PART I

BASIC CONCEPTS
CHAPTER 1

Theory of Size, Confinement, and Oxidation Effects

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1.1. INTRODUCTION

Both the processes of oxidation and the size reduction form the essential entities that dictate the behavior of a nanostructured oxide. The electronic processes of oxidation destroy the initially metallic bonds to create new kinds of bonds with specific properties, such as polarization, localization, and transportation of charge, which determine the behavior of the oxides to vary from their parent metals (1). Oxygen interaction with atoms of metals relates to the technical processes of corrosion, bulk oxidation, heterogeneous catalysis, and so on (2). Studies of these processes laid the foundations for applications in microelectronics (gate devices and deep submicron integrated circuit technologies), photo-electronics (photoluminescence, photo-conductance, and field emission), magneto-electronics (superconductivity and colossal magneto-resistance) and dielectrics (ferro-, piezo-, and pyro-electrics) (3).

Nanoparticles are entities that appear in between extended solids and molecules or even in an isolated atom. Properties of nanosolids determined by their shapes and sizes are indeed fascinating, which form the basis of the emerging field of nanoscience and nanotechnology that has been recognized as the key significance in science, technology, and economics in the 21st century. When examining nanostructures, many concepts developed in both molecular chemistry and solid-state physics have to be considered. One may develop a “top-down” theory on the behavior of nanosystems starting from a solid and confining it to a limited size. Another chemical-like “bottom-up” approach is to start with a molecular system and expand its size. Each approach
has different advantages and disadvantages. There is a challenge to bridge these two approaches and develop new concepts for nanostructures.

The size-induced property change of nanostructures has inspired tremendous theoretical efforts. For instance, several models have been developed to explain how the size reduction could induce the blue shift in the photoluminescence (PL) of nanosemiconductors. An impurity luminescent center model (4) assumed that the PL blue shift arises from different types of impurity centers in the solid and suggested that the density and types of the impurity centers vary with particle size. Surface states and the surface alloying mechanism (5,6) proposed that the PL blue shift originates from the extent of surface passivation that is subject to the processing parameters, aging conditions, and operation temperatures (7). The model of inter-cluster interaction and oxidation (8) also claimed responsibility for the PL blue shift. The most elegant model for the PL blue shift could be the “quantum confinement (QC)” theory (9–13). According to the QC theory, the PL energy corresponds to the band gap expansion dictated by electron-hole (e-h) pair (or exciton) production:

$$E_G(R) - E_G(\infty) = \frac{\pi^2 \hbar^2}{(2\mu R^2)} - 1.786\varepsilon^2/(\varepsilon_r R) + 0.284E_R$$ (1.1)

where $\mu = m_h^*m_e^*/(m_h^* + m_e^*)$, being the reduced mass of the e-h pair, is an adjustable parameter. The $E_G$ expansion originates from the addition of the kinetic energy $E_K$ and the Coulomb interaction $E_p$ of the e-h pairs that are separated by a distance of the particle radius $R$ and contribution of the Rydberg or spatial correlation (electron–electron interaction) energy $E_R$ for the bulk semiconductor. The effective dielectric constant $\varepsilon_r$ and the effective mass $\mu$ describe the effect of the homogeneous medium in the quantum box, which is simplified as a mono-trapping central potential by extending the dimension of a single atom $d_0$ to that of the solid $D$. According to the QC theory, electrons in the conduction band and holes in the valence band are confined spatially by the potential barrier of the surface or are trapped by the potential well of the quantum box. Because of the confinement of both the electrons and the holes, the lowest energy optical transition from the valence to the conduction band increases in energy, effectively increasing the $E_G$. The sum of the kinetic and potential energy of the freely moving carriers is responsible for the $E_G$ expansion, and therefore, the width of the confined $E_G$ grows as the characteristic dimensions of the crystallites decrease.

In contrast, a free-exciton collision model (14) suggested that the $E_G$ expansion arises from the contribution of thermally activated phonons in the grain boundaries rather than from the QC effect. During a PL measurement, the excitation laser heats the free excitons that then collide with the boundaries of the nanometer-sized fragments. The laser heating the free-excitons up to the temperature in excess of the activation energy required for the self-trapping gives rise to the extremely hot self-trapping excitons (STEs). Because the resulting temperature of the STEs is much higher than the lattice temperature, the cooling of the STEs is dominated by the emission of phonons. However, if the STE temperature comes into equilibrium with the lattice temperature, the absorption of lattice phonons becomes possible. As a result, the blue shift of the STE–PL band is suggested to originate from the activation
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of hot-phonon-assisted electronic transitions. The blue shift of the STE–PL band depends on the temperature of laser-heated free-excitons that in turn is determined by the size of nanofragments. This event happens because the temperature (kinetic energy) of the laser-heated free-exciton increases with the number of boundary collisions, which tends to be higher with decreasing size of the nanofragments. The energy gained from laser heating of the exciton increases with decreasing nanosolid size in an $\exp(1/R)$ way.

Another typical issue of nanostructures is their thermal stability. The melting point ($T_m$) of an isolated nanosolid, or a system with weakly linked nanoparticles, drops with solid size (called supercooling), whereas the $T_m$ may rise (called superheating) for an embedded nanosystem because of the interfacial effect. The $T_m$ is characterized by the Lindemann’s criterion (15) of atomic vibration abruption or Born’s criterion (16) of shear modulus disappearance at the $T_m$. The $T_m$ elevation or suppression and the mode of melting in the nanometer regime have been described with the following models: (1) homogeneous melting and growth (17,18); (2) random fluctuation melting (19); (3) liquid shell nucleation and growth (20–23); (4) liquid-drop (24) formation; (5) lattice-vibrational instability (25,26); and (6) surface-phonon instability (27,28).

Often, numerous modeling arguments exist for a specific phenomenon. The challenge is how to correlate all outstanding arguments for all observations to the effect of bond order loss of the under-coordinated surface atoms or the effect of confinement. The origin for one phenomenon must intrinsically sustain to others. Understanding the mechanisms for both size reduction and oxidation and their joint contribution of the two entities is critical to understanding the behavior of nanostructured oxide materials and related devices.

This chapter describes a bond order–length–strength (BOLS) correlation mechanism (29) for the effect of physical size (bond breaking) and a chemical-bond–valence-band–potential-barrier (BBB) correlation mechanism (1) for the effect of oxidation (bond making) on the performance of a nanostructured oxide. The BBB correlation indicates the essentiality of sp-orbital hybridization of an oxygen atom upon reacting with atoms in the solid phase. In the process of oxidation, electronic holes, non-bonding lone pairs, lone-pair-induced antibonding dipoles, and hydrogen bonds are involved through charge transportation, localization, and polarization, which dictate the performance of an oxide. Charge transport from metal to oxygen creates the band gap, which turns the metal to be a semiconductor or an insulator; lone-pair-induced charge polarization lowers the work function of the surface, whereas hydrogen bond-like formation caused by overdosing with the oxygen additives restores the work function. The often-overlooked events of nonbonding and antibonding are expected to play significant roles in the functioning of an oxide.

The BOLS correlation mechanism indicates the significance of bond order loss of an atom at a site surrounding a defect or near the edge of a surface or in an amorphous phase in which the coordination (CN) reduction (deviation of bond order, length, and angle) distributes randomly. Bond order loss causes the remaining bonds of the under-coordinated atom to contract spontaneously associated with bond-strength gain or atomic potential well depression, which localizes electrons and enhances the
density of charge, mass, and energy in the relaxed region. The energy density rise in the relaxed region perturbs the Hamiltonian and the associated properties such as the band gap width, core-level energy, Stokes shift (electron–phonon interaction), and dielectric susceptibility. On the other hand, bond order loss lowers the cohesive energy of the under-coordinated atom, which dictates the thermodynamic process such as self-assembly growth, atomic vibration, thermal stability, and activation energies for atomic dislocation, diffusion, and chemical reaction.

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1.2.1. Basic Concepts

Involvement of interatomic interaction causes the performance of a solid, or a cluster of atoms, to vary from that of an isolated atom; adjustment of the relative number of the under-coordinated surface atoms provides an additional freedom that allows one to tune the properties of a nanosolid with respect to that of its bulk counterpart. Hence, contribution from the under-coordinated atoms and the involvement of interatomic interaction could be the starting points of consideration to bridge the gap between an isolated atom and a bulk solid in chemical and physical performance.

1.2.1.1. Intra-atomic Trapping

Electrons of a single atom confined by the intra-atomic trapping potential $V_{\text{atom}}(r)$ move around the central ion core in a standing-wave form inside the potential well. The $V_{\text{atom}}(r)$ describes the electron–nucleus interaction, and it takes a value that varies from several electronvolts to infinity, depending on the orbitals in which electrons are revolving. The Hamiltonian and the corresponding eigenwave functions and the eigenenergies for an electron in the isolated atom are given as

$$\hat{H}_0 = -\frac{\hbar^2 \nabla^2}{2m} + V_{\text{atom}}(r)$$

$$\phi_n(r) \propto \sin^2(k_n r)$$

and

$$E(n) = \hbar^2 k_n^2 / 2m; \quad k_n = 2n\pi / d_0, \quad n = 1, 2, 3, \ldots$$

(1.2)

the atomic diameter $d_0$ corresponds to the dimension of the potential well of the atom. The branch numbers ($n$) correspond to different energy levels. The energy separation between the nearest two levels depends on $(n+1)^2 - n^2 = 2n + 1$.

