Physics of

MAGNETIC
NANOSTRUCTURES

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PREFACE

When solids have dimensions of nanometers, the properties of the solids change. Such properties as strength, melting temperature, color, electrical conductivity, thermal conductivity, reactivity, and magnetic properties are affected, and the magnitude of the 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. Thus, size in the nanometer regime can be used 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 potential, nanotechnology and nanoscience have generated much interest in recent years 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 various subfields of nanotechnology.

Nanostructured magnetic materials have a particularly strong possibility for developing new and interesting applications. In fact, there are already a number of technologies that employ nanostructured magnetic materials such as computer data storage and ferrofluids. The development of digital computers capable of handling large software programs has created a strong need for increased storage capability. Storage density has almost doubled every year. This is a result of a major research thrust in developing magnetic nanoparticles of smaller sizes with appropriate properties, which enables increased storage density. This increased density of smaller magnetic nanoparticles has driven the need to develop more

sensitive methods of reading the storage devices because smaller particles have lower magnetizations. Nanosized magnetoresistive materials such as magnetic tunnel junctions have the potential to increase the sensitivity of reading devices.

Presently, there is also active research to develop new applications in the medical field. Such ideas as using magnetic nanoparticles for targeted delivery of drugs and enhancement of images in magnetic resonance imaging are presently under investigation. Using magnetic nanoparticles loaded with chemotherapeutic drugs to deliver them directly to the tumor has a large potential to eliminate the negative side effects of the drugs. Understanding this research and its possibilities requires knowledge of the basic ideas and properties of magnetic materials, how they are measured, and how nanosizing affects these properties.

This book, *The Physics of Magnetic Nanostructures*, is intended to provide this understanding as an introduction to the subject for those who wish to learn about the field or become involved in research on the subject. With omission of some sections, the book could also be the basis of a senior undergraduate or graduate level textbook on how and why reducing the size of solids to nanodimensions changes magnetic properties. Thus, exercises have been included at the end of each chapter. The objectives of the book are to describe how magnetic properties depend on the size and dimension in the nanometer regime and to explain using relatively simple models of the solid state why these changes occur. Experimental methods for measuring the magnetic properties are described as the data from them are first presented.

The first chapter presents a basic overview of the effect reducing the size of a solid to nanometers on the

fundamental properties of the materials. The next chapter reviews the physics of magnetism and methods of measuring magnetic properties, which is necessary to understand how nanosizing affects magnetism. The remaining chapters discuss various kinds of magnetic structures and how nanosizing influences their magnetic properties. This includes two chapters that present potential and actual applications, one on devices and the other on medical applications.

ACKNOWLEDGMENT

1
PROPERTIES OF NANOSTRUCTURES

Nanostructures are generally considered to consist of a number of atoms or molecules bonded together in a cluster with at least one dimension less than 100 nm. A nanometer is 10^{-9} m or 10 Å. Spherical particles having a radius of about 1000 Å or less can be considered to be nanoparticles. If one dimension is reduced to the nano range, while the other two dimensions remain large, then we obtain a structure known as a well. If two dimensions are reduced, while one remains large, the resulting structure is referred to as a wire. The limiting case of this process of size reduction in which all three dimensions reach the low nanometer range is called a dot. Figure 1.1 illustrates the structures of rectangular wells, wires, and dots. This chapter will discuss how the important properties of materials such as the cohesive energy and the electronic and vibrational structure are affected when materials have at least one length in the nanometer range. Elementary models of the solid state will be used to explain why the changes occur on nanosizing.
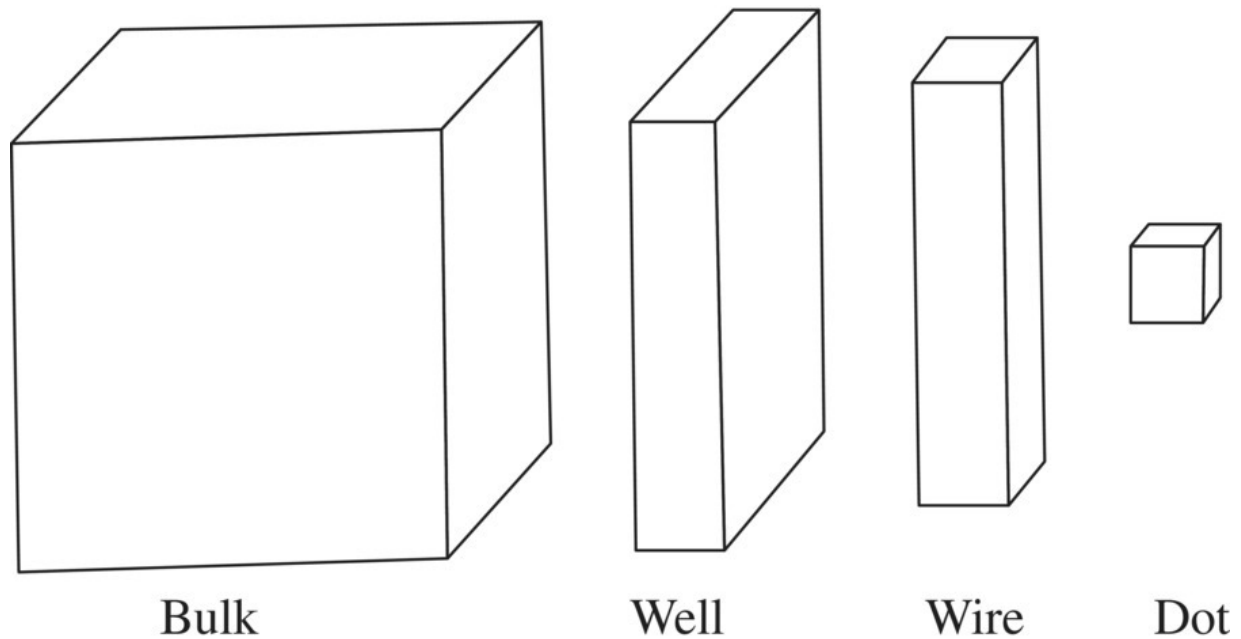
FIGURE 1.1 Structures corresponding to a rectangular well, wire, and dot having one, two, and three dimensions of nanometer length, respectively.

1.1 COHESIVE ENERGY

The atoms or ions of a solid are held together by interactions between them, which can be electrostatic and/or covalent. The electrostatic interaction is described by the Coulomb potential between charged particles. Covalent bonding involves overlap of wave functions of outer electrons of nearest neighbor atoms in the lattice. A crystal is stable if the total energy of the lattice is less than the sum of the energies of the atoms or molecules that make up the crystal when they are isolated from each other. The energy difference is the cohesive energy of the solid. As materials approach nanometer dimensions, the percentage of atoms on the surface increases. Figure 1.2 demonstrates a plot of the percentage of atoms on the surface of a hypothetical face-centered cubic (fcc) structure having a lattice parameter of 4 Å. Appendix A provides a

