Size Effects in 11-VI Semiconductor Nanocrystals

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We review size effects on optical transition energies in CdS, CdSe and CdSSe crystallites with diameter less tlian 20 nm. We first compare metliods for tlie measurement of particle and grain size and then review methods for determining the eiiergy of tlie lowest optical transition. There are many studies in the literature which report quantum size effects in II-VI crystallites, but relatively few which report both optical transition energies and particle size for more than one size particle. A review of tlie literature indicates quite disparate results for tlie size dependence of tlie lowest excited state. We suggest that surface states and the interaction between the particle and the material in which it is embedded may play an important role in the size dependence.

I. Introduction

CdS, CdSe and CdS_xSe_{1-x} nanocrystals or large clusters are one of the most extensively studied classes of quantum dot systems, but there still remain uncertainties about the basic size-dependent properties of the electronic wavefunctions in sucli systems. The first and most important question for our fundamental understanding of cadmium chalcogenide nanocrystals is: How does the iiature of the first excited state clíange with particle size? The answer to this question has ramifications for tlie development of our theoretical understanding of nanocrystals and quantum dots in general as well as for applications in nonlinear optics. This question must be addressed experimentally since the tlieoretical answer requires knowledge of quasi-particle (i.e.- electron-hole, electron-phonon) iiiteractions, crystal structure, and surface or interface structure. Tlie principal experimental tools for such studies are optical, including optical absorption, photoluminescence, and nonlinear or electromodulated absorption. In this paper we collect and compare experimental reports on tlie size dependence of the optical transition energy for the lowest excited state in CdS-CdSe crystallite systems prepared by a variety of techniques and embedded in a variety of insulating matrices. It is believed that the crystallites are well isolated in all of these situations. We observe that tlie size dependence of the first excited state is different for similar systems and we propose that it is necessary to consider the details of surface and interface termination as well as matrix effects.

II. Preparation Techniques

Nanocrystalline 11-VI materials have been prepared by several techniques but two major approaches dominate tlie literature, liquid pliase and solid phase precipitation. Liquid phase preparation is usiially a low temperature process (T<50C) whereas solid pliase preparation usiially involves high temperature (T=500-800°C) growth and annealing of particles in a glass matrix. Another approach involves the growtli of extremely small CdS crystallites inside of a molecular cage (zeolite.)[1]

Many aqueous and non-aqueous liquid preparatioiis have led to tlie successful growtli of nanocrystals[2-8]. The inverse micelle technique is an example of a liquid-pliase technique which has led to excellent control over particle size and size distribution[9-13]. Particles are grown inside of water micelles in an organic liquid sucli as heptane. Tlie surface of the resulting particles are terminated with specific molecules, sucli as pyridine, effectively isolating tlíe particles electronically and chemically.

In solid phase precipitation, less than one atom percent Cd and the chalcogenide (S, Se or Te) are dissolved in a borosilicate glass matrix at high temperature. The glass is quenched to room temperature, creating a supersaturated solution of Cd and the chalcogenide, but particles do not precipitate because the constituents of the particles are not mobile. Upon raising the temperature to 500-600°C, crystallite nuclei form and upon annealing at 600-750°C crystallites grow[14-24]. There remain many questions about tlie nucleation, Cd and chalcogenide diffusion, and particle growth and dissolution over time, but particles of size from 2-20 nm aiid

with a fairly narrow size distribution of 10-20% in diameter have been demonstrated.