1.2.1.2. Interatomic Bonding and Intercluster Coupling

When two atoms or more joined as a whole, interatomic interaction comes into play, which causes the performance of a cluster of atoms to be different from that of an isolated atom.
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The interatomic bonding is essential to make a solid or even a liquid. Considering an assembly composed of \( n \) particles of mean size \( K_j \) and with each particle, there are \( N_j \) atoms, the total binding energy \( V_{\text{cry}}(r, n, N_j) \) is (30):

\[
V_{\text{cry}}(r, n, N_j) = \sum_n \sum_{l \neq i} \sum_i v(r_{li}) = \frac{n}{2} \left[ N_j \sum_{i=1} v(r_{ii}) + \sum_{k \neq j} V(K_{kj}) \right] \\
\approx \frac{n}{2} \left[ N_j^2 v(d_0) + nV(K_j) \right] \tag{1.3}
\]

The \( V_{\text{cry}}(r, n, N_j) \) sums over all \( N_j \) atoms and the \( n \) particles. The high order \( r_{li} \) is a certain fold of the nearest atomic spacing \( d_0 \). Interaction between the nearest clusters, \( k \) and \( j \), \( V(K_{kj}) \), is negligible if the \( K_{kj} \) is considerably large. Normally, the intercluster interaction, \( V(K_{kj}) \), is much weaker than the interatomic interaction, if the cluster is treated as an electric or a magnetic dipole of which the Van der Waals or the super-paramagnetic potentials dominate.

1.2.1.3. Hamiltonian and Energy Band

According to the band theory, the Hamiltonian for an electron inside a solid is in the form:

\[
\hat{H} = \hat{H}_0 + \hat{H}' = -\frac{\hbar^2 \nabla^2}{2m} + V_{\text{atom}}(r) + V_{\text{cry}}(r + R_C) \tag{1.4}
\]

where the \( \hat{H}_0 \) is the Hamiltonian for an isolated atom as given in Eq. 1.2. \( \hat{H}' = V_{\text{cry}}(r) = V_{\text{cry}}(r + R_C) \) is the periodic potential of the crystal, describing the interaction between the specific electron with the ion cores of all other atoms. The term of electron–electron interaction is treated in a mean field as a constant background from the first-order approximation. \( R_C \) is the lattice constant. According to the nearly free-electron approximation, the \( E_G \) between the valence and the conduction bands originates from the crystal potential. The width of the gap depends on the integral of the crystal potential in combination with the Bloch wave of the nearly free electron \( \phi(k_l, r) \):

\[
E_G = 2|V_1(k_l)| \quad \text{and} \quad V_1(k_l) = \langle \phi(k_l, r)|V(r + R_C)|\phi(k_l, r) \rangle \tag{1.5}
\]

where \( k_l \) is the wave-vector and \( k_l = 2l\pi/R_C \). Actually, the \( E_G \) is simply twice the first Fourier coefficient of the crystal potential.

As illustrated in Figure 1.1, the energy levels of an isolated atom will evolve into energy bands when interatomic bonding is involved. When two atoms are bonded together, such as \( H_2 \) dimer-like molecules, the single energy level of the initially
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Figure 1.1. The involvement of interatomic interaction evolves a single energy level to the energy band when a particle grows from a single atom to a bulk solid that contains \( N_j \) atoms. Indicated is the work function \( \phi \), band gap \( E_G \), core level shift \( \Delta E_c \), and bandwidth \( E_B \). The number of allowed sublevels in a certain band equals the number of atoms of the solid (33).

Isolated atom splits into two sublevels. The presence of interatomic interaction lowers the center of the two sublevels, which is called the core level shift. Increasing the number of atoms up to \( N_j \), the single energy level will expand into a band within which there are \( N_j \) sublevels.

What distinguishes a nanosolid from a bulk chunk is that for the former the \( N_j \) is accountable, whereas for the latter, the \( N_j \) is too large to be accounted despite the portion of the under-coordinated atoms in the surface skin. Therefore, the classic band theories are valid for a solid over the whole range of sizes or for containing any number of atoms. As detected with X-ray photoelectron spectroscopy (XPS), the density-of-states (DOS) of the valence region for a nanosolid exhibits band-like features rather than the discrete spectral lines of a single atom. If the \( N_j \) is sufficiently small, the separation between the sublevels is resolvable. The energy level spacing between the successive sublevels in the valence band, known as the Kubo gap (\( \delta_K = 4E_F/3N_j \)), decreases with the increase of the number of valence electrons of the system \( N_j \) (31). Where \( E_F \) is the Fermi energy of the bulk. Because of the presence of the \( \delta_K \) in an individual nanosolid, properties such as electron conductivity and magnetic susceptibility exhibit quantized features (32).

According to the tight-binding approximation, the energy dispersion of an electron in the \( v \)th core band follows the relation:

\[
E_v(k) = E_v(1) + \Delta E_v(\infty) + \Delta E_B(k_i, R_C, z) \\
= E_v(1) - \langle \beta + 2\alpha \rangle + 4\alpha \Omega(k_i, R_C, z) \tag{1.6}
\]

where

- \( E_v(1) = \langle \phi_v(r) | \hat{H}_0 | \phi_v(r) \rangle \) is the \( v \)th energy level of an isolated atom.
- \( \beta = -\langle \phi_v(r) | V_{\text{cry}}(r) | \phi_v(r) \rangle \) is the crystal potential effect on the specific core electron at site \( r \).
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\[ \alpha = -\langle \phi_v(r - R_C)V_{\text{cry}}(r - R_C)|\phi_v(r - R_C) \rangle \]

is the crystal potential effect on the coordinate neighboring electrons. For an fcc structure example, the structure factor \( \Omega(k_i, R_C) = \sum_z \sin^2(k_i R_C/2) \). The sum is over all contributing coordinates \( z \) surrounding the specific atom in the solid.

Equations 1.5 and 1.6 indicate that the \( \Delta E_v(\infty) = -(\beta + 2\alpha) \) of the \( E_v(1) \) and the bandwidth \( \Delta E_B \) (last term in Eq. 5.16) are all functions of interatomic interaction or crystal potential. Any perturbation to the crystal potential will vary these quantities accordingly as the change of the Block wavefunction is negligible in the first-order approximation. The band structure has nothing to do with the actual occupancy of the particular orbitals or events such as electron-hole pair creation or recombination, or the processes of PL and PA that involve the electron–phonon coupling effect. Without interatomic interaction, neither the \( E_v \) expansion nor the core-level shift would be possible; without the interatomic binding, neither a solid nor even a liquid would form.

If one intends to modify the properties of a solid, one has to find ways of modulating the crystal potential physically or chemically. Bond nature alteration by chemical reaction or bond length relaxation by size reduction, as discussed in the following sections, will be the effective ways of modulating the interatomic potential.

1.2.1.4. Atomic Cohesive Energy and Thermal Stability

Another key concept is the cohesive energy per discrete atom. The binding energy density per unit volume contributes to the Hamiltonian that determines the entire band structure and related properties, whereas the atomic cohesive energy determines the activation energy for thermally and mechanically activated processes, including self-assembly growth, phase transition, solid–liquid transition, evaporation, atomic dislocation, diffusion, and chemical reaction.

The cohesive energy (\( E_{\text{coh}} \)) of a solid containing \( N_j \) atoms equals to the energy dividing the crystal into individually isolated atoms by breaking all bonds of the solid. If no atomic CN reduction is considered, the \( E_{\text{coh}} \) is the sum of bond energy over all \( z_b \) coordinates of all \( N_j \) atoms:

\[
E_{\text{coh}}(N_j) = \sum_{N_j} \sum_{z_i} E_i \cong N_j z_b E_b = N_j E_B \tag{1.7}
\]

The cohesive energy for a single atom \( E_B \) is the sum of the single bond energy \( E_b \) over the atomic CN, \( E_B = z_b E_b \). One may consider a thermally activated process such as phase transition in which all bonds are loosened to a certain extent due to thermal activation. The energy required for such a process is a certain portion of the atomic \( E_B \) although the exact portion may change from process to process. If one considers the relative change to the bulk value, the portion will not be accounted. This approximation is convenient in practice, as one should be concerned with the origins and the trends of changes. Therefore, bulk properties such as the thermal stability of a solid could be related directly to the atomic cohesive energy—the product of the bond number and bond energy of the specific atom.
1.2.2. Boundary Conditions

1.2.2.1. Barrier Confinement vs. Quantum Uncertainty  The termination of lattice periodicity in the surface normal direction has two effects. One is the creation of the surface potential barrier (SPB), work function, or contact potential, and the other is the reduction of the atomic CN. The SPB is the intrinsic feature of a surface, which confines only electrons that are freely moving inside the solid. However, the SPB has nothing to do with the strongly localized electrons in deeper core bands or with those form sharing electron pairs in a bond. The localized electrons do not suffer such barrier confinement at all as the localization length is far shorter than the particle size.

According to the principle of quantum uncertainty, reducing the dimension ($D$) of the space inside which energetic particles are moving increases the fluctuation, rather than the average value, of the momentum ($p$) or kinetic energy ($E_k$) of the moving particles:

\[
\Delta p D \geq \hbar/2
\]

\[
p = \bar{p} \pm \Delta p
\]

\[
E_k = \bar{p}^2/(2\mu)
\]

where $\hbar$ being the Plank constant corresponds to the minimal quanta in energy and momentum spaces and $\mu$ is the effective mass of the moving particles. The kinetic energy of a freely moving carrier is increased by a negligible amount due to the confinement effect on the fluctuation that follows the principle of quantum uncertainty.

