ions (+1 and −1 for NaCl, −2 and +3 for Al_2O_3, etc.). When z_1 and z_2 are of opposite signs, E_{pot} is negative, which is consistent with the fact that energy is released as the ions are brought together from infinity. A plot of Eq. (2.11) is shown in Fig. 2.4*a* (lower curve), from which it is clear that when the ions are infinitely separated, the interaction energy vanishes, as one would expect. Equation (2.11) also predicts, however, that as the distance between the ions goes to zero, the ions should fuse together and release an infinite amount of energy! That this does not happen is obvious; NaCl does, and incidentally we also, exist.

It follows that for a stable lattice to result, a repulsive force must come into play at short distances. As discussed above, the attraction occurs from the *net* charges on the ions. These ions, however, are themselves made up of positive and negative entities, namely, the nuclei of each ion, but more importantly, the electron cloud surrounding each nucleus. As the ions approach each other, these like charges repel and prevent the ions from coming any closer.

The repulsive energy term is positive by definition and is usually given by the empirical expression:

$$E_{rep} = \frac{B}{r^n} \tag{2.12}$$

where B and n are empirical constants that depend on the material in question. Sometimes referred to as the **Born exponent**, **n**, usually lies between 6 and 12. Equation (2.12) is also plotted in Fig. 2.4*a* (top curve), from which it is clear that the repulsive component dominates at small r, but decreases quite rapidly as r increases. The Born exponent should not be confused with the principle quantum number, n; they are not related in any way.

The net energy E_{net} of the system is the sum of the attractive and repulsive terms, or

$$E_{net} = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 r} + \frac{B}{r^n} \tag{2.13}$$

When E_{net} is plotted as a function of r (middle red curve in Fig. 2.4*a*), it goes through a minimum, at a distance denoted by r_0. The minimum in the curve corresponding to the equilibrium situation can be found readily from

$$\left.\frac{dE_{net}}{dr}\right|_{r=r_0} = 0 = -\frac{z_1 z_2 e^2}{4\pi\varepsilon_0 r_0^2} - \frac{nB}{r_0^{n+1}} \tag{2.14}$$

By evaluating the constant B and removing it from Eq. (2.13), it can be shown that the depth of the energy well E_{bond} is given by

$$\boxed{E_{bond} = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 r_0}\left(1 - \frac{1}{n}\right)} \tag{2.15}$$

Here, r_0 is the equilibrium separation between the ions. The occurrence of this minimum is of paramount importance since it defines a bond; i.e., when two ions are brought closer together from infinity, they will

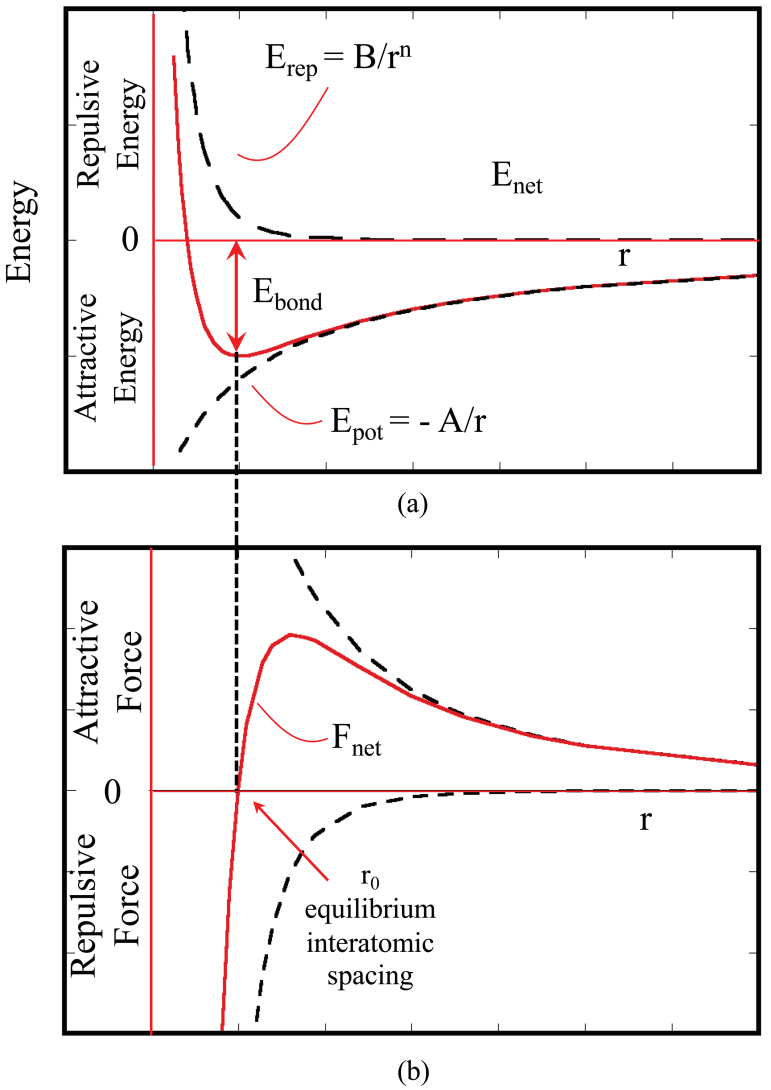

FIGURE 2.4 (*a*) Energy versus distance curves for an ionic bond. The net energy is the sum of attractive and repulsive energies, which gives rise to an energy well. (*b*) Corresponding force versus distance curve. This curve is the derivative of the net energy curve shown in (*a*). Note that when the energy is at a minimum, the net force is zero.

attract each up to an **equilibrium distance**, $\mathbf{r_o}$, and liberate an amount of energy given by Eq. (2.15). Conversely, E_{bond} can be thought of as the energy required to pull the ions apart from a distance r_o to infinity.

It is important to note that Eq. (2.14) is also an expression for the *net* force between the ions, since by definition

$$F_{net} = \frac{dE_{net}}{dr} = -\frac{z_1 z_2}{4\pi\varepsilon_0 r^2} - \frac{nB}{r^{n+1}} \tag{2.16}$$

F_{net} is plotted in Fig. 2.4*b*. For distances > r_o, F_{net} on the ions is attractive; for distances < r_o, the net force is repulsive. At r_o the net force on the ions is zero [Eq. (2.14)], which is why r_o is the equilibrium interatomic spacing. Figure 2.4*a* and *b* illustrate a fundamental law of nature, namely, that at equilibrium the energy is minimized and the net force on a system is zero.

2.5 IONICALLY BONDED SOLIDS

The next logical question is, how do such bonds lead to the formation of a solid? After all, a solid is made up of roughly 10^{23} bonds. The other related important question has to do with the energy of the solid lattice. The latter is related to the stability of a given structure and directly, or indirectly, determines such properties as melting temperatures, thermal expansion, stiffness and others, discussed in Chap. 4. This section addresses how the lattice energy is calculated and experimentally verified, starting with the simple electrostatic model that led to Eq. (2.15).