III. Methods for Determining Particle Size

The best method for determining particle size is transmission electron microscopy (TEM). This is relatively straightforward for particles in powder form which can be dispersed on a carbon grid. As an example, in Fig. 1 we show a TEM bright field micrograph of CdS particles with mean diameter of 6 nm. These particles were prepared by liquid phase precipitation and have aggregated during drying for TEM observations[5].
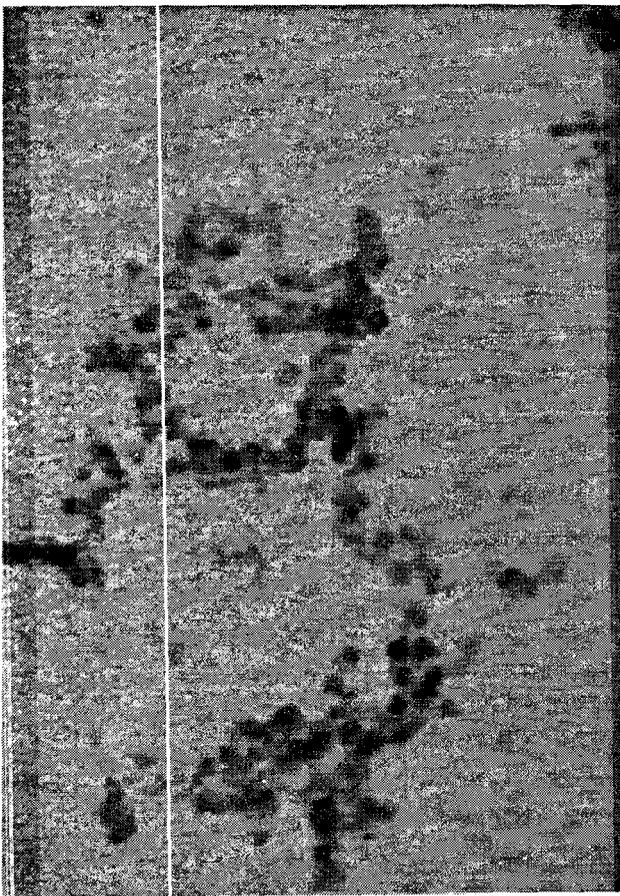
Figure 1: Transmission electron micrograph of 6 nm CdS particles formed by precipitation from aqueous solution [Ref.5].

Particles embedded in glass present many problems for TEM analysis. The glass matrix scatters electrons and limits resolution. It is thermally and electrically insulating and limits heat dissipation and therefore electron beam currents. The glass must be thinned to a few tens of nanometers, which is a difficult task.

X-ray diffraction can give an average measure of crystal grain size from Debye-Scherrer broadening. A simple determination of crystal size from peak width should be interpreted with care however because x-ray diffraction peak height for a given particle is proportional to the square of the volume of the crystal and therefore x-ray diffraction weights the size measurement toward large crystallites[16].

It has become clear from recent x-ray studies on powders that particles may consist of several crystal grains and that the stacking sequence in particles may differ radically from either wurzite or zincblende crystals[25]. A similar proposal has been made to explain inconsistencies between x-ray diffraction and small angle x-ray scattering measurements of particle size[16] for particles embedded in glass.

A new optical technique has recently been demonstrated which has great promise for the measurement of particle size, low frequency inelastic Raman scattering (LOFIRS)[24-26]. In this measurement, laser light is scattered from size-quantized low frequency (acoustic-like) vibrational modes of the particle. The lowest energy mode is given by: $v = c2\pi/d$ where d is the particle diameter and c is the speed of sound. In Fig. 2 we show an example of the LOFIRS spectrum for 4 nm diameter CdS nanoparticles (A, B, C peaks) and for 2 nm CdS nanoparticles (A', B' peaks) embedded in glass. Like optical phonon Raman scattering in bulk and nanocrystalline 11-VI materials, LOFIRS is resonant with real optical transitions. This could prove to be a valuable property of LOFIRS because it can allow us to associate a set of optical transitions with particles of a certain size. Further study into this technique is clearly indicated.
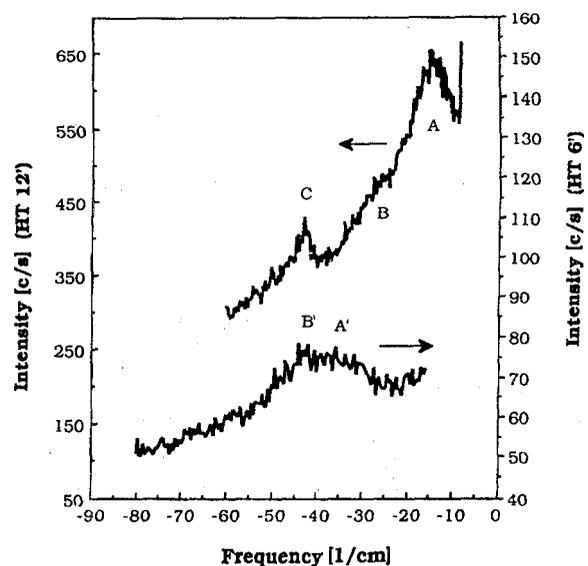
Figure 2: Low frequency Raman scattering from normal modes of 2.2 nm and 4.3 nm CdS particles in glass.