1.2.2.2. Atomic CN Reduction  The atomic CN reduction is referred to the standard value of 12 in the bulk of an fcc structure irrespective of the bond nature or the crystal structure. Atomic CN reduction is referred to an atom with a coordinate less than the standard value of 12. The CN is 2 for an atom in the interior of a monatomic chain or an atom at the open end of a single-walled carbon nanotube (CNT); while in the CNT wall, the CN is 3. For an atom in the fcc unit cell, the CN varies from site to site. The CN of an atom at the edge or corner differences from the CN of an atom in the plane or the central of the unit cell. Atoms with deformed bond lengths or deviated angles in the CNT are the same as those in amorphous states that are characterized with the band tail states (34). For example, the effective CN of an atom in diamond tetrahedron is the same as that in an fcc structure as a tetrahedron unit cell is an interlock of two fcc unit cells. The CN of an atom in a highly curved surface is even lower compared with the CN of an atom at a flat surface. For a negatively curved surface (such as the inner side of a pore or a bubble), the CN may be slightly higher than that of an atom at the flat surface. Therefore, from the atomic CN reduction point of view, there is no substantial difference in nature among a nanosolid, a nanopore, and a flat surface. This premise can be extended to the structural defects or defaults, such as voids; atoms surrounding these defects also suffer from CN reduction. Unlike
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1.2.3. Surface-to-Volume Ratio

It is easy to derive the volume or number ratio of a certain atomic layer, denoted $i$, to that of the entire solid by differentiating the natural logarithm of the volume:

$$\gamma_{ij} = \frac{N_i}{N_j} = \frac{V_i}{V_j} = \frac{d\ln(V_j)}{dR_j} = \frac{\tau d c_i}{K_j}$$

(1.9)

where $K_j = R_j/d_0$ is the dimensionless form of size, which is the number of atoms lined along the radius of a spherical dot ($\tau = 3$), a rod ($\tau = 2$), or cross the thickness of a thin plate ($\tau = 1$). The volume of a solid is proportional to $R_j^\tau$. For a hollow system, the $\gamma_{ij}$ should count both external and internal sides of the hollow structure.

With reducing particle size, the performance of surface atoms becomes dominant because at the lower end of the size limit, ($K_j \to \tau c_i$)$\gamma_1$ approaches unity. At $K_j = 1$, the solid will degenerate into an isolated atom. Therefore, the $\gamma_{ij}$ covers the whole range of sizes and various shapes. The definition of dimensionality ($\tau$) herein differs from the convention in transport or quantum confinement considerations in which a nanosphere is zero-dimension (quantum dot), a rod as one dimension (quantum wire), and a plate two dimension (quantum well). If we count atom by atom, the number ratio and the property change will show quantized oscillation features at smaller sizes, which varies from structure to structure (35).

1.2.4. BOLS Correlation

1.2.4.1. Bond Order-Length Correlation

As the consequence of bond order loss, the remaining bonds of the under-coordinated atoms contract spontaneously. As asserted by Goldschmidt (36) and Pauling (37), the ionic and the metallic radius of the atom would shrink spontaneously if the CN of an atom is reduced. The CN reduction-induced bond contraction is independent of the nature of the specific bond or structural phases (38). For instances, a 10% contraction of spacing between the first and second atomic surface layers has been detected in the liquid phase of Sn, Hg, Ga, and In (39). A substitutional dopant of As impurity has induced 8% bond contraction around the impurity at the Te sublattice in CdTe has also been observed using extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge spectroscopy (XANES) (40). Therefore, bond order loss-induced bond contraction is universal.

Figure 1.2 illustrates the CN dependence of bond length. The solid curve $c(z_i$)formulates the Goldschmidt premise, which states that an ionic radius contracts by 12%, 4%, and 3%, if the CN of the atom reduces from 12 to 4, 6 and 8, respectively. Feibelman (41) has noted a 30% contraction of the dimer bond of Ti and Zr, and a 40% contraction of the dimer-bond of Vanadium, which is also in line with the formulation.
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Figure 1.2. Illustration of the BOLS correlation. Solid curve in (a) is the contraction coefficient $c_i$ derived from the notations of Goldschmidt (36) (open circles) and Feibelman (41) (open square). As a spontaneous process of bond contraction, the bond energy at equilibrium atomic separation will rise in absolute energy $E_i = c_i^{-m}E_b$. The $m$ is a parameter that represents the nature of the bond. However, the atomic cohesive energy $z_iE_i$ changes with both the $m$ and the $z_i$ values. (b) Atomic CN reduction modified pairing potential energy. CN reduction causes the bond to contract from one unit (in $d_0$) to $c_i$, and the cohesive energy per coordinate increases from one unit to $c_i^{-m}$ unit. Separation between $E_i(T)$ and $E_i(0)$ is the thermal vibration energy. Separation between $E_i(T_{m,i})$ and $E_i(T)$ corresponds to melting energy per bond at $T$, which dominates the mechanical strength. $T_{m,j}$ is the melting point. $\eta_{2i}$ is $1/z_i$ fold energy atomizing an atom in molten state.

1.2.4.2. Bond Length-Strength Correlation As the atomic CN reduction-induced bond contraction is a spontaneous process, the system energy will be lowered with an association of bond strength gain. The contraction coefficient and the associated bond energy gain form the subject of the BOLS correlation mechanism that is formulated as

\[
\begin{align*}
    c_i(z_i) &= d_i/d_0 = 2/[1 + \exp((12 - z_i)/(8z_i))] \quad \text{(BOLS-coefficient)} \\
    E_i &= c_i^{-m}E_b \quad \text{(Single-bond-energy)} \\
    E_{B,i} &= z_iE_i \quad \text{(Atomic-cohesive-energy)}
\end{align*}
\]

Subscript $i$ denotes an atom in the $i$th atomic layer, which is counted up to three from the outermost atomic layer to the center of the solid as no CN-reduction is expected for $i > 3$. The index $m$ is a key indicator for the nature of the bond. Experience (42) revealed that for Au, Ag, and Ni metals, $m \equiv 1$; for alloys and compounds, $m$ is around four; for C and Si, the $m$ has been optimized to be 2.56 (43) and 4.88 (44), respectively. The $m$ value may vary if the bond nature evolves with atomic CN (45). If the surface bond expands in cases, we simply expand the $c_i$ from a value that is
smaller than unity to greater, and the \( m \) value from positive to negative to represent the spontaneous process of which the system energy is minimized. The \( c_i(z_i) \) depends on the effective CN rather than a certain order of CN. The \( z_i \) also varies with the particle size due to the change of the surface curvature. The \( z_i \) takes the following values \((44)\):

\[
z_1 = \begin{cases} 
4(1 - 0.75/K_j) & \text{curved-surface} \\
4 & \text{flat-surface}
\end{cases}
\]  

Generally, \( z_2 = 6 \) and \( z_3 = 8 \) or 12.

Figure 1.2b illustrates schematically the BOLS correlation using a simple interatomic pairing potential, \( u(r) \). When the CN of an atom is reduced, the equilibrium atomic distance will contract from one unit (in \( d_0 \)) to \( c_i \) and the cohesive energy of the shortened bond will increase in magnitude from one unit (in \( E_b \)) to \( c_i^{-m} \). The solid and the broken \( u(r) \) curves correspond to the pairing potential with and without CN reduction. The BOLS correlation has nothing to do with the particular form of the pairing potential as the approach involves only atomic distance at equilibrium. The bond length-strength correlation herein is consistent with the trend reported by Bahn and Jacobsen \((46)\) although the extent of bond contraction and energy enhancement therein vary from situation to situation.

Several characteristic energies in Figure 1.2b correspond to the following facts:

1. \( T_{m,i} \), being the local melting point, is proportional to the cohesive energy \( z_iE_i(0) \) per atom with \( z_i \) coordinate \((47)\).

2. Separation between \( E = 0 \) and \( E_i(T) \), or \( \eta_{1i}(T_{m,i} - T) + \eta_{2i} \), corresponds to the cohesive energy per coordinate \( E_i \) at \( T \), being energy required for bond fracture under mechanical or thermal stimulus. \( \eta_{1i} \) is the specific heat per coordinate.

3. The separation between \( E = 0 \) and \( E_i(T_m) \), or \( \eta_{2i} \), is the \( 1/z_i \) fold energy that is required for atomization of an atom in molten state.

4. The spacing between \( E_i(T) \) and \( E_i(0) \) is the vibration energy purely due to thermal excitation.

5. The energy contributing to mechanical strength is the separation between \( E_i(T_m) \) and the \( E_i(T) \), as a molten phase is extremely soft and highly compressible \((49)\).

Values of \( \eta_{1i} \) and \( \eta_{2i} \) can be obtained with the known \( c_i^{-m} \) and the bulk \( \eta_{1b} \) and \( \eta_{2b} \) values that vary only with crystal structures as given in Table 1.1.

### 1.2.4.3. Densification of Mass, Charge, and Energy

Figure 1.3 compares the potential well in the QC convention with that of the BOLS for a nanosolid. The QC convention extends the monotrapping potential of an isolated atom by
TABLE 1.1. Relation Between the Bond Energy $E_b$ and the $T_m$ of Various Structures (24). $\eta_{2b} < 0$ for an fcc Structure Means that the Energy Required for Breaking All Bonds of an Atom in Molten State is Included in the Term of $\eta_{1b}T_m$, and Therefore, the $\eta_{2b}$ Exaggerates the Specific Heat per CN.

