

Size dependence of electron–LO-phonon coupling in semiconductor nanocrystals

G. Scamarcio,* V. Spagnolo, G. Ventruti, and M. Lugará
INFN–Dipartimento di Fisica, Università di Bari, 70126 Bari, Italy

G. C. Righini
IROE–CNR, 50127 Firenze, Italy

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An increase in the Fröhlich–electron–LO-phonon interaction strength with decreasing nanocrystal size in the strong confinement limit is reported. This results from the size dependence of resonant Raman scattering by $\text{CdS}_x\text{Se}_{1-x}$ nanocrystals embedded in a glass slab. The mean particle radius $20 < \bar{R} < 30 \text{ \AA}$ increases monotonically with the position along the slab so that, for each laser line, the resonance has been tuned by scanning the sample with a microprobe. The relative strength between Fröhlich and deformation-potential contributions is determined by analyzing the polarization properties of the scattering. [S0163-1829(96)51716-9]

Coupling between electronic and vibrational excitations plays a central role in the physics of crystalline materials, e.g., determining their transport properties and the energy relaxation rate of excited carriers. Semiconductor nanocrystals as small as a few hundred unit cells make it possible to investigate the electron-phonon interaction beyond the bulk approximation. In this regime, strong quantum-size effects influence the electronic and vibrational states and their coupling.¹ Also, phonon broadening of the exciton linewidth competes with quantization in determining the energy spectrum, thereby posing an intrinsic limit to the strength of the absorption nonlinearities achievable in nanostructures.²

The important issue on the size dependence of the electron-phonon coupling has recently kindled great interest.^{2–12} However, contradictory results have been published, leaving ambiguous the answer to this basic question. As far as theory is concerned, Schmitt-Rink, Miller, and Chemla,² using simple charge neutrality arguments, suggested that the exciton–LO-phonon coupling mediated by the Fröhlich interaction should vanish in small spherical nanocrystals. This should be true only if the electron and hole charge distribution were identical. Klein *et al.*,³ using a donorlike exciton model but neglecting electron-hole correlation, predicted a size-independent coupling. However, an increased coupling to short-wavelength phonons is expected when the crystal size is reduced.² In fact, more recently, Efros,⁴ Marini *et al.*,⁵ and Nomura and Kobayashi,⁶ taking into account electron-hole correlation, valence-band degeneracy, conduction-band nonparabolicity, and proper confined phonon wave functions, have shown that the Huang-Rhys parameter S , which measures the strength of the Fröhlich interaction, increases at decreasing the nanocrystal size in the limit of small mean particle radius $\bar{R} \lesssim 100 \text{ \AA}$. Experimentally, the analysis of absorption,^{6–9} photoluminescence,^{7–9} and spectral hole burning¹⁰ measurements indicate that the electron–LO-phonon coupling is larger in nanocrystals with smaller radii. Surprisingly, in previous resonant Raman scattering (RRS) experiments, in which in principle the electron-phonon interaction can be directly probed, either a size-independent coupling³ or even a decrease of the electron-phonon interaction strength at decreasing the nanocrystal radius has been suggested.^{11,12}

In this work we unambiguously demonstrate that the strength of the electron–LO-phonon coupling increases with increasing confinement (decreasing size) in the strong confinement limit. This conclusion results from the size dependence of the ratio between two-phonon and one-phonon Raman cross sections in a prototype system: $\text{CdS}_x\text{Se}_{1-x}$ nanocrystals embedded in a glass matrix. It is important to stress that, in our experiments, *the resonance condition has been kept constant (within $< 1 \text{ meV}$) for each investigated nanocrystal size.* This has been achieved by fully exploiting the advantages of a Raman microprobe apparatus and a suitable sample in which the mean nanoparticle size increases monotonically along one direction. Due to the strong energy dependence of the Raman cross section, keeping constant the resonance condition is mandatory for a meaningful comparison of spectra associated with nanocrystals having different sizes and hence different electronic transitions. Our approach represents an improvement with respect to previous RRS investigations in which the challenging experimental problem of keeping constant the resonance condition has not been properly solved.^{3,11,12} Also, we report a polarization analysis of the Raman spectra in nanocrystals. Our results show that the electron-phonon coupling mediated by the Fröhlich interaction increases stronger than that mediated by the deformation potential with increasing confinement.