2.5.1 LATTICE ENERGY CALCULATIONS

The **lattice energy**, $\mathbf{E_{latt}}$, is defined as the energy released when x moles of cations, A, and y moles of anions, B, react to form the solid A_xB_y. To calculate E_{latt} a structure or packing arrangement of the ions has to be assumed,[14] and all the interactions between the ions have to be taken into account. To illustrate consider NaCl, which has one of the simplest ionic structures known (Fig. 2.5*a*), wherein each Na ion is surrounded by six Cl ions and vice versa. Referring to Fig. 2.5*b*, the central cation—depicted in light gray—is attracted to 6 Cl^- anions at a distance r_o, repelled by 12 Na^+ cations at distance $\sqrt{2}r_o$ (Fig. 2.5*c*), attracted to 8 Cl^- anions at $\sqrt{3}r_o$ (Fig. 2.5*d*), etc. Summing up the electrostatic interactions,[15] one obtains

[14] This topic is discussed in greater detail in the next chapter and depends on the size of the ions involved, the nature of the bonding, etc.

[15] Strictly speaking, this is not exact, since in Eq. (2.17) the repulsive component of the ions that were not nearest neighbors was neglected. If that interaction is taken into account, an exact expression for E_{sum} is given by

$$E_{sum} = \frac{-z_1 z_2 e^2 a}{4\pi\varepsilon_0 r} + \frac{B\beta}{r^n}$$

where β is another infinite series. It is important to note that such a refinement does not in any way alter the result, namely, Eq. (2.18).

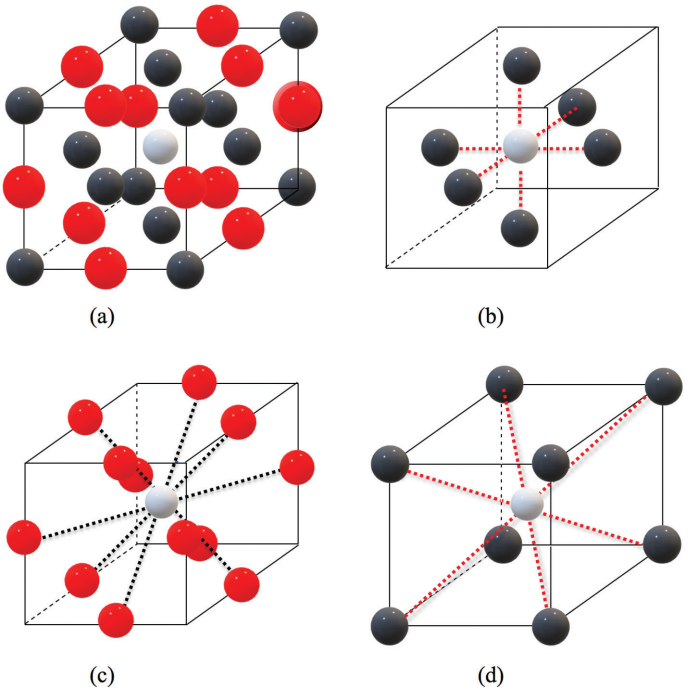

FIGURE 2.5 (*a*) Schematic of the NaCl structure. (*b*) The first six nearest neighbors are attracted to the central cation, (*c*) the second 12 nearest neighbors at a distance $\sqrt{2}r_o$ are repelled, (*d*) third eight nearest neighbors are attracted, etc.

$$E_{sum} = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 r_o}\left(1-\frac{1}{n}\right)\left(\frac{6}{1}-\frac{12}{\sqrt{2}}+\frac{8}{\sqrt{3}}-\frac{6}{\sqrt{4}}+\frac{24}{\sqrt{5}}-\cdots\right)$$
$$= \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 r_o}\left(1-\frac{1}{n}\right)\alpha \qquad (2.17)$$

The second term in parentheses is an alternating series that converges to some value α, known as the **Madelung constant.** Evaluation of this constant, though straightforward, is tedious because the series converges quite slowly. The Madelung constants for a number of crystal structures are listed in Table 2.4.

The total electrostatic attraction or lattice energy to form 1 mol of NaCl in which there are twice Avogadro's number N_{Av} of ions but only N_{Av} bonds is

$$E_{latt} = \frac{N_{Av} z_1 z_2 e^2 \alpha}{4\pi\varepsilon_0 r_o}\left(1-\frac{1}{n}\right) \qquad (2.18)$$

According to this equation, sometimes referred to as the *Born–Lande equation*, the information required to calculate E_{latt} is the crystal structure, which determines α, the equilibrium interionic spacing, both easily

TABLE 2.4 Madelung constants for some common ceramic crystal structures (see Chap. 3)

Structure	Coordination number	α[a]	α_{conv}[b]
NaCl	6: 6	1.7475	1.7475
CsCl	8: 8	1.7626	1.7626
Zinc blende	4: 4	1.6381	1.6381
Wurtzite	4: 4	1.6410	1.6410
Fluorite	8: 4	2.5190	5.0387
Rutile	6: 3	2.4080[c]	4.1860[c]
Corundum	6: 4	4.1719[c]	25.0312[c]

[a] Assumes structure is made of isocharged ions that factor out.

[b] The problem of structures with more than one charge, such as Al_2O_3, can be addressed by making use of the relationship

$$E_{sum} = \alpha_{conv} \frac{(Z\pm)^2 e^2}{4\pi\varepsilon_0 r_0}\left(1-\frac{1}{n}\right)$$

where $Z\pm$ is the *highest common factor* of z_1 and z_2, i.e., 1 for NaCl, CaF_2 and Al_2O_3, 2 for MgO, TiO_2, ReO_3, etc.

[c] Exact value depends on c/a ratio.

obtainable from X-ray diffraction and n, which is obtainable from compressibility data. Note that E_{latt} is not greatly affected by small errors in n.

In deriving Eq. (2.18), a few terms were ignored. A more exact expression for E_{latt} is

$$E_{latt} = \frac{dE_{net}}{dr} = -\frac{A}{r_o} + \frac{B}{r^n} + \left(\frac{C}{r_o^6} + \frac{D}{r_o^8}\right) + \frac{9}{4} h\nu_{max} \tag{2.19}$$

The first two terms, discussed in detail up to this point, dominate. Note the term $z_1 z_2 e^2/4\pi\varepsilon_0$ in Eq. (2.13) is replaced by the constant A in Eq. (2.19). The term in parentheses represents dipole–dipole and dipole–quadrapole interactions between the ions. The last term represents the zero-point correction, with ν_{max} being the highest frequency of the lattice vibration modes. Lastly, in this section it is worth noting that this ionic model is a poor approximation for crystals containing large anions and small cations, where the covalent contribution to the bonding becomes significant (see Chap. 3).

Worked Example 2.3

(a) Calculate the lattice energy of NaCl given that n = 8.
(b) Repeat part (a) assuming the structure is CsCl instead and comment on the difference.
(c) Repeat part (a) for MgO.