<table>
<thead>
<tr>
<th>$E_b = \eta_{1b}T_m + \eta_{2b}$</th>
<th>fcc</th>
<th>bcc</th>
<th>Diamond Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta_{1b}$ ($10^{-4}$ eV/K)</td>
<td>5.542</td>
<td>5.919</td>
<td>5.736</td>
</tr>
<tr>
<td>$\eta_{2b}$ (eV)</td>
<td>-0.24</td>
<td>0.0364</td>
<td>1.29</td>
</tr>
</tbody>
</table>

expanding the size from $d_0$ to $D$. BOLS scheme covers contribution from individual atoms that are described with multi-trapping-center potential wells and the effect of atomic CN reduction on the surface skin. Atomic CN reduction-induced bond-strength gain depresses the potential well of trapping in the surface skin. Therefore, the density of charge, energy, and mass in the relaxed surface region are higher than other sites inside the solid. Consequently, surface stress that is in

Figure 1.3. Schematic illustration of conventional quantum well (a) with a monotrapping center extended from that of a single atom, and the BOLS-derived nanosolid potential (b) with multi-trap centers and CN reduction-induced features. In the relaxed surface region, the density of charge, energy, and mass will be higher than other sites due to atomic CN reduction.
the dimension of energy density will increase in the relaxed region. Electrons in the relaxed region are more localized because of the depression of the potential well of trapping, which lowers the work function and conductivity in the surface region due to boundary scattering (50, 51), but it enhances the angular momentum of the surface atoms (35).

1.2.4.4. Oxide Long-Range Interaction For an oxide nanosolid, the long-order dipole–dipole interaction is involved, which may change the Madelung potential in the ionic oxide nanosolid (52). The value of Madelung potential shifts their effective electronic levels, thus renormalizing their electronegativity. The concept of electronegativity in the oxide nanosolid is very useful for discussing the ability of under-coordinated atoms to bind to adatoms or molecules. The Madelung potential value also enters the energetic balance that fixes the local atomic arrangement, and its long-range character may induce peculiar effects, for example, the stabilization of noncompact structures especially in small clusters. These aspects are akin to insulating compounds with a non-negligible ionic character of the oxygenation bonding and are not met in metals or compound semiconductors in low dimensionality.

The immediate effect of long-range interaction is its contribution to the atomic cohesive energy that dominates the ferroelectric properties of oxides (53). For a spherical dot with radius $R = K d$, we need to consider the interaction between the specific central atom and its surrounding neighbors within the critical volume $V_C = 4\pi K^3_C/3$, in addition to the BOLS correlation in the surface region, as illustrated in Figure 1.4. The ferroelectric property drops down from the bulk value to a value smaller than $5/16$ (estimated from Figure 1.4) when one goes from the central atom to the edge along the radius to the correlation radius $K_C$. If the surrounding volume of the central atom is smaller than the critical $V_C$, the ferroelectric feature of this central atom attenuates; otherwise, the bulk value remains. For an atom in the $i$th surface layer, the number of the lost exchange bonds is proportional to the volume $V_{vac}$ that is the volume difference between the two caps of the $V_C$-sized spheres as illustrated in Figure 1.4a. Therefore, the relative change of the ferroelectric exchange energy of an atom in the $i$th atomic layer compared with that of a bulk atom becomes

$$\frac{\Delta E_{exc,i}}{E_{exc}(\infty)} = \frac{V_C - V_{vac}}{V_C} - 1 = -\frac{V_{vac}}{V_C}$$  \hspace{1cm} (1.12)$$

1.2.5. Shape-and-Size Dependency

1.2.5.1. Scaling Relation Generally, the mean relative change of a measurable quantity of a nanosolid containing $N_j$ atoms, with dimension $K_j$, can be expressed as $Q(K_j)$ and as $Q(\infty)$ for the same solid without contribution from bond order loss. The correlation between the $Q(K_j)$ and $Q(\infty) = N_j q_0$ and the relative change of $Q$
Figure 1.4. (a) Schematic illustration of the long-range exchange bonds lost in an atom in a spherical oxide nanosolid with radius \( K \) (\( K = R/d \) is the number of atoms of size \( d \) lined along the radius \( R \) of a sphere or cross a thin plate of \( R \) thick). \( K_C \) is the critical correlation radius. The volume loss \( V_{\text{vac}} \) (the shaded portion) is calculated by differencing the volumes of the two spherical caps:

\[
V_{\text{vac}} = \pi (K_C + K_I - K \cos \theta)^2 \left( K_C - \frac{K_C + K_I - K \cos \theta}{3} \right) - \pi (K - K \cos \theta)^2 \left( K - \frac{K - K \cos \theta}{3} \right)
\]

where the angle \( \theta \) is determined by the triangle \( O_1O_2A \). (b) Correlation radius \( K_C \) dependence of the atomic cohesive energy. For the \( K_C = 5 \) example, the BOLS lowers the \( E_B \) by \(-41.1\%\) (follows the curve in Figure 1.4a), and the long-range bond loss contribution that is a constant lowers the \( E_B \) by \(-53\%\) (53).

---

\( V_{\text{vac}} \) — volume loss
\( K_C \) — critical correlation radius
\( K_I \) — number of atoms of size \( d \) lined along radius \( R \)
\( \theta \) — angle determined by triangle \( O_1O_2A \)
\( E_B \) — atomic cohesive energy

---

The volume loss \( V_{\text{vac}} \) is calculated by differencing the volumes of the two spherical caps.

\[
V_{\text{vac}} = \pi \left( K_C + K_I - K \cos \theta \right)^2 \left( K_C - \frac{K_C + K_I - K \cos \theta}{3} \right) - \pi \left( K - K \cos \theta \right)^2 \left( K - \frac{K - K \cos \theta}{3} \right)
\]
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caused by bond order loss is given as

\[ Q(K_j) = N_j q_0 + N_s (q_s - q_0) \]
\[ \frac{\Delta Q(K_j)}{Q(\infty)} = \frac{Q(K_j) - Q(\infty)}{Q(\infty)} = \frac{N_s}{N_j} \left( \frac{q_s}{q_0} - 1 \right) \]
\[ = \sum_{i \leq 3} \gamma_{ij} \frac{\Delta q_i}{q_0} = \Delta_{ij} \quad (1.13) \]

The weighting factor \( \gamma_{ij} \) represents the geometrical contributions from dimension \( K_j \) and dimensionality \( \tau \) of the solid, which determines the magnitude of change. The quantity \( \Delta q_i/q_0 \) is the origin of change. The \( \sum_{i \leq 3} \gamma_{ij} \) drops in a \( K_j^{-1} \) fashion from unity to infinitely small when the solid grows from atomic level to infinitely large. For a spherical dot at the lower end of the size limit, \( K_j = 1.5 \) (\( K_j d_0 = 0.43 \) nm for an Au spherical dot example), \( \gamma_1 = 2, \gamma_{2j} = 1, \) and \( \gamma_{3j} = 0 \), which is identical in situation to an atom in a monatomic chain (MC) despite the orientation of the two interatomic bonds. Actually, the bond orientation is not involved in the modeling iteration. Therefore, the performance of an atom in the smallest nanosolid is a mimic of an atom in an MC of the same element without the presence of an external stimulus such as stretching or heating. At the lower end of the size limit, the property change of a nanosolid relates directly to the behavior of a single bond.

Generally, experimentally observed size-and-shape dependence of a detectable quantity follows a scaling relation. Equilibrating the scaling relation to Eq. 1.10, one has

\[ Q(K_j) - Q(\infty) = \begin{cases} \frac{bK_j^{-1}}{Q(\infty)} \times K_j & \text{(measurement)} \\ \frac{Q(\infty)}{Q(\infty)} & \text{(theory)} \end{cases} \]

where the slope \( b \equiv Q(\infty) \times \Delta_{ij} \times K_j \equiv \text{constant} \) is the focus of various modeling pursues. The \( \Delta_{ij} \propto K_j^{-1} \) varies simply with the \( \gamma_{ij}(\tau, K_j, c_i) \) if the functional dependence of \( q(z_i, c_i, m) \) on the atomic CN, bond length, and bond energy is given.

1.2.5.2. Cohesive Energy Modification

The heat energy required for loosening an atom is a certain portion of the atomic \( E_B \) that varies with not only the atomic CN but also the bond strength. The variation of the mean \( E_B \) with size is responsible for the fall (supercooling) or rise (superheating) of the \( T_C \) (critical temperature for melting, phase transition, or evaporation) of a surface and a nanosolid. The \( E_B \) is also responsible for other thermally activated behaviors such as phase transition, catalytic reactivity, crystal structural stability, alloy formation (segregation and diffusion), and stability of electrically charged particles (Coulomb explosion). The cohesive energy also determines crystal growth and atomic diffusion and atomic gliding displacement that determines the ductility of nanosolids.

