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Size effects on the phonon spectra of quantum dots in CdTe-doped glasses

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We studied the confinement effects on the phonon spectra of CdTe quantum dots by means of resonant Raman scattering measurements. The spectra show clearly longitudinal optical phonons, surface phonons and some of their overtone combinations. We show that the scattering due to surface phonons increases as the quantum dot size decreases. The results are obtained by tuning the laser excitation energy to resonance for quantum dots of different sizes inside the broad size distribution in CdTe-doped glasses. © 1996 American Institute of Physics.

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The quantum-confinement effects on the optical properties of nanocrystallites in semiconductor doped glasses is the subject of much current research. The interest arises because of the great potential of these materials for optical device applications due to their nonlinear optical properties.¹⁻⁶ Experimental and theoretical studies showing the confinement effects on the electron states and their confined energy levels are now quite well established.⁷⁻¹⁴ Nonetheless, the size-effects on their phonon modes and on the electron-phonon interaction are still somewhat controversial. Theoretical studies based on a dielectric continuum model^{15,16} predict that in small ionic crystals there exist transverse (TO) and longitudinal (LO) optical bulk modes, and also surface optical modes (SO). The surface modes being an infinite series of modes with frequencies between the TO and LO modes. Schmitt-Rink *et al.*¹⁷ predicted a decrease in the coupling of the LO bulk modes to electrons, as the crystal decreases. Klein *et al.*¹⁸ have observed the bulk LO modes and have shown evidence for the SO modes in CdSe nanocrystals, but their results show no size dependence on the electron-phonon coupling. However, Shiang and co-workers¹⁹ presented second-order Raman scattering results for CdS nanocrystals that show the decrease on the electron-phonon coupling as the nanocrystal size is decreased. In addition, Scamarcio *et al.*²⁰ have observed LO modes with shifted frequencies in CdS_{1-x}Se_x, which they attributed to compressive strain due to the glass matrix.

In this letter we present Raman scattering results for CdTe nanocrystals which clearly show the confinement effects on the phonon spectra as a function of the quantum dot size. We observed the LO-phonon modes, surface phonons and some of their overtone combinations. Our results confirm the decrease on the electron-phonon coupling as the nanocrystal size is decreased. We show also that the surface phonon scattering intensity increases as the quantum dot size decreases. These confinement effects are observed by changing the laser excitation energy, and thus tuning to resonance with the optical transitions for quantum dots of different

sizes within their broad size distribution in semiconductor doped glasses.

The glass samples were prepared by melting a glass host containing SiO₂, B₂O₃, Na₂O and ZnO mixed with CdO and metallic Te. The semiconductor nanocrystallites are produced by a subsequent heat treatment. We present results for a sample annealed at 580 °C for 25 min. The CdTe quantum dot mean-radius obtained from the first peak in the absorption spectra considering the quantum confinement energy given by a $\mathbf{k} \cdot \mathbf{p}$ model is 3.6 nm.¹⁴ For this sample, the width of the quantum dot distribution estimated from the absorption spectrum is about 10%.

We used a dye laser and an argon laser as excitation sources and the Raman spectra were measured with a Jobin-Yvon triple spectrometer (resolution of 1 cm⁻¹) and a multichannel detector. The spectra were obtained in a back scattering geometry. The sample was held in a closed cycle helium cryostat, where the temperature could be controlled from 10 K to 300 K.

Figure 1 compares the 10 K and 300 K Raman scattering spectra for excitation at 594 nm (2.09 eV). Both spectra show a main peak at the bulk CdTe LO-phonon frequency. By cooling the sample we get thinner and better resolved phonon peaks. There is also a small shift in the LO frequency which agrees with the measured bulk temperature shift.²¹ In addition, we can clearly observe a peak at about 149 cm⁻¹, which we attribute to scattering from the surface phonon mode with $l=1$, the first mode of the infinite series of surface modes, the so-called Fröhlich mode.¹⁵ We believe it is at too high frequency to be associated with the TO mode (the bulk TO mode is at 142 cm⁻¹ Ref. 21). Note, also the asymmetry of the LO-phonon peak to lower frequencies. The sloping background is the photoluminescence.