The sample is a 15-cm-long glass bar containing $\text{CdS}_{0.35}\text{Se}_{0.65}$ nanocrystals prepared from the same melt used for the fabrication of commercial Schott filters RG610 and RG630. The nanocrystal growth is promoted by heating the pristine slab for 72 h in a temperature gradient (500 °C–700 °C). As a result, the crystallite mean radius is a monotonic function $\bar{R}(x)$ of the position x along the rod. In fact, due to the size dependence of the nanocrystal energy gap, the glass color changes from pale yellow to deep red by moving from one end of the slab to the opposite. $\bar{R}(x)$, which varies in the range 20–30 Å, has been determined at 12 K from the blueshift ΔE_c of the first absorption band with respect to the bulk by using the well-tested relation⁷ $\Delta E_c(x) = \pi^2 \hbar^2 / 2M^* \bar{R}^2(x)$. For the exciton effective mass, we used the value $M^* = (1/m_e + 1/m_h)^{-1} = 0.112$, calculated considering a linear interpolation between the CdS and CdSe elec-

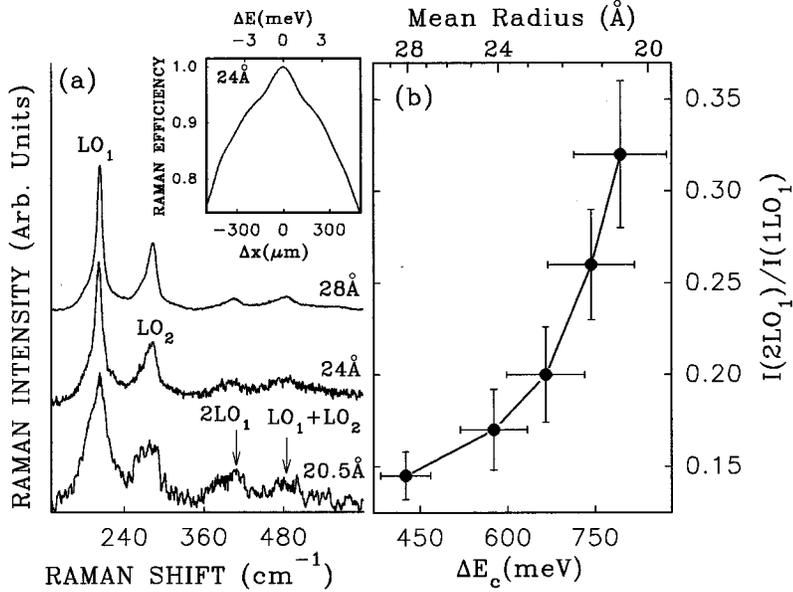


FIG. 1. (a) Representative set of resonance Raman spectra of CdS_{0.35}Se_{0.65} nanocrystals with different mean radii, recorded with the exciting laser wavelengths 4579 Å (bottom), 4880 Å (middle), and 5145 Å (top), each under the same resonance condition corresponding to the maximum enhancement of the first-order bands. The spectra have been normalized to show the relative intensities between one-phonon and two-phonon bands. The resonance is found by moving a 15-cm-long sample, in which the mean nanoparticle size is a monotonic function of the position along the slab, under the 1-μm-diameter laser spot created by the focusing objective of the microprobe. The inset shows the resonance profile obtained at 4880 Å as a function of the distance Δx along the slab from the position of strongest resonance. (b) Ratio between two-phonon and one-phonon Raman bands as a function of the confinement energy and the mean nanocrystal radius. The line joining the points is a guide for the eye.

tron (m_e) and hole (m_h) effective masses.² The spread in the particle size at a given position x has been determined in a previous investigation of the present sample by x-ray diffraction to be 10–15%.¹⁰