Considering both the BOLS correlation in the surface region and the long-range bond loss, we have a universal form for the cohesive energy suppression for an oxide
nanosolid:

\[
\frac{\Delta E_B(K_j)}{E_B(\infty)} = \begin{cases} 
\sum_{i \leq 3} \gamma_{ij}(z_{ib}c_i^{-1} - 1) = \Delta_B & \text{(BOLS)} \\
\sum_{i \leq K_C} \gamma_{ij} \left(-\frac{V_{vac}}{V_C}\right) + \Delta_B = \Delta_{COH} & \text{(BOLS + long-range)}
\end{cases}
\]

For the short spin–spin interaction, it is sufficient to sum over the outermost three atomic layers; for a ferroelectric and a superconductive solid, the sum should be within the sphere of radius \(K_C\). The BOLS correlation considers only contribution from atoms in the shells of the surface skin, whereas the long-range contribution involves the concept of correlation radius that is used in ferroelectric systems. The BOLS contribution is obtained by considering the shell structures:

\[
\langle E_{coh}(N_j) \rangle = N_jz_bE_b + \sum_{i \leq 3} N_i(z_iE_i - z_bE_b)
\]

\[
= N_jE_B(\infty) + \sum_{i \leq 3} N_i z_bE_b(z_{ib}E_{ib} - 1)
\]

\[
= E_{coh}(\infty) \left[1 + \sum_{i \leq 3} \gamma_{ij}(z_{ib}c_i^{-m} - 1)\right] = E_{coh}(\infty)(1 + \Delta_B)
\]

or

\[
\frac{\Delta E_B(K_j)}{E_B(\infty)} = \sum_{i \leq 3} \gamma_{ij}(z_{ib}c_i^{-m} - 1) = \Delta_B
\]

where \(E_{coh}(\infty) = N_jz_bE_b\) represents the ideal situation without \(CN\) reduction. The \(z_{ib} = z_i/z_b\) is the normalized \(CN\), and the \(E_{ib} = E_i/E_b \cong c_i^{-m}\) is the normalized binding energy per coordinate of a surface atom. For an isolated surface, \(\Delta_B < 0\); for an intermixed interface, \(\Delta_B\) may be positive depending on the strength of interfacial interaction. Therefore, the relative change of \(T_C(K_j)\) and activation energy \(E_A(K_j)\) for thermally and mechanically activated process can be expressed as

\[
\frac{\Delta T_C(K_j)}{T_C(\infty)} = \frac{\Delta E_A(K_j)}{E_A(\infty)} = \frac{\Delta E_B(K_j)}{E_B(\infty)} = \Delta_B(K_j)
\]

Interestingly, the critical temperature for sensing operation could be lowered from 970 to 310 K of SrTiO\(_3\) by ball milling to obtain 27 nm-sized powders (54). The resistivity of the SrTiO\(_3\) increases when the SrTiO\(_3\) particle size is decreased (55). Decreasing the particle sizes of ferroelectric BaTiO\(_3\) could lower the \(T_C\) to 400 K and the refractive index (dielectric constant) and, hence, the transmittance of BaTiO\(_3\) infilled SiO\(_2\) photonic crystals, as a consequence (56,57). The suppression of the
critical temperatures for sensing and phase transition results and the modulation of resistivity and refractive index could be consequences of energy densification and cohesive energy suppression in the surface skin.

1.2.5.3. Hamiltonian Perturbation The perturbation to the energy density in the relaxed region that contributes to the Hamiltonian upon assembly of the nanosolids is

\[ \Delta H(K_j) = \frac{V\text{cry}(r,n,N_j)}{V\text{cry}(d_0,n,N_j)} - 1 \]

\[ = \sum_{i=3}^\infty \frac{\Delta v(d_i)}{v(d_0)} + \delta_{ij} \]

\[ = \sum_{i=3}^\infty \gamma_{ij} (c_i^m - 1) + \delta_{ij} \]

where

\[ \delta_{ij} = \frac{nV(K_j)}{N_j^2 v(d_0)} \]  

(1.18)

With the perturbation, the \( \hat{H}' \) in Eq. 1.4 becomes \( \hat{H}'(\Delta H) = V\text{cry}(r)[1 + \Delta_H(K_j)] \), which dictates the change of not only the \( E_G \) width, but also the core-level energy:

\[ \frac{\Delta E_G(K_j)}{E_G(\infty)} = \frac{\Delta E_v(K_j)}{E_v(\infty)} = \Delta_H(K_j) \]

(1.19)

where \( \Delta E_v(K_j) = E_v(K_j) - E_v(1) \). This relation also applies to other quantities such as the bandwidth and band tails (33).

Most strikingly, without triggering electron–phonon interaction or electron–hole generation, the scanning tunneling microscopy/spectroscopy (STM/S) measurement at low temperature revealed that the \( E_G \) of Si nanorod varies from 1.1 to 3.5 eV with decreasing the rod diameter from 7.0 to 1.3 nm associated with \( \sim 12\% \) Si–Si bond contraction from the bulk value (0.263 nm) to \( \sim 0.23 \) nm. The STS findings concur excitingly with the BOLS premise: CN reduction shortens the remaining bonds of the under-coordinated atoms spontaneously with an association of \( E_G \) expansion.

1.2.5.4. Electron–Phonon Coupling The electron–phonon (e–p) interaction contributes to the processes of photoemission, photoabsorption, photoconduction, and electron polarization that dominates the static dielectric constant. Figure 1.5 illustrates the effect of e–p coupling and crystal binding on the energy of photoluminescence and absorbance \( E_{PL} \) and \( E_{PA} \). The energies of the ground state (\( E_1 \)) and the excited
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Figure 1.5. Mechanisms for $E_{PA}$ and $E_{PL}$ of a nano-semiconductor, involving crystal binding ($E_G$) and electron-phonon coupling ($W$). Insertion illustrates the Stokes shift from $E_{PA}$ to $E_{PL}$. Electron is excited by absorbing a photon with energy $E_G + W$ from the ground minimum to the excited state, then undergoes a thermalization to the excited minimum, and then transmits to the ground emitting a photon with energy $E_G - W$ (58).

The vertical distance between the two minima is the true $E_G$ that depends uniquely on the crystal potential. The lateral displacement ($q_0$) originates from the e–p coupling that can be strengthened by lattice contraction. Therefore, the blue shift in the $E_{PL}$ and in the $E_{PA}$ is the joint contribution from crystal binding and e–p coupling.

In the process of carrier formation, or electron polarization (34), an electron is excited by absorbing a photon with $E_G + W$ energy from the ground minimum to the excited state with creation of an electron-hole pair. The excited electron then undergoes a thermalization and moves to the minimum of the excited state, and eventually it transmits to the ground and combines with the hole. The carrier recombination is associated with emission of a photon with energy $E_{PL} = E_G - W$. The transition state ($E_2$) are expressed in parabola forms (34):

\[
\begin{align*}
E_1(q) &= Aq^2 \\
E_2(q) &= A(q - q_0)^2 + E_G
\end{align*}
\]  

Constant $A$ is the slope of the parabolas. The $q$ is in the dimension of wave-vector.
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processes (e-h pair production and recombination) follow the rule of momentum and energy conservation, although the conservation law may be subject to relaxation for the short-ordered nanosolid. Relaxation of the conservation law is responsible for the broad peaks in the PA and PL.

The insertion illustrates the Stokes shift, \(2W = 2Aq_0^2\), or the separation from \(E_{PL}\) to \(E_{PA}\). The \(q_0\) is inversely proportional to atomic distance \(d_i\), and hence, \(W_i = A/(c_i d_i)^2\), in the surface region. Based on this premise, the blue shift of the \(E_{PL}\), the \(E_{PA}\), and the Stokes shift can be correlated to the CN reduction-induced bond contraction (58).

\[
\begin{align*}
\frac{\Delta E_{PL}(K_j)}{E_{PL}(\infty)} & = \frac{\Delta E_G(K_j)}{E_G(\infty)} \mp \frac{\Delta W(K_j)}{W(\infty)} \equiv \sum_{i \geq 3} \gamma_i[(c_i^{-m} - 1) \mp B(c_i^{-2} - 1)] \\
& = \Delta H \mp B\Delta e_p
\end{align*}
\]

\(\Delta H \mp B\Delta e_p\)

\(B = \frac{A}{E_G(\infty)d^2} ; \frac{W(\infty)}{E_G(\infty)} \approx 0.007 \approx 1.12\)

Compared with the bulk \(E_G(\infty) = 1.12\) eV for silicon, the \(W(\infty) \sim 0.007\) eV obtained using tight-binding calculations (59) is negligible. One can easily calculate the size-dependent \(E_{PL}\), \(E_{PA}\), and \(E_G(\infty)\) using Eq. 21. Fitting the measured data gives the values of \(m\) and \(A\) for a specific semiconductor.