table relating the diameter of spherical nanoparticles to the number of atoms in the particle and the percentage on the surface. Below about 14 nm, more than 10% of the atoms are on the surface. This holds true for metallic particles as well as ionically and covalently bonded materials. Since the atoms on the surface have less nearest neighbor atoms, this means that the cohesive energy of an ionic solid decreases as the size is reduced in the nanometer range. One of the results of this decrease in cohesive energy is an increase in the separation of the constituents of the lattice. Figure 1.3 shows an X-ray diffraction measurement of the lattice parameter of the ionic solid CeO_2 as a function of particle size showing the increase in the lattice parameter as the particle size is reduced. This results in a reduction of the strength of the interaction between the ions of the solid and thus a reduction in the cohesive energy.
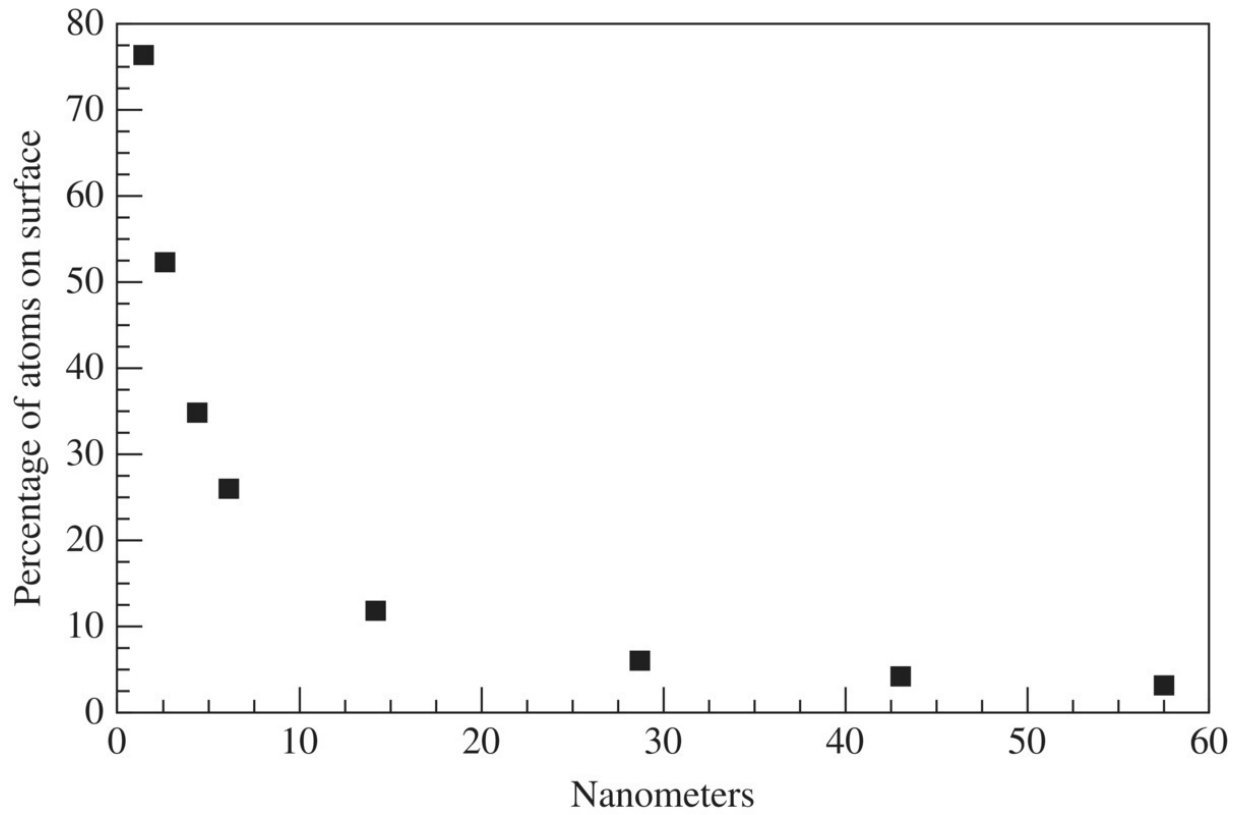
FIGURE 1.2 Percentage of atoms on surface of a face-centered cubic lattice versus particle size. The lattice parameter is 4 Å.
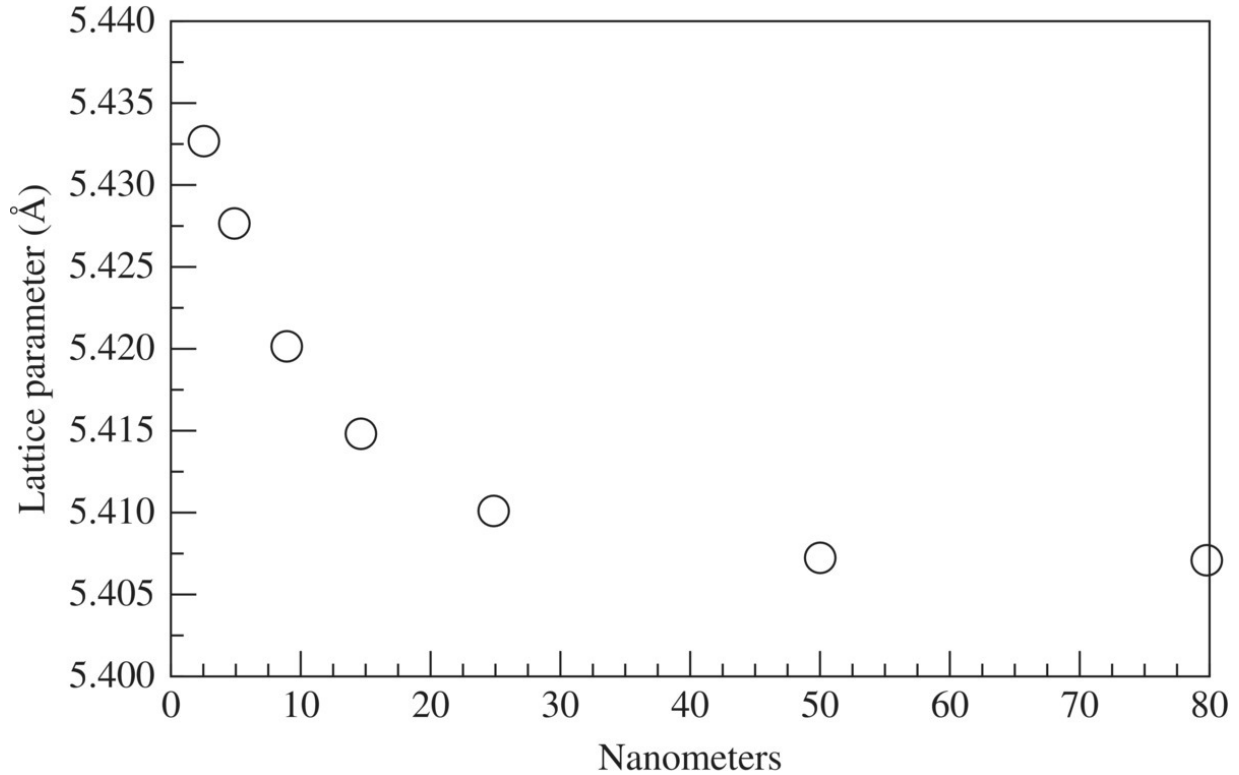
FIGURE 1.3 Experimental measurement of the lattice parameter of the ionic crystal, CeO_2, versus particle size.

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Ionic solids are ordered arrays of positive and negative ions such as sodium chloride, which is an fcc structure of positive sodium ions and an interpenetration of fcc negative chlorine ions. The interaction potential between the ions of charge Q is electrostatic, $\pm Q/r$. Ions of opposite sign are attracted, while ions of the same sign repel each other. The total electrostatic energy of any one ion i is U_i given by the sum of all the Coulomb interactions between the ith ion and all positive and negative ions of the lattice:

$$U_i = \sum_j U_{ij} = \sum_j \pm \frac{Q^2}{r_{ij}}$$

(1.1)

where r_{ij} is the distance between ions i and j. In the case of the interaction between the nearest neighbors, a term has to be added to [Equation 1.1](#) to take into account that the electron core around the nucleus repels those of the nearest neighbors. The form of this has been derived from experiment and is given by

