

OPTICAL PHONONS IN CdS NANOCRYSTALS: EFFECTS OF SIZE, SHAPE AND PACKING DENSITY

A.G. ROLO^{*}, M.I. VASILEVSKIY^{*}, M.I.M. GOMES^{*}, O.V. VIKHROVA[♦], Yu.P. RAKOVICH^{*#}, M.V. ARTEMYEV[‡]

^{*}Departamento de Física, Universidade do Minho, 4700-320 Braga, Portugal,

E-mail: mikhail@fisica.uminho.pt

[♦]Faculty of Physics, Nizhni Novgorod University, Russia

[#]Department of Physics, Brest Polytechnic Institute, Brest, Belarus

[‡]Physico-Chemical Research Institute, Belarussian State University, Minsk, Belarus

ABSTRACT

Optical vibrations confined in CdS nanocrystals (embedded in a glass film or forming a close-packed film with some organic-molecule links between them) have been studied experimentally, by means of FIR and Raman spectroscopies, and theoretically. The asymmetric Raman lineshape can be modelled considering resonant and non-resonant scattering on spherical modes with $l=0$ (those with $n>1$ are responsible for the low-frequency wing). A phonon-related dielectric response of the nanocrystal composites has been studied by measuring FIR reflectivity and transmission spectra. The theoretical consideration consists of the (i) calculation of the single-particle polarisability due to the confined $l=1$ modes and (ii) including the dipole-dipole interaction between the particles. We show that, for the smallest particles, the FIR response has a bimodal structure, which disappears as the nanocrystal size increases. However, the experimentally observed bulk-CdS-like reflection band at 230-300 cm^{-1} is too broad and can not be explained by the model. Only making further assumptions, namely, of a fractal structure of the nanocrystal composites, enables us to fit well the experimental FIR spectra.

INTRODUCTION

Optical vibrations in semiconductor quantum dots (QD) are important because they affect their electronic properties and are responsible for the Raman scattering of light. The latter can be used to measure the QD size, on the condition that the lattice dynamics of such a small crystal are properly described theoretically. As in the case of bulk materials, far-infrared (FIR) spectroscopy would provide additional information concerning the optical vibration modes, complementary to that obtained from Raman spectra. Although Raman spectroscopy is now a standard tool for the study of semiconductor QD [1-3], there are very few papers devoted to small size effects on the FIR-active lattice vibration modes [4]. In this communication, we report the results of our experimental and theoretical studies of FIR and Raman-active optical vibrations in small CdS crystals. An emphasis will be on the effects of QD size (phonon mode confinement) and QD concentration (interaction between them).

THEORY

Our consideration of confined optical vibrations in QD is based on the macroscopic equation for the relative displacement of the positive and negative ions [5]:

$$(\omega^2 - \omega_{TO}^2)\vec{U} = \beta_L \vec{\nabla}(\vec{\nabla} \cdot \vec{U}) - \beta_T \vec{\nabla} \times (\vec{\nabla} \times \vec{U}) + \frac{e_T}{\rho v} \vec{\nabla} \varphi, \quad (1)$$

where ρ is the reduced mass density, ω_{TO} the TO bulk frequency, e_T the transverse charge, v the unit cell volume, and β_L and β_T are phenomenological bending parameters. We consider β_L and β_T as functions of frequency, chosen to reproduce approximately the bulk [111] dispersion curves [6]. The general solution of this equation is given in ref.[5]. We used the following boundary conditions (b.c.) at the interface: (i) all the components of the displacement vanish, (ii) the electrostatic potential and (iii) the normal component of the electric displacement are continuous. Applying these b.c., one can obtain equations which determine the frequencies of the Raman active ($l=0$ and $l=2$) and FIR-active ($l=1$) modes. These equations can be found in [3,5] and [6], respectively, so, we do not reproduce them here.