1.2.5.5. Mechanical Strength

The mechanical yield strength is the strain-induced internal energy deviation that is proportional to energy density or the sum of bond energy per unit volume (17). Considering the contribution from heating, the strength (stress, flow strength), the Young’s modulus, and the compressibility (under compressive stress) or extensibility (under tensile stress) at a given temperature can be expressed by

\[
P_i(z_i, T) = -\frac{\partial u(r, T)}{\partial V}\Bigg|_{d_i,T} \sim \frac{N_i \eta_i (T_{m,i} - T)}{d_i^2} \\
\beta_i(z_i, T) = -\frac{\partial V}{\partial P}|_T = [Y_i(z_i, T)]^{-1} = \left[ -V \frac{\partial u^{(1)}(r, T)}{\partial V} \right]^{-1}|_T \\
= \frac{d_i^2}{N_i \eta_i (T_{m,i} - T)} = [P_i(z_i, T)]^{-1}
\]

\(\beta\) is an inverse of dimension of the Young’s modulus or the hardness. \(N_j\) is the total number of bonds in \(d^3\) volume. If calibrated with the bulk value at \(T\) and using the size-dependent specific heat, melting point, and lattice parameter, the temperature,
bond nature, and size-dependent strength and compressibility of a nanosolid will be

\[
\frac{P(K_j, T)}{P(\infty, T)} = \frac{Y(K_j, T)}{Y(\infty, T)} = \frac{\beta(\infty, T) \eta_1(\infty)}{\beta(K_j, T) d(K_j)} \left( \frac{d(\infty)}{d(K_j)} \right)^3 \times \frac{T_m(K_j, m) - T}{T_m(\infty) - T} \quad (1.23)
\]

The bond number density between the circumferential neighboring atomic layers does not change upon relaxation \((N_f = N_0)\). Equation 1.23 indicates that the mechanical strength is dictated by the value of \(T_m(K_j) - T\) and the specific heat per bond. At \(T\) far below the \(T_m\), a surface or a nanostructure is harder than the bulk interior. However, the \(T_m\) drops with size \(K_j\), and therefore, the surface or nanosolid become softer when the \(T_m(K_j) - T\) value becomes smaller. This relation has led to quantification of the surface mechanical strength, the breaking limit of a single bond in monatomic chain, and the anomalous Hall–Petch relationship in which the mechanical strength decreases with size in a fashion of \(D^{-0.5}\) and then deviates at the order of 10 nm from the Hall–Petch relationship \((49)\).

### 1.2.6. Summary

If one could establish the functional dependence of a detectable quantity \(Q\) on atomic separation or its derivatives, the size dependence of the quantity \(Q\) is then certain. One can hence design a nanomaterial with desired functions based on such prediction. The physical quantities of a solid can be normally categorized as follows:

1. Quantities that are directly related to bond length, such as the mean lattice constant, atomic density, and binding energy.
2. Quantities that depend on the cohesive energy per discrete atom, \(E_{B,i} = z_i E_i\), such as self-organization growth; thermal stability; Coulomb blockade; critical temperature for liquidation, evaporation, and phase transition of a nanosolid; and the activation energy for atomic dislocation, diffusion, and bond unfolding \((60)\).
3. Properties that vary with the binding energy density in the relaxed continuum region such as the Hamiltonian that determine the entire band structure and related properties such as band gap, core-level energy, photo-absorption, and photo-emission.
4. Properties that are contributed from the joint effect of the binding energy density and atomic cohesive energy such as mechanical strength, Young’s modulus, surface energy, surface stress, extensibility and compressibility of a nanosolid, as well as the magnetic performance of a ferromagnetic nanosolid.

Using the scaling relation and the BOLS correlation, we may derive solutions to predict the size and shape dependence of various properties. Typical samples are given in Table 1.2 and Figure 1.6.
TABLE 1.2. Summary of Functional Dependence of Various Quantities on Particle Size and Derived Information.

<table>
<thead>
<tr>
<th>Quantity Q</th>
<th>( \Delta Q(K_j)/Q(\infty) = \Delta_q(K_j) )</th>
<th>Refs.</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant ((d))</td>
<td>( \sum_{i \leq 3} \gamma_i (c_i - 1) )</td>
<td>42</td>
<td>Only outermost three atomic layers contribute</td>
</tr>
<tr>
<td>Bond energy ((E_i))</td>
<td>( \sum_{i \leq 3} \gamma_i (c_i^{m} - 1) = \Delta H )</td>
<td>29, 33</td>
<td>( \Delta H )—Hamiltonian perturbation</td>
</tr>
<tr>
<td>Band gap ((E_G))</td>
<td>( \sum_{i \leq 3} \gamma_i (c_i^{m} - 1) = \Delta H )</td>
<td>29, 33</td>
<td>( \Delta H )—Hamiltonian perturbation</td>
</tr>
<tr>
<td>Core-level shift ((\Delta E_v))</td>
<td>( \sum_{i \leq 3} \gamma_i (c_i^{m} - 1) = \Delta H )</td>
<td>29, 33</td>
<td>( \Delta H )—Hamiltonian perturbation</td>
</tr>
<tr>
<td>Electron–phonon coupling energy ((W))</td>
<td>( B \sum_{i \leq 3} \gamma_i (c_i^{m} - 1) = B\Delta_{e-p} )</td>
<td>58</td>
<td>( B )-constant</td>
</tr>
<tr>
<td>Photoemission and photoabsorption energy ((E_{PL}, E_{PA}))</td>
<td>( \Delta H = B\Delta_{e-p} )</td>
<td>58</td>
<td>( E_G = (E_{PA} + E_{PL})/2 )</td>
</tr>
<tr>
<td>Critical temperature for phase transition ((T_C)); activation energy for thermally and mechanically activated processes</td>
<td>( \sum_{i \leq 3} \gamma_i (c_i^{m} - 1) = \Delta B ) \text{(Ferromagnetic)}&lt;br&gt;( \sum_{i \leq K_C} \gamma_i \left( \frac{-V_{\text{vac}}}{V_C} \right) + \Delta B = \Delta_{\text{COH}} ) \text{(else)}</td>
<td>47, 53</td>
<td>( \Delta B )—atomic cohesive perturbation&lt;br&gt;( V_{\text{vac}} )—volume loss&lt;br&gt;( V_C )—correlation volume</td>
</tr>
<tr>
<td>Quantity Q</td>
<td>( \Delta Q(K_j)/Q(\infty) = \Delta_d(K_j) )</td>
<td>Refs.</td>
<td>Comments</td>
</tr>
<tr>
<td>------------</td>
<td>---------------------------------</td>
<td>-------</td>
<td>-----------</td>
</tr>
<tr>
<td>Mechanical strength and Yung’s modulus of monatomic bond ((P, Y))</td>
<td>( \frac{\eta_1 d^3 (T_{m,j} - T)}{\eta_1 d^3 (T_m(\infty) - T)} - 1 )</td>
<td>61</td>
<td>( \eta_1 )—specific heat per bond ( T_m )—melting point</td>
</tr>
<tr>
<td>Inverse Hall–Petch relation; solid–semisolid–liquid transition</td>
<td>( \frac{\eta_1 (K_j) d^3 (T_m(K_j) - T)}{\eta_1 d^3 (K_j)(T_m(\infty) - T)} - 1 )</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td>Optical phonon frequency ((\omega))</td>
<td>( \sum_{i \leq 3} \gamma_j (\varepsilon_{\delta} e_i^{-(m/2+1)} - 1) )</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>Fermi level</td>
<td>( \sum_{i \leq 3} \gamma_j (c_i^{-2\tau/3} - 1) )</td>
<td>63, 64</td>
<td></td>
</tr>
<tr>
<td>Dielectric permittivity ((\chi = \varepsilon_r - 1))</td>
<td>( \Delta_d - (\Delta_H - B\Delta_{\varepsilon-p}) )</td>
<td>65</td>
<td></td>
</tr>
</tbody>
</table>

Typical samples of consistency are shown in Figure 1.6.
Figure 1.6. Comparison of BOLS predictions with measured size dependence of (a) Lattice contraction of Pr$_2$O$_3$ films on Si substrate (66). (b) Atomic cohesive energy of Mo and W (67). (c) Mechanical strength (Inverse Hall–Petch relationship, IHPR) of TiO$_2$ (68) nanosolids; straight line is the traditional Hall–Petch relationship (HPR). (d) $T_m$ suppression of Bi (69–73) and CdS (74); (e) $T_C$ suppression of ferromagnetic Fe$_3$O$_4$ nanosolids (75). (f) $T_C$ suppression of ferroelectric PbTiO$_3$ (76), SrBi$_2$Ta$_2$O$_9$ (77), BaTiO$_3$ (78), and anti-ferroelectric PbZrO$_3$ (79) nanosolids. High-order CN reduction is considered for dipole–dipole interaction.
Figure 1.7. Comparison of BOLS predictions with measured size dependence of (a) $E_G$-expansion measured using STS (80) and optical method, Data-1 ($E_G = E_{PA} - W$) (81), Data-2 ($E_G = (E_{PL} + E_{PA})/2$) (82). (b) Core-level shift of Au capped with Thiol (83) and deposited on Octan (84) shows three-dimensional features, whereas core-level shift of Au deposited on TiO$_2$ (85) and Pt (86) show one-dimensional pattern. (c) Raman acoustic frequency shift of TiO$_2$-a and TiO$_2$-b (87) SnO$_2$-a (88) nanostructures caused by interparticle interaction. (d) Raman optical frequency shift of CeO$_2$ (89), SnO$_2$-1 (90), SnO$_2$-2 (88), InP (91). (e) Dielectric suppression of nanosolid silicon with Data 1, 2, and 3 (92); Data 4 and 5 (93); and Data-6 (94). (f) Temperature and size dependence of magnetization.
1.3. EFFECT OF OXIDATION

1.3.1. Bond–Band–Barrier (BBB) Correlation

The BBB correlation mechanism indicates that it is necessary for an atom of oxygen, nitrogen, and carbon to hybridize its sp orbitals upon interacting with atoms in the solid phase. Because of tetrahedron formation, nonbonding lone pairs, anti-bonding dipoles, and hydrogen-like bonds are produced, which add corresponding features to the DOS of the valence band of the host, as illustrated in Figure 1.8 (95). Bond forming alters the sizes and valences of the involved atoms and causes a collective dislocation of these atoms. Alteration of atomic valences roughens the surface, giving rise to corrugations of surface morphology. Charge transportation not only alters the nature of the chemical bond but also produces holes below the $E_F$ and thus creates or enlarges the $E_G$ (96). In reality, the lone-pair-induced metal dipoles often direct into the open end of a surface because of the strong repulsive forces among the lone pairs and among the dipoles. This dipole orientation leads to the surface dipole layer with lowered $\Phi$. For a nitride tetrahedron, the single lone pair may direct into the bulk center, which produces an ionic layer at the surface. The ionic surface network deepens the well depth, or increases the $\Phi$, as the host surface atoms donate their electrons to the electron acceptors. For carbide, no lone pair is produced, but the weak antibonding feature exists because of the ion-induced polarization. However, hydrogen adsorption neither adds DOS features to the valence band nor expands the $E_G$ as hydrogen adsorption terminates the dangling bond at a surface, which minimizes the midgap impurity DOS of silicon, for instance (34).

