



PHYSICS OF
**MAGNETIC
NANOSTRUCTURES**

FRANK J. OWENS

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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.

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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.

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

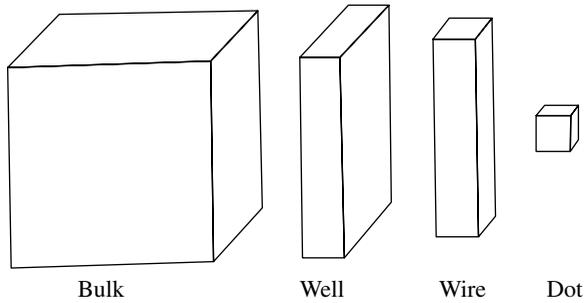


FIGURE 1.1 Structures corresponding to a rectangular well, wire, and dot having one, two, and three dimensions of nanometer length, respectively.

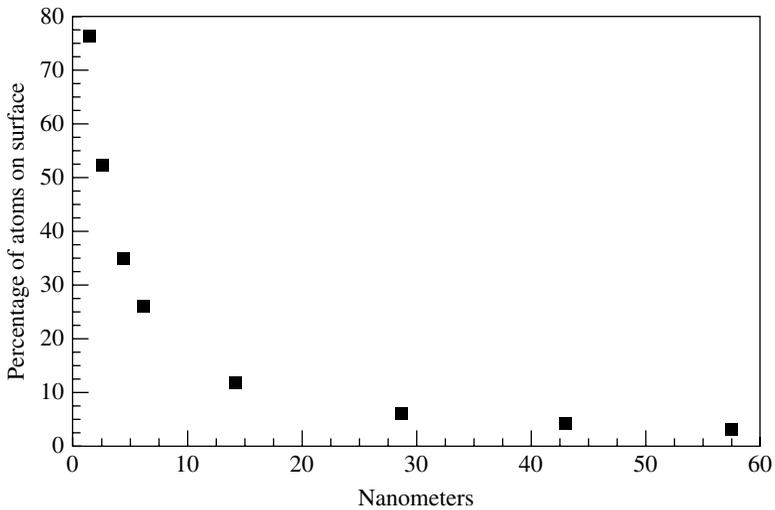


FIGURE 1.2 Percentage of atoms on surface of a face-centered cubic lattice versus particle size. The lattice parameter is 4\AA .

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.

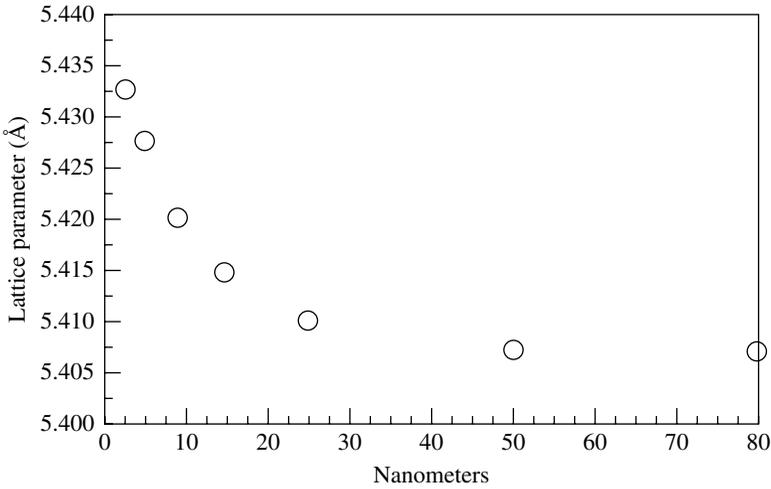


FIGURE 1.3 Experimental measurement of the lattice parameter of the ionic crystal, CeO_2 , versus particle size. (Reproduced with permission from Zhang et al. [1]. © 2002, AIP Publishing LLC.)