IV. Methods for Determining Particle Exciton Energy

The principal teclinique for the study of optical transitions is optical absorption. In Fig. **3** we show the optical absorption spectrum for different size CdSSe particles in glass and in Fig. 4 we show the spectrum for CdS particles in glass. Hole burning and photolumines-cence excitation spectroscopies have demonstrated that the spectra in Figs. 3 and 4 are inhomogeneously broad-ened by a particle size distribution. Studies on materi-als prepared by the micelle approach demonstrate sig-nificantly narrower absorption peaks[29], indicative of a narrower size distribution. Quantitative measurements of size distribution for particles with an average diam-eter of **3** nm is quite difficult.

Figure 4: Optical absorption spectra of CdS-doped glass wliicli lias undergone a series of lieat treatments at 700 C. HT 12 was annealed for 12 minutes. IIT 6 was annealed for 6 minutes. UT was quenched slowly from a high tempera-ture melt. Sample M was quenched rapidly to about 500 C (approximately 30 seconds) from a melt at 1100 C.

Figure 3: Optical absorption spectrum of CdSSe particles in glass which lias undergone a series of lieat treatments. The spectra progress from right to left (long dash, dot, solid, short dash) as the annealing temperature is increased from 625 C to 750 C. Tlie dot-dash spectrum was measured on an as-received sample of RG630 from Sliott glassworks.

Picking out the energy of the first excited state in an absorption spectrum such as that in Figs. **3** and 4 is somewhat ambiguous. We have also employed elec-tromodulation spectroscopy to determine average exci-tation energy for a set of particles, an example set of spectra is shown in Fig. 5 (see ref. [30]). The peak at the center of the spectrum matches the peak in the absorption spectrum closely when there is a clear peak in tlie absorption spectrum. The peak in modulation spectroscopy is found to be quite close to the shoulder in the absorption spectrum when there is only a shoulder. The first excited state gives the strongest electromod-ulation response so absorption due to higher levels in a given particle is suppressed and the first level appears clearly[30].

Figure 5: Electromodulation spectra of the same series of glasses as shown in figure **3**. Sample C2 corresponds to the long-dash spectrum in figure **3** and C8 corresponds to tlie short-dash spectrum. Sample RG630 is an as-received sample from Schott glassworks.

We caution that photoluminescence emission spec-troscopy does not appear to yield consistent iesults for

the first excited state energies. In CdSe-rich solid so-
lutions there is a well-defined PL peak quite close to
(but slight lower in energy tlian) tlie absorption peak.
In CdS-rich crystals tlie PL is dominated by emis-
sion from defects a few hundred millivolts below the
band-edge peak iii the excitation spectrum[31]. On tlie
other hand, excitation spectra appear to be reliable -
they agree with absorption spectra, modulation spec-
tra, and Ranan excitation spectra. We note that we
have recently observed unexpectedly high efficiency lu-
minescence when tlie excitation energy exceeds 4 eV in
CdS-doped glasses which suggests tliat excitation pro-
cesses may be quite complex and tliat excitation spectra
should always be coiisidered carefully[31].