The second step is to calculate the relative contributions of these modes with different n to Raman or FIR spectra. Let us first consider briefly the Raman-active $l=0$ modes (the quadrupole modes are active only under resonance conditions and their contribution is much smaller). The Raman cross-section can be written as:

$$\frac{d^2\sigma}{d\Omega d\omega_s} = \frac{\omega_i \omega_s}{\pi c^4} v^2 [n(\omega) + 1] \left[-\text{Im} \sum_n \frac{|\Theta_n|^2}{\omega^2 - \omega_n^2 + i0} \right], \quad (2)$$

where ω_i and ω_s are the incident and scattered light frequencies, n is the Bose factor and ω_n^2 are the $l=0$ eigenfrequencies. The matrix element Θ_n depends on the scattering mechanism. If the excitation energy is in resonance with some particular electron-hole (e-h) state (with energy E_1), the Fröhlich mechanism of the electron-phonon interaction is the most efficient, and

$$|\Theta_n|^2 = \left(\frac{e^2 P}{m_0^2 \omega_i \omega_s v} \right)^2 \frac{\left[\int e \varphi_n (|\psi_e|^2 - |\psi_h|^2) d\vec{R} \right]^2}{(E_1 - \hbar \omega_i)^2 (E_1 - \hbar \omega_s)^2}, \quad (3)$$

where P is the dipole moment matrix element of the e-h transition, m_0 is the free electron mass, ψ_e and ψ_h are the electron and hole wavefunctions, respectively, and φ_n is the potential associated with the n -th mode. The situation when the excitation is off-resonance was considered in [3].

The dielectric response of a single QD is described, in the dipole approximation, by its polarisability. The polarisability can be written in terms of the dipolar ($l=1$) eigenmodes as follows:

$$\alpha = R^3 \left\{ \frac{\epsilon_\infty^{(1)} - \epsilon_\infty^{(2)}}{\epsilon_\infty^{(1)} + 2\epsilon_\infty^{(2)}} - \frac{3\epsilon_\infty^{(2)}}{\epsilon_\infty^{(1)} + 2\epsilon_\infty^{(2)}} \sum_n \frac{B_n}{\omega^2 - \omega_n^2 + i0} \right\}, \quad (4)$$

where $\varepsilon_{\infty}^{(1)}$ and $\varepsilon_{\infty}^{(2)}$ are the high-frequency dielectric constants of the QD and matrix, respectively, R is sphere's radius and

$$B_n = \frac{e_T Z_n w_n^{(0)}}{V} \int d\vec{R} (\vec{e}_z \cdot \vec{w}_n) \quad (5)$$

In (5), \vec{w}_n is a normalised eigenmode of eq. (1) (with amplitude $w_n^{(0)}$), Z_n is the effective charge associated with the n -th mode (defined from the potential which the mode produces outside the sphere), and \vec{e}_z is a unit vector along the external electric field direction.

In reality, people always deal with *ensembles* of QD. This means that some collective effects can arise, unless the QD concentration is very small. Moreover, there always is some dispersion of QD sizes. However, the Raman-active $l=0$ modes do not produce any field outside the sphere, so, different QD do not interact. The ensemble scattering cross-section is simply a superposition of the individual QD contributions. Note that the QD cross-section $\sim R^3$ for non-resonant scattering [3], while the R^{-1} dependence follows from eq. (3).

Modes with $l>0$ confined in different QD can couple to each other via the electric field, which they produce outside the QD. The collective dielectric response of an ensemble of QD can be described by its effective dielectric function (EDF). The EDF of a composite containing separate spherical inclusions in a dielectric matrix can be calculated using an approach based on the coupled-dipole equations. This is done by introducing a renormalised polarisability, which can be expressed in terms of the usual polarisability (given by (4)) by a kind of Dyson equation. The EDF is related to the polarisability by the classical Maxwell-Garnett equation. This approach allows for taking into account a continuous distribution of sizes of the spheres [7]. The necessary formulas are given in refs.[7,8].

EXPERIMENTAL AND CALCULATED RESULTS

In this work we studied experimentally two kinds of samples: (i) CdS- doped glass films and (ii) matrix-free films of close-packed (CP) CdS nanocrystals (NC). They were produced by RF-sputtering using targets of SiO₂ with CdS chips atop, and the drying of a colloidal solution of CdS NC on a substrate, respectively. The NC mean radius was in the range of 2-4nm and 1-3nm for the two types of samples, respectively. Raman spectra were measured with a Jobin-Yvon T64000 spectrometer at room temperature in a back-scattering geometry using

