Theoretical investigation of the surface vibrational modes in germanium nanocrystals

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Quantum dots (QD’s) and nanocrystals (NC’s) have received great attention in recent years both for their fundamental science and potential applications. In particular, when the size of NC is decreased the number of atoms located on its surface increases proportionally. These atoms are subject to forces different from those in the interior of the NC. As a result, their vibrational frequencies differ from those of the bulk. Furthermore, their interaction with electrons confined in the NC are also expected to be different from those of the bulk phonon modes. While the Raman spectra of Ge NC of different sizes have been reported, there is no breakdown of the Raman modes into those dominated by surface atoms and those dominated by atoms in the interior. Typically two features attributed to the formation of the NC have been noted in the experimental spectra. A “redshift” of the zone center optical phonon has been attributed to the quantum confinement effect. In the low frequency range, Raman modes whose frequency increases with decrease in NC size have been reported and were attributed to distortion modes of a continuum sphere calculated theoretically by Lamb. Such continuum models are expected to breakdown for nm size NC. So far microscopic calculation of the vibration modes and Raman spectra has been reported in Ge and other NC. However, the theoretical calculations have not separated the predicted modes into surface and bulk modes. In this Brief Report, we have analyzed the “surface” characteristics of phonon modes in Ge NC by comparing the relative vibration-amplitude squared (or VAS in the rest of this article) of atoms located near the NC surface with those in the interior of the NC. We have also been able to relate the NC phonon modes to the Lamb modes.

The theoretical model that we have used to investigate phonon modes in Ge NC is the same valence force field model (VFFM) that we have developed in recent years to calculate phonon modes in semiconductor NC (these have also been referred to as quantum dots or QD’s in our previous publications; in this paper we will use the terms interchangeably) including complex nanostructures, such as NC’s containing a core of GaAs surrounding by a shell of AlAs. In this model, the change in the total energy of a NC due to the lattice vibration is described in terms of two bond stretching and bending parameters: C0 and C1 (assumed to be equal to 47.2 and 0.845 eV respectively, for Ge). To simplify the diagonalization of the dynamical matrix, we classify the vibration modes according to the point group symmetry of the atoms in the NC (which is tetrahedral or Td for Ge). This simplification allows us to study NC whose vibrational modes are normally too complex to compute numerically. In the present paper we have studied NC’s containing as many as 7289 Ge atoms (a sphere of diameter approximately = 6.8 nm). All the NC are assumed to have a stress-free surface.

In Fig. 1 we plot the phonon density of states (PDOS) after a small Lorentzian broadening for five Ge NC’s with different numbers (N) of atoms. In this paper we shall define “surface atoms” as those atoms containing at least one dangling bond. Atoms with no dangling bonds are defined as interior or “body atoms.” For the largest NC (N = 1147) in Fig. 1 we noticed that there are two relatively sharp peaks (around 25 and 37 cm⁻¹ and high-lighted by arrows) in the 0–100 cm⁻¹ frequency range of the PDOS. Two similar peaks are also observable in the N = 873 NC at slightly different frequencies. To determine whether a mode involve mainly surface atoms or body atoms we have adopted the following approach. We first calculated the vibration-amplitude-squared (VAS) for each atom in the NC corresponding to a given eigenmode. We then select the atom with the maximum VAS (MVAS) and determine whether this atom is a surface or body atom. This approach is similar to the inverse partition ratio method described in Refs. 14 and 15. In case of a surface mode the atom with the MVAS will be a surface atom and, in addition, the value of its MVAS will be large. Depending on whether this atom is a body or surface atom its MVAS are plotted separately in Fig. 2 for Ge NC containing up to 1147 atoms (d ~ 3.7 nm) as a function of vibrational frequencies. From these plots it is clear that modes with the lowest frequencies (<50 cm⁻¹) involve relatively larger motion of surface atoms and, therefore, can
be classified as surface modes. In the frequency range of 50 to 200 cm$^{-1}$ the phonon modes involve both surface and body atoms so it is not meaningful to classify them as bulk or surface modes. The modes in the highest frequency range (200 cm$^{-1}$) correspond to the optical phonons in bulk Ge and involve mostly body atoms. The exception is a mode around 260 cm$^{-1}$ where surface atoms have relatively large MVAS. This mode is not strong enough to appear as a sharp peak in the PDOS in Fig. 1. In other words this surface mode is really a resonant mode. The reason is because there is no true gap in the PDOS of bulk Ge in this region between the acoustic and optical branches. Surface atoms in a NC have at least one dangling bond which tends to weaken their spring constants. In bulk crystals a weakening of the spring constant can result in the appearance of “gap modes” if there is a gap in the PDOS. In bulk Ge there is only a region of low PDOS or a “pseudogap” as a result of crystal symmetry and hence only resonant surface modes exist in Ge NC.

