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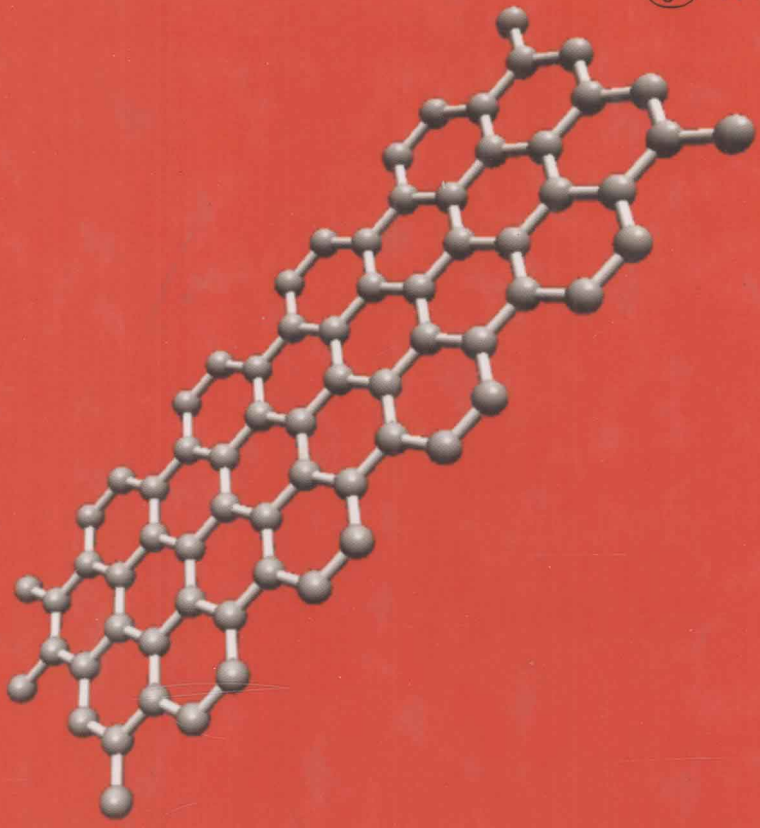
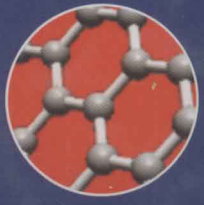


THE PHYSICS AND CHEMISTRY OF NANOSOLIDS



FRANK J. OWENS
CHARLES P. POOLE JR.

THE PHYSICS AND CHEMISTRY OF NANOSOLIDS

Frank J. Owens and Charles P. Poole, Jr.

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THE PHYSICS AND CHEMISTRY OF NANOSOLIDS

PREFACE

The prefix *nano* in the word *nanotechnology* means a billionth (1×10^{-9}). *Nanoscience* is a science that studies the properties of matter that has at least one dimension of the order of a billionth of a meter, called a *nanometer*. Its importance lies in the fact that when solids have dimensions of nanometers, the properties of these solids change. Properties such as strength, melting temperature, color, electrical conductivity, thermal conductivity, reactivity, and magnetic properties are affected, and the magnitude of change depends on the size of the solid in the nanometer regime. The changes also depend on the number of dimensions that are nanometers in size. This introduces the possibility of using size in the nanometer regime to design and engineer materials with new and possibly technologically interesting properties. The development of applications based on nanoscience research is referred to as *nanotechnology*. Because of this, nanotechnology and nanoscience have generated much interest in recent years (as of 2007) in the materials science, chemistry, physics, and engineering communities. As a result, chemistry, physics, materials science, and engineering departments at universities are developing courses in the subject. However, there is no textbook available to meet the needs of the development of the courses that describes the changes in properties and explains why they occur. This book, *The Physics and Chemistry of Nanosolids*, is intended as a senior undergraduate or graduate-level textbook on how and why reducing the size of solids to nanodimesions changes their properties. An undergraduate course in modern physics, physical chemistry, or materials science that has some introduction to quantum theory, is a prerequisite. The objectives of the book are to describe how properties depend on size in the nanometer regime, and explain, using relatively simple models of the physics and chemistry of the solid state, why these changes occur. This means that the student needs some understanding of the physics and chemistry of macroscopic solids and models developed to explain properties such as the theory of phonon and lattice vibrations and electronic band structure. Many of the chapters examine these models to see what they predict when one or more dimensions of a solid have a nanometer length. In some instances this will lead to unexplored territory where no experimental information exists. Chapter 1 provides an overview of the basic principles of solids. For those students who have had a course in the chemistry or physics of solids or materials science, this chapter can be skipped or used as a brief review. For those who have not, the chapter should be used as a guide to what subjects they may need to study in further detail in books such as Kittel's *Introduction to Solid State Physics* or Ashcroft and Mermin's *Solid State Physics*. Chapter 2 describes the various experimental

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methods used to measure the properties of the nanosolids. This chapter is important because the results of measurements using many of the methods are discussed throughout the remainder of the book. Chapter 3 is an overview of changes in properties of nanometer-size materials. Chapters 4–5 for the most part present data on how various properties of solids are affected by nanosizing and examine, in the context of the theories of macroscopic solids, why these changes occur. Because of the importance of carbon in biological materials and the potential applications of carbon nanostructures, a separate chapter is devoted to this subject. Each chapter is followed by a series of exercises designed to enhance the student's understanding of the reasons for changes in properties in the nanometer region.