Considering the particle size dispersion and assuming for R a Gaussian distribution $f(R)$, the total Raman cross section for an n -phonon process can be written as¹¹

$$\sigma_n = \int \sigma_n^R(\omega) f(R) dR, \quad (1)$$

$$\sigma_n^R(\omega) = \mu^4 \left| \sum_{m=0}^{\infty} \frac{\langle n|m \rangle \langle m|0 \rangle}{E_0 + n\hbar\omega_{LO} - \hbar\omega + i\hbar\Gamma} \right|^2, \quad (2)$$

where μ is the electronic dipole transition moment, E_0 is the (size-dependent) energy of the electronic transition, $\hbar\omega$ and $\hbar\omega_{LO}$ are the energies of the incident photon and the LO phonon, respectively, m denotes the intermediate vibrational level in the excited state, and Γ is the homogeneous linewidth. The overlap integral between the ground and excited states wave functions can be written as¹¹

$$\langle n|m \rangle = (n!/m!)^{1/2} \exp(-\Delta^2/2) \Delta^{(n-m)} L_m^{n-m}(\Delta^2), \quad (3)$$

where L_m^{n-m} denotes a Laguerre polynomial and Δ is the dimensionless displacement of the harmonic oscillator in the excited state. Δ is known to be related to the Huang-Rhys parameter S by the relation $S = \Delta^2$. Therefore the ratio η between two-phonon and one-phonon scattering cross sections is a very sensitive function of the electron-phonon coupling strength. However, η is also strongly dependent from the exciting photon energy. Clearly, in order to extract the size dependence of the coupling from η by comparing measurements on crystals with different sizes and hence different E_0 values, the resonance condition must be kept constant for each measurement.

In order to meet the above condition we have adopted the following procedure. For each of the five lines λ_j , $j=1-5$ ($\lambda_1=5145$ Å, $\lambda_2=4880$ Å, $\lambda_3=4765$ Å, $\lambda_4=4658$ Å, $\lambda_5=4579$ Å) of an Ar⁺ laser we have scanned the sample along the x direction while seeking the positions x_j corresponding to the maximum resonant enhancement of the first-

order Raman bands. We have used a high-resolution microprobe Raman setup with typical laser spot diameter <1 μm.¹³ Due to the monotonic variation of the mean nanoparticle size along the x direction and the size dependence of the nanocrystal energy gap, the corresponding energy resolution is ~ 0.01 meV. A typical resonance profile, recorded with the excitation wavelength λ_2 in proximity of the corresponding position x_2 is shown in the inset of Fig. 1(a). Each spectrum recorded at the positions x_j as defined above has been associated with the mean nanocrystal radius $\bar{R}(x_j)$.

Figure 1 shows a representative set of resonant Raman spectra recorded at room temperature. The bands labeled LO₁ and LO₂, peaked at 202 and 282 cm⁻¹, are due to CdSe- and CdS-like phonons, respectively. The asymmetric broadening on the low-energy side is a well-documented effect induced by the localization of the phonon wave function.¹⁴ The peak at 404 cm⁻¹ is due to the overtone 2LO₁, while the peak at 480 cm⁻¹ is due to the sum LO₁+LO₂. Figure 1(b) shows the size dependence of the ratio $\eta = I(2LO_1)/I(1LO_1)$. Due to the constant resonance condition, the increase of η at decreasing the crystal size can be solely ascribed to the corresponding increase of the electron-phonon coupling. We note that surface effects, such as hole surface localization, which have been shown to increase the exciton-LO-phonon coupling in the temperature range below 10 K (Refs. 15 and 16), cannot play a role in our room-temperature measurements. Our results are in agreement with the theoretical predictions of Refs. 4–6 and with absorption,^{6–9} photoluminescence,^{7–9} and spectral hole burning¹⁰ experiments, and support the notion that the cancellation induced by the increased overlap of electron and hole wave functions in small nanocrystals is overwhelmed by the increased coupling to short-wavelength phonons.² The different results and even opposite conclusions reported in previous Raman investigations^{11,12} may be ascribed to the comparison of spectra recorded under inconstant resonance conditions.

A deeper insight can be obtained by analyzing the polarization properties of the scattering. The electron-phonon in-