So far, low frequency (~10–20 cm$^{-1}$) Raman modes have been reported in spherical NC of Ge, CdS, and CdSSe (Ref. 5) embedded in glasses. One characteristic of these low frequency modes is that their frequencies scale inversely with the diameter ($d$) of the NC. These experimental results have typically been interpreted in terms of the vibrations of a homogeneous and spherical elastic body under stress-free boundary conditions first worked out theoretically by Lamb. These vibrational modes can be classified as either spheroidal (pictured as breathing modes of a sphere) or torsional (involve twisting of the sphere). The frequencies of these modes are quantized and depend on two integers: a branch number $n$ and the angular momentum $l$. For brevity, we shall denote the Lamb modes with $n$ and $l$ as ($n,l$). The torsional mode frequencies depend on the transverse acoustic phonon velocity ($v_t$) while the spheroidal mode frequencies depend on both the longitudinal acoustic phonon velocity ($v_l$) and $v_t$. In Ge NC with $d=13$ nm Ovsyuk et al. have observed two Raman modes with frequencies of 10.2 and 7.3 cm$^{-1}$ which they interpreted as due, respectively, to the spheroidal and torsional modes of Ge spheres. The frequencies of such modes (in cm$^{-1}$) calculated according to the Lamb theory are $f_s = 0.7 \left( \frac{v_l}{dc} \right)$ (where $c$ is the speed of light in vacuum) and $f_t = 0.85 \left( \frac{v_t}{dc} \right)$, respectively. From the experimental frequencies, Ovsyuk et al. determined the ratio of $v_l/v_t = 1.67$ in Ge. By averaging the acoustic phonon velocities in bulk Ge over several high symmetry directions, they obtained the values of $v_l = 5.25 \times 10^5$ cm/s and $v_t = 3.25 \times 10^5$ cm/s leading to a ratio of $v_l/v_t = 1.62$, in good agreement with their Raman result.

To extract the frequencies of Lamb modes from our microscopic calculation for comparison with experiment, we
first calculate the displacement pattern for the Lamb modes with \( n = 0 \) and different values of \( l \). To determine their frequencies, we project the atomic displacements of the NC eigenmodes from our lattice dynamical calculation along the Lamb mode vectors. After that we sum over the displacement amplitudes projections and then square the sum. In this calculation we can either include only lattice modes of a particular symmetry or modes of all symmetries. Although the Lamb modes are defined for a system with spherical symmetry, the contributions to a particular Lamb mode are sometimes dominated by lattice modes of a particular symmetry. The results obtained in this way for the \( n = 0 \) and \( l = 3 \) torsional Lamb mode are shown in Fig. 3 for NC with two different sizes. As can be seen from Fig. 3, the \( l = 3 \) torsional modes are dominated by the \( T_2 \) symmetry lattice modes. The contributions of lattice modes of other symmetries are many orders of magnitude smaller than that of \( T_2 \) symmetry. We find also that the low frequency regions of the plots (with \( T_2 \) symmetry) in Fig. 3 become dominated by only one peak as \( N \) becomes larger. If we repeat the calculation for torsional modes with different values of \( l \) (while keeping \( n = 0 \)) we find there is usually a low frequency peak which dominates the plot but the strength of these lowest frequency peaks is largest for \( l = 3 \). Thus the frequency of the experimentally observed torsional Lamb mode can be attributed mainly to that of the \( n = 0 \) and \( l = 3 \) mode. Furthermore, this frequency can be deduced from a plot of the lattice modes with \( T_2 \) symmetry, such as those shown in Fig. 3. We have also performed similar computations for the Lamb spheroidal modes. In this case the strongest contribution comes from the \( n = 0 \) and \( l = 0 \) mode. A projection of the lattice mode onto this Lamb spheroidal mode shows that it is dominated by lattice modes of \( A_1 \) symmetry.

