Consistent insight is presented into the atomistic origin and temperature ($T$) dependence of the redshift of Raman optical modes in nanostructures from the perspective of surface bond unsaturation and the bond-order-length-strength (BOLS) correlation [Sun et al., Phys Rev B 72, 134301 (2005)]. It turns out that: (1) the size-induced redshift of Raman optical modes results from the effect of bond order deficiency of atoms on the surface and its consequences on the force constants of bonds between the under-coordinated surface atoms; (2) the temperature-induced redshift arises from thermally induced bond expansion and bond weakening and (3) the magnitude of vibration of atoms in the surface or surrounding defects is always greater than the fully coordinated bulk atoms, while the frequency of such under-coordinated atoms are relatively lower. It is demonstrated that a combination of the freedoms of solid size and temperature of testing with Raman spectroscopy could lead to information about the vibrational frequency of a monatomic chain and single-bond energy, which is beyond the scope of the traditional size- and temperature-independent approaches. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: Raman optical modes; nanostructure; surface bond contraction

INTRODUCTION

The vibration of under-coordinated atoms at a surface and in a nanosolid is of great importance because the behavior of surface phonons influences directly the electrical, optical, and dielectric properties in semiconductor materials and devices, such as electron–phonon coupling, photoabsorption, and photomission, as well as phonon scattering in the transport dynamics of electrons, phonons, and photons in devices.1–5 With miniaturization of a solid down to nanometer scales, the optical Raman modes shift toward lower wavenumbers.6 On the other hand, when the temperature is increased, the Raman peaks also shift down to low wavenumbers monotonically yet nonlinearly at low temperatures.7–9 It is expected that the magnitude of vibration for a surface atom is always greater than that in the bulk.10,11 However, the underlying mechanisms behind the size- and temperature-induced Raman redshift of the optical modes remain ambiguous.

Size-induced Raman redshift

The size-induced redshift of Raman optical modes has usually been suggested to be activated by surface disorder,12 surface stress,13–15 quantum confinement,16–19 local heating effects,20–22 or surface chemical passivation. The Raman shifts of TiO$_2$ particles are attributed to the effects of decreasing particle size on the force constants and the amplitudes of vibration of the nearest atomic neighbors.23 However, the effect of stress can usually be ignored for hydrogenated silicon,24,25 in which hydrogen atoms terminate the surface dangling bonds, which reduce the bond strains and hence the residual stress. The phonon quantum confinement argument16 attributes the redshift of the asymmetric Raman line to the relaxation of the $q$-vector selection rule for the excitation of the Raman active phonons due to their localization. The relaxation of the momentum conservation rule arises from the finite crystalline size and the distribution of the diameters of the nanosolid in the films. When the size is decreased, the rule of momentum conservation will be relaxed and the Raman active modes will not be limited to the center of the Brillouin zone.13 However, Alim et al.21,22 who have measured resonant and nonresonant Raman scattering spectra for ZnO nanocrystals with an average diameter of 20 nm, proposed that the observed phonon redshift can be attributed to the local heating effects instead of phonon...
confinement effects. A Gaussian-type phonon confinement model\(^7\) that has been used to fit the experimental data indicates that strong phonon damping is present, whereas calculations\(^26\) using the correlation functions of the local dielectric constant ignore the role of phonon damping in the nanosolid. The large surface-to-volume ratio of a nanosolid strongly affects the optical properties mainly because of the introduction of surface polarization and surface states.\(^27\) Using a phenomenological Gaussian envelope function of phonon amplitudes, Tanaka \(\text{et al.}\)\(^7\) showed that the size dependence of the redshift of Raman optical modes originated from the relaxation of the \(q = 0\) selection rule based on the confinement argument with negative phonon dispersion. The phonon energies for all the glasses are reduced, and the values of the phonon energies of CdSe nanosolids are found to be quite different for different host glasses because of interfacial interaction.