$$\lambda \exp\left(\frac{-r_{ij}}{\rho}\right) \tag{1.2}$$

The constants λ and ρ for NaCl are 1.75×10^{-9} ergs and 0.321. The larger the r_{ij}, the smaller the cohesive energy. Thus, for ionic crystals, the cohesive energy decreases as the lattice parameter increases. [Figure 1.4](#) shows a plot of the experimentally determined cohesive energy of crystals having the NaCl structure versus lattice parameter. The reduction of the cohesive energy also affects other properties such as the melting temperature. [Figure 1.5](#) illustrates a plot of the melting temperature of some alkali halides versus cohesive energy. In general, when materials have nanometer dimensions, the melting temperature decreases.
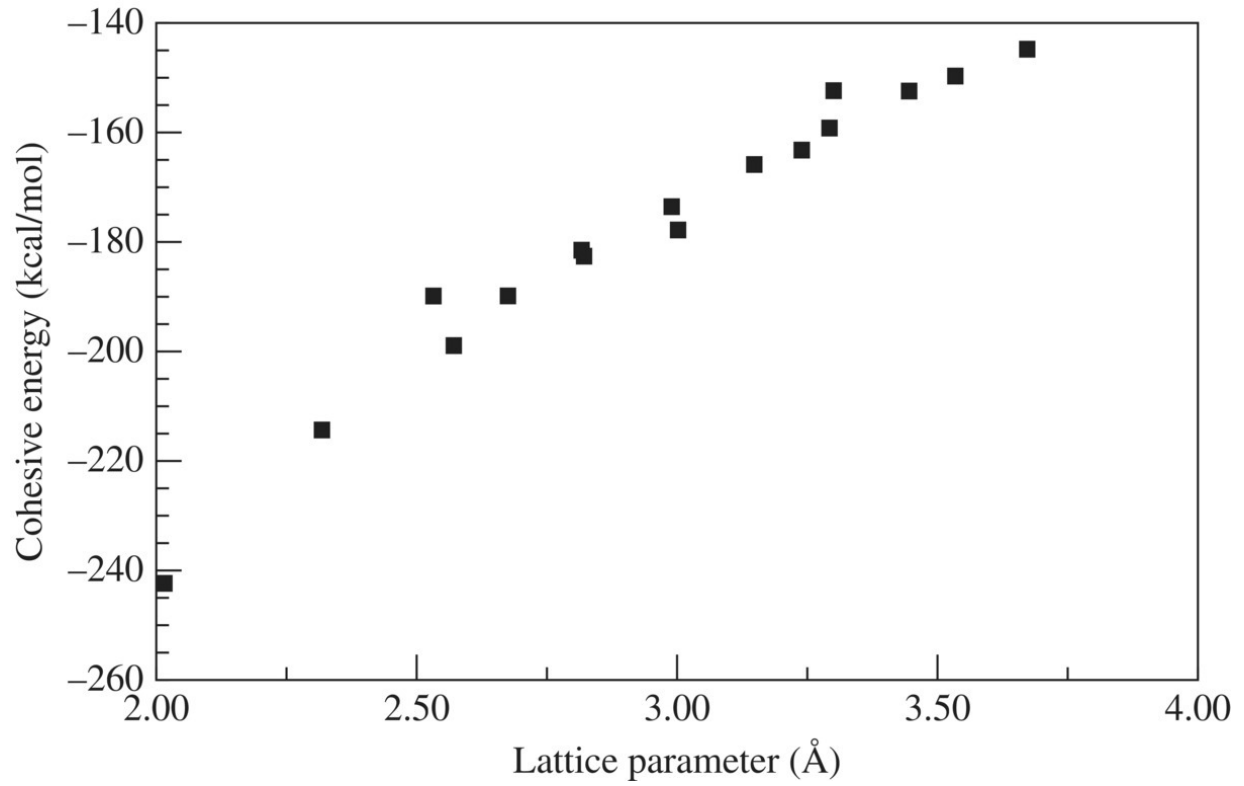
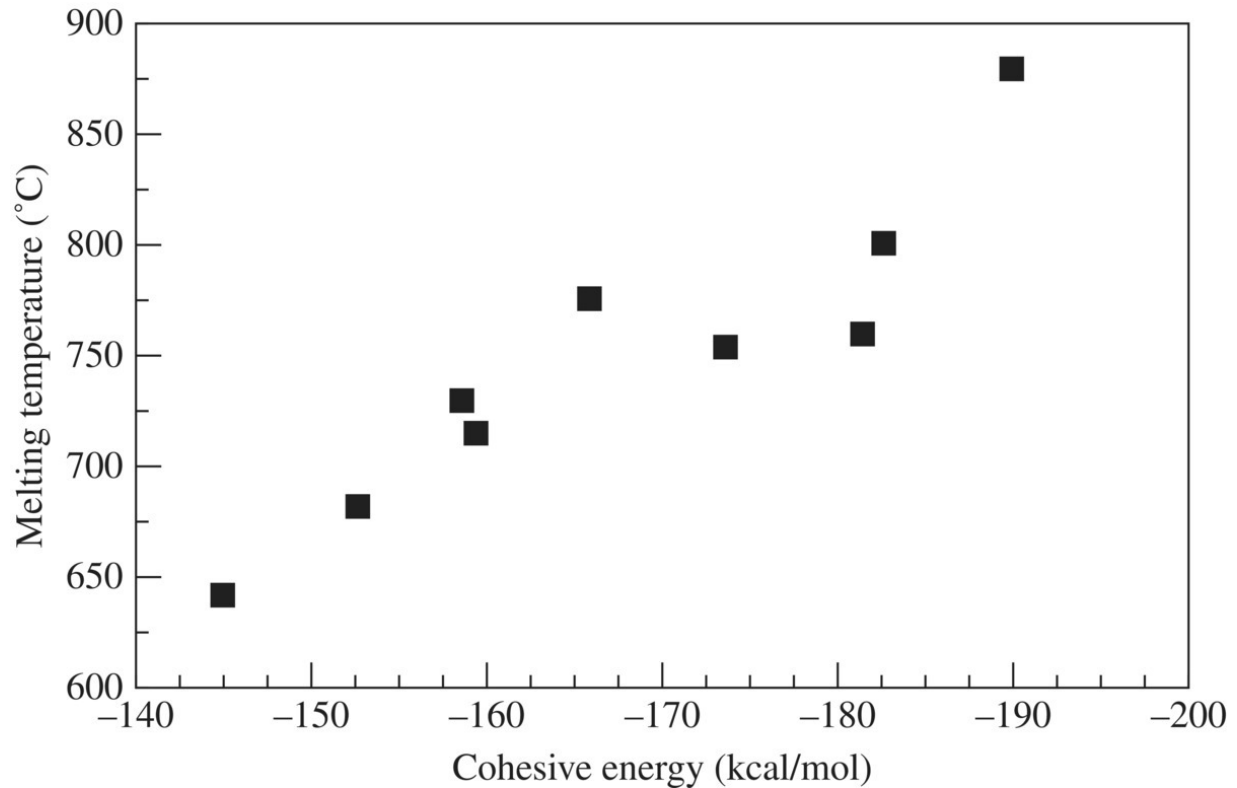**FIGURE 1.4** Cohesive energy of ionic alkali halide crystal having NaCl structure versus lattice parameter.

Melting temperature of some alkali halide crystals versus cohesive energy.

Most of the experimental observations of the effect of size of metal nanoparticles on the lattice parameters show it decreases as the diameter decreases. The decrease is attributed to the effect of surface stress. The surface stress causes small particles to be in a state of compression where the internal pressure is inversely proportional to the radius of the particle. Figure 1.6 demonstrates a plot of the measured decrease in the lattice parameter of copper versus the diameter in angstroms. Notice that the changes don't occur until the diameter reaches a very small value of 0.9 nm. In the case of gold, measurements show that at 3.5 nm the lattice parameter has decreased to 0.36% of the bulk value. In aluminum, significant changes are not observed until the particle size is below 1.8 nm. In the discussion of models of the electronic properties of metals in the following section, it will be assumed that the lattice

parameter is not significantly dependent on particle sizes for values greater than 4 nm. As will be seen, the number of atoms in a metal nanoparticle has a much more significant influence on the electronic structure.
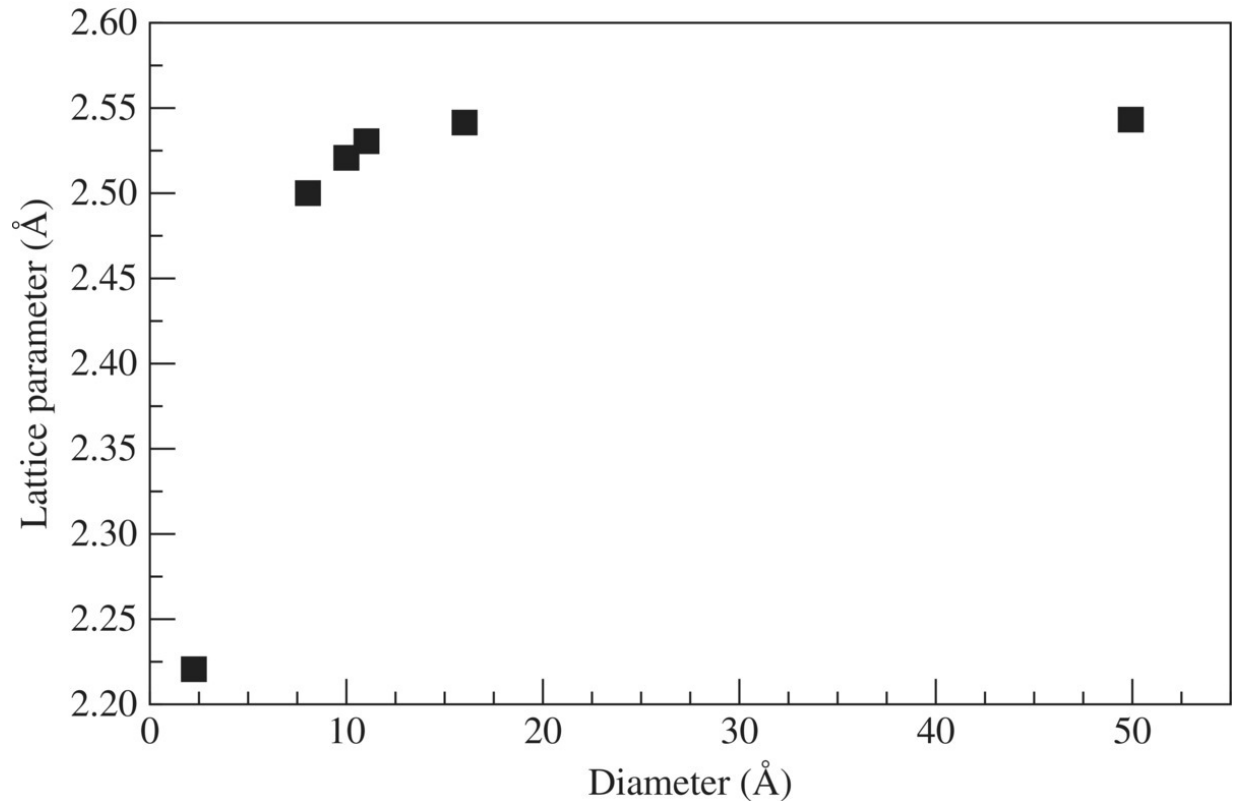
Metals conduct electricity because the outer electrons of the atoms of the solid are delocalized and hence free to move about the lattice. This makes the development of a theory of binding energy of metals a bit more complex than for ionic or covalent solids. Because the outer electrons of the atoms can be itinerant, the atoms can be considered to be positively charged. The binding energy of a metal can be treated as arising from the Coulomb interaction of a lattice of positive ions embedded in a sea of negative conduction

