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LETTER TO THE EDITOR

The vibrational density of states and specific heat of Si nanocrystals

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Abstract

The vibrational density of states and phonon specific heat of Si nanocrystals are studied by means of a lattice dynamical calculation. The vibrational density of states of Si nanocrystals is distinct from the bulk one at low and high frequencies owing to the finite-size effect. At low frequencies there is an excess of the vibrational modes, while there is a deficit at high frequencies. At low frequencies the dependence of the vibrational density of states on frequency is intermediate between linear and quadratic. The specific heat of Si nanocrystals is enhanced as compared to that of the bulk with a maximal excess at around 90 K. The dependence of the specific heat on temperature deviates from the known T^3 -law for crystalline systems at low temperatures.

Recently, the electronic and optical properties of nanocrystals, also known as quantum dots, have attracted much attention owing to their interesting physical properties and potential applications as well. The wavefunctions of electrons and phonons in nanocrystals are considerably modified compared to the counterparts in the corresponding crystalline phases due to the finite-size effects. Although a variety of physical properties of nanocrystalline materials have been extensively studied, their thermodynamical properties have received less attention. It has been found by experiments that there are interesting lattice dynamical properties of metallic nanocrystals [1–7]. The vibrational density of states (VDOS) in metallic nanocrystals at low frequencies is enhanced as compared to that of the bulk [1–7]. Moreover, the dependence of the VDOS on frequency is linear at low frequencies, rather than quadratic as for the bulk. These features have been confirmed by a theoretical calculation for Ag nanocrystals [8]. Experimental measurements have revealed an enhancement of the phonon specific heat in Pd [9, 10] and Cu [9] nanocrystals. Atomistic simulations of nanocrystalline model materials based on the Lennard-Jones potential showed an anomaly of the specific heat [11]. The binding and structural properties of semiconductors are rather different from those of metals. Therefore, it is of interest to study the vibrational and thermodynamical

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properties of semiconductor nanocrystals. Vibrational properties of Si nanocrystals have been investigated by Raman spectroscopy [12–17] and by means of theoretical calculations based on either phenomenological models [17–19] or microscopic ones [20–22]. To our knowledge, there have, however, been few studies on the thermodynamic properties of Si nanocrystals.

In the present work, a microscopic lattice dynamical calculation is carried out to study the VDOS and phonon specific heat for Si nanocrystals. Si nanocrystals are modelled by spherical bulk-terminated Si clusters. The nanocrystal surface is assumed to be free without relaxation and reconstruction, as adopted in the study of the electronic [23] and vibrational properties [20, 24] of semiconductor nanocrystals, since the x-ray characterizations revealed that the relaxation is very small [15]. The force constants in Si nanocrystals are taken to be the same as those in the bulk. We use the same force constants for Si nanocrystals as are used for bulk Si. The force constants up to the fifth-nearest neighbours are obtained by a partial density approach [25], which can give an overall satisfactory description of the lattice dynamical properties of bulk Si.

The computational procedure is as follows. First we use the force constants to construct the dynamical matrix for a given Si nanocrystal. We then solve the standard eigen-problem of the secular equation resulting from the dynamical matrix. The eigen-frequencies and eigenfunctions can be obtained, from which the VDOS or local VDOS will be calculated. From the VDOS obtained the phonon specific heat of a nanocrystal at constant volume can then be calculated from [26]

$$C_V(T) = k_B \int \left(\frac{\hbar\omega}{k_B T} \right)^2 \rho(\omega) \frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2} d\omega \quad (1)$$

where k_B is the Boltzmann factor, T is the temperature, and $\rho(\omega)$ is the VDOS.

The size of a spherical Si nanocrystal is defined as its diameter, given by $L = (3N/4\pi)^{1/3}a$, where a is the lattice constant of crystalline Si and N is the number of Si atoms in the nanocrystal. Nanocrystals consisting of 239, 471, and 943 atoms with sizes 2.09, 2.52, and 3.30 nm, respectively, are studied.