We present in Fig. 2 the spectra for different laser excitation energies. The luminescence background were subtracted and the intensity was normalized by the LO-phonon peak intensity. We observed clearly the SO₁ and LO-phonons and also some of their overtone combinations 2LO and LO+SO₁. The peak at about 190 cm⁻¹ may be due to 2LO-SO₁ scattering. It should also be pointed out that we observe no shift of the LO-phonon frequency within the experimental resolution of 1 cm⁻¹. The resonance profile fol-

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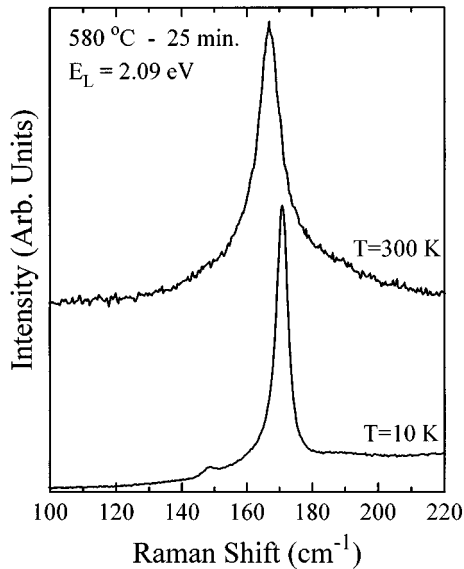


FIG. 1. Raman scattering spectra at room temperature ($T=300$ K) and at 10 K with the laser excitation at 594 nm (2.09 eV). The intensity was normalized to the peak intensity of the LO-phonon and the spectra were vertically shifted for clarity.

lows the first peak in the absorption spectrum, however, as we tune to higher energies the spectra change: the LO-phonon peak broadens, the “shoulder” at the low frequency side becomes more apparent and the ratio of the second to first order scattering decreases. This decrease is in agreement with the results of Shiang *et al.*¹⁹ obtained with the laser in resonance with the first transition for samples with decreasing nanocrystal mean-radii. We have also observed this same trend for samples with different nanocrystal mean-radii. These results indicate that as we change the laser excitation energy we can get resonance with quantum dots of different radius within the broad quantum dot distribution. As a result we can study the size effects with just one sample — at higher excitation energy we probe the first transition of the smaller quantum dots in the distribution. The overall resonance profiles for quantum dots in doped glasses follow the

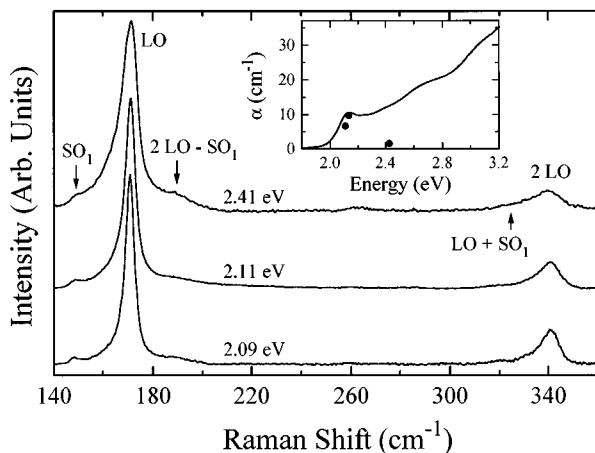


FIG. 2. Raman scattering spectra at 10 K for different laser excitation energies. The spectra were normalized to the LO-phonon peak intensity and vertically shifted for clarity. The inset shows the absorption spectrum; the dots are the LO-phonon intensities for each laser excitation energy.