electrons. One relatively simple model is to consider the binding energy to be the interaction of a positive point charge e with a negative charge −e distributed uniformly over a sphere of radius R_0 and volume V_0 equal to the atomic volume. The cohesive energy on this simple model can be shown to be [3]

$$U_c = -\frac{0.9e^2}{R_0} + \left(\frac{3}{5}\right)[E_f]$$

(1.3)

where E_f is the Fermi level, the top occupied energy level, of the metal nanostructure. One would not expect the atomic volume to change significantly with reduced size, and thus, the first term in Equation 1.3 will not change much with nanosizing. In the next section, it will be shown that the magnitude of the Fermi energy E_f increases as the particle size is reduced. From Equation 1.3, this implies that the cohesive energy of metals decreases as the particle size decreases in the nanometer regime. However, this decrease will not happen until the particle size is quite small.

Solids such as silicon are covalently bonded, meaning that the bonding involves overlap of the wave functions of nearest neighbors. Reduction in particle size would lead to a decrease in the binding energy. Figure 1.7 shows a plot of the calculated binding energy per monomer as a function of the length of a polyacetylene polymer in the nanometer range. Polyacetylene is a chain of covalently bonded monomers, C_2H_2. The binding energy of the monomer in the chain is given by

$$BE = BE_{pa} - nBE_{monomer}$$

(1.4)

where BE_{pa} is the binding energy of the polymer, $BE_{monomer}$ is the binding energy of the monomer, and n is the number
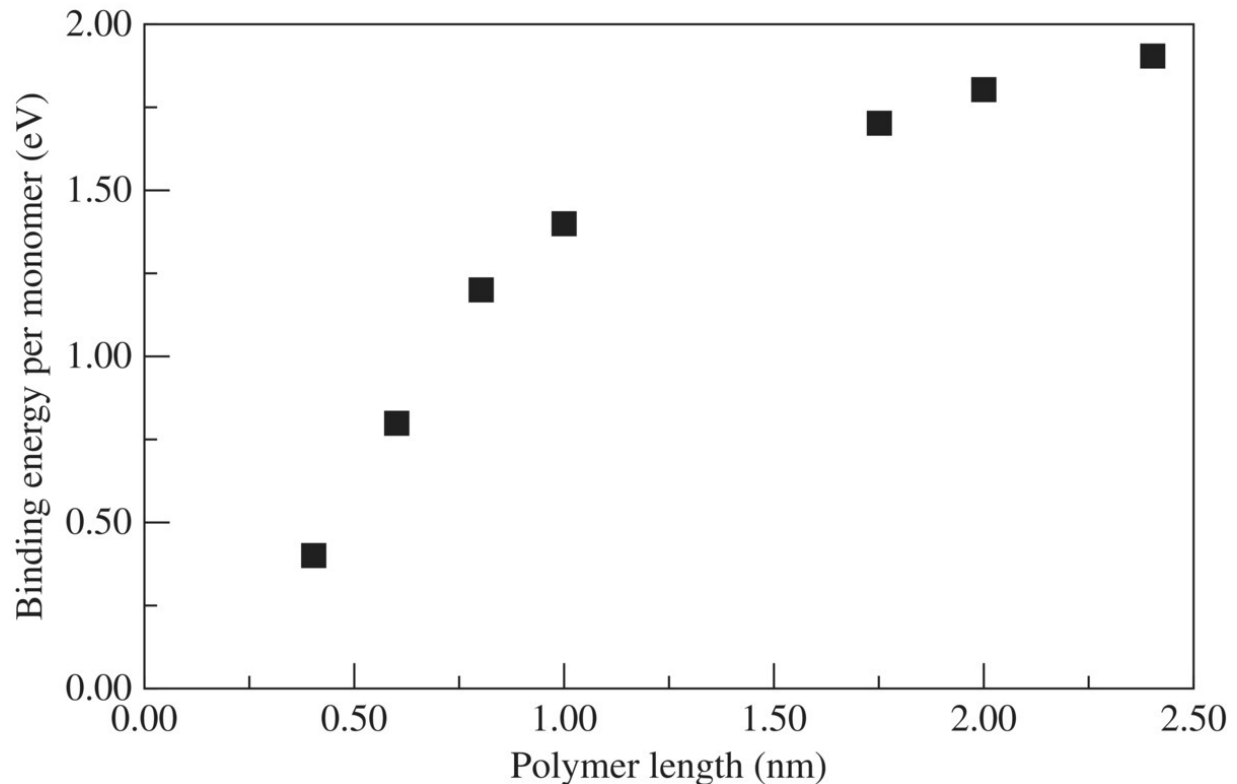
of monomers in the chain.

FIGURE 1.7 Density functional calculation of binding energy per monomer, C_2H_2, of the linear chain polymer, polyethylene versus polymer length.

(Adapted from Ref. [4].)

Generally, the interaction between the constituents of organic crystals is a dipole–dipole potential, which depends on their separation as $1/R^3$. Because of its short range, the crystals would have to be quite small to affect the lattice parameter. The potential describing the interaction between atoms in inert gas solids is the Lennard–Jones potential, which has a $1/R^6$ dependence on the atomic separation, meaning that the reduction in the size of the crystal to nanometers will have little effect on the cohesive energy. However, there have been no experimental studies of the effect of size on the lattice parameters of organic or inert gas solids.

1.2 ELECTRONIC PROPERTIES

One of the simplest models of the electronic structure of metals treats the conduction electrons as though they see no potential at all, but are confined to the volume of the solid. The model is best applicable to monovalent metals such as lithium, sodium, or potassium, where the ion cores only occupy about 15% of the volume of the solid. The energies are obtained by solving the Schrödinger wave equation for $V(r) = 0$, with boundary conditions. For the case of a one-dimensional system, the wave equation has the form

$$-\left[\frac{h^2}{2m}\right]\frac{d^2\Psi_n}{dx^2} = E_n\Psi_n \qquad (1.5)$$

where Ψ_n is the wave function of the electron in the nth state and E_n is the energy. The boundary conditions for a one-dimensional lattice of length L are

$$\Psi_n(0) = 0 \text{ and } \Psi_n(L) = 0 \qquad (1.6)$$

The eigenvalues obtained by solving Equation 1.5 are [3]

$$E_n = \left[\frac{h^2}{2m}\right]\left[\frac{n}{2L}\right]^2 \qquad (1.7)$$

where n is a quantum number having integer values 0, 1, 2, 3,..., etc.