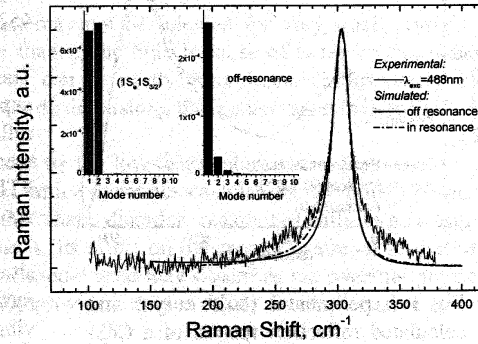


Fig.1 Raman lineshapes for a CdS-doped glass sample ($R=3\text{nm}$) obtained with the 488nm Ar^+ laser line. Two theoretical curves were calculated using the spherical QD model assuming the excitation to be in resonance with the $(1s_e, 1S_{3/2})$ $e-h$ state (full curve) and off resonance (dashed one). The phonon damping used was 14cm^{-1} . Two histograms show the relative contributions of different phonon confined modes.

several lines of an Ar⁺ laser (output power was 100mW). The spot size and spectral resolution were 1 μ m and 1cm⁻¹, respectively.

A typical spectrum is shown in Fig. 1. Generally, it was found that the shift and broadening of the Raman peak corresponding to CdS LO-type confined vibrations increase as the NC mean size decreases. The lineshape is rather asymmetric for all the samples studied. It was modelled as explained in the previous section. Since the excitation photon energy falls slightly below the absorption edge for samples with larger NC size (like that presented in Fig. 1), both the model of ref.[3] and that given by eqs.(2) and (3) were tried. In the latter case, we assumed that the ground e-h pair state is (1s_e 1s_{3/2}). The electron and hole wavefunctions necessary for the calculation of Θ_n can be found, for example, in ref.[8]. The relative contributions of the spherical vibration modes with different n are shown in Fig. 1. Somewhat unexpectedly, the $n=2$ mode gives the largest contribution to the scattering. Both models reproduce the lineshape asymmetry reasonably well, while the non-resonant one provides a slightly better fit to the experimental spectrum. This is in an agreement with the fact that

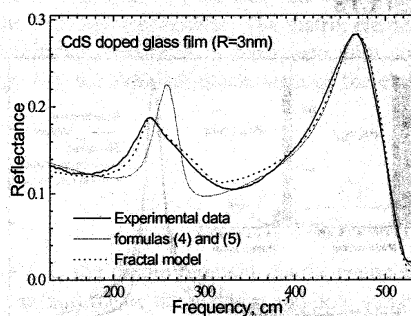


Fig. 3 Experimental (bold curve) and calculated reflection spectra of a CdS-doped glass sample ($R=3\text{nm}$, film thickness $1.7\mu\text{m}$). Theoretical curves were calculated using the modified Maxwell-Garnett model explained in the text and the fractal model of ref. [10]. In both cases $f=0.13$, CdS-like phonon damping $=14\text{cm}^{-1}$.

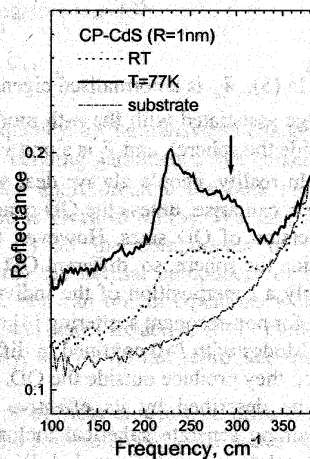


Fig. 2 Experimental reflectivity spectra of a CP CdS film on glass substrate (measured at 300K and 77K), and of the substrate itself.

we did not observe any significant change in the experimental lineshape when changing the excitation wavelength from 457.9nm to 514.5nm.

Let us turn to the FIR-active modes. The phonon-related dielectric response was experimentally studied by measuring reflectivity spectra. FIR measurements were performed with a Bruker IFS66V FTIR spectrometer. Some representative results are shown in Figs. 2 and 3.

From the theoretical viewpoint, the situation is as follows. In a QD of a given radius R , there are several dipolar vibrational modes, whose number grows as R increases. Note that the Fröhlich mode, an electrostatic 'surface' mode in a sphere [9], is *not* an eigenmode of eq.(1) with rigid b.c.. However, those confined modes, which are close in frequency to the Fröhlich mode, produce most of the FIR activity of a QD of $R>2\text{nm}$ (see Fig. 4).