Figure 1 shows the VDOS for the three nanocrystals studied together with the differential VDOS with respect to that of the bulk. The calculated VDOS is smoothed by using a Lorentzian function with a width of 15 cm^{-1} . The VDOS for each nanocrystal is normalized to 1. It is found that even for a nanocrystal with size smaller than 2 nm (not shown here), the general features of the VDOS resemble those of the bulk except for low and high frequencies. The similarity in VDOS between nanocrystals and the crystalline phase increases with the size of the nanocrystals. In the intermediate frequency range the difference in VDOS between nanocrystals and bulk is rather small. Note that there are, however, two features of the VDOS for the nanocrystals that differ significantly from those of the bulk at low and high frequencies.

At high frequencies, corresponding to the optical-like vibrations, the VDOS of Si nanocrystals is lower than that of the bulk and decreases with decreasing size. The peak position at around 500 cm^{-1} is found to be shifted downward in frequency with decreasing size owing to the confinement effects. For metallic nanocrystals [4–8] there exists a high-frequency tail that extends beyond the top of the bulk band. The high-frequency tail is attributed to the global shrinking of the metallic nanocrystals [8], leading to an enhancement of the force constants. In Si nanocrystals there is no such feature owing to the difference in structural and binding properties between metal and semiconductor nanocrystals.

At low frequencies, corresponding to the acoustic-like vibrations, an excess of vibrational modes is found as compared to the bulk. The maximal excess occurs at around 100 cm^{-1} . The enhancement of the VDOS at low frequencies increases with decreasing size. This characteristic has been reported recently for metallic nanocrystals experimentally [1–7] and has

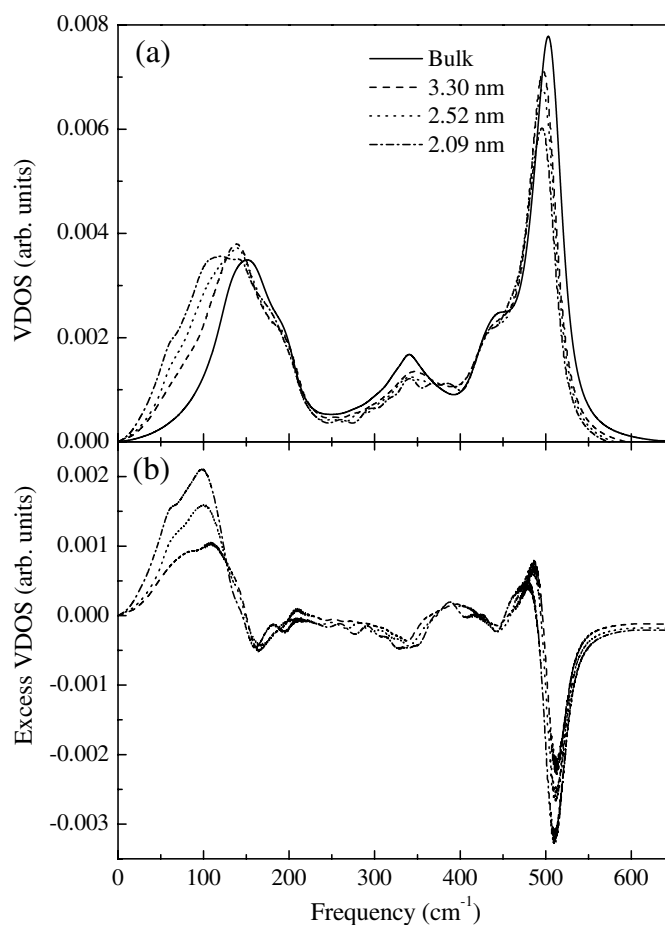


Figure 1. (a) The total VDOS for Si nanocrystals of size 2.09 nm (dash-dotted line), 2.52 nm (dotted line), and 3.30 nm (dashed line). The bulk VDOS (solid line) is also given for comparison. (b) The excess of the VDOS of Si nanocrystals with respect to that of the bulk.

been confirmed by a lattice dynamical calculation for Ag nanocrystals [8]. The enhancement of the VDOS at low frequencies is related to the finite-size effect. The coordination number of the surface atoms is less than that of the bulk atoms, leading to changes in the force field, which are responsible for the enhancement of the low-frequency modes.