Equation 1.7 is useful in understanding how the electronic structure of metals is affected when the dimensions are nanometers. The separation between the energy levels of state n and $n + 1$ is

$$E_{n+1} - E_n = \left[\frac{h^2}{8mL^2}\right][1 + 2n] \tag{1.8}$$

It is seen from Equation 1.8 that as the length of the chain, L, decreases, the separation between energy levels increases, and eventually, the band structure opens up into a set of discrete levels. This also means that the density of states, the number of energy levels per interval of energy, will decrease with size. When the energy levels are filled with electrons, only two electrons are allowed in each level because of the Pauli exclusion principle. These two electrons must have different spin quantum numbers m_s of $+1/2$ and $-1/2$, meaning that the two electron spins in each level n are antiparallel and there is no net spin in the level. The Fermi energy is the energy of the top filled level, which for a monovalent metal will have the quantum number $n_f = N/2$ where N is the number of atoms in the solid. Thus, for the one-dimensional solid, the Fermi energy is obtained from Equation 1.7 to be

$$E_f = \left[\frac{h^2}{2m}\right]\left[\frac{N}{4L}\right]^2 \tag{1.9}$$

In a manner analogous to the derivation of Equation 1.9 for the Fermi level in one dimension, the Fermi level in the free electron model of metals in three dimensions is obtained to be

$$E_f = \left[\frac{h^2}{2m(\pi)^2}\right]\left[\frac{3\pi^2 N}{V}\right]^{2/3} \tag{1.10}$$

Figure 1.8 demonstrates a calculation of the relative change of the Fermi level for the face-centered copper lattice versus diameter. The plot shows that the Fermi level

does not increase significantly until the particle size is quite small, less than 2.5 nm for copper.
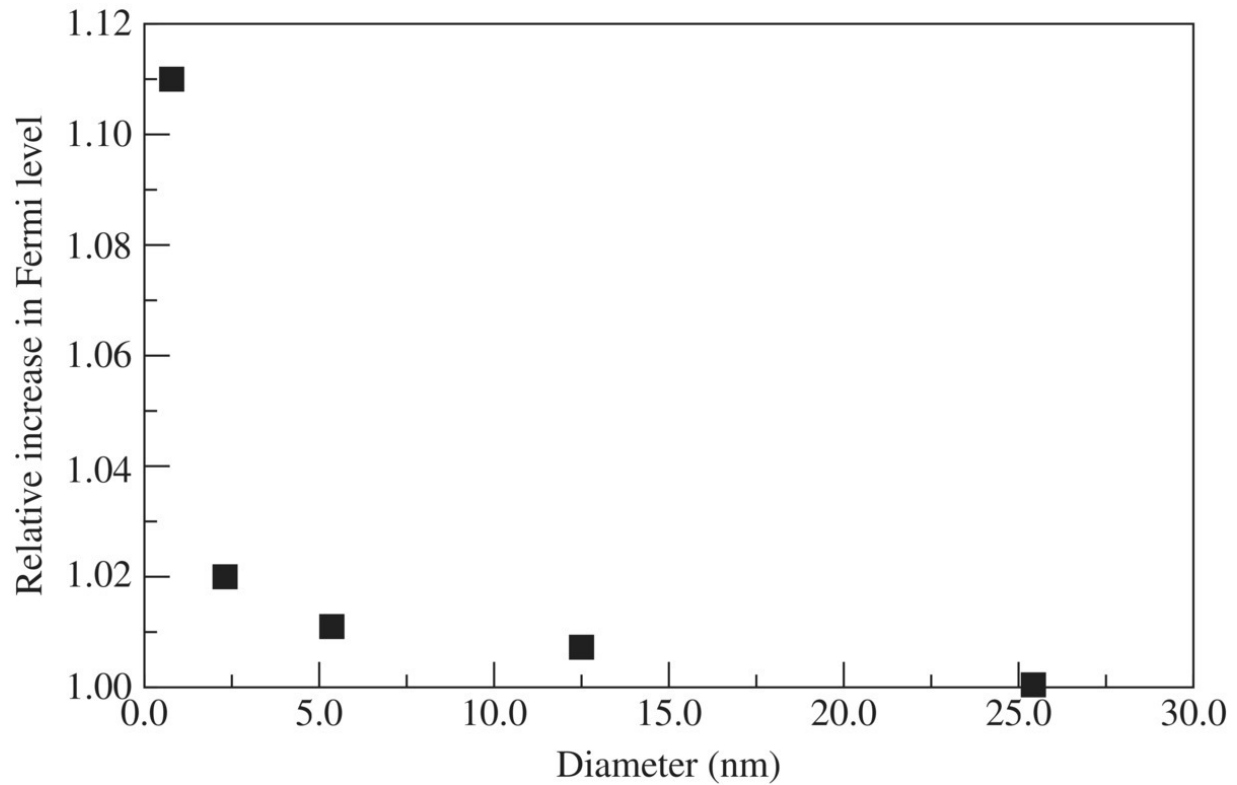

FIGURE 1.8 Calculation of the relative shift of the Fermi level for copper versus particle diameter.

An important property of solids is the density of states, that is, the number of energy levels per interval of energy given by $D(E) = dN/dE$. The density of states determines a number of properties of solids such as the electronic specific heat and the magnetic susceptibility arising from the conduction electrons. The density of states depends on the dimensionality of the material. For a wire, a one-dimensional material, the density of states can be calculated from Equation 1.7 and has the form $1/2\ C_1 E^{-1/2}$. For two dimensions, a well, the density of states can be shown to be $D(E) = C$, and for three dimensions, $D(E) = C_3 E^{1/2}$. Thus, we see that the density of states of a material

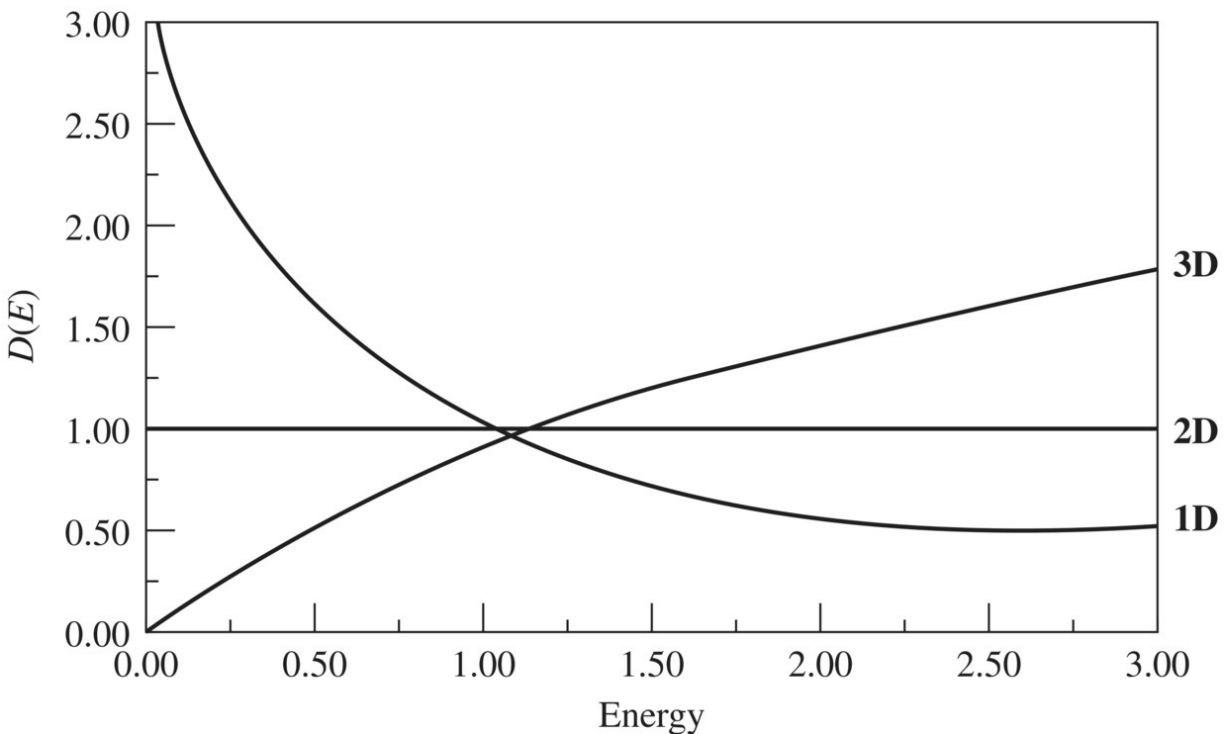depends on its dimensions. Figure 1.9 gives a plot of the density states for the different dimensions.

FIGURE 1.9 Plot of the density of states versus energy based on the free electron model of metals for structures having one, two, and three dimensions of nanometer length.