Figure 1.8. Oxygen-induced DOS differences between a compound and the parent metal (upper) or the parent semiconductor (lower). The lone-pair polarized anti-bonding state lowers the $\Phi$, and the formation of bonding and anti-bonding generates holes close to $E_F$ of a metal or near the valence band edge of a semiconductor. For carbide, no lone-pair features appear, but the ion-induced anti-bonding states will remain.
1.3.2. Experimental Evidence

1.3.2.1. Surface Potential Barrier and Bond Geometry

The work function is expressed as $\Phi = E_0 - E_F(\rho(E)^{2/3})$ (97), which is the energy separation between the vacuum level $E_0$ and the Fermi energy $E_F$. The $\Phi$ can be modulated by enlarging the charge density ($\rho(E)$) through lattice contraction or by raising the energy where the DOS is centered via dipole formation (63). Dipole formation could lower the $\Phi$ of a metal surface by $\sim$1.2 eV (1). The work function varies from site to site with strong localized features. However, if additional oxygen atoms are adsorbed to the surface, the $\Phi$ will restore to the original value or even higher because the metal dipoles donate the polarized electrons to the additional electronegative additives to form a “+/dipole” at the surface (1).

Figure 1.9 shows a typical STM image and the corresponding model for the Cu(001)-(2×1)-O$_2^-$ phase. The round bright spots of 0.8 ± 0.2 Å in height correspond to the lone-pair-induced Cu dipoles. In contrast, the protrusion for the clean Cu(110) surface is about 0.15 Å (98). Single O–Cu–O strings are formed along the [010] direction associated with every other row missing because of the tetrahedron bond saturation.

Dynamic XRD and very-low-energy electron diffraction (VLEED) optimization have led to quantification of atomic positions that are determined by the bond geometry, such as the bond length and bond angles. A simple conversion between
1.3. EFFECT OF OXIDATION

TABLE 1.3. Geometrical Parameters for the Cu$_2$O Tetrahedron Deduced from the XRD Data of O–Cu(110) Phase (99) and the Cu$_3$O$_2$ Paired Tetrahedra Derived from VLEED Calculation of O–Cu(001) Surface (100). Bond Contraction with Respect to the Ideal Length of 1.85 Å. Results from the Effect of Bond Order Loss. The “:” Represents the Lone-Pair Interaction.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>O–Cu(110)</th>
<th>O–Cu(001)</th>
<th>Conclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic bond length (Å)</td>
<td>1.675 (Cu$^+$–O$^{2-}$)</td>
<td>1.628 (Cu$^{2+}$–O$^{2-}$)</td>
<td>&lt;1.80</td>
</tr>
<tr>
<td>Ionic bond length (Å)</td>
<td>1.675 (Cu$^+$–O$^{2-}$)</td>
<td>1.776 (Cu$^{2+}$–O$^{2-}$)</td>
<td>&lt;1.80</td>
</tr>
<tr>
<td>Lone-pair length (Å)</td>
<td>1.921 (Cu$^{2+}$:O$^{2-}$)</td>
<td>1.926 (Cu$^{2+}$:O$^{2-}$)</td>
<td>~1.92</td>
</tr>
<tr>
<td>Ionic bond angle (°)</td>
<td>102.5</td>
<td>102.0</td>
<td>~104.5</td>
</tr>
<tr>
<td>Lone-pair angle (°)</td>
<td>140.3</td>
<td>139.4</td>
<td>~140.0</td>
</tr>
</tbody>
</table>

atomic position and bond parameters could give the bond geometry for O–Cu examples as shown in Table 1.3.

1.3.2.2. Valence Density of States Oxygen-derived DOS features can be detected using STS and ultraviolet photoelectron spectroscopy (UPS). The STS spectra in Figure 1.10 for an O–Cu(110) surface (98) revealed the lone-pair and dipole features. Spectrum A was taken from the clean Cu(110) surface, whereas B and C were taken from, respectively, the site above the bright spot (dipole) and the site between two bright spots along a “O$^{2-}$ : Cu$^{2+}$dipole : O$^{2-}$” chain at the Cu(110)–(2 × 1)–O$^{2-}$ surface. On the clean surface, empty DOS at 0.8 ~ 1.8 eV above $E_F$ are resolved and no extra DOS structures are found below $E_F$. The STS spectra recorded from the Cu(110)–(2 × 1)–O$^{2-}$ islands reveal that the original empty-DOS above $E_F$ are partially occupied by electrons upon chemisorption, which result in a slight shift of the empty DOS to higher energy. Additional DOS features are generated around ~2.1 eV below the $E_F$. The sharp features around ~1.4 eV have been detected with angular-resolved photoelectron spectroscopy (ARPES) (101) and with the de-excitation spectroscopy of metastable atoms (102). The DOS for Cu-3d electrons are between ~2 and ~5 eV (103), and the O–Cu bonding derivatives are around the 2p-level of oxygen, ~5.6 ~ ~7.8 eV below $E_F$ (104). The DOS features for Cu-3d and O–Cu bonding are outside the energy range of the STS ($E_F$ ± 2.5 eV). The band-gap-expansion mechanism implies that it is possible to discover or invent new sources for light emission with a desired wavelength by controlling the extent of the catalytic reaction. Intense blue-light emission from P(Zr$_{x}$Ti$_{1-x}$)O$_3$ ceramics under Ar$^+$ ultraviolet (UV) irradiation could be direct evidence for this mechanism (105).

It has been found that the crystal geometry and the surface morphology may vary from surface to surface and from material to material; the oxygen-derived DOS features are substantially the same in nature, as summarized in Table 1.4. The O-derived DOS features include oxygen-metal bonding (~5 ~ ~8 eV), nonbond lone-pair of oxygen (~1 ~ 2 eV), holes of metal ions (~$E_F$) and antibonding metal-dipole states (~$E_F$).
Figure 1.10. (a) STS profiles of a Cu(110) surface (98) with and without chemisorbed oxygen. Spectra in panel (a) were obtained (A) at a metallic region, (B) on top of, and (C) between protrusions of the \( \text{O}^2^- : \text{Cu}_{\text{dipole}} : \text{O}^2^- \) chain (95) on the Cu(110)-(2 x 1)-O\(^2^-\) surface. (b) Oxygen-derived DOS features (shaded areas) in the valence band of O–Pd(110) (106) and O–Cu(110) (107) surfaces. Although the microscopy and crystallography of these two systems are different, the PES features are substantially the same. A slight difference in the feature positions results from the difference in electronegativity. Features around \(-1 \sim -2\) eV and \(-5 \sim -8\) eV correspond to the nonbonding lone pairs and the O sp-hybrid bond states, respectively.
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### TABLE 1.4. Oxygen-Derived DOS Features Adding to the Valence Band of Metals (unit in eV). Holes are Produced Below $E_F$. All the Data were Probed with Angular-Resolved Photoelectron Spectroscopy Unless Otherwise Indicated.