Hwang \(\text{et al.}\)\(^28\) and Kim and Jang\(^29\) indicated for the first time that the effect of lattice contraction must be considered to explain the observed differences in the redshift of phonon energies for CdSe nanodots embedded in different glass matrices and in ZrTiO\(_3\) nanocrystals. Interface bond contraction has been confirmed recently by Pan \(\text{et al.}\)\(^30\) using fluorescence X-ray absorption fine structure and X-ray diffraction. To obtain the phonon frequency as a function of the solid radius \(K_j\) with contribution of lattice contraction, it was assumed that:\(^28\)

\[
\omega(K_j) - \omega_l(\infty) = \Delta \omega_{\text{D}}(K_j) + \Delta \omega_{\text{C}}(K_j)
\]

where \(\omega_l\) is the LO phonon frequency of the bulk, \(\Delta \omega_{\text{D}}(K_j)\) is the peak position shift due to phonon dispersion, and \(\Delta \omega_{\text{C}}(K_j)\) is the peak shift due to lattice contraction, which are given by:

\[
\frac{\Delta \omega_{\text{D}}(K_j)}{\omega_l} = \left[1 - \frac{\beta_0}{\omega_l} \left(\frac{\mu_{np}}{Kjd} \right)^2 \right]^{-1/2} - 1 \approx -\frac{\beta_0^2}{2\omega_l} \left(\frac{\mu_{np}}{Kjd} \right)^2
\]

\[
\frac{\Delta \omega_{\text{C}}(K_j)}{\omega_l} = \left(1 + \frac{3\Delta d(K_j)}{d} \right)^{-\gamma} - 1 \approx -\frac{3\gamma \Delta d(K_j)}{d}
\]

(1)

where the parameter \(\beta_0\) describes the phonon dispersion, assumed to be parabolic, \(\mu_{np}\) is the nonzero \(np\)th root of the equation of \(\tan(\mu_{np}) = \beta_{np}\), and

\[
\frac{\Delta d(K_j)}{d} = (\alpha' - \alpha)(T - T_g) - \frac{2\beta_c}{3} \left(\frac{\sigma_\infty}{Kjd} + \frac{b}{2(Kjd)^2} \right)
\]

\[
\approx (\alpha' - \alpha)(T - T_g) - \frac{\beta_c b}{3(Kjd)^2}
\]

(2)

Here, \(\gamma\) is the Grüneisen parameter and \(\alpha'\) and \(\alpha\) are the linear thermal expansion coefficients of the host glass and the nanosolid, respectively. \(T\) and \(T_g\) are the testing and the heat-treatment temperature, respectively. \(\beta_c\) and \(\sigma_\infty\) are the compressibility and the surface tension of the bulk, respectively, and \(b\) is the parameter describing the size-dependent surface tension of the crystal. The surface tension for the bulk crystals is assumed to be small. The first term describes the lattice contraction by thermal expansion mismatch between the glass matrix and the crystal, and the second term arises from the increase of surface tension with the decrease of the crystal size. Substituting Eqn (2) into Eqn (1), the phonon frequency change at a given temperature is obtained:

\[
\frac{\Delta \omega(K_j)}{\omega_l(\infty)} = -3\gamma(\alpha' - \alpha)(T - T_g)
\]

\[
-\left[\frac{1}{2} \left(\frac{\beta_0^2}{\omega_l(\infty)} \right)^2 - \gamma \beta_c b \right] (Kjd)^{-2}
\]

\[
= A(T) - BK_j^{-2}
\]

(3)

For the free surface, \(\alpha' = \alpha\), and \(A(T)\) and \(b\) are 0. The redshift will follow a \(K_j^{-2}\) relation. There are some difficulties however in using this equation, as remarked by Hwang \(\text{et al.}\)\(^28\) The thermal expansion coefficients are hardly detectable within the temperature range \(T\) and \(T_g\). The value of \(B\) in Eqn (3) is given by the difference of the phonon negative dispersion and the size-dependent surface tension. Thus, a positive value of \(B\) indicates that the phonon negative dispersion exceeds the size-dependent surface tension and consequently causes a redshift of the phonon frequency. On the contrary, if the size-dependent surface tension is stronger than the phonon negative dispersion, a blueshift of phonon frequency occurs. In case of balance of the two effects, i.e. \(B = 0\), the Raman peaks will remain unchanged with size. Furthermore, the parameter \(b\) introduced by the size-dependent surface tension is also not known.