The band gap of a material is the energy separation between the top filled energy level and the first unfilled level. One way to measure the effect of nanosizing on the band gap of a nanosized semiconductor is to measure the absorption of light as a function of the wavelength for different particle sizes. An absorption will occur when the energy of the photon of the light is equal to or greater than the band gap. When this happens, an electron is excited from the valence band to the conduction band and light energy is absorbed. Nanosized cadmium selenide is a semiconductor. Figure 1.10 illustrates a plot of the measured band gap of cadmium selenide versus the inverse

square of the particle radius showing a nearly straight line dependence. A nanowire is a nanostructure in which two dimensions have nanometer size, and the other is large, generally greater than microns. Figure 1.11 shows the result of the measurement of the band gap of a silicon nanowire versus its diameter, showing the band gap increasing as the diameter of the wire is reduced.
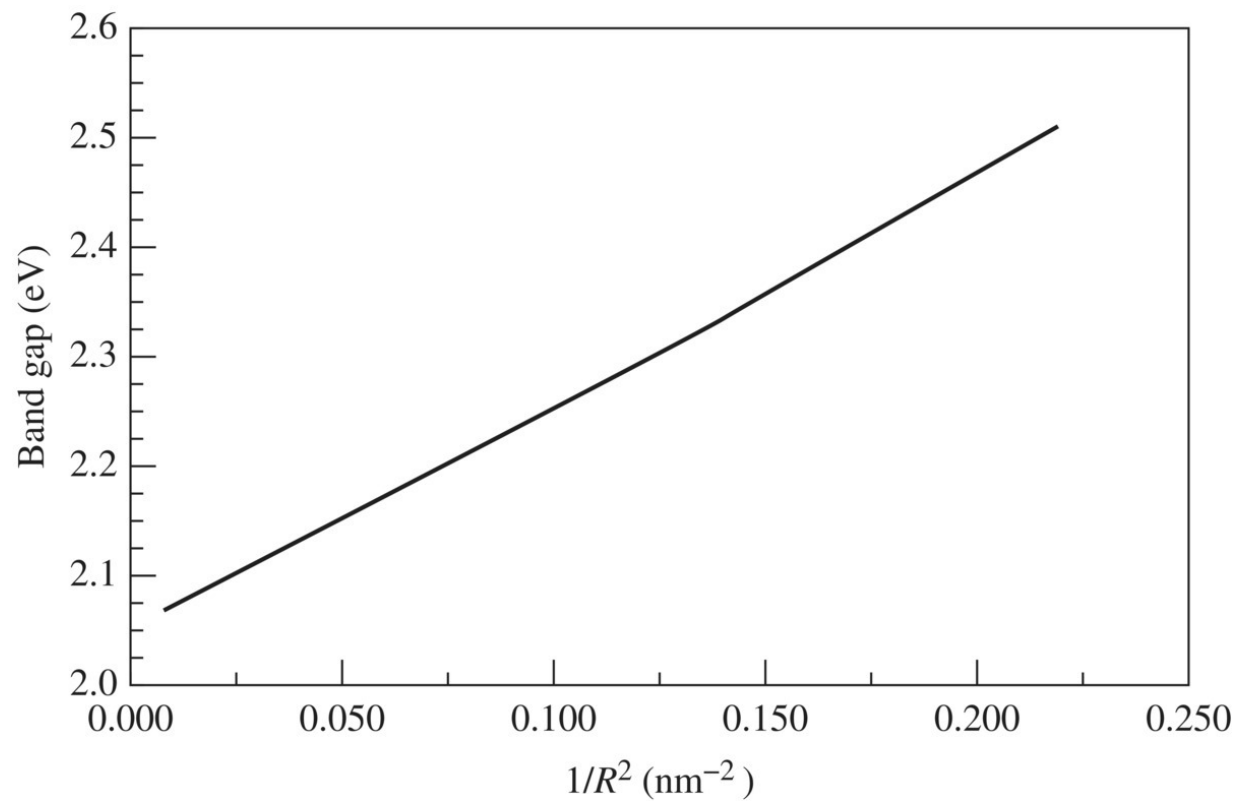

FIGURE 1.10 Band gap of CdSe versus inverse square of particle radius.
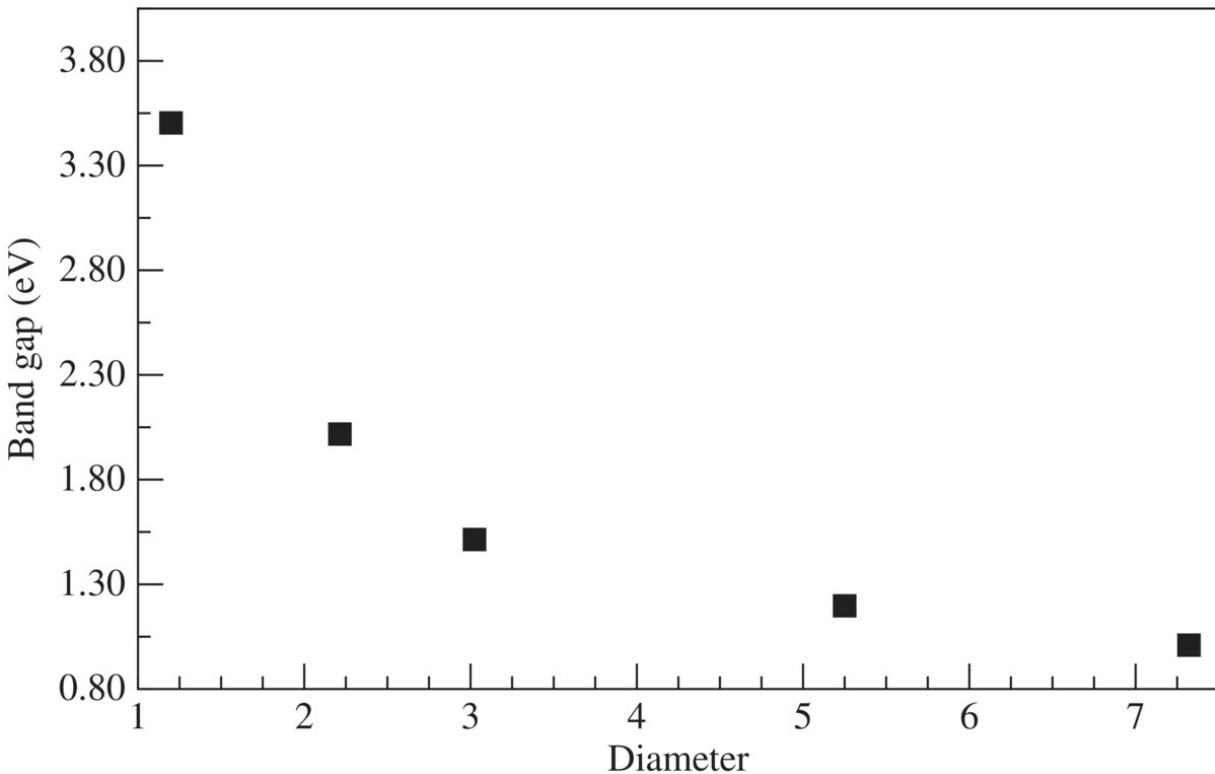
(Adapted from Ref. [5].)

FIGURE 1.11 Measured band gap of silicon nanowire versus diameter in nanometers

(Adapted from Ref. [6].)

1.3 QUANTUM DOTS

Semiconductors are materials having small band gaps typically ranging from 2.5 to 0.18 eV such that an electron at higher temperatures can be excited from the valence band to the conduction band providing a source of charge carriers for current. For example, silicon, which is widely used in transistor devices, has four valence electrons that are shared in covalent bonds with four neighboring silicon atoms in the lattice. The electronic structure of the lattice is determined by this covalent bonding. Thus, Equations 1.6, 1.7, 1.8, 1.9, and 1.10 cannot be used to describe the electronic structure of bulk semiconductors. There is one situation where similar equations can be used to describe

the energy levels. This is at the size where quantum confinement occurs. As the dimensions of wires, wells, and dots are decreased, there is a size where the separation of the surfaces of the particles is in the order of the wavelength of the charge carriers. The charge carriers are said to be confined, and the effect is referred to as the quantum size effect. At these sizes, the structures in <u>Figure 1.1</u> are referred to as quantum wires, wells, and dots. At this size, the energy levels of the structures are not determined by the chemical nature of the atoms of the material but by the dimensions of the structure. It is interesting to note that the quantum size effect occurs in semiconductors at larger sizes because of the longer wavelength of conduction electrons and holes in semiconductors due to the larger effective mass. In a semiconductor, the wavelength can be as long as 1 μm, whereas in a metal, it is in the order of 0.5 nm.