It is known that the VDOS of a perfect crystal satisfies $\rho(\omega) \propto \omega^{d-1}$ variation at low frequencies, where d is the dimension [26]. For three-dimensional crystalline systems a quadratic relation is expected. It has been found experimentally that the dependence of the VDOS on frequency at low frequencies is linear for Pd nanocrystals [3, 7]. A theoretical calculation on Ag nanocrystals also gave a linear relation [8]. The linear dependence of metallic nanocrystals indicates that they behave like two-dimensional crystals at low frequencies. For Si nanocrystals, however, this dependence at low frequencies is found to be neither quadratic nor linear. A close examination of the VDOS of Si nanocrystals gives a relation intermediate between linear and quadratic at low frequencies for the three nanocrystals studied. The difference in behaviour of the VDOS for Si and metallic nanocrystals at low frequencies reflects the difference in binding and structural properties between semiconductor and metal.

The VDOS at low frequencies also reveal a tendency of approaching the bulk relation with the increase in nanocrystal size, as expected.

To display the origin of the enhancement of the VDOS of Si nanocrystals at low frequencies, the local VDOS of a Si nanocrystal with size 3.3 nm projected into different shells is shown in figure 2. The central atom is defined as the first shell and the first-nearest-neighbour atoms as the second shell. The subsequent shells are defined accordingly. For a Si nanocrystal with the size of 3.3 nm, there are in total 35 shells. At low frequencies the VDOS of the inner shells is close to that of the bulk. An obvious deviation occurs after the 25th shell. Evidently the outer atoms are responsible for the excess of the low-frequency modes.

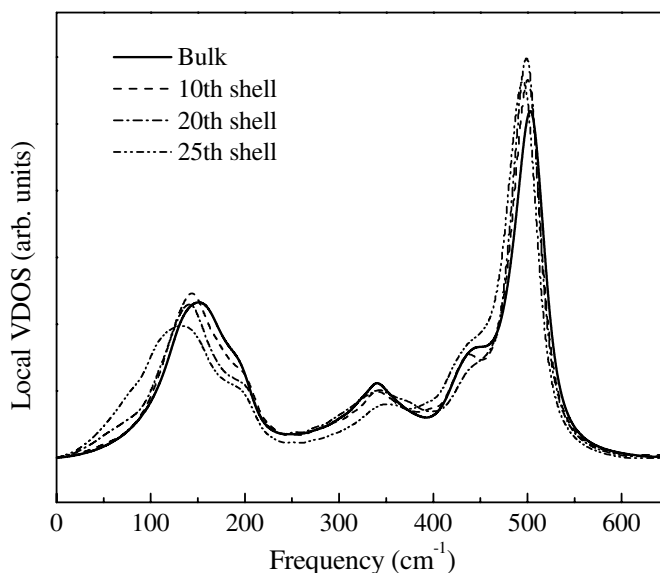


Figure 2. The projection of the local VDOS for the Si nanocrystal of size 3.2 nm into the 10th shell (dashed line), 20th shell (dash-dotted line), and 25th shell (dash-dot-dotted line) together with the bulk one (solid line) for comparison. The local and bulk VDOS are normalized to 1.