**Temperature-induced Raman redshift**

From the classical thermodynamics point of view, the temperature-induced change of phonon frequency was attributed to the anharmonic terms in the lattice potential energy.\(^31\) The anharmonic constants are found to be highly size-dependent and increase greatly with decreasing dimensions.\(^32\) Surface and surface phonon modes are considered as the main contributions to the asymmetry of the spectra.\(^33\) In the common condition, the volume of the specimen always increases with the temperature of operation. The measured frequency change at a constant pressure was suggested as:\(^34\)

\[
\frac{\Delta \omega(T)}{\omega(T_0)} = \frac{1}{\omega(T_0)} \left(\frac{d\omega}{dT} |_V + \frac{d\omega}{dV} |_T \frac{dV}{dT} |_P \right) \Delta T
\]

\[
= \frac{1}{\omega(T_0)} (\chi_T + \chi_P) \Delta T
\]

where \(\omega(T_0)\) is the intrinsic frequency of the optical phonon measured at \(T_0\). The first term describes the pure temperature effect and the second the thermal expansion effect. The
volume dependence of frequency can be calculated using the Gr"uneisen constant model:
\[
\frac{\chi \nu \Delta T}{\omega(T)} = \frac{\Delta \omega(T)}{\omega(T_0)} = -3y \int_0^T \alpha(T)dT - 1
\]
where \(\alpha(T)\) is the thermal expansion coefficient.

On the other hand, from the quantum mechanical point of view, the temperature-induced relative Raman redshift can be fitted to a negative Bose–Einstein population, or equivalently:
\[
\frac{\omega(K_j, T) - \omega(K_j, T_0)}{\omega(K_j, T) - \omega(2, T_0)} = \left\{ \frac{A}{\frac{\Delta \nu}{\nu_0}} - 1 \right\} \left[ 1 + \frac{2}{\epsilon^2 - 1} \right] + D \left[ 1 + \frac{3}{\epsilon^2 - 1} + \frac{3}{(\epsilon^2 - 1)^2} \right] = f(T, \omega(T_0))
\]
where \(A, B, C, \) and \(D\) are fitting parameters.

**Motivation and objectives**
Most of the existing models for the size-induced Raman shift are based on a continuum dielectric mechanism assuming that the materials are homogeneous and isotropic, which is valid only in the long-wavelength limit. When the size of the nanosolid is in the range of several nanometers, the continuum dielectric models exhibit limitations. The physics behind the temperature dependence is not clear, though the temperature-induced shift agrees with the negative Bose–Einstein population that describes the density population rather than the energy distribution of the phonons. Therefore, an atomicistic understanding is highly desired for the dependence of the Raman shift on the size, temperature, and the bond nature.

The objective of this work is to show that the observed size, temperature, and bond nature dependence of the Raman shift of nanostructures can be unified in terms of the effect of broken bond, which follows the recently developed bond-order-length-strength (BOLS) correlation mechanism.

**PRINCIPLES**

**Vibrational modes and frequency**
When a solid contains numerous Bravais unit cells and each cell contains \(n\) atoms, there will be \(3n\) modes of vibration in total. Among the \(3n\) modes, there will be three acoustic modes, LA, TA\(_1\) and TA\(_2\), and \(3(n - 1)\) optical modes. The acoustic mode represents the in-phase motion of the mass center of the unit cell or the entire solid as a whole. The optical mode is the relative motion of the individual atoms in the Bravais unit cell which contains more than one atom. For elemental bulk solids with a simple structure, such as the fcc structure of Ag, there are no optical modes. For elemental nanosolid, however, additional acoustic modes can be observed because of the interparticle interaction or particle–matrix interaction in the embedded systems. The structure for silicon or diamond is an interlock of two fcc structures, which contains in each Bravais unit cell two atoms in nonequivalent positions, so there will be three acoustic modes and three optical modes.