A simple model that exhibits the principal characteristics of such a potential well is a square well in which the boundary is very sharp or abrupt. Square wells can exist in one, two, three, and higher dimensions, and for simplicity, a one-dimensional case will be considered.

Standard quantum mechanical texts show that for an infinitely deep square potential well of width, a, in one dimension, the coordinate x has the range of values $-\frac{1}{2}(a) \leq x \leq \frac{1}{2}(a)$ inside the well, and the energies there are given by the expressions

$$E_n = \frac{h^2}{2m}\left(\frac{n^2}{a^2}\right)$$ (1.11a)

$$= E_0 n^2$$ (1.11b)

where $E_0 = h^2/2ma^2$ is the ground state energy and the quantum number n assumes the values $n = 1, 2, 3,....$ The electrons that are present fill up the energy levels starting from the bottom, until all available electrons are in place. An infinite square well has an infinite number of energy levels, with ever-widening spacings as the quantum number n increases. If the well is finite, then its quantized energies E_n are smaller than the corresponding infinite well energies, and there are only a limited number of them. Figure 1.12 illustrates the case for a finite well of potential depth $V_0 = 7E_0$, which only has three allowed energies. No matter how shallow the well, there is always at least one bound state E_0. For the case of a cubic quantum dot having edges of length, a, the energy levels will be

$$E_n = \left[\frac{h^2}{2ma^2} \right] (n_x^2 + n_y^2 + n_z^2)$$
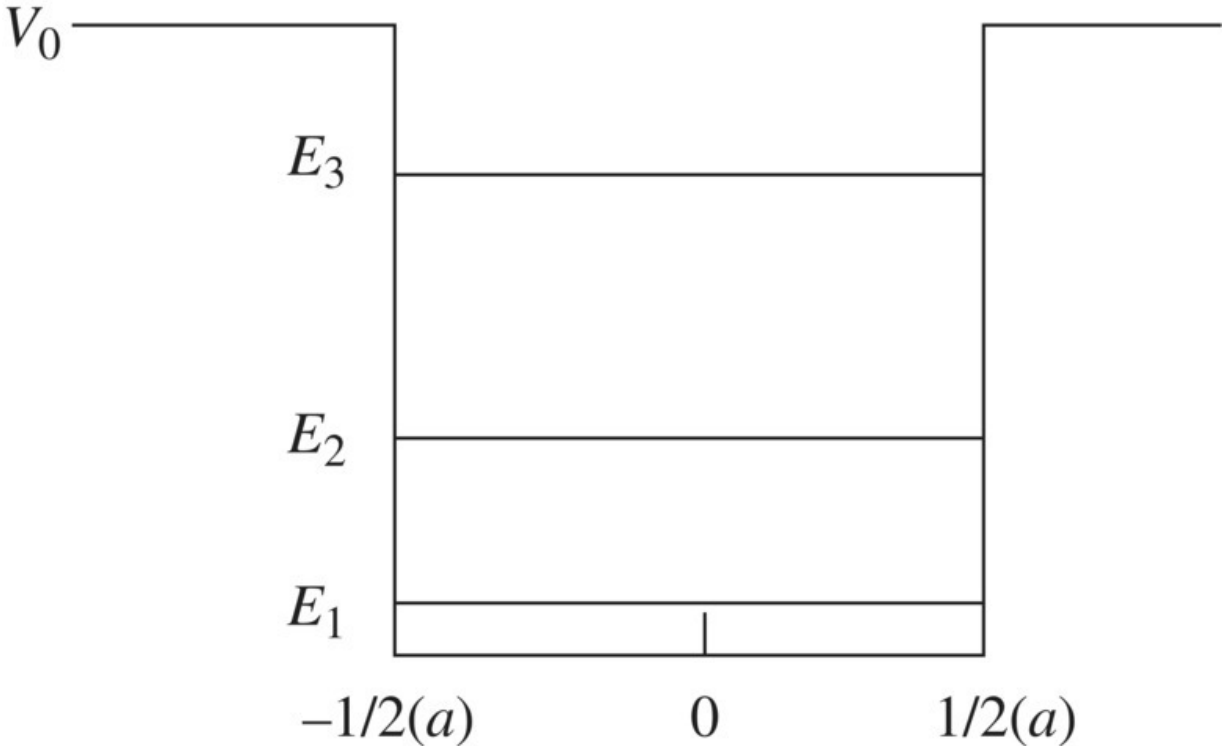
(1.12)

FIGURE 1.12 Energy levels of a finite potential well.

Quantum dots such as the cubic dot, having energy levels given by the above equation, have been developed into one of the major applications of nanotechnology. The quantum dot laser is used in CD players to read the groves on the disk. The separation between the levels in the dot can be chosen by the value of a in Equation 1.12. There is a value of a in which the separation of the energy levels from the conduction band can be in the infrared (IR) frequency range. This means an IR photon can excite an electron to the conduction band and application of a voltage produces a current. This is the basis for the use of the quantum dot as an IR detector. It is possible with appropriate excitation to produce a population inversion in the energy levels of the dot. This means that one of the upper levels has more electrons than a lower level, which is necessary to produce laser light.