ANSWER

(a) To calculate E_{latt}, r_o, n and the structure of NaCl all are needed. As noted above, the structure of NaCl is the rock salt structure (Fig. 2.5) and hence its Madelung constant is 1.748 (Table 2.4). The equilibrium interionic distance, r_o, is simply the sum of the radii of the Na^+ and Cl^- ions. The values are listed at the end of Chap. 3 in Appendix 3A. Looking up the values, the equilibrium interionic distance $r_o = 181 + 102 = 283$ pm. Applying Eq. 2.18, it follows that

$$E_{latt} = \frac{(-1)(+1)(6.02\times10^{23})(1.6\times10^{-19})^2(1.748)}{4\pi(8.85\times10^{-12})(283\times10^{-12})}\left(1-\frac{1}{8}\right) \approx -749 \text{ kJ/mol}$$

(b) If one assumes the structure is CsCl, then the only terms that change in the above equation are the Madelung constant and the radii of the ions. In this case the Na^+ ion is in 8 fold coordination and its radius is 118 pm. The radius on Cl^- in 8 fold coordination is not given in Appendix 3A, so we assume it to remain unchanged. It follows that $r_o = 181 + 118 = 299$ pm and

$$E_{latt} = \frac{(-1)(+1)(6.02\times10^{23})(1.6\times10^{-19})^2(1.7626)}{4\pi(8.85\times10^{-12})(299\times10^{-12})}\left(1-\frac{1}{8}\right) \approx -714.8 \text{ kJ/mol}$$

These calculations make the following points amply clear: (i) E_{latt} of NaCl in the rock salt structure is lower in energy—more stable—than had it crystallized in the CsCl structure, which is why it crystallizes in the former. (ii) The differences in energy is less than 5%. It follows that it is crucial that our models and the parameters used in them be quite accurate. In many cases, the differences in energy between different polymorphs are even smaller. (iii) Knowing the exact values of the ionic radii is crucial when considering which polymorph is more stable.

(c) For MgO, $r_o = (72+140) = 212$ pm, and assuming n = 8, then

$$E_{latt} = \frac{(-2)(+2)(6.02\times10^{23})(1.6\times10^{-19})^2(1.748)}{4\pi(8.85\times10^{-12})(212\times10^{-12})}\left(1-\frac{1}{8}\right) \approx -4000 \text{ kJ/mol}$$

2.5.2 BORN–HABER CYCLE

So far, a rather simple model has been introduced in which it was assumed that an ionic solid is made up of ions attracted to each other by Coulombic attractions. How can such a model be tested? The simplest thing to do would be to compare E_{latt} to experimental results. This is easier said than done, however, given that E_{latt} is the energy released when 1 mol of gaseous *cations and anions* condense into a solid—an experiment that, needless to say, is not easy, if not impossible, to perform.

An alternate method is to make use of the first law of thermodynamics, namely, that energy can be neither created nor destroyed. If a cycle can be devised where all the energies are experimentally known

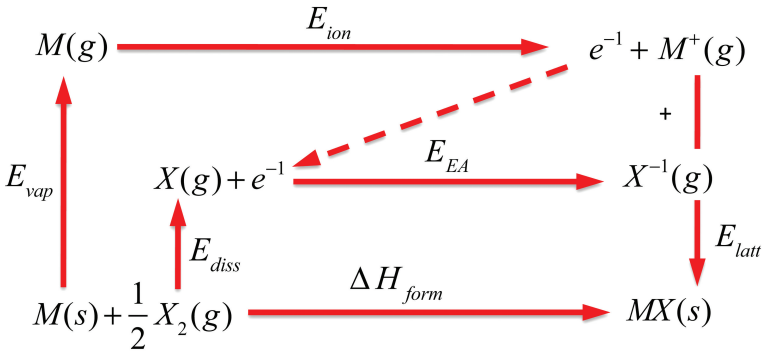

FIGURE 2.6 The Born–Haber cycle.

except E_{latt}, then it can be calculated. For such a cycle, known as the *Born–Haber cycle*, shown in Fig. 2.6, it is necessary that

$$\Delta H_{form}(\text{exo}) = E_{latt}(\text{exo}) + E_{ion}(\text{endo}) + E_{EA}(\text{endo or exo})$$
$$+ E_{diss}(\text{endo}) + E_{vap}(\text{endo})$$

Each of these terms is discussed in greater detail below with respect to NaCl.

ENTHALPY OF FORMATION OR REACTION

The enthalpy of formation, ΔH_{form} of a reaction is the experimental energy absorbed or released when that reaction occurs. In the case of NaCl, the reaction is

$$Na(s) + \tfrac{1}{2}Cl_2(g) \rightarrow NaCl(s)$$

Since energy is liberated, this reaction is exothermic and thus by convention ΔH_{form} is negative. For NaCl at 298 K, the experimentally determined $\Delta H_{form} = -411$ kJ/mol. The enthalpies of formation of most compounds are exothermic.

DISSOCIATION ENERGY

The dissociation energy, E_{diss}, of a molecule is the energy needed to break it up into its constituent atoms. For NaCl, it is energy change for the reaction

$$\tfrac{1}{2}Cl_2 \rightarrow Cl(g)$$

This energy is always endothermic and thus positive. For this reaction as written, $E_{diss} = +121$ kJ/mol.

HEAT OF VAPORIZATION

The **latent heat of vaporization**, $\mathbf{E_{vap}}$, is the energy required for the reaction

$$M(s) \rightarrow M(g)$$

which is always endothermic. In this case of Na, this value is 107.3 kJ/mol.

Values of ΔH_{form}, E_{diss} and E_{vap} can be found in various sources[16] and are well documented for most elements and compounds.

IONIZATION ENERGY

The **ionization energy**, $\mathbf{E_{ion}}$, is the energy required to completely remove an electron from an isolated atom in the gas phase. Ionization energies are endothermic since in all cases work has to be done to remove an electron from its nucleus. Table 2.2 lists the first and second ionization potentials for select elements. For Na, that value is 5.14 eV or 495.8 kJ/mol.

ELECTRON AFFINITY

The electron affinity, $\mathbf{E_{EA}}$, is a measure of the energy change that occurs when an electron is added to the valence shell of an atom. Some selected values of E_{EA} for nonmetals are listed in Table 2.5. The addition of the first electron is usually exothermic (e.g., oxygen, sulfur); further additions, when they occur, are by necessity endothermic since the second electron is now approaching a negatively charged entity. The electron affinity of Cl is –348.7 kJ/mol.