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 i th ion and all positive and negative ions of the lattice:

$$U_i = \sum_j U_{ij} = \sum_j \pm \frac{Q^2}{r_{ij}} \quad (1.1)$$

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

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

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

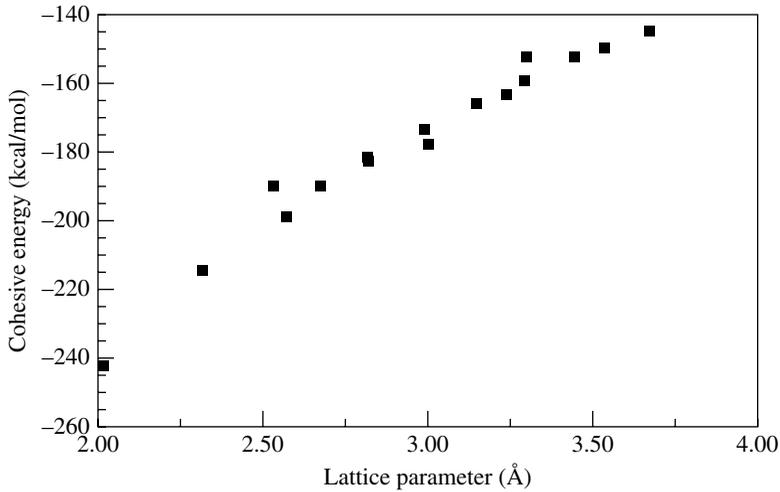


FIGURE 1.4 Cohesive energy of ionic alkali halide crystal having NaCl structure versus lattice parameter.

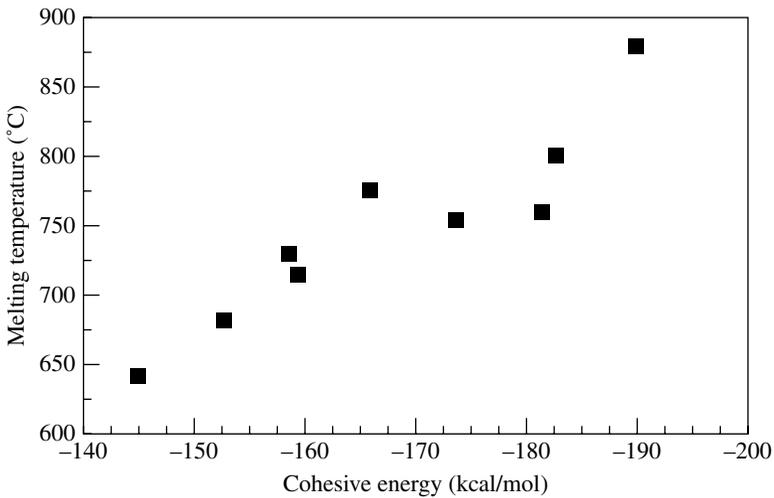


FIGURE 1.5 Melting temperature of some alkali halide crystals versus cohesive energy.

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.

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

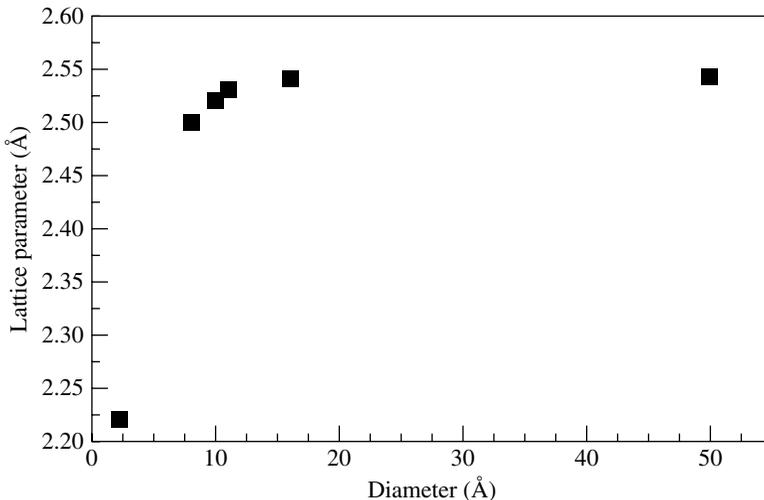


FIGURE 1.6 Measured lattice parameter of copper versus particle size. (Reprinted with permission from Ref. [2]. © 1986 by the American Physical Society.)

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]

$$U_c = -\frac{0.9e^2}{R_0} + \left(\frac{3}{5}\right)[E_f] \quad (1.3)$$

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