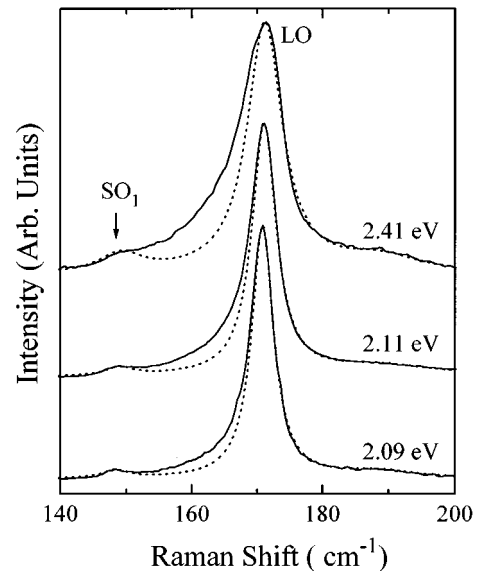


FIG. 3. Raman scattering spectra at 10 K for different laser excitation energies. Same spectra as in Fig. 2, showing in more detail the first order scattering region. The dash lines are fitted spectra considering Lorentzian line shapes.

first peak in the absorption spectra²² with no enhancement of the Raman scattering intensities for other higher transitions, thus we expect that the excitation of electrons into the higher states of the larger quantum dots would not significantly influence the scattering intensities. The probing of quantum dots of different sizes within the size distribution in CdTe-doped glasses has also been observed in photoluminescence excitation measurements.¹⁴

Figure 3 shows in more detail the first order scattering frequency region. The dashed lines are calculated curves considering a Lorentzian line shape for the phonon modes. We fitted the Lorentzian line to the high energy side of the LO-phonon peak. The fitted LO-phonon widths are 4.0, 4.5 and 6.5 cm^{-1} for the 2.09, 2.11 and 2.41 eV spectra, respectively. We used these values also for the SO_1 peak widths. The second order peaks are about twice as broad and the $2\text{LO}-\text{SO}_1$ peak three times broader. It can be clearly seen that the “shoulder” at the low energy side of the LO peak increases intensity for higher excitation energies. There is also an increase of the scattering due to the first surface phonon (SO_1) at 149 cm^{-1} .

Our results may be explained using the dielectric continuum model of Ruppin and Engman.¹⁵ It should be noted that the interface phonon frequencies of GaAs-AlAs quantum wells and superlattices^{23,24} were successfully explained by a dielectric continuum model. In this model the sphere surface mode frequencies are given by¹⁵:

$$\omega_{\text{SO}_l}^2 = \omega_{\text{TO}}^2 \frac{\epsilon_0 + \epsilon_M(l+1)/l}{\epsilon_\infty + \epsilon_M(l+1)/l}, \quad l=1,2,3, \dots, \quad (1)$$

where ϵ_0 and ϵ_∞ are the semiconductor static and high-frequency dielectric constant, and ϵ_M the dielectric constant of the surrounding medium. l is the order of the spherical harmonic in the phonon mode electric potential expression. Using the CdTe parameters²¹ and the glass dielectric constant as $\epsilon_M=5.1$ (the value for a Corning borosilicate

glass²⁵) we get for the lowest ($l=1$) and highest ($l\rightarrow\infty$) modes $\omega_{\text{SO}_1} = 153 \text{ cm}^{-1}$ and $\omega_{\text{SO}_\infty} = 159 \text{ cm}^{-1}$, respectively. These frequencies are consistent with the observed spectra, the uncertain value for the glass dielectric constant may account for the small differences. The “shoulder” between the SO_1 and the LO peaks are due to scattering from all the higher surface phonon modes ($l=2,3,\dots$). For smaller quantum dots the scattering from the surface modes increases and the “shoulder” gets more apparent. The scattering from the first surface mode is expected to be more efficient even for the larger quantum dots, as it has a constant electric field amplitude over the whole volume of the sphere.¹⁶

Other simple phonon confinement models, for instance that of Campbell and Fauchet,²⁶ have predicted a low energy asymmetric broadening of the LO-phonon peak. However it predicts a shift of the main peak frequency to low energy which is not observed experimentally. Also the presence of the extra peak is not explained. In diatomic polar crystals, such as CdTe, the electric polarizability is too strong and should not be neglected in the phonon confinement model.

In conclusion we have clearly shown the size effects on the phonon spectra of small CdTe nanocrystallites. We observed LO-phonons as well as surface phonons. The scattering from the surface modes increases as the nanocrystals decrease.

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