FRANK J. OWENS
CHARLES P. POOLE JR.

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CHAPTER 1

Physics of Bulk Solids

In this text we will be discussing the physics and chemistry of nanostructures. The materials used to form these structures generally have bulk properties that become modified when their sizes are reduced to the nanorange; the present chapter presents background material on bulk properties of this type. Much of what is discussed here can be found in a standard text on solid-state physics.[1–4]

1.1. STRUCTURE

1.1.1. Size Dependence of Properties

Many properties of solids depend on the size range over which they are measured. Microscopic details become averaged when investigating bulk materials. At the macro- or large-scale range ordinarily studied in traditional fields of physics such as mechanics, electricity and magnetism, and optics, the sizes of the objects under study range from millimeters to kilometers. The properties that we associate with these materials are averaged properties, such as the density and elastic moduli in mechanics, the resistivity and magnetization in electricity and magnetism, and the dielectric constant in optics. When measurements are made in the micrometer or nanometer range many properties of materials change, such as mechanical, ferroelectric, and ferromagnetic properties. The aim of the present book is to examine characteristics of solids at the next lower level of size, namely, the nanoscale level, perhaps from 1 to 100 nm. Below this there is the atomic scale near 0.1 nm, followed by the nuclear scale near a femtometer (10^{-15} m). In order to understand properties at the nanoscale it is necessary to know something about the corresponding properties at the macroscopic and mesoscopic scales, and the present chapter aims to provide some of this background.

Many important nanostructures are composed of the group IV elements Si or Ge, types III–V semiconducting compounds such as GaAs or types II–VI semiconducting materials such as CdS, so these semiconductor materials will be used to illustrate some of the bulk properties that become modified when their dimensions are reduced

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to the nanometer range. These Roman numerals IV, III, V, and, so on refer to columns of the periodic table. Tabulations of various bulk properties of these semiconductors are found in Appendix B.

1.1.2. Crystal Structures

Most solids are crystalline with their atoms arranged on sites of a regular lattice structure. They possess "long-range order" because this regularity extends throughout the entire crystal. In contrast to this amorphous materials such as glass and wax lack long-range order, but they have "short-range order," which means that the local environment of each atom is similar to that of other equivalent atoms, but this regularity does not persist over appreciable distances. In other words, each atom of a particular type might have, for example, six nearest neighbors, and these neighboring atoms might be at positions that approximate an octahedral configuration. Liquids also have short-range order, but lack long-range order, and this short-range order is undergoing continual rearrangements as a result of Brownian motion. Gases lack both long-range and short-range order. Their constituent molecules undergo rapid translational motion in all directions, so the disorder is continually rearranging at a rapid rate.

Figure 1.1 shows the five regular arrangements of lattice points that can occur in two dimensions, namely, the square (a), primitive rectangular (b), centered rectangular (c), hexagonal (d), and oblique (e) kinds. These arrangements are called *Bravais lattices*. The general or oblique Bravais lattice has two unequal lattice constants $a \neq b$ and an arbitrary angle θ between them. For the perpendicular case when $\theta = 90^\circ$, the lattice becomes rectangular, and if in addition $a = b$, the lattice is called *square*. For the special case $a = b$ and $\theta = 60^\circ$, the lattice is hexagonal, formed from equilateral triangles. Each lattice has a unit cell, indicated in the figures, which can replicate throughout the plane and generate the lattice.

A crystal structure is formed by associating with a lattice a regular arrangement of atoms or molecules. Figure 1.2 presents a two-dimensional crystal structure based on a primitive rectangular lattice containing two diatomic molecules A–B in each unit cell. A single unit cell can generate the overall lattice.

In three dimensions there are three lattice constants, a, b, and c, and three angles: α between b and c, β between a and c, and γ between lattice constants a and b. There are 14 Bravais lattices, ranging from the lowest symmetry triclinic type in which all three lattice constants and all three angles differ from each other ($a \neq b \neq c$

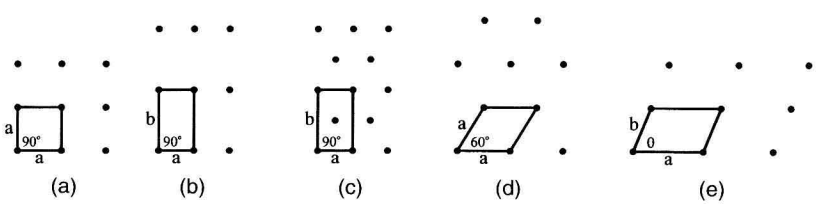

Figure 1.1. The five Bravais lattices that occur in two dimensions, with the unit cells indicated: (a) square; (b) primitive rectangular; (c) centered rectangular; (d) hexagonal; (e) oblique.

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