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Lattice reorganization in electronically excited semiconductor clusters

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Upon electronic excitation of a binary bulk semiconductor the lattice reorganizes, the extent of the deformation depending on the ionicity of the lattice.¹⁻⁴ We demonstrate here that when the crystal dimension becomes comparable to the bulk exciton diameter, this well-known effect in bulk solids depends strongly on the size of the crystal.

Cadmium sulfide is the prototypical material for studies of the effects of quantum confinement on the electronic and optical properties of semiconductors.⁵ The absorption edge of CdS shifts to higher energy when the crystal is comparable in size to the bulk exciton diameter of 60 Å (Bohr radius of 45 Å). This shift is the signature of major changes in the spatial wave functions of the electron and hole in the electronic excited state. In the bulk, the electron and hole are coulombically bound to each other in a hydrogenic state, with the electron, the lighter of the two particles, significantly more delocalized than the hole. In particles much smaller than the bulk exciton diameter, the spatial wave functions of electron and hole become particle-in-a-spherical-box type functions, with much greater spatial overlap between electron and hole.

Electronic excitation in *bulk* CdS produces a lattice deformation, which is manifested in the resonance Raman spectrum as a strong (up to nine) overtone progression of long wavelength longitudinal optical vibrations.⁶ In the Frohlich coupling model,¹⁻⁴ an excess negative charge in the semiconductor induces a distortion of the ionic lattice. An excess positive charge induces a distortion opposite in direction. The amount of lattice distortion induced by optical excitation is determined by the spatial overlap of the electron and the hole, greater electron-hole overlap leads to smaller lattice distortions.

A previous study of the resonance Raman spectrum of 40 Å diameter CdSe showed a progression in the *LO* overtones with different relative intensities of the overtones compared to the bulk.⁷ In this experiment we show that: 1) the relative intensities of the overtones in the resonance Raman spectrum of CdS depend smoothly on cluster size; and 2) absolute cross-section measurements are essential to determine the cause for the observed changes.

Crystalline CdS particles with bulk lattice constant and "capped" with thioglycolate molecules have been prepared and characterized by well-established methods, including x-ray powder diffraction and transmission electron microscopy.⁸⁻⁹ The variation in diameter about the mean is $\pm 15\%$. A full report on the synthesis of these samples is in preparation. Figure 1 shows the size dependent resonance Raman spectra measured using a tunable dye laser as the excitation source, a SPEX triple monochromator to isolate the inelastically scattered light, and a CCD camera to record the spectrum. For each sample relative resonance Raman excitation spectra were recorded at ambient temperature.

Figure 2 shows the absolute resonance Raman excitation spectrum of 70 Å diameter CdS clusters.

Our data shows two trends with size. First, the relative size of the overtone decreases with respect to the fundamental in smaller clusters. Second, the *absolute* efficiency of the resonance Raman scattering decreases with decreasing cluster size. To quantitate these observations, we model our data using the Albrecht *A* term single mode offset harmonic oscillator description of the resonance Raman process which has been proposed to explain the bulk data.^{1,10,11} In this model, three parameters describe the resonance Raman process: the oscillator offset between ground and excited states, Δ , and the sum of the population and dephasing lifetimes of the electronic excited state and the temperature. Changing the offset directly affects the Franck-Condon factors and thus the overtone ratio, and shifts the peak of the resonance Raman excitation spectrum. Reducing the excited state lifetime decreases the absolute intensity of the resonance Raman signal and increases the strength of the fundamental relative to the overtone. The temperature determines the ground electronic state vibrational populations; including this effect changes the calculated excitation profiles by approximately 10%. For 70 Å diameter CdS, the absolute cross section and wavelength dependent overtone ratio data are fit by $\Delta = 2$ (in units of the oscillator zero point motion) and an excited state lifetime of 50 fs. For the bulk case $\Delta = 3$ and the lifetime is on the order of nanoseconds. The total energy depos-

FIG. 1. Resonance Raman spectra of CdS clusters, scaled to illustrate the size dependence of the ratio of fundamental to overtone. In each case, the exciting radiation wavelength was at the peak of the resonance Raman excitation spectrum.

FIG. 2. Absolute resonance Raman excitation spectrum for 70 Å diameter CdS clusters. The curve represents the best fit to a single offset harmonic oscillator model.

ited into the lattice upon electronic excitation, $\Delta^2 \hbar \omega_{lo}$, is reduced by a factor of two in 70 Å diameter CdS particles, compared to the bulk solid.

We conclude that two effects are responsible for the observed changes in the resonance Raman process with crystal size. First, increased spatial overlap of electron and hole in

the clusters, relative to the bulk, leads to reduced Frohlich coupling. Second, trapping of the electronic excited state by defects, especially those on the surface, reduces the excited-state lifetime. By measuring overtone ratios and absolute cross sections for different size clusters as a function of temperature these effects can be separated, and this work is now in progress.

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Anisotropic effects in x-ray Raman scattering from graphite

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Extended x-ray absorption fine structure (EXAFS) is now widely applied to study local structures around a selected central atom in amorphous materials. Wide application of EXAFS to low *Z* elements is, however, hampered because they have characteristic absorptions in the soft x-ray region, where experiment is plagued with various technical difficulties. Very recently we have reported EXAFS-like wiggles in the x-ray Raman spectra of graphite and diamond, and showed that they coincide very well with those observed in

soft x-ray absorption^{1,2}; thus it was proved for the first time that x-ray Raman scattering is capable of providing the same information as absorption, as was suggested over 30 years ago.^{3,4} By combining the theories for x-ray Raman scattering and EXAFS, the equation proposed for EXAFS analysis of isotropic materials⁵ was successfully applied to extract structural parameters.

For anisotropic materials additional information can be obtained, since the momentum transfer or scattering vector *s*