The lattice energy of NaCl was calculated in Worked Example 2.3 to be –750 kJ/mol. If we put all the pieces together, the Born–Haber summation for NaCl yields

$$\begin{aligned}\Delta H_{form}(\text{exo}) &= E_{latt}(\text{exo}) + E_{ion}(\text{endo}) + E_{EA}(\text{exo}) \\ &\quad + E_{diss}(\text{endo}) + E_{vap}(\text{endo}) \\ &= -750 + 495.8 - 348.7 + 121 + 107.3 = -374.6 \text{ kJ/mol}\end{aligned}$$

TABLE 2.5 Electron affinities[a] of selected nonmetals at 0 K

Element	EA (kJ/mol)	Element	EA (kJ/mol)
$O \rightarrow O^-$	141 (exo)	$Se \rightarrow Se^-$	195 (exo)
$O^- \rightarrow O^{2-}$	780 (endo)	$Se^- \rightarrow Se^{2-}$	420 (endo)
$F \rightarrow F^-$	322 (exo)	$Br \rightarrow Br^-$	324.5 (exo)
$S \rightarrow S^-$	200 (exo)	$I \rightarrow I^-$	295 (exo)
$S^- \rightarrow S^{2-}$	590 (endo)	$Te \rightarrow Te^-$	190.1 (exo)
$Cl \rightarrow Cl^-$	348.7 (exo)		

[a] Electron affinity is usually defined as the energy *released* when an electron is added to the valence shell of an atom. This can be quite confusing. To avoid confusion, the values listed in this table clearly indicate whether the addition of an electron is endo- or exothermic. Data taken from https://en.wikipedia.org/wiki/Electron_affinity_(data_page).

[16] A reliable source for thermodynamic data is JANAF *Thermochemical Tables*, 4th ed., which lists the thermodynamic data of over 1800 substances. http://kinetics.nist.gov/janaf/.

which compares favorably with the experimentally determined value of −411 kJ/mol. If Eq. (2.19) is used, even better agreement is obtained.

This is an important result for two reasons. First, it confirms that our simple model for the interaction between ions in a solid is, for the most part, correct. Second, it supports the notion that NaCl can be considered an ionically bonded solid.

2.6 COVALENT BOND FORMATION

The second important type of primary bond is the covalent bond. Whereas ionic bonds involve electron transfer to produce oppositely charged species, covalent bonds arise as a result of electron sharing. In principle, the energetics of the covalent bond can be understood if it is recognized that electrons spend more time in the area *between* the nuclei than anywhere else. The mutual attraction between the nuclei and the electrons between them lowers the potential energy of the system, resulting in a bond. Several theories and models have been proposed to explain the formation of covalent bonds. Of these, **molecular orbital theory** has been particularly successful and is the one discussed in some detail below. As the name implies, molecular orbital (MO) theory treats a molecule as a single entity and assigns orbitals to the *molecule as a whole*. In principle, the idea is similar to that used to determine the energy levels of isolated atoms, except that now the wave functions have to satisfy Schrödinger's equation with the appropriate expression for the potential energy, which has to include *all* the charges making up the molecule. The solutions, in turn, give rise to various MOs, with the number of filled orbitals determined by the number of electrons needed to balance the nuclear charge of the molecule as a whole, subject to Pauli's exclusion principle.

To illustrate, consider the simplest possible molecule, namely, the H_2^+ molecule, which has one electron but two nuclei. This molecule is chosen in order to avoid the complications arising from electron–electron repulsions alluded to earlier.

2.6.1 HYDROGEN ION MOLECULE

The procedure is similar to that used to solve for the electronic wave function of the H atom [i.e., the wave functions have to satisfy Eq. (2.1)] except that the potential energy term has to account for the presence of *two* positively charged nuclei rather than one. The Schrödinger equation for the H_2^+ molecule thus reads

$$\frac{\partial^2\psi}{\partial x^2}+\frac{8\pi^2 m_e}{h^2}\left(E_{tot}+\frac{e^2}{4\pi\varepsilon_0 r_a}+\frac{e^2}{4\pi\varepsilon_0 r_b}-\frac{e^2}{4\pi\varepsilon_0 R}\right)\psi=0 \tag{2.20}$$

where the distances, r_a, r_b and R are defined in Fig. 2.7*a*. If the distance R between the two nuclei is fixed, then an exact solution exists, which is quite similar to that of the H atom, except that now *two solutions* or *wave functions* emerge. One solution results in an increase in the electron density between the nuclei (Fig. 2.7*c*) whereas the second solution decreases it (Fig. 2.7*d*). In the first case, both nuclei are attracted to the electron between them, which results in the lowering of the energy of the system relative to the isolated

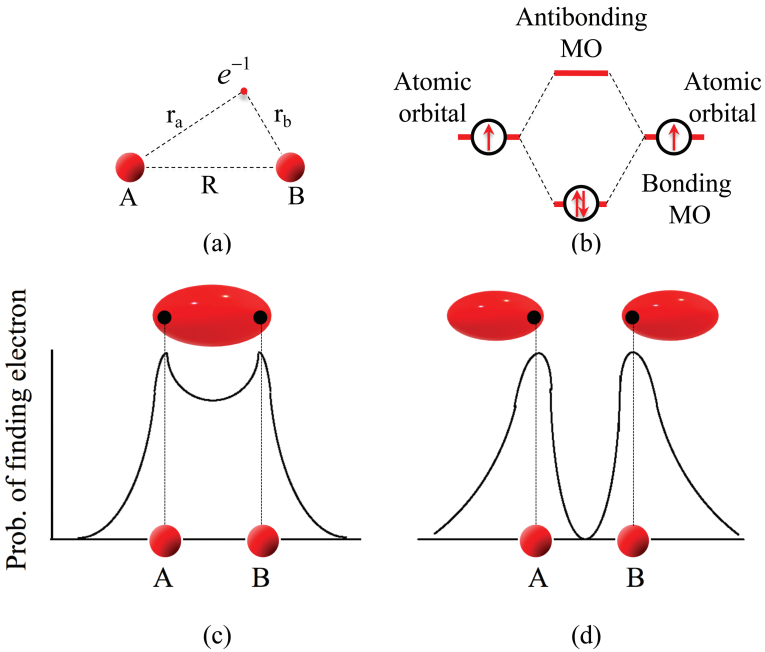

FIGURE 2.7 (*a*) Coordinates for the H_2^+ molecule used in Eq. (2.20). (*b*) Interaction of the two atomic orbitals results in bonding and antibonding orbitals. (*c*) Probability function for the bonding case in which the electron density between the nuclei is enhanced. (*d*) Probability function for the antibonding case, where the probability of finding the electron in the volume between the nuclei is decreased resulting in a higher-energy orbital.

atom case and is thus known as a **bonding orbital** (Fig. 2.7*b*). The second results in an increase in energy relative to the isolated atoms because now the unsheathed, or partially bared, nuclei repel one another. This is known as the **antibonding orbital**, also shown in Fig. 2.7*b*.

It is important to note that in order to obtain an energy-distance curve typical of a bond (see Fig. 2.4*a*), Eq. (2.20) would have to be solved for many values of R, the distance between the protons. It is only by doing so, that an energy distance curve is obtained from which the equilibrium interatomic distance can be predicted and ultimately compared with experimental values.