From our calculations described above we have obtained the variations in the frequencies of the strongest Lamb spheroidal mode \((0,0)\) and torsional mode \((0,3)\) with the size of the NC (see open squares and circles and the solid lines drawn through them in Fig. 4) for comparison with experiment. The crosses in Fig. 4 indicate the \( d = 13 \) nm Ge NC results of Ovsyuk et al.\cite{Ovsyuk2001} From our calculation we predict that, for \( d = 13 \) nm, the frequencies of the \((0,0)\) spheroidal and \((0,3)\) torsional modes are equal to 10.0 and 4.8 cm\(^{-1}\), respectively. The value of the spheroidal mode is in good agreement with the experimental value. The value of the torsional mode is too small compared with the experimental value of 7.3 cm\(^{-1}\). The reason for this discrepancy is that our force constants have been chosen to fit the zone-edge acoustic phonon frequencies.\cite{Ovsyuk2001} We expect that agreement between theory and experiment will be improved if we choose a different set of values for \( C_0 \) and \( C_1 \) (equal to and 47.7 and 2.8 eV, respectively) which have been obtained by fitting the elastic constants. The Lamb modes frequencies calculated with this alternate set of force constants are shown in Fig. 4 as broken lines. From these curves we obtained the Lamb spheroidal and torsional mode frequencies for \( d = 13 \) nm spheres to be 10.2 and 8.3 cm\(^{-1}\), respectively. We note that
the good agreement between theory and experiment is preserved for the spheroidal mode while the discrepancy between theory and experiment for the torsional mode is greatly reduced.

For NC with \( N < \sim 800 \) (or \( d < 3 \) nm) we found that the projection of the lattice modes onto the Lamb modes no longer produce sharp peaks similar to the Lamb modes. However, one should not confuse these peaks in the PDOS with the Lamb modes. While the Lamb mode frequencies depend on the sphere size, the frequencies of the surface lattice modes are independent of the NC size and do not scale as (1/d). This result indicates that the Lamb model is no longer valid for such small NC but instead discrete surface lattice modes dominate the low frequency region of the PDOS.

In summary, we have applied a microscopic VFFM to investigate theoretically the phonon properties of Ge NC as a function of their size. We have identified both high frequency resonant surface mode and low frequency surface modes. In the larger NC these latter surface modes of specific symmetry contribute predominantly to the Lamb spheroidal and torsional modes of a continuum sphere. Our calculated Lamb modes frequencies are in good agreement with available experimental data in Ge. We also show that the Lamb model starts to break down for Ge NC with diameter smaller than 4 nm.

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13. W. A. Harrison, Electronic Structures and the Properties of Solids (Freeman, San Francisco, 1980). It should be noted that two different sets of values of \( C_0 \) and \( C_1 \) are given in this book. The set with \( C_0 = 47.2 \) eV and \( C_1 = 0.845 \) eV (from Table 9-1) have been obtained by fitting the zone-edge phonon frequencies. A different set of values with \( C_0 = 47.7 \) eV and \( C_1 = 2.8 \) eV (in Table 8-4) have been obtained by fitting the elastic constants.