1.4 VIBRATIONAL PROPERTIES

The constituents of a solid lattice vibrate. The specific frequencies, called the normal modes of vibration, are determined by the nature of the interaction between constituents of the lattice and the symmetry of the lattice. The vibrational frequencies of solids can be measured by IR spectroscopy and Raman spectroscopy. IR spectroscopy measures the absorption of IR light when it induces a transition from the $N = 0$ vibrational state to the $N = 1$ state. The basis of Raman spectroscopy is illustrated in Figure 1.13. Laser light is used to excite the lowest energy level of a vibration to some higher level. The higher level excited state then decays back to the lowest level. However, some of decay goes to a vibrational state above the ground state. The frequency of this emitted light is measured, and the difference between the frequencies of exciting laser light and the emitted light measures the vibrational frequency. When solids are reduced to nanometer dimensions, the frequencies generally decrease. Figure 1.14 shows a plot of the decrease in the frequency of the longitudinal optical mode of silicon as a function of particle size measured by Raman spectroscopy. There are two reasons for this decrease. It is seen earlier that the lattice parameter generally increases as the particle size decreases. This weakens the interaction between the constituents of the lattice and thus causes a lowering of the frequencies. The other reason for the decrease is phonon confinement, a process similar to electron confinement discussed earlier. This occurs when the dimensions of the solid are in the order of the wavelength of the lattice vibrations. The uncertainty principle can be used to explain phonon confinement.
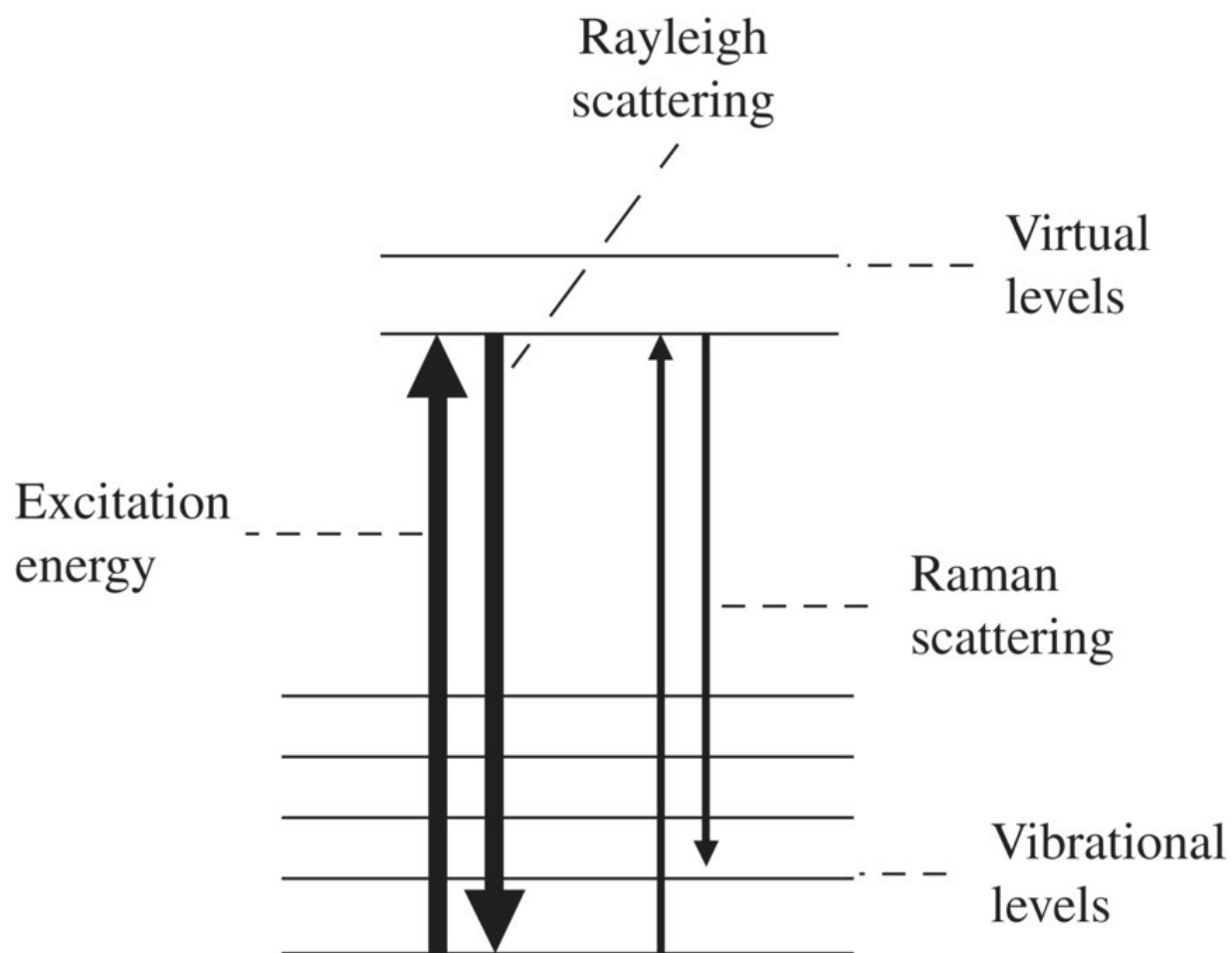
FIGURE 1.13 Illustration of excitation and emission of light from vibrational energy levels providing the basis of Raman spectroscopy.
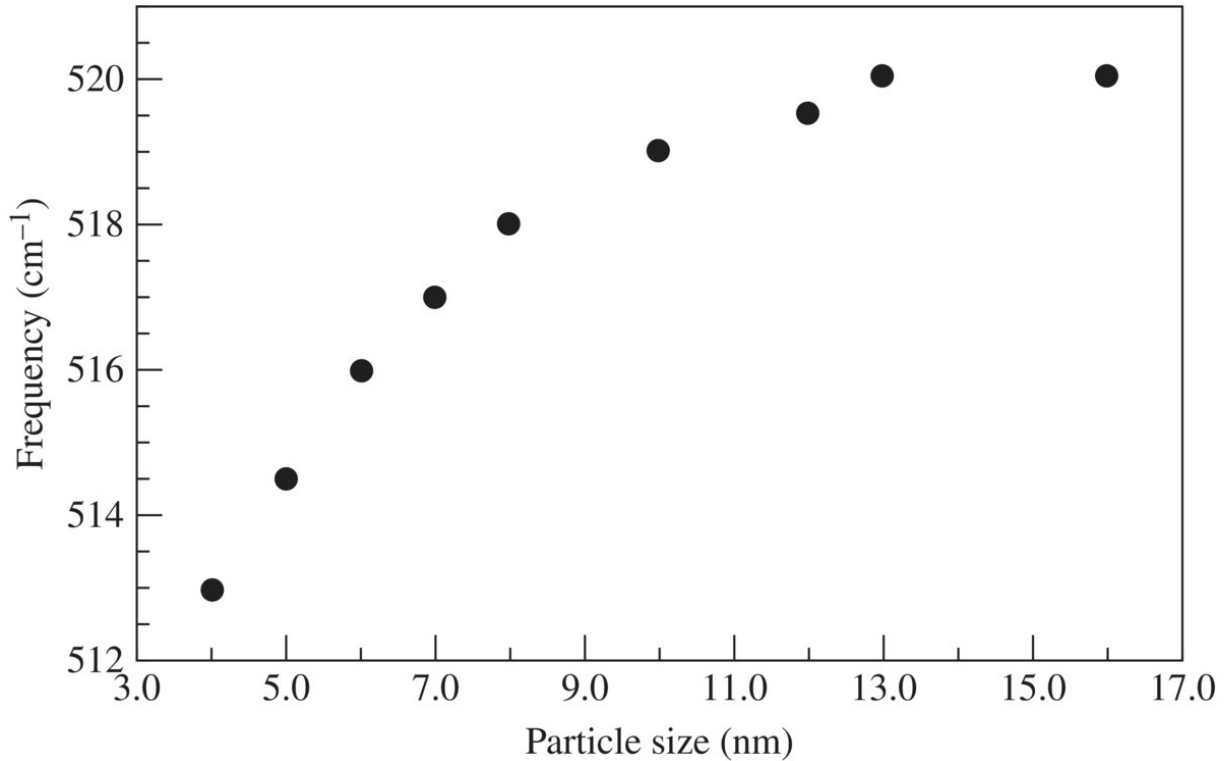
FIGURE 1.14 Plot of the frequency of the longitudinal optical mode of silicon versus the particle size measured by Raman spectroscopy.

(Adapted from Ref. [7].)

The uncertainty principle says that the order of magnitude of the uncertainty in position ΔX times the order of magnitude of the uncertainty in momentum ΔP must at least be Planck's constant, h, divided by 2π, that is,

$$\Delta X \Delta P \geq \frac{h}{2\pi} \qquad (1.13)$$

Let us assume that ΔX is the diameter of the nanoparticle, D, and that it can be measured accurately by some technique such as scanning electron microscopy. This means the uncertainty in the momentum P will have a range of values. It can be shown that the momentum of a phonon is $hk/2\pi$ where k is the wave vector given by ω/c

and c is the velocity of light. Thus, we have $D\Delta k \geq 1$ or the minimum uncertainty in k is

$$\Delta k \sim \frac{1}{D}$$

Raman spectroscopy measures frequencies at the center of the Brillouin zone, $k = 0$.

However, that is a precise value that Equation 1.14 shows has some uncertainty, meaning that there is a spread of values for k for a Raman measurement in small particles. This means nonzero values of k will contribute to the Raman spectrum. Let us assume that for small values of k, the dependence of the frequency on k, that is, the dispersion relationship, is quadratic:

$$\Delta\omega = ak^2 \qquad (1.15)$$

From this, it follows that

$$\Delta K = C\Delta\omega^{1/2} \qquad (1.16)$$

where C is a constant. Thus,

$$\Delta\omega = C\left[\frac{1}{D^2}\right] \qquad (1.17)$$

However, if the dependence of the frequency on k is other than k^2, say k^γ, then the dependence of the frequency shift on particle diameter will be $1/D^\gamma$, which is what is observed with γ ranging from 1 to 1.5 depending on the material.

The vibrational density of states $D(\omega)$ is the number of vibrational modes per interval of frequency, $dN/d\omega$. For a

one-dimensional line having N atoms, the number of vibrational modes is N. For a three-dimensional lattice, it is $3N$. The normal modes may be considered a set of independent oscillators with each oscillator having the energy ε_n given by

$$\varepsilon_n = \left(n+\frac{1}{2}\right)\left(\frac{h}{2\pi}\right)\omega \qquad (1.18)$$

where n is a quantum number having integral values ranging from 0, 1, 2,... to n.

The average energy of a harmonic oscillator assuming a Maxwell–Boltzmann distribution function is

$$\langle\varepsilon\rangle = \frac{h\omega}{2\pi}\left[\frac{1}{2}+\frac{1}{\exp\left(\dfrac{\dfrac{h\omega}{2\pi}}{k_\mathrm{B}T}\right)-1}\right] \qquad (1.19)$$

The total energy of a collection of oscillators is

$$E = \sum_k <\varepsilon_k>\left(\frac{h}{2\pi}\right)\omega_k \qquad (1.20)$$

When there is a large number of atoms, the allowed frequencies are very close and can be treated as a continuous distribution allowing replacement of the summation by an integral, where $D(\omega)d\omega$ is the number of modes of vibration in the range ω to $\omega + d\omega$. It turns out it is more convenient to work in k space and deal with the number of modes $D(k)dk$ in the interval k to $k + dk$. As shown in Figure 1.15, the number of values of k in three dimensions between k and $k + dk$ will be proportional to the volume element on a sphere of radius k, which is given by