The solution for the H_2 molecule is quite similar, except that now an extra potential energy term for the repulsion between the two electrons has to be included in Schrödinger's equation. This is nontrivial, but fortunately the end result is similar to that of the H_2^+ case; the individual energy levels split into a bonding and an antibonding orbital. The atomic orbital overlap results in an increased probability of finding the electron between the nuclei. Note that in the case of the H_2 molecule, the two electrons are accommodated in the bonding orbital. A third electron, i.e., H_2^-, would have to go into the antibonding orbital because of Pauli's exclusion principle.

Before proceeding, it is illustrative to consider another slightly more complicated example: the HF molecule.

2.6.2 HF MOLECULE

In the preceding section, the electronegativities of the two atoms and the shapes (both spherical) of the interacting orbitals making up the bond were identical. The situation becomes more complicated when one considers bonding between dissimilar atoms. The HF molecule provides a good example. The electron configuration of H is $1s^1$, and that of F is $(He)2s^22p^5$. The valence orbitals of the F atom are shown in Fig. 2.8*a* (the inner core electrons are ignored since they are not involved in bonding). The atoms are held at the distance that separates them, which can either be calculated or obtained experimentally, and the molecular orbitals of HF are calculated. The calculations are nontrivial and beyond the scope of this book; the result, however, is shown schematically in Fig. 2.8*b*. The total number of electrons that have to be accommodated in the MOs is eight (seven from F and one from H). Placing two in each orbital fills the first four orbitals and results in an energy for the molecule that is *lower* (more negative) than that of the sum of the two noninteracting atoms, which in turn renders the HF molecule more stable relative to the isolated atoms.

Figure 2.8 can also be interpreted as follows: the F 2s electrons, by virtue of being at a much lower energy than hydrogen (because of the higher charge on the F nucleus), remain unperturbed by the hydrogen atom.[17] The 1s electron wave function of the H atom and one of the 2p orbitals on the F atom overlap to form a primary σ bond (Fig. 2.8*d*). The remaining electrons on the F atom (the so-called lone pairs) remain unperturbed in energy and in space.

As mentioned above, the calculation for Fig. 2.8 was made for a given interatomic distance. The same calculation can be repeated for various interatomic separations. At infinite separation, the atoms do not

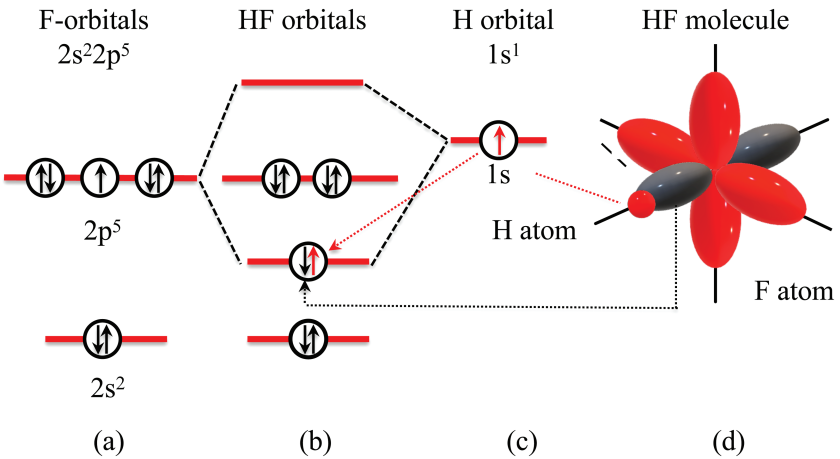

FIGURE 2.8 (*a*) F atomic orbitals. (*b*) HF molecular orbitals. (*c*) H atomic orbital. (*d*) Interaction of H 1s orbital with one of the F p orbitals. The overlap of these two orbitals results in a lowering of the system's energy. Dotted lines joining (*b*) to (*d*) emphasize that it is only the F p orbital that overlaps with the H orbital that lowers its energy. The two pairs of unpaired electrons (red lobes) have the same energy in the molecule that they did on the F atom, since these so-called lone pairs are unperturbed by the presence of the H atom.

[17] For orbitals to overlap, they must be relatively close to each other in energy.

interact, and the system's energy is just the sum of the energies of the electrons on the separate atoms. As the atoms are brought closer together, the attractive potential energy due to the mutual attraction between the electrons and the nuclei decreases the energy of the system up to a point beyond which a repulsive component comes into play and the energy starts increasing again. In other words, at some interatomic distance, a minimum in the energy occurs, and a plot of energy versus interatomic distance results in an energy well that is not unlike the one shown in Fig. 2.4*a*.

2.7 COVALENTLY BONDED SOLIDS

Up to this point the discussion was focused on the energetics of a single covalent bond between two atoms. Such a bond, however, will not lead to the formation of a strong solid, i.e., one in which all the bonds are primary. To form such a solid, each atom has to be simultaneously bonded to at least two other atoms. For example, at room temperature, HF does not form a solid because once a HF bond is formed, both atoms attain their most stable configuration—He for H and Ne for F—which in turn implies that there are no electrons available to form covalent bonds with other atoms. This is why HF is a gas at room temperature, despite the fact that the HF bond is quite strong.[18]

As discussed in greater detail in the next chapter, many predominantly covalently bonded ceramics, especially Si-based ones such as silicon carbide, silicon nitride, and the silicates, are composed of Si atoms simultaneously bonded to four other atoms in a tetrahedral arrangement. Examining the ground-state configuration of Si, that is, (Ne) $3s^2\ 3p^2$ (Fig. 2.9*a*), one would expect only two primary bonds to form, when in fact four bonds are known to form. This apparent contradiction has been explained by postulating that **hybridization** between the s and p wave functions occurs. Hybridization consists of a mixing of, or linear combinations of, s and p orbitals in an atom in such a way as to form new hybrid orbitals. This hybridization can occur between one s orbital and one *p* orbital (forming a sp orbital), or one s and two p orbitals (forming a sp^2 trigonal orbital). In the case of Si, the s orbital hybridizes with all three p orbitals to form what is known as **sp^3 hybrid orbitals.** The latter possesses both s and p character and directionally reaches out in space as lobes in a tetrahedral arrangement, with a bond angle of 109°, as shown in Fig. 2.9*c*. If each of these orbitals is populated by one electron (Fig. 2.9*b*), then each Si atom can now bond to *four* other Si atoms, or any other *four* atoms for that matter, which in turn can lead to three-dimensional structures. Note that the promotion of the electron from the s to the sp^3 hybrid orbital requires some energy, which is more than compensated for by the formation of four primary bonds.

2.8 BAND THEORY OF SOLIDS

One of the more successful theories developed to explain a wide variety of electrical and optical properties in solids is the **band theory of solids.** In this model, the electrons are consigned to bands. Bands that are incompletely filled (Fig. 2.10*a*) are termed **conduction bands**, while those that are full are called

[18] If sufficiently cooled, HF will form a solid as a result of secondary bonds.