The energy \(E_{\text{total}}\) of a bond can be expanded in a Taylor series as equilibrium energy of binding at 0 K, \(E_k(d) < 0\), and the thermal vibration energy, \(E_V(T) > 0\):
\[
E_{\text{total}}(r, T) = \sum_{n=0}^{\infty} \left( \frac{d^n u(r)}{n! dr^n} \right)_{r=0} (r-d)^n
\]
\[
= u(d) + \left( \frac{d^2 u(r)}{2! dr^2} \right)_{r=0} (r-d)^2 + \left( \frac{d^3 u(r)}{3! dr^3} \right)_{r=0} (r-d)^3 + \ldots
\]
\[
= E_k(d) + \left( \frac{K_2}{2} + \frac{K_3}{6} (r-d) \right) (r-d)^2 + 0 [(r-d)^{n-3}] + \ldots
\]
\[
= E_k(d) + E_V(T)
\]
Here \(r-d\) is the magnitude of lattice vibration, which is smaller than 3% at melting. The term with index \(n = 0\) corresponds to the minimum binding energy at \(T = 0\) K, \(E_k(d)\). The \(n = 1\) term is the force \([du(r)/dr]_r=0\) at equilibrium and terms with \(n \geq 2\) correspond to the thermal vibration energy, \(E_V(T)\). By definition, the thermal vibration energy of a single bond is:
\[
E_V(T) = \left( \frac{k}{2} + \frac{K_3}{6} (r-d) \right) (r-d)^2 + 0 [(r-d)^{n-3}] + \ldots
\]
\[
\approx \mu \omega^2 (r-d)^2/2 + 0 [(r-d)^{n-3}]
\]
\[
\approx k_v (r-d)^2/2 = \int_0^T \eta_1(t)dt
\]
\(\mu\) is the reduced mass of a monatomic chain of concern and \(\eta_1(t)\) is the temperature-dependent specific heat per bond following the Debye formulation. \(\omega\) is the angular frequency of vibration. The force constant for lattice vibration with the anharmonic term contribution is:
\[
k_v = \mu \omega^2 = k + \frac{K_3}{3} (r-d) = \left( \frac{d^2 u(r)}{dr^2} \right)_{r=0} + \left( \frac{d^3 u(r)}{3 dr^3} (r-d) \right)_{r=0}
\]
\[
\propto E_k/d^2 + 0
\]
Actually, the high-order anharmonic terms corresponding to the nonlinear contribution can be neglected in the first-order approximation because at equilibrium, \(r = d\).

**Broken bond rule and the BOLS correlation**
The BOLS correlation mechanism indicates that the coordination (\(z_i\)) deficiency of an atom denoted \(i\) at a site surrounding a defect (void, stacking fault, impurity, etc.) or near the surface edge causes the remaining bonds of the under-coordinated atom to contract spontaneously.
from the bulk value \( d \) to \( d_i \) with a coefficient \( c_i \). This spontaneous process is associated with bond strength gain or trapping potential well depression, from the bulk value \( E_b \) to \( E = E_i^m E_b \), the index \( m \) being an indicator of the nature of the bond. Consequently, densification and localization of charge, energy, and mass would take place at the surface and interface skins, yet the core interior undergoes little change if no impurity is involved. The atomic cohesive energy, being the sum of bond energy over all the coordinates of the specific \( i \)th atom, will change from the bulk value \( E_b \) to \( E \) given by \( E_i = \frac{z_i}{z_2 d_i^{-m}} = \frac{z_2 c_i^{-m}}{2} \). The BOLS correlation mechanism can be expressed as:

\[
\begin{align*}
E_i = c_i^{-m} E_b & \quad \text{(Single bond energy)} \\
E_{B,i} = z_i E_i & \quad \text{(Atomic cohesive)}
\end{align*}
\]

The subscript \( i \) denotes an atom in the \( i \)th atomic layer, which may be counted up to three from the outermost atomic layer to the center of the solid as no coordination (CN) reduction is expected for \( i > 3 \). The bond nature indicator \( m \) is intrinsic to a specific material, which cannot be adjusted freely. For metals, such as Au, Ag, and Ni, \( m = 1 \); for alloys and compounds \( m \) is around four; for C and Si, the \( m \) value has been optimized to be 2.56 \(^{39} \) and 4.88 \(^{30} \) respectively. The \( m \) value may vary if the bond nature evolves with atomic CN, such as the III-A and IV-A elements in the periodic table.\(^ {51} \) If the surface bonds expand in certain cases, we simply expand the \( c_i \) from a value that is smaller than unity to greater, and \( m \) from positive to negative to represent the spontaneous process for which the system energy is minimized. The \( c_i(z_i) \) should be anisotropic and depend on the effective CN rather than a certain order of CN. \( z_i \) also varies with the particle size owing to the change of the surface curvature. Experience reveals that the \( z_i \) takes the following values:

\[
z_i = \begin{cases} 4(1 - 0.75/K_1) & \text{curved surface} \\ 4 & \text{flat surface} \end{cases}
\]

Generally, \( z_2 = 6 \) and \( z_3 = 8 \) or 12 would be sufficient. The BOLS correlation has nothing to do with the particular form of the pairing potential, as the approach involves only the atomic distance at equilibrium. There are several characteristic energies in Fig. 1, which correspond to the following facts:

1. \( T_{m,i} \) being the local melting point is proportional to the atomic cohesive energy, \( z_i E_i(0) \), per atom with \( z_i \) coordinate.\(^ {53} \)
2. The separation between \( E = 0 \) and \( E_i(T_m) \), or \( \eta_2 \), is \( 1/z_i \) fold of energy that is required for atomization of an atom in molten state.
3. Separation between \( E = 0 \) and \( E_i(T) \), or \( \int_{T}^{T_m} \eta_1(t)dt + \eta_2 \), corresponds to the cohesive energy per coordinate, \( E_i \), at \( T \), being the energy required for the bond fracture under mechanical or thermal stimulus.
4. The spacing between \( E_i(T_m,t) \) and \( E_i(0) \) is the thermal vibration energy, \( \int_{T}^{T_m} \eta_1(t)dt \).

**Coordination- and temperature-dependent force constant and frequency**

According to the BOLS correlation, the force constant \( k_e \) for a single bond is strengthened; for an under-coordinated atom, the resultant \( k_e \) could be lower or higher depending on the production of the reduced CN and the CN-reduction-induced bond strength gain.\(^ {51} \) Since the short-range interaction on each atom results from its neighboring coordinated atoms, the atomic vibrating dislocation is

![Figure 1](https://www.interscience.wiley.com/journal/jrs)

**Figure 1.** (a) Atomic coordination-imperfection-modified pairing potential energy (solid curve) compared with the bulk situation (broken curve). CN imperfection causes the bond to contract from one unit (in \( d \)) to \( c_i \) and the cohesive energy per coordinate increases from one unit to \( c_i^{-m} \) unit. The bond energy \( E_i(T) = E_i(0) - \int_{0}^{T} \eta_1(t)dt - \frac{z_i}{z_2} \eta_2(T_m,t) \), \( T_{m,i} \) being the melting point, \( \eta_1(t) \) the specific heat per bond that follows Delye’s formulation, and \( \eta_2 \) the latent heat per coordinate for atomization of the \( i \)th atom in molten state. Figure 1(b) illustrates the temperature dependence of the reduced specific heat (inset) and bonding energy \( E_B(T)/E_B(0) \) when \( \eta_2/(\chi_1 T_m) \) chosen to be 10. For consideration of a single bond, one has to divide the values by the atomic CN. The \( C_v(T/\theta_2) \) and \( U(T/\theta_2) \) are sensitive to the Debye temperature. This figure is available in colour online at www.interscience.wiley.com/journal/jrs.
the contribution from all the surrounding coordinates, \(z\).

Considering the vibration amplitude \(z \ll d\), it is convenient and reasonable to take the mean contribution from each coordinate to the force constant and to the magnitude of dislocation as the first-order approximation, i.e.

\[
k_1 = k_2 = \ldots = k_z = \mu(z^2)
\]

and

\[
x_1 = x_2 = \ldots = x_z = (r - d)/z
\]

Therefore, the total energy of a certain atom with \(z\)-coordinates is the sum over all coordinates:

\[
E_z = \sum_z \left[ -E_0 + \frac{\mu c^2 a z^2}{2} \left( \frac{r - d}{z} \right)^2 + \ldots \right]
\]

\[
= -2E_0 + \frac{z d^2 u(r)}{2d^2 r^2} \left| (r - d)^2 + \ldots \right|
\]

where \(c\) is the velocity of light in vacuum. This relation leads to an immediate expression for the phonon frequency as a function of atomic CN, bond length, and bond energy:

\[
\omega(0) = \frac{z}{c} \left[ \frac{d^2 u(r)}{d^2 r^2} \right]^{1/2} \propto \frac{z(E_b)^{1/2}}{d}
\]

(5)

Extending to temperature domain, we have:

\[
E_b(T) = E_b(0) - \int_0^T \eta_1(t) dt
\]

\[
= \int_0^T \eta_1(t) dt + \eta_2
\]

\[
d(T) = d(1 + \alpha T/T_m)
\]

Equation (5) evolves into

\[
\omega(T) \propto \frac{z}{d(1 + \alpha T/T_m)} \left[ \frac{E_b(0) - \int_0^T \eta_1(t) dt}{d(1 + \alpha T/T_m)} \right]^{1/2}
\]

(6)

in which \(\eta_1(t)\) follows the Debye specific heat model as:

\[
\eta_1(t/\theta_b) = \frac{c_v(T/\theta_b)}{z} = \frac{9R}{z} \left( \frac{T}{\theta_b} \right)^3 \int_0^{\theta_b/\theta} x^2 \exp(x) (e^x - 1)^2 dx
\]

\[
u(T/\theta_b) = \frac{U(T/\theta_b)}{z} = \int_0^T \frac{c_v(T) dt}{z} = \frac{9TR}{z} \left( \frac{T}{\theta_b} \right)^3 \int_0^{\theta_b/\theta} x^2 \exp(x) (e^x - 1)^2 dx
\]

where \(U(T/\theta_b)\) is the internal energy.