Only for smaller QD (e.g. of $R=1\text{nm}$), there is another group of modes, which produce a polarisability peak at a lower frequency, closer to the bulk TO frequency. Thus, as one can see from Fig. 4, the FIR polarisability of small QD has some structure. The collective effects (dipole-dipole interaction of QD) shift the peaks a little bit downwards. The structure has a tendency to disappear if the dispersion of QD sizes increases. Nevertheless, we can clearly see this structure in the experimental low-temperature reflectivity spectrum of the CP NC film (it is marked by the arrow in Fig. 2).

Larger NC's are not supposed to produce any structure in the FIR response of a composite, just a (broadened and slightly shifted) peak near the Fröhlich frequency (see the theoretical curve in Fig. 3). However, the experimental spectra of CdS NC embedded in glass show a broad bulk-CdS-like reflection band at about $230\text{--}300\text{ cm}^{-1}$, which can not be explained in terms of the present model. One can suggest a few different explanations for this. The bulk phonon parameters (the TO and LO frequencies) may not be relevant for very small crystals. For example, the ionic charge can be larger than in the bulk because of stress produced by the surface tension. Also, the semiconductor can be partly amorphous. Unfortunately, X-ray diffraction spectroscopy does not allow for distinguishing these cases unambiguously for very small crystals.

One may also argue that NC produced by the low-temperature techniques would hardly be perfect spheres. We performed model lattice dynamics calculations for binary clusters of irregular shape [10,11] and found that the 'shape disorder' results basically in an additional broadening of the Raman lineshape. That is, its effect on the spectra is similar to that of the size dispersion. Thus, we believe that the model used here describes the essential physics of the FIR response of semiconductor QD, provided they are just small pieces of the bulk material.

There is a more intriguing explanation to the broad FIR spectra observed for the QD ensembles. If we assume that the spatial distribution of NC is random but correlated (e.g., if NC form a fractal fragment), their dipole-dipole interaction can result in a broad spectral distribution of the dipolar modes [12]. For CdS-doped glass films, a model of fractal aggregates consisting of small crystalline particles was proposed in [10]. The reflectivity spectrum calculated using this model (Fig. 3) fits much better the experimental curve than

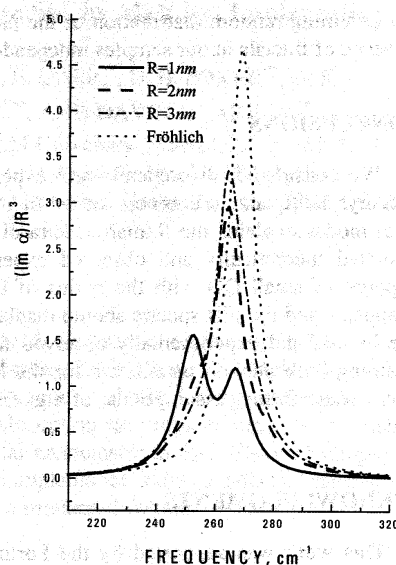


Fig. 4 Imaginary (left) and real (right) parts of the polarisability calculated according to eqs. (4) and (5) for CdS spheres of different radii embedded in SiO_2 glass. Dotted curves correspond to the Fröhlich mode, which is independent of the QD radius.

that assuming random distribution of the particles. However, we were not able to prove the presence of fractals in our samples independently so far.

CONCLUSIONS

We considered, theoretically and experimentally, optical vibrations confined in small CdS crystals (quantum dots) embedded in a matrix. The non-resonant scattering on $l=0$ (LO-type) modes explains the Raman spectra obtained using different lines of the Ar laser. We predicted theoretically and observed experimentally the two-mode structure of the FIR response of small QD with the radius of the order of 1nm. For larger QD, this structure disappears and the FIR spectra should display a single mode close to the Fröhlich frequency. The broad band experimentally observed for both types of samples can not be explained assuming bulk phonon parameters for the NC and treating properly the small-size effects, unless some further assumptions, of e.g. fractal structure of the QD/matrix composite, are made.

ACKNOWLEDGMENTS

This work was supported by the Portuguese Foundation for Science and Technology through project PBIC/C/CTM/1923/95. MIV wishes to acknowledge the FCT (PRAXIS/XXI/BCC/11974/97) Fellowship and travel support from the Luso-American Foundation for Development. YPR acknowledges the INVOTAN/ICCTI Fellowship (Portugal). The authors are grateful to J.L. Ribeiro and L.G. Vieira for help in performing FIR measurements at the IMAT (University of Minho).