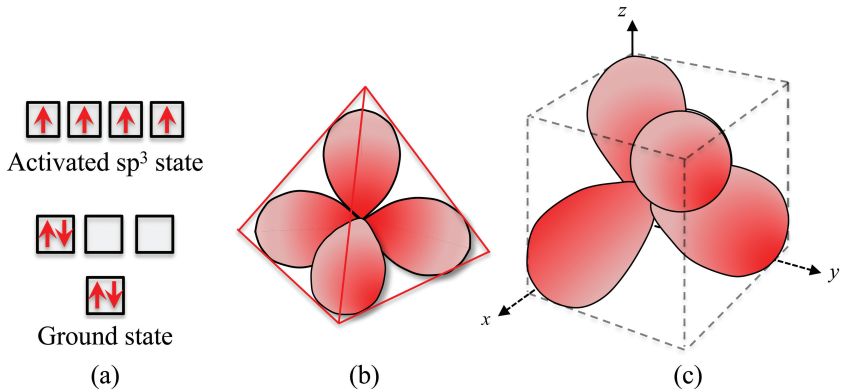

FIGURE 2.9 (*a*) Electronic configuration of ground state of the Si atom (bottom) and after hybridization (top). (*b*) Directionality of sp^3 bonds relative to a tetrahedral. (*c*) *Same as* (b) *but now embedded in a cube, where each lobe points to a different corner.* By so doing the electrons are kept as far away from each other as possible. Note that each bond lobe contains one electron, and thus the atom can now form *four* covalent bonds with other atoms.

valence bands. The electrons occupying the highest energy in a conduction band can rapidly adjust to an applied electric or magnetic field and give rise to the properties characteristic of a metal, such as high electrical and thermal conductivities, ductility and reflectivity. Solids where the valence bands are completely filled (Fig. 2.10*b*), on the other hand, are poor conductors of electricity and, at 0 K, are perfect insulators. It follows that understanding this model of the solid state is of paramount importance if the electrical and optical properties of solids in general, and ceramics in particular, are to be understood.

The next three subsections address the not-so-transparent concept of how, and why, bands form in solids. Three approaches are discussed. The first is a simple qualitative model. The second is slightly more quantitative and sheds some light on the relationship between the properties of the atoms making up a solid and

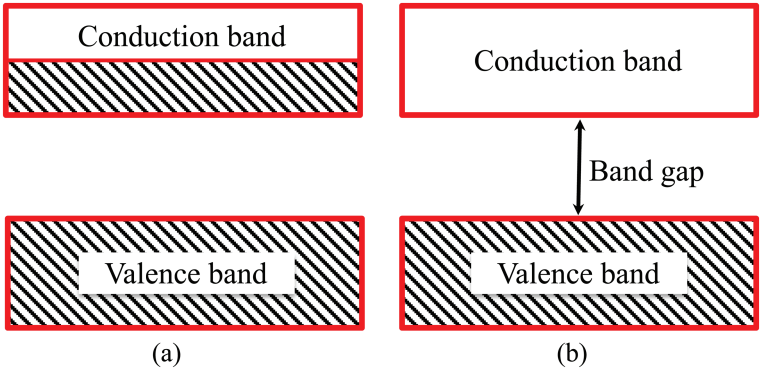

FIGURE 2.10 Band structure of, (*a*) a metal with an incompletely filled conduction band and (*b*) an insulator or semiconductor. At 0 K, such a solid is an insulator because the valence band is totally filled and the conduction band is totally empty. As the temperature is raised, some electrons are promoted into the conduction band and the material starts to conduct.

its band gap. The last model is included because it is physically the most tangible and because it relates the formation of bands to the total internal reflection of electrons by the periodically arranged atoms.

2.8.1 INTRODUCTORY BAND THEORY

In the same way that the interaction between two hydrogen atoms gave rise to two orbitals—one bonding and the other antibonding—the interaction or overlap of the wave functions of $\approx 10^{23}$ atoms in a solid gives rise to energy bands. To illustrate, consider 10^{23} atoms of Si in their ground state (Fig. 2.11*a*). The band model is constructed as follows:

1. Assign four localized tetrahedral sp^3 hybrid orbitals to each Si atom, for a total of 4×10^{23} hybrid orbitals (Fig. 2.11*b*).
2. The overlap of each of two neighboring sp^3 lobes forms one bonding and one antibonding orbital, as shown in Fig. 2.11*d*.
3. The two electrons associated with these two lobes are accommodated in the bonding orbitals (Fig. 2.11*d*).
4. As the crystal grows, every new atom added brings *one orbital to the bonding and one to the antibonding orbital set*. As the orbitals or electron wave functions overlap, they must *broaden* as shown in Fig. 2.11*c*, because of the Pauli exclusion principle.

   Thus, in the solid a spread of orbital energies develops within each orbital set, and the separation between the **highest occupied molecular orbital** (HOMO) and the **lowest unoccupied molecular orbital** (LUMO) in the molecule becomes the **energy band gap**, $\mathbf{E_g}$ (Fig. 2.11*c*). Note that the new orbitals are created near the original diatomic bonding σ and antibonding σ^* energies (Fig. 2.11*d*) and move toward the band edges as the size of the crystal increases.
5. In the case of Si, each atom starts with four valence electrons, and the total number of electrons that has to be accommodated in the valence band is 4×10^{23}. But since there are 2×10^{23} levels in that band

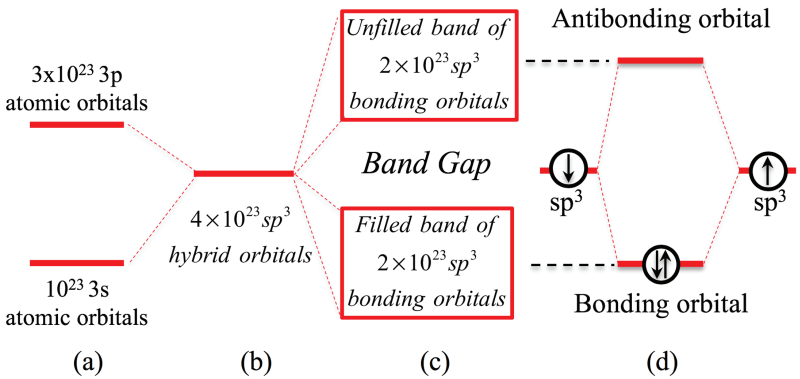

FIGURE 2.11 (*a*) Ground state of Si atoms. (*b*) sp^3 hybrid orbitals. (*c*) Interaction of sp^3 orbitals to form energy bands. (*d*) Localized orbital energy levels between two Si atoms to form a Si_2 molecule. Note that the energy bands are centered on the energy of the diatomic bonds.

and each level can accommodate two electrons, *it follows that at 0 K the valence band is completely filled and the conduction band is empty.*[19]

This last statement has far-reaching implications. If the band gap, usually denoted by E_g, lies somewhere between ≈0.02 and 3 eV, the material is considered to be a semiconductor. For higher values of E_g, the solid is considered an insulator. Said otherwise, if all the electrons are used in bonding, none are left to move freely and conduct electricity. Table 2.6, in which the band gaps of a number of binary and ternary ceramics are listed, clearly indicates that most ceramics are insulators.

