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We have used a microscopic lattice dynamical model to study phonon modes in germanium (Ge) NC with size varying between 47 to 7289 atoms (diameter$\sim$6.8 nm). By separating these atoms into bulk and surface atoms we have found that surface modes can exist in Ge NC both at low frequencies (<50 cm^{-1}) and at high frequency (~ 260 cm^{-1}). The latter mode is a resonant mode which occurs in the ''pseudogap'' between the acoustic and optical phonon branches in bulk Ge. From the low frequency surface modes we have been able to reconstruct the spheroidal and torsional Lamb modes which have been used to interpret experimental results. Finally, we found that the Lamb model starts to deviate from the lattice dynamical results for Ge NC with diameter <4 nm and breaks down for NC smaller than 3 nm.

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Quantum dots (QD's) and nanocrystals (NC's) have received great attention in recent years both for their fundamental science[1] 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,[2,3] 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.[3] In the low frequency range, Raman modes whose frequency *increases* with decrease in NC size have been reported[2,4,5] and were attributed to distortion modes of a continuum sphere calculated theoretically by Lamb.[6] 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-amplitudes 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 two terms interchangeably) including complex nanostructures, such as NC's containing a core of GaAs surrounding by a shell of AlAs.[7–12] 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: C_0 and C_1 (assumed to be equal to 47.2 and 0.845 eV,[13] 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 T_d 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 d 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 ($d\sim 3.7$ 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

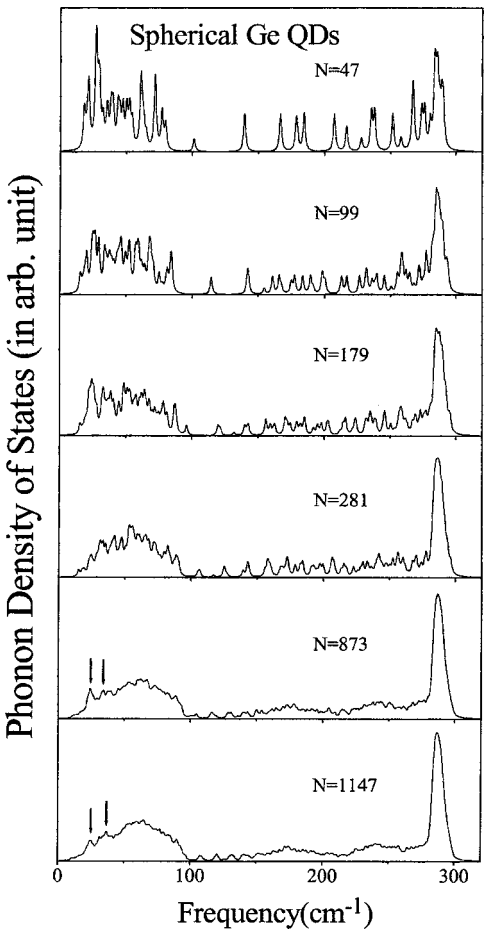

FIG. 1. Phonon density-of-states of Ge nanocrystals (NC) with varying number of atoms. The largest NC with 1147 atoms has an approximate diameter of 3.7 nm. The two vertical arrows indicate the surface modes that remain visible even as the NC size becomes larger.

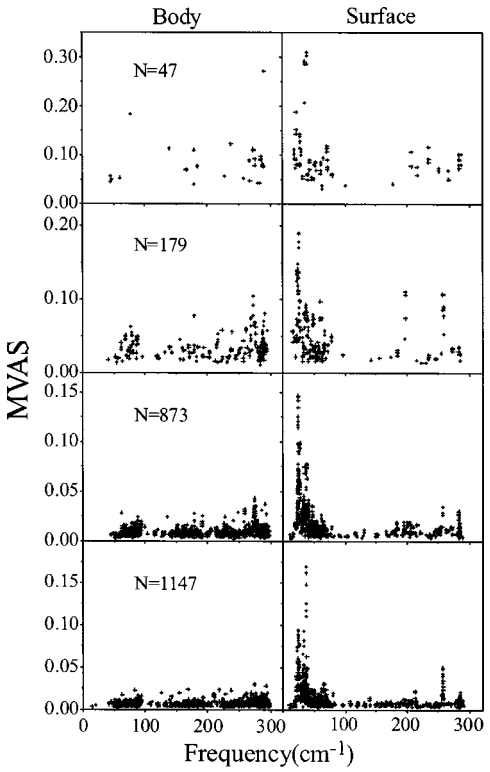

FIG. 2. Surface and body atoms with the maximum-value-of-amplitude-squared (MVAS) in Ge NC with total number of atoms $N=1147$, 873, 179, and 47 atoms with their MVAS plotted as a function of the mode frequency.