The thermal expansion coefficient \(\alpha\) can be omitted because it is insignificantly small at melting, and \(\alpha\) is at a maximum of 3–5% of the lattice constant.\(^{66}\)

Size, temperature, and bond-nature dependence of vibrational frequency

Generally, the mean relative change of a measurable quantity of a nanosolid containing \(N_j\) atoms can be expressed as \(Q(K_j)\) and as \(Q(\infty)\) for the same solid without the effect of CN imperfection being involved. \(Q(K_j)\) relates to \(Q(\infty) = Nq\) through a core–shell configuration and a scaling relation:

\[
Q(K_j) = N_q \sum_{i=3} \frac{N_i(q_i - q)}{K_j}
\]

\[
\Delta Q(K_j) \frac{Q(\infty)}{Q(K_j)} = \sum_{i=3} \frac{\Delta \eta_i}{\eta_j} = \Delta \eta_j
\]

\[
\eta_j = \frac{N_i}{N_j} = \frac{\tau_0}{K_j} < 1
\]

Here, \(q\) and \(q_i\) correspond to the local density of \(Q\) inside the bulk and in the region of the \(i\)th atomic layer, respectively, \(K_j\) being the dimensionless form of size, is the number of atoms lined along the radius of a sphere and across the thickness of a thin plate. The weighting factor, \(\eta_j\), represents the geometrical contributions from dimension \((K_j)\) and dimensionality \((\tau)\) of the solid, which determine the magnitude of the change. The quantity \(\Delta \eta_j/\eta_j\) in the surface skin originates the change, which depends functionally on the temperature and bond nature. Interestingly, investigations revealed that the size-induced property change of a nanosolid follows the \(K_j^{-1}\) fashion. Equating the theoretical and the experimentally observed scaling relations for the size dependence of a nanosolid with given \(m\) value, we have:

\[
Q(K_j) - Q(\infty) = \left\{ \begin{array}{l}
A^mK_j^{-1} \quad \text{(measurement)} \\
Q(\infty) \times \Delta \eta_j(K_j, T) \quad \text{(theory)}
\end{array} \right\}
\]

For the current case, \(Q(\infty, T_0) = \omega(\infty, T_0, ) - \omega(2, T_0)\), with \(\omega(2, T_0)\) being the vibrational frequency of a monatomic chain measured at \(T_0\), which is the reference point for the optical redshift upon nanosolid and bulk formation. The scaling relation becomes:

\[
\frac{\omega(K_j, T) - \omega(2, T_0)}{\omega(\infty, T_0) - \omega(2, T_0)} - 1 = \frac{\omega(K_j, T) - \omega(\infty, T_0)}{\omega(\infty, T_0) - \omega(2, T_0)} = \Delta \eta(K_j, T) = \sum_{i=3} \gamma_i \delta \eta_i(z_i, T)
\]

or

\[
\omega(K_j, T) - \omega(\infty, T_0) = \left\{ \begin{array}{l}
A^m(T_0)/K_j \\
\left[ \omega(\infty, T_0) - \omega(2, T_0) \right] \Delta \eta(K_j, T) \quad \text{(measurement)}
\end{array} \right\}
\]

(7)

Using the relations: \(E_i = c_i^{-m}E_0\), and \(E_b(T_0) = \eta_1(T_m)T_m + \eta_2\) we have, \(\eta_1(T_m) = z_2\eta_1(T_m)\), and \(\eta_2 = c_i^{-m}\eta_2\), with \(z_2 = z_3/z_1\) and \(z\) taking the standard bulk value\(^{55}\) of 12. Therefore, the size, temperature, and bond nature dependence of the Raman shift originates from:

\[
\delta \eta(z_i, T) = \frac{\omega(z_i, T) - \omega(z, T_0)}{\omega(z, T_0) - \omega(2, T_0)}
\]
Atomistic origin and temperature dependence of Raman redshift in nanostructures