Note that the degree of interaction between the orbitals depends on the interatomic distance or the spatial delocalization of the interacting electrons (the two are not unrelated). For example, the band gaps of C (diamond), Si and Ge are, respectively, 5.33, 1.12 and 0.74 eV. In C, the interaction is between the n = 2 electrons, whereas for Si and Ge one is dealing with the n = 3 and n = 4 electrons, respectively. As the interacting atoms become larger, the interaction of their orbitals increases, widening the bands that in turn reduces the band gap.[20]

Orbital overlap, while important, is not the only determinant of band gap width. Another important factor is how tightly the lattice binds the electrons. This is dealt with in the following model.

2.8.2 TIGHT BINDING APPROXIMATION[21]

In this approach, not unlike the one used to explain the formation of a covalent bond, Schrödinger's equation

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m_e}{h^2}[E_{tot} - E_{pot}(x)]\psi = 0 \tag{2.21}$$

is solved by assuming that the electrons are subject to a periodic potential E_{pot}, which has the same periodicity as the lattice. By simplifying the problem—to one dimension, with interatomic spacing a and assuming that $E_{pot}(x) = 0$ for regions near the nuclei and $E_{pot} = E_o$ for regions in between, and further assuming that the width of the barrier to be w (see Fig. 2.12*a*)—Eq. (2.21) can be solved. Despite these simplifications, the details of the solution are still beyond the scope of this discussion, and only the final results are presented.[22] It turns out that solutions are possible only if the following *restricting* conditions are satisfied:

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[19] As discussed subsequently, this is only true at 0 K. As the temperature is raised, the thermal energy will promote some of the electrons into the conduction band.

[20] Interestingly enough, a semiconducting crystal can be made conductive by subjecting it to enormous pressures, which increase the level of interaction of the orbitals to such a degree that the bands widen and eventually overlap.

[21] Also known as the Kronig–Penney model.

[22] The method of solving this problem lies in finding the solution for the case when E = 0, that is,
$\psi_o = A\exp(i\phi x) + B\exp(i\phi x)$
with $\phi = \sqrt{2\pi m E_{tot}}/h$. And the solution for the case where $E = E_o$, that is,
$\psi_v = C\exp\beta x + D\exp(-\beta x)$
where $\beta = 2\pi\sqrt{2\pi m(E_o - E_{tot})/h}$. By using the appropriate boundary conditions, namely, continuity of the wave function at the boundaries, and ensuring that the solution is periodic, A, B, C and D can be solved for. If it is further assumed that the barrier area, i.e., the product of wE_o, is a constant, Eqs. (2.22) and (2.23) follow. See R. Bube, *Electrons in Solids*, 2nd ed., Academic Press, New York, 1988, for more details.

TABLE 2.6 Band gaps, E_g, for various ceramics

Material	Band gap, eV	Material	Band gap, eV
Halides			
AgBr	2.8	MgF_2	11.0
BaF_2	8.8	MnF_2	15.5
CaF_2	12.0	NaCl	7.3
KBr	7.4	NaF	6.7
KCl	7.0	SrF_2	9.5
LiF	12.0	TlBr	2.5
Binary oxides, carbides and nitrides			
AlN	6.2	Ga_2O_3	4.6
Al_2O_3 parallel	8.8	MgO (periclase)	7.7
Al_2O_3 perpendicular	8.85	SiC (α)	2.6–3.2
BN	4.8	SiO_2 (fused silica)	8.3
C (diamond)	5.3	UO_2	5.2
CdO	2.1		
Transition metal oxides			
Binaries		Ternaries	
CoO	4.0	$BaTiO_3$	2.8–3.2
CrO_3	2.0	$KNbO_3$	3.3
Cr_2O_3	3.3	$LiNbO_3$	3.8
CuO	1.4	$LiTaO_3$	3.8
Cu_2O	2.1	$MgTiO_3$	3.7
FeO	2.4	$NaTaO_3$	3.8
Fe_2O_3	3.1	$SrTiO_3$	3.4
MnO	3.6	$SrZrO_3$	5.4
MoO_3	3.0	$Y_3Fe_5O_{12}$	3.0
Nb_2O_5	3.9		
NiO	4.2		
Ta_2O_5	4.2		
TiO_2 (rutile)	3.0–3.4		
V_2O_5	2.2		
WO_3	2.6		
Y_2O_3	5.5		
ZnO	3.2		

$$\cos ka = P\frac{\sin \phi a}{\phi a} + \cos \phi a \tag{2.22}$$

where

$$P = \frac{4\pi^2 ma}{h^2} E_o w \tag{2.23}$$

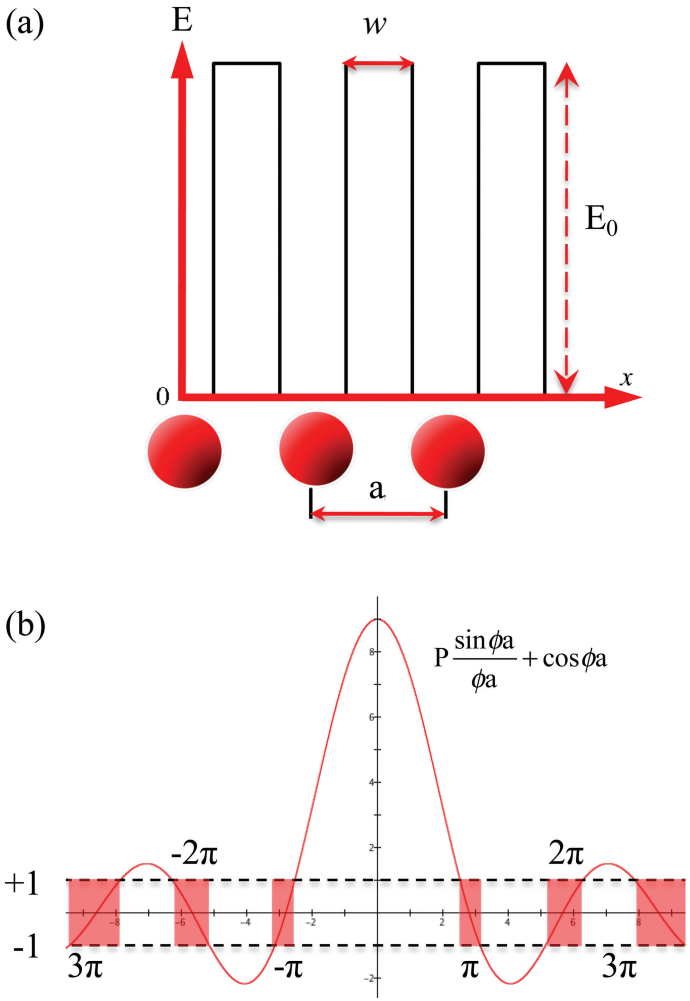

FIGURE 2.12 (*a*) Approximation of periodic potential that an electron is subjected to in a one-dimensional crystal of periodicity a. Here w is the width of the barrier and E_o is the depth of the energy well. (*b*) Plot of right-hand side of Eq. (2.22) versus ϕa. The x-axis is proportional to the energy of the electron, and the shaded areas denote energies that are permissible, whereas the energies between the these areas are not permissible.