The VDOS in nanocrystals being different from that in bulk will certainly affect their thermodynamical properties. In figure 3 the calculated phonon specific heat of Si nanocrystals is given. It is obvious that there is an excess of the specific heat of Si nanocrystals over that of the bulk. As discussed above, there is an enhancement of the VDOS of Si nanocrystals at low frequencies. Consequently, the specific heat of Si nanocrystals is expected to be enhanced compared to that of the bulk. This behaviour has been found in metallic nanocrystals [9, 10]. Note that the maximal excess occurs at around 90 K. It is found that the specific heat of Si nanocrystals increases with decreasing size and will approach the bulk value eventually with the increase in size, as expected. At low temperatures, a T^3 -dependence of the specific heat of the bulk is desired [26]. For Si nanocrystals the T^3 -dependence is, however, not maintained since the dependence of the VDOS on frequency at low frequencies is intermediate between linear and quadratic. A dependence intermediate between quadratic and cubic is expected. It should be stressed that the difference in phonon specific heat between Si nanocrystals and the bulk is about a few per cent and could be observable by experiment, especially at around 90 K.

In summary, we have studied the VDOS and phonon specific heat of Si nanocrystals by means of a lattice dynamical calculation. The enhancement of the VDOS of Si nanocrystals at low frequencies is caused by the finite-size effect. At low frequencies the dependence of

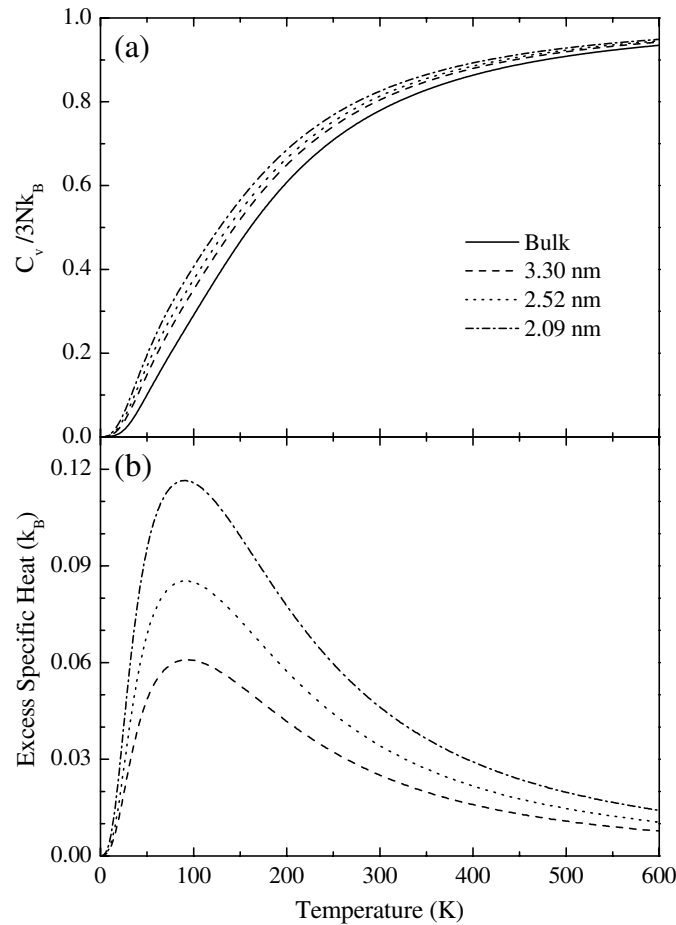


Figure 3. (a) The phonon specific heat for Si nanocrystals of size 2.09 nm (dash-dotted line), 2.52 nm (dotted line), and 3.30 nm (dashed line). The bulk values (solid line) are also given for comparison. (b) The excess of the specific heat of Si nanocrystals with respect to that of the bulk.

the VDOS in Si nanocrystals on frequency is intermediate between linear and quadratic. At high frequencies the VDOS of Si nanocrystals is depressed and there is a downward shift of frequency for the peak position owing to the confinement effects. The specific heat of Si nanocrystals is enhanced as compared to that of the bulk. The maximal excess occurs at around 90 K. At low temperatures the dependence of the specific heat on temperature is intermediate between quadratic and cubic.

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