785

where $1 + \Delta_i = z_{\beta C_i}^{-m}$ with $\Delta_i$ being the perturbation to the atomic coherency. $T_{m_i} = (1 + \Delta_i)T_m$, and the subscript 2 corresponds to a monatomic chain. Generally, at temperature above the Debye temperature, $\eta_i(t)$ can be taken as constant; otherwise it follows the universal Debye relation of temperature dependence. For bulk materials, from Eqn (6), we have a simpler form:

$$\frac{\omega(T)}{\omega(T_0)} = 1 + \frac{\alpha T_0}{\alpha T/T_m} \left( \frac{E_0(0) - \int_0^T \eta_i(t)dt}{E_0(0) - \int_0^T \eta_i(t)dt} \right)^{1/2}, \quad (T_0 \neq 0)$$

$$= \frac{1 + \alpha T_0/T_m}{1 + \alpha T/T_m} \left( 1 + \frac{\int_0^T \eta_i(t)dt}{E_0(0) - \int_0^T \eta_i(t)dt} \right)^{1/2}, \quad (T_0 \neq 0)$$

$$\equiv \begin{cases} 
\frac{1 + \alpha T_0/T_m}{1 + \alpha T/T_m} \exp \left\{ \frac{\int_0^T \eta_i(t)dt}{2E_0(0)} \right\}, & (T_0 \neq 0) \\
\exp \left\{ \frac{-\int_0^T \eta_i(t)dt/[2E_0(0)]}{1 + \alpha T/T_m} \right\}, & (T_0 = 0)
\end{cases}$$

Note the fact that temperature-induced Raman shift can be numerically fitted to the negative Bose–Einstein population, $f(T, \omega(T_0))$, as given in Eqn (3). Equilibrating the $f(T, \omega(T_0))$ and theoretical prediction of temperature dependence, we also have:

$$\omega(K_i, T) - \omega(\infty, T_0) = [\omega(\infty, T_0) - \omega(2, T_0)]$$

$$\times \left\{ \sum_{\delta \eta} \gamma_i \delta \eta_i(z_i, T) \right\} (\text{measurement})$$

$$\times \left\{ \frac{A'(T_0)/[\omega(\infty, T_0) - \omega(2, T_0)]}{K_f(T_0, \omega(T_0))} \right\} (\text{K}-\text{dependent})$$

$$\times \left\{ \frac{K_f(T_0, \omega(T_0))}{T-\text{dependent}} \right\}$$

Equilibrating the measurements to the predictions of size Eqn (7) and temperature Eqn (10) dependence, we always have:

$$\sum_{\delta \eta} \gamma_i \delta \eta_i(z_i, T_0)$$

$$= \left\{ \frac{A'(T_0)/[\omega(\infty, T_0) - \omega(2, T_0)]}{K_f(T_0, \omega(T_0))} \right\} (\text{K}-\text{dependent})$$

$$\times \left\{ \frac{K_f(T_0, \omega(T_0))}{T-\text{dependent}} \right\}$$

RESULTS AND DISCUSSION

Calculations

A least square fitting of the measured size-dependent data gives the slope $A'(T_0)$ and the intersection $\omega(\infty, T_0)$ using Eqn (7). In order to minimize the errors in measurement, several datasets are used to find the best fit to all the data. Another numerical fitting of the temperature-dependent data will give the values of $A$, $B$, $C$, and $D$ and hence $f(T_0, \omega(T))$. We can also get the ratio of $\eta_2/\eta_1$ in $\delta \eta_i(z_i, T)$ and $\omega(2, T_0)$ by solving a combination of equations derived from Eqn (11). $T_0$ is set as 300 K. $\eta_2$ is replaced with $\eta_2^* = [\eta_2(T_{m_2})/\eta_1(T_{m_2})]$, if $T_0 < \theta_D$, to reproduce the $T$-dependent data over the whole temperature range. Temperature dependence of $\theta_D(T)$ is neglected in the current exercise.