and

$$\phi = \frac{2\pi}{h}\sqrt{2mE_{tot}} \tag{2.24}$$

k is the wave number, defined as:

$$k = \frac{2\pi}{\lambda} \tag{2.25}$$

where λ is the electron's wavelength. Recall the wave number of an electron is a direct measure of its momentum, p, since, according to DeBroglie, $p = 2\pi k/h$ [see Eq. (2A.3)].

Since the left-hand side of Eq. (2.22) can take only values between +1 and –1, the easiest way to find possible solutions to this equation is to do it graphically by plotting the right-hand side of Eq. (2.22) as a function of ϕ a, as shown in Fig. 2.12*b*. Whenever that function lies between +1 and –1 (shaded areas in Fig. 2.12*b*), that represents a solution. Given that ϕ is proportional to the energy of the electron [Eq. (2.24)], what is immediately apparent from Fig. 2.12*b* is that there are regions of energy that are permissible (shaded areas in Fig. 2.12*b*) and regions that are forbidden. This implies that *an electron moving in a periodic potential can only move in so-called allowed energy bands that are separated from each other by forbidden energy zones*. Furthermore, the solution clearly indicates that the E_{tot} *of the electron is a periodic function of the wave function*, k.

The advantage of this model over others is that a semiquantitative relationship between the bonding of an electron to its lattice and the size of the band gap can be construed. This is reflected in the term P—for atoms that are highly electronegative, E_o, and consequently P, is large. As P increases, the right-hand side of Eq. (2.22) becomes steeper, the *bands narrow and the regions of forbidden energy widen*. It follows that if this model is correct, an empirical relationship between the electronegativities of the atoms, or ions, making up a solid and its band gap should exist. That such a relationship, namely,

$$E_g\,(\text{eV}) \approx -15 + 3.75\left(\sqrt{|10X_A - 17.5|} + \sqrt{|10X_B - 17.5|}\right)$$

does exist is illustrated nicely in Fig. 2.13. Here X_A and X_B represent the electronegativities of the atoms making up the solid.

Before moving on, it is instructive to look at two limits of the solution arrived at above:

1. The interaction between the electrons and the lattice vanishes, In that case, E_o or P approaches 0. If $P = 0$ in Eq. (2.22), then $\cos ka = \cos k\phi$, and $k = \phi$, which when substituted in Eq. (2.24) and upon rearranging yields

$$E_{tot} = \frac{h^2k^2}{8\pi^2 m} \tag{2.26}$$

   which is nothing but the well-known relationship for the energy of a free electron (see App. 2A).
2. At the boundary of an allowed band, i.e., when $\cos ka = \pm 1$ or

$$k = \frac{n\pi}{a} \quad \text{where } n = 1,2,3 \tag{2.27}$$

   This implies that discontinuities in energy occur whenever this condition is fulfilled. When this result is combined with Eq. (2.26) and the energy is plotted versus k, Fig. 2.14 results. The essence of this figure lies in appreciating that at the bottom of the bands the electron dependence on k is parabolic; in other words, the electrons are behaving as if they were free. However, as their k increase, periodically, Eq. (2.27) will be satisfied and a band gap develops. The reason for the formation of such a gap is discussed in the next section.

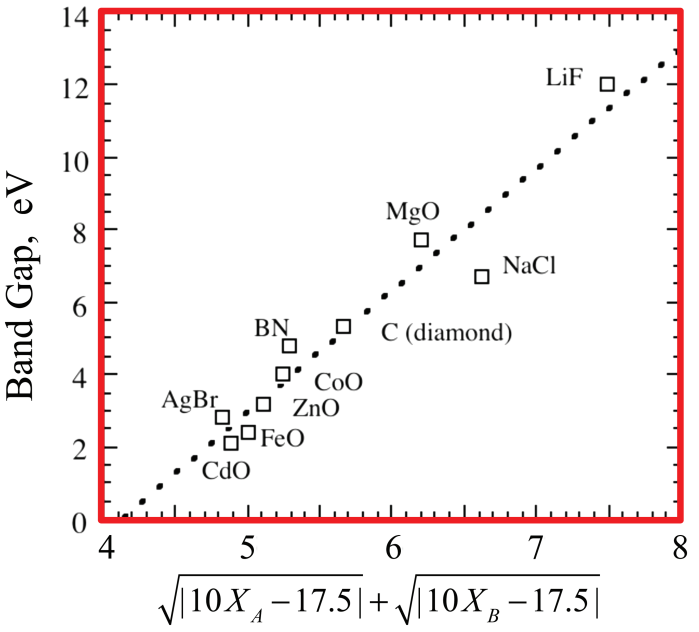

FIGURE 2.13 Empirical correlation between the electronegativities of the atoms making up a solid and its band gap; X_A and X_B are the electronegativities of the constituent atoms or ions.

2.8.3 NEARLY FREE ELECTRON APPROXIMATION

The physical origin of the band gap predicted in the previous model can be understood as follows: as a totally empty band is filled with electrons, they have to populate levels of higher energies or wave numbers, k. As they do, their momentum, p, increases and their wavelength decreases (see Eq. 2A.2). Consequently, at some point the condition $k = n\pi/a$ will be fulfilled, which is another way of saying that a pattern of *standing waves* is set up, and the electrons no longer propagate freely through the crystal because as the waves propagate to the right, they are reflected to the left, and vice versa.[23]

It can be shown further that[24] these standing waves occur with amplitude maxima either at the positions of the lattice points, that is $\psi^2 = (\text{const})\cos^2(n\pi x/a)$ (bottom curve in Fig. 2.15), or in between the lattice points, that is $\psi^2 = (\text{const})\sin^2(n\pi x/a)$ (top curve in Fig. 2.15). In the former case, the attraction of the electrons to the cores reduces the energy of the system—an energy that corresponds to the top of the valence band. In the latter case, the energy is higher and corresponds to that at the bottom of the conduction band. The difference in energy between the two constitutes E_g.

[23] The condition $k = n\pi/a$ is nothing but the well-known Bragg reflection condition, $n\lambda = 2a\cos\theta$, for $\theta = 0$. See Chap. 3 for more details.

[24] See, e.g., L. Solymar and D. Walsh, *Lectures on the Electrical Properties of Materials*, 4th ed., Oxford University Press, New York, 1988, p. 130.