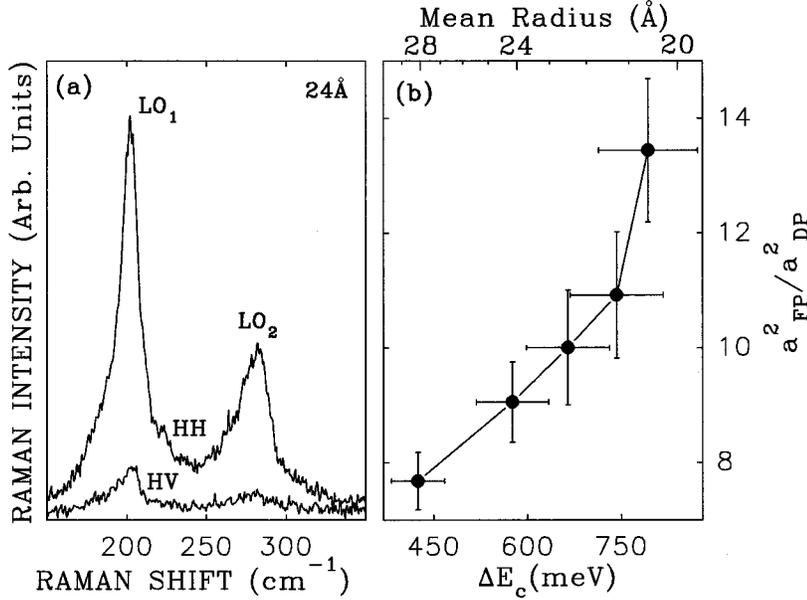


FIG. 2. (a) Resonant Raman spectra recorded under 4880 Å in parallel (*HH*) and crossed (*HV*) scattering polarizations at the position along the sample corresponding to the maximum resonant enhancement of the one-phonon band intensities. (b) Ratio $a_{\text{FP}}^2/a_{\text{DP}}^2$ between Fröhlich and deformation-potential Raman polarizabilities as a function of the confinement energy and the mean nanocrystal radius. The line joining the points is a guide for the eye.

teraction is governed by two mechanisms: the Fröhlich potential (FP) and the deformation potential (DP). In a bulk crystal, the two contributions can be experimentally resolved by comparing the polarization properties of the scattering with selection rules. As an example, in the case of zinc-blende crystals, DP-mediated scattering can be observed in backscattering from (001) surface when the polarization vectors of incident and scattered photons lie along different crystallographic axes, whereas the observation of FP-mediated scattering requires parallel polarization vectors. In a glass composite material the embedded nanocrystals are randomly oriented and a statistical average must be carried out. Following the same approach used for randomly oriented molecules,¹⁷ the depolarization ratio ρ between the scattered intensities polarized perpendicular and parallel to the incident radiation can be written as

$$\rho = 3\gamma^2 / (45\alpha^2 + 4\gamma^2), \quad (4)$$

where $\alpha = 1/3[a_{xx} + a_{yy} + a_{zz}]$ and

$$\gamma = \left\{ \frac{1}{2} [(a_{xx} - a_{yy})^2 + (a_{yy} - a_{zz})^2 + (a_{zz} - a_{xx})^2 + 6(a_{xy})^2 + 6(a_{yz})^2 + 6(a_{xz})^2] \right\}^{1/2}$$

are the isotropic and anisotropic parts of the scattering tensor, respectively. $\text{CdS}_x\text{Se}_{1-x}$ crystallizes either in the wurtzite (hexagonal) or the zinc-blende (cubic) form. However, a

common feature of the growth of II-VI nanocrystals in different host media is the cubic modification.¹ In this case, the ratio between Fröhlich and deformation potential Raman polarizabilities can be written as

$$a_{\text{FP}}^2/a_{\text{DP}}^2 = 3(3 - 4\rho)/5\rho. \quad (5)$$

Figure 2(a) shows two typical spectra recorded under 4880 Å excitation in parallel (*HH*) and crossed (*HV*) polarizations, at the position of maximum enhancement of the one-phonon bands intensities, as discussed above. Special care has been taken to avoid artifacts. A scrambler was placed in front of the entrance slit of the monochromator in order to get rid of the polarization response of the gratings. The polarization of the scattered light was analyzed with a Polaroid plate by keeping constant the polarization of the exciting photons. Introducing the experimental values in Eq. (5), we obtain for the ratio $a_{\text{FP}}^2/a_{\text{DP}}^2$ the values plotted in Fig. 2(b) as function of the crystal size. The ratio increases by a factor 1.7 ± 0.3 when the radius decreases from 28 to 20.5 Å. This shows that the enhancement of the electron-LO-phonon scattering at decreasing the nanocrystal size is mainly associated with the Fröhlich interaction.

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*Present address AT&T Bell Laboratories, Murray Hill, NJ 07974; electronic address: nino@physics.att.com

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