Predictions – general trends

In theoretical predictions of $m$, $K_i$, and $T$ dependence of the Raman redshift, we may assume $\eta_2 = 0$ for numerical convenience because the $\eta_2$ only leads to a negligible offset of the predicted trends. In this prediction, $m = 3, 5$ and $T/T_m = 1/3$ and $2/3$ are used because $m = 1$ applies only to pure metals with simple Bravais unit cells possessing no optical modes of vibration. For the general trend prediction, we used $T_0 = 0$. For comparison between predictions and the measured data of size dependence, $T = T_0 = 300 \text{ K}$ was taken. In Fig. 2(a) and (b), the $K_i$ and $T$ dependence of the Raman shift is shown, which is obtained from Eqns (7) and (10).
Figure 2. Predictions of (a) size-dependent Raman shift for $m = 3$ and $5$, $T/T_m = 1/3$ and $2/3$. The Raman redshift increases with increasing $m$ and $T$; (b) temperature-dependent Raman shift with $m = 3$, $5$ and $\theta_p/T_m = 0.25$ and $0.50$. The specific heat per bond $\eta_1(T)$ is considered to be a constant when $T > \theta_0$ and follows Debye’s formulation for specific heat when $T < \theta_0$. A plateau is observed at low temperature due to the reduced specific heat $\eta_1(T)$ at low temperature. This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

Figure 3. Comparison of prediction to the measured size- and $T$-dependent shifts: (a) least square fitting to obtain $\omega(\infty, T_0 = 300 \text{ K}) = 518.5 \text{ cm}^{-1}$ for Si; (b) compares our prediction using Eqn (7), the prediction agreeing very well with the experimental data when $\eta_21$ is $0.1 T_m$; (c) compares the temperature-dependent Raman shift for bulk GaN$^{37}$ and Eqn (9), where $\omega(0) = 568.4 \text{ cm}^{-1}$ and $\eta_21$ is $0.9 T_m$, our prediction matching the experimental data quite well; (d) $K_j = 11$ and $\eta_21$ is $0.1 T_m$ for Si nanocrystal.
Size-dependent Raman shift and monatomic chain vibration

According to Eqn (7), the Raman shift is inversely proportional to the size of nanocrystal. Figure 3(a) shows the least square fitting of the measured size-dependent data\(^3\) from which \(\omega(\infty, T_0)\) is obtained as 518.5 cm\(^{-1}\) at 300 K. Furthermore, from our BOLS prediction, a good agreement of the size-dependent Raman shift at \(T_0 = 300\) K with experimental data is also obtained in Fig. 3(b).

Temperature-dependent Raman shift and specific heat per bond

Figures 3(c) and (d) show the consistency between predictions and measurement of the temperature-induced Raman shift. In Fig. 3(c), the temperature-dependent Raman shift for bulk GaN\(^5\) is predicted using Eqn (9), where \(T_0\) is set to 0 K, and \(\omega(T_0) = 568.4\) cm\(^{-1}\). When the materials are reduced to the nanometer scale, both size and temperature will affect the Raman redshift. The combination effect can be obtained in Eqn (7). Figure 3(d) shows both the experimental data\(^3\) and prediction of the Raman redshift with respect to temperature for 5.1 nm nanoparticles.

Surface atom vibration

We may extend Einstein’s relation for gaseous phase to the surface atomic vibration, to derive that

\[
\frac{\omega_b}{\omega_b^\prime} = \frac{z_3}{z_3^\prime} = \frac{2}{3} \frac{\omega (0)}{\omega (z)} = \frac{\omega (0)}{\omega (z)} = \frac{\omega (0)}{\omega (z) / (m/2 + 1)} = \frac{\omega (0)}{\omega (z) / (m/2 + 1)}
\]

\[
= \sqrt{\frac{3}{2}} \times 0.883^{1/2} = 1.12 \quad \text{Si}
\]

The vibrational amplitude of an atom at the surface of an MC is indeed greater than that of a bulk atom while the frequency is lower. The magnitude and frequency are sensitive to the \(m\) value and vary insignificantly with the curvature of a spherical dot when \(K_p > 3\). This result verifies the assumption\(^10\) that the vibrational amplitude of the broken surface atom is always greater than the bulk value and it is constant for all particle sizes.

SUMMARY

An analytical form has been presented for the atomistic origin and temperature dependence of Raman optical redshift in nanostructures from the perspective of surface bonds. Most strikingly, the combination of the freedom of solid size, temperature domain, and Raman spectroscopy has allowed us to gain quantitative information about the vibrational frequency of a monatomic chain and the ratio between the latent heat of atomization and the specific heat per bond, which is beyond the scope of traditional size- and temperature-independent approaches. As the approach follows a bond-by-bond, atom-by-atom, shell-by-shell approach, no other constraints for the continuum medium are applied. This approach may be extended to the vibration of atoms in a junction interface and surrounding point defects.

REFERENCES

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