REFERENCES

1. C. Trallero-Giner, A. Debenardi, M. Cardona, E. Menendez-Proupin. and A.I. Ekimov, Phys. Rev. B **57**, p. 4664 (1998).
2. K.K. Nanda, S.N. Sarangi, S.N. Sahu, S.K. Deb and S.N. Behera, Physica B **262**, p.31 (1999).
3. M.I. Vasilevskiy, A.G. Rolo and M.J.M. Gomes, Solid State Commun. **104**, p. 381 (1997).
4. T.D. Krauss, F.W. Wise and D.A. Tanner, Phys. Rev. Lett. **76**, p.1376 (1996).
5. R. Roca, C. Trallero-Giner and M. Cardona, Phys. Rev. B **49**, p. 13704 (1994).
6. M.P. Chamberlain, C. Trallero-Giner and M. Cardona, Phys. Rev. B **51**, p. 1680 (1994).
7. M.I. Vasilevskiy and E.V. Anda, Phys.Rev. B **54**, p. 5844 (1996).
8. M.I. Vasilevskiy, A.M. de Paula, E.I. Akinkina and E.V. Anda, Semiconductors **32**, p. 1229 (1998).
9. R. Ruppini and R. Englman, Rep. Prog. Phys. **33**, p. 149 (1970).
10. M.I. Vasilevskiy, A.G. Rolo, and M.J.M. Gomes, Microelectronics Engineering **43-44**, p. 715 (1998).
11. M.I. Vasilevskiy, A.G. Rolo, M.J.M. Gomes, O. V. Vikhrova and A.Yu. Savinov, in: *Proc. 24-th Conf. Physics of Semiconductors, Jerusalem, Israel, August 1998*, edited by M.Heiblum and E.Cohen, World Scientific, Tu P10.
12. V.A. Markel, V.M. Shalaev, E.B. Stechel, W. Kim and R.L. Armstrong, Phys. Rev. B **53**, p. 2425 (1996).

MATERIALS RESEARCH SOCIETY
SYMPOSIUM PROCEEDINGS VOLUME 571

Semiconductor Quantum Dots

Symposium held April 5-8, 1999, San Francisco, California, U.S.A.

EDITORS:

Steven C. Moss

*The Aerospace Corporation
Los Angeles, California, U.S.A.*

Daryush Ila

*Alabama A&M University
Normal, Alabama, U.S.A.*

Howard W.H. Lee

*Lawrence Livermore National Laboratory
Livermore, California, U.S.A.*

David J. Norris

*NEC Research Institute
Princeton, New Jersey, U.S.A.*

ORGANIZERS:

A. Paul Alivisatos

*University of California, Berkeley
Berkeley, California, U.S.A.*

Anupam Madhukar

*University of Southern California
Los Angeles, California, U.S.A.*



Materials Research Society
Warrendale, Pennsylvania

Single article reprints from this publication are available through
University Microfilms Inc., 300 North Zeeb Road, Ann Arbor, Michigan 48106

CODEN: MRSPDH

Copyright 2000 by Materials Research Society.
All rights reserved.

This book has been registered with Copyright Clearance Center, Inc. For further
information, please contact the Copyright Clearance Center, Salem, Massachusetts.

Published by:

Materials Research Society
506 Keystone Drive
Warrendale, PA 15086
Telephone (724) 779-3003
Fax (724) 779-8313
Web site: <http://www.mrs.org/>

Library of Congress Cataloging-in-Publication Data

Semiconductor quantum dots : symposium held April 5-8, 1999, San Francisco,
California, U.S.A. / editors, Steven C. Moss, Daryush Ila, Howard W.H. Lee,
David J. Norris

p.cm.—(Materials Research Society symposium proceedings,

ISSN 0272-9172 ; v. 571)

Includes bibliographical references and index.

ISBN 1-55899-478-5

I. Quantum dots—Congresses. I. Moss, Steven C. II. Ila, Daryush
III. Lee, Howard W.H. IV. Norris, David J. V. Materials Research Society
symposium proceedings ; v. 571

TK7874.88 S46 2000

537.6'22—dc21

99-088300

Manufactured in the United States of America