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 ($\sim 10-20$ cm^{-1}) Raman modes have been reported in spherical NC of Ge,[2] CdS,[4] 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 homogenous and spherical elastic body under stress-free boundary conditions first worked out theoretically by Lamb.[6] These vibrational modes can be classified as either spheroidal (pictured as breathing modes of a sphere[5]) 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.*[2] have observed two Raman modes with frequencies of 10.2 and 7.3 cm^{-1} which they interpreted as due, respectively, to the spheriodal and torsional modes of Ge spheres. The frequencies of such modes (in cm^{-1}) calculated according to the Lamb theory are $f_s=0.7$ (v_l/dc) (where c is the speed of light in vacuum) and $f_t=0.85$ (v_t/dc), respectively. From the experimental frequencies, Ovsyuk *et al.*[2] 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 $v_l=5.25\times10^5$ cm/s and $v_t=3.25\times10^5$ 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

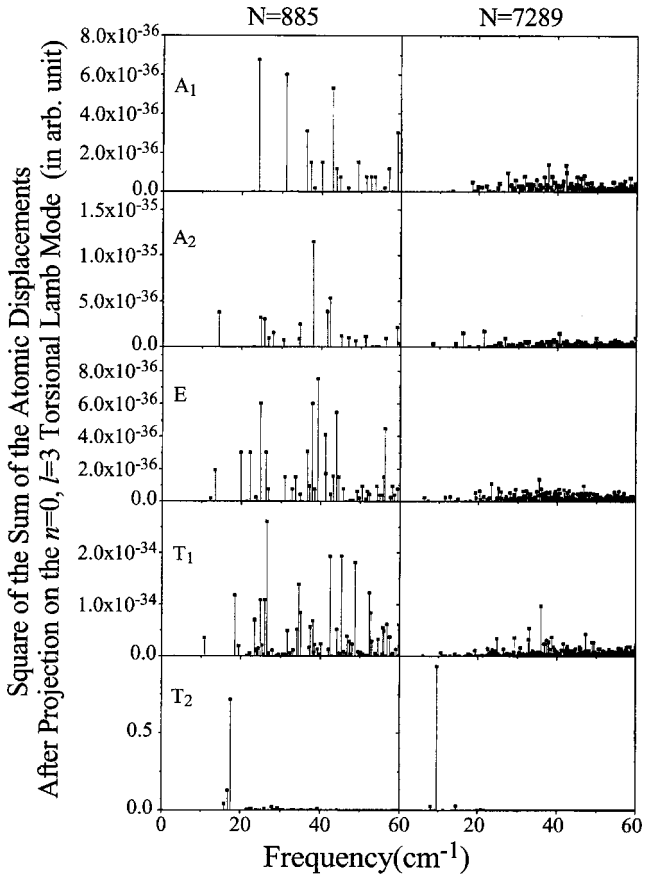

FIG. 3. The square of the sum of the projection of atomic displacements of lattice modes of different symmetries of the T_d group along the eigenvector of the $n=0$, $l=3$ torsional Lamb mode plotted as a function of the lattice mode frequency for nanocrystals of two different numbers (N) of Ge atoms.

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 torional 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

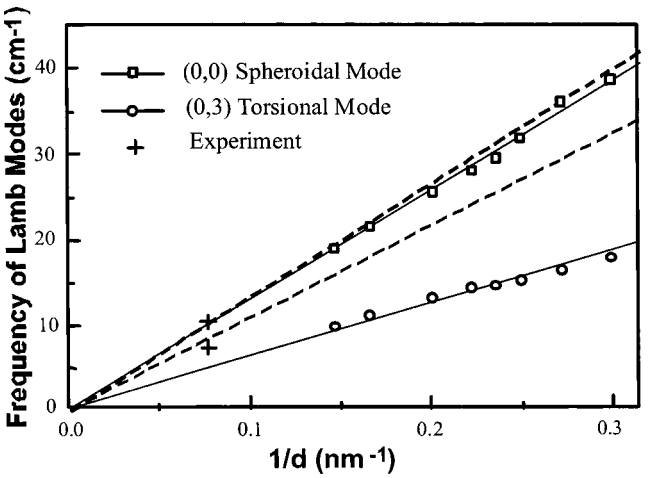

FIG. 4. The NC size dependence of the theoretical frequencies of the Lamb (0,0) spheroidal and (0,3) torsional modes (open square and circles, respectively) with the largest strength deduced from plots similar to those in Fig. 3 (using the force constants $C_0=47.2$ eV and $C_1=0.845$ eV). The solid lines are least square fits to the theoretical points. The broken lines were obtained by repeating the calculation with an alternate set of force constants $C_0=47.7$ eV and $C_1=2.8$ eV. The crosses represent the mode frequencies measured by Ovsyuk *et al.* (Ref. 2) in NC with diameter of 13 nm.

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.*[2] 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.[13] 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.[13] 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 in stead 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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