<table>
<thead>
<tr>
<th>Oxide Surfaces</th>
<th>Refs.</th>
<th>Methods</th>
<th>Anti-Bond Dipole $&gt; E_F$</th>
<th>Lone Pair $&lt; E_F$</th>
<th>O–M Bond $&lt; E_F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O–Cu(001)</td>
<td>108,109</td>
<td>VLEED (1)</td>
<td>−1.5 ± 0.5</td>
<td>−6.5 ± 1.5</td>
<td></td>
</tr>
<tr>
<td>O–Cu(110)</td>
<td>101,107,</td>
<td>STS (98)</td>
<td>1.2</td>
<td>−2.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>110,111</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O–Cu(poly)</td>
<td>103</td>
<td></td>
<td>1.3 ± 0.5</td>
<td>−2.1 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>O–Cu/Ag(110)</td>
<td>112</td>
<td></td>
<td>−1.5</td>
<td>−3.0; −6.0</td>
<td></td>
</tr>
<tr>
<td>O–Rh(001)</td>
<td>113</td>
<td>DFT</td>
<td>1.0</td>
<td>−3.1</td>
<td>−5.8</td>
</tr>
<tr>
<td>O–Pd(110)</td>
<td>114</td>
<td></td>
<td>−2.0 ± 0.5</td>
<td>−4.5 ± 1.5</td>
<td></td>
</tr>
<tr>
<td>O–Gd(0001)</td>
<td>115</td>
<td></td>
<td>−3.0</td>
<td>−6.0</td>
<td></td>
</tr>
<tr>
<td>O–Ru(0001)</td>
<td>116</td>
<td></td>
<td>−1.0 ± 1.0</td>
<td>−5.5 ± 1.5</td>
<td></td>
</tr>
<tr>
<td>O–Ru(0001)</td>
<td>117</td>
<td></td>
<td>−0.8</td>
<td>−4.4</td>
<td></td>
</tr>
<tr>
<td>O–Ru(0001)</td>
<td>118</td>
<td>Ab initio</td>
<td>1.5</td>
<td>−4</td>
<td>−5.5; −7.8</td>
</tr>
<tr>
<td>O–Ru(0001)</td>
<td>119</td>
<td></td>
<td>1.7</td>
<td>−3.0</td>
<td>−5.8</td>
</tr>
<tr>
<td>O–Ru(1010)</td>
<td>120</td>
<td>DFT</td>
<td>2.5</td>
<td>−2 ~ −3.0</td>
<td>−5.0</td>
</tr>
<tr>
<td>O–Co(Poly)</td>
<td>121</td>
<td></td>
<td>−2.0</td>
<td>−5.0</td>
<td></td>
</tr>
<tr>
<td>O–diamond (001)</td>
<td>122</td>
<td></td>
<td>−3.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(O, S)–Cu(001)</td>
<td>123</td>
<td></td>
<td>−1.3</td>
<td>−6.0</td>
<td></td>
</tr>
<tr>
<td>(N, O, S)–Ag</td>
<td>124</td>
<td></td>
<td>−3.4</td>
<td>−8.0</td>
<td></td>
</tr>
</tbody>
</table>

1.3.2.3. Lone-Pair Interaction A direct determination of the lone-pair interaction is to measure the frequency of vibration in metal oxide surfaces using Raman and high-resolution electron energy loss spectroscopy (EELS) (125–127) in the frequency range below 1000 cm$^{-1}$ or the shift energy of $\sim 50$ meV. Typical Raman spectra in Figure 1.11 show the lone pair vibration features in Al$_2$O$_3$ and TiO$_2$ powders (128). The energy of the stretching vibration of O–M in EELS around 50 meV coincides with the energy of hydrogen bond detected using infrared and Raman spectroscopy from H$_2$O, protein and DNA (129). The energy for an ionic bond is normally around 3.0 eV, and the energy for a Van der Waals bond is about 0.1 eV. The $\sim 0.05$-eV vibration energies correspond to the weak nonbonding interaction between the host dipole and the oxygen adsorbate.

A nuclear inelastic scattering of synchrotron radiation measurement (130) revealed that additional vibrational DOS present at energies around 18 meV and 40–50 meV for the oxide-caped nanocrystalline $\alpha$-Fe (6–13-nm sizes) compared with that of the coarse-grained $\alpha$-Fe. The 50-meV DOS corresponds apparently to the lone-pair states, whereas the 18-meV modes could be attributed to intercluster interaction that should increase with the inverse of particle size (Figure 1.7c).
1.3.2.4. Bond-Forming Kinetics The spectral signatures of LEED, STM, PES/STS, TDS, and EELS can be correlated to the chemical bond, surface morphology, valence DOS, and the bond strength, which enables the kinetics of oxide tetrahedron formation to be readily understood. It has been found generally that an oxide tetrahedron forms in four discrete stages: (1) $O^{1-}$ dominates initially at very low oxygen dosage; (2) $O^{2-}$ hybridization begins with lone-pair and dipole formation upon second bond formation; (3) interaction develops between lone pairs and dipoles; and finally, (4) H-bond-like forms at higher dosages. These processes give rise to the corresponding DOS features in the valence band and modify the surface morphology and crystallography, accordingly. Therefore, the events of $sp$-hybrid bonding, nonbonding lone pair, anti-bonding dipole, and the H-like bonding are essential in the electronic process of oxidation, which should dominate the performance of an oxide.

1.3.3. Summary

It is essential that an oxygen atom hybridizes its $sp$-orbitals upon reacting with atoms in the solid phase. In the process of oxidation, electronic holes, nonbonding lone pairs, anti-bonding dipoles, and hydrogen-like bonds are involved, which add corresponding density-of-states features to the valence band of the host. Formation of
TABLE 1.5. Summary of Special Bonding Events and Potential Applications of Oxide Nanomaterials.

<table>
<thead>
<tr>
<th>Events</th>
<th>Functions</th>
<th>Potential Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anti-bonding(dipole) &gt; $E_F$</td>
<td>Work function-reduction $(\Delta\phi)$</td>
<td>Cold-cathode</td>
</tr>
<tr>
<td>Holes &lt; $E_F$</td>
<td>Band gap expansion</td>
<td>Field emission</td>
</tr>
<tr>
<td>Nonbonding (Lone pair) &lt; $E_F$</td>
<td>Polarization of metal electrons</td>
<td>PL blue-shift</td>
</tr>
<tr>
<td></td>
<td></td>
<td>UV detection</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High-elasticity</td>
</tr>
<tr>
<td>Bond order loss</td>
<td>$\Delta\phi$-recovery</td>
<td>Raman and Far-infrared low-frequency activity</td>
</tr>
<tr>
<td></td>
<td>BOLS correlation charge, mass, and energy densification</td>
<td>Bond network stabilization</td>
</tr>
<tr>
<td></td>
<td>Cohesive energy Hamiltonian</td>
<td>Origin for the tunability of nanosols</td>
</tr>
</tbody>
</table>

Knowing the bonding events and their consequences would help us to scientifically design the synthesis of oxide nanostructures with desired functions. The predictions of the functions and the potential applications of the bonding events at a surface with chemisorbed oxygen are summarized in Table 1.5. Oxidation modifies directly the occupied valence DOS by charge transportation or polarization, in particular the band gap and work function. The involvement of the often-overlooked events of lone pair and dipoles may play significant roles in many aspects of the performance of an oxide. The bond contraction is not limited to an oxide surface, but it happens at any site, where the atomic CN reduces.

1.4. CONCLUSION

The impact of the often-overlooked event of atomic CN reduction is indeed tremendous, which unifies the performance of a surface, a nanosolid, and a solid in amorphous
state consistently in terms of bond relaxation and its consequences on bond energy. The unusual behavior of a surface and a nanosolid has been consistently understood and systematically formulated as functions of atomic CN reduction and its derivatives on the atomic trapping potential, crystal binding intensity, and electron–phonon coupling. The properties include the lattice contraction (nanosolid densification and surface relaxation), mechanical strength (resistance to both elastic and plastic deformation), thermal stability (phase transition, liquid–solid transition, and evaporation), and lattice vibration (acoustic and optical phonons). They also cover photon emission and absorption (blue shift), electronic structures (core-level disposition and work function modulation), magnetic modulation, dielectric suppression, and activation energies for atomic dislocation, diffusion, and chemical reaction. Structural miniaturization has indeed given a new freedom that allows us to tune the physical properties that are initially nonvariable for the bulk chunks by simply changing the shape and size to make use of the effect of atomic CN reduction.

The effect of size reduction and the effect of oxidation enhance each other in an oxide in many aspects such as the charge localization, band gap expansion, and work function reduction. For instance, the enhancement of the energy density in surface skin enlarges the band gap intrinsically through the Hamiltonian modification, whereas charge transport from metal to oxygen enlarges the $E_G$ extrinsically by hole production at the upper edge of the valence band (131). A theoretical calculation (132) suggested that the band gap of nanosolid Si decreases with increasing dot size. Furthermore, the band gap increases as much as 0.13 eV and 0.35 eV on passivating the surface of the dot with hydrogen and oxygen, respectively. So both size and surface passivation contribute to the optical and electronic properties of Si nanosolids. The lone-pair-induced dipoles in oxidation will add a new DOS above the $E_F$, whereas charge densification due to bond contraction will intensify the DOS. Therefore, both oxidation and size reduction could lower the work function.

We need to note that the bond contraction for under-coordinated metal atoms and oxygen-metal bonds is general. In particular, in cases such as V, Mo, W, and other oxides, atoms at surfaces will have double bonds and the average M–O distance will decrease. However, at surfaces terminated by hydroxyl groups, the bond contraction is not so clear. For example, earlier EXAFS measurements suggested an average distance decreases in TiO$_2$, but new results using cumulant expansion (a more sophisticated analysis) give the opposite result (3). The bond expansion in the latter case and the hydroxyl-terminated surface may be connected with the fact that the TiO$_2$, CeO$_2$, and other “reducible” oxides have a certain quantity of oxygen vacancies and reduced (Ti$^{3+}$, Ce$^{3+}$) cation states; the corresponding radii are larger than the ones of fully oxidized states and, typically, display larger average M–O bond distances. This latter is also observed in α- and γ-Fe$_2$O$_3$, but several “synthesis” details concerning the coexistence of Fe$^{2+}$/Fe$^{3+}$ are still unclear. Alternative explanations indicate that M–OH bond distances would be larger than M–O and dominate the first coordinating distance behavior. Therefore, we could not exclude the situation of bond expansion as observed in compound nanostructures. Both situations, e.g., distance increase and decrease, are covered by the BOLS correlation as consequences on the bond energy disregarding the possible origins for the bond expansion.
It is the practitioner’s view that we are actually making use of the effect of bond order loss in size reduction and the effect of bond nature alteration in oxidation in dealing with oxide nanomaterials. Grasping with the factors controlling the process of bond making, breaking and relaxing would be more interesting and rewarding.

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