V. Comparison of Quantum Size Shifts Observed for Similar Systeins

We have collected together data from several reports
on tlie size dependence of tlie optical transition energy
for tlie first excited state in CdS, CdSe aiid their solid
solutions. In Fig. 6 we sliow tlie energy of the first ex-
cited state in CdS particles plotted as a function of par-
ticle radius for particles embedded in organic liquid[1]
or in glass[14,15].
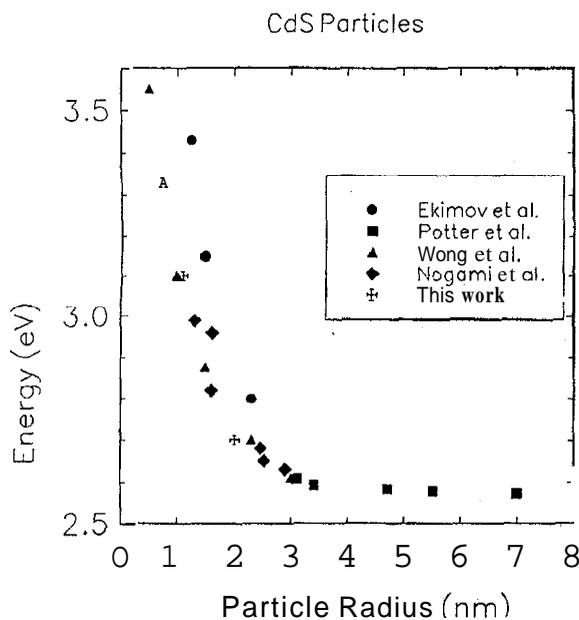
CdS Particles

Figure 6: Energy of tlie first excited state in CdS nanopar-
ticles. Data lias been transcribed from references 15 (circle,
CdS in glass), 19 (square, CdS in glass), 1 (triangle, CdS in
organic liquid), and our own work (diamond, CdS in glass).

In Fig. 7 we show tlie first excited state energy for
$CdS_{0.4}Se_{0.6}$ particles embedded in glass, again plotted

as a function of particle radius. In Fig. 8 we show
tlie lowest excited state energy plotted against particle
radius for CdSe particles embedded in various media.
The effective masses and bulk exciton radii are quite
similar for CdS, CdSe and tlieir solid solutions. We also
believe tliat tlie particles are electronically isolated by
liigli potential barriers for all of tliese systems, tlierefore
we might expect all of tliese systems to beliave similarly.
We have only included studies here in which several
particle sizes of a single coinposition and preparation
approach have been ieported because we want to focus
here on how tlie excitation energy clianges with size.
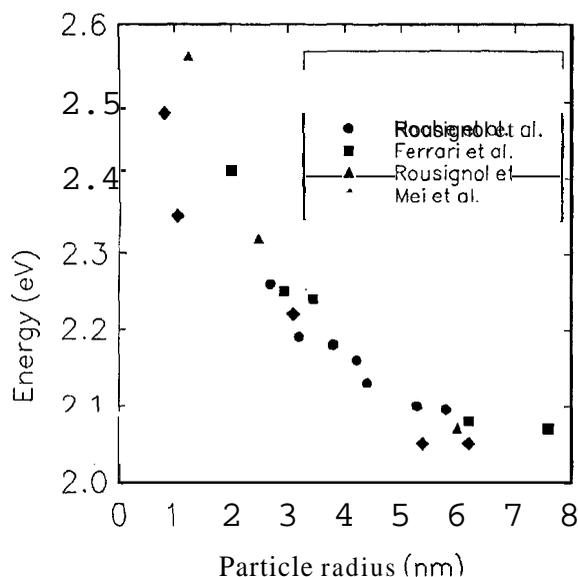
Figure 7: Energy of the first excited state in $Cd_{0.4}Se_{0.6}$ in
glass. References are marked in the legend within the figure.

We observe that tlie first excited state energy clearly
increases witli reduction in particle size for all particle
systeins, tlie inost significant changes are observed for
particles smaller than 4 nm in diameter. There are
significant differences between energy shifts in the small
particle portion of the spectruin when the results for
different studies are compared. There do not appear
to be striking systematic differences (i.e.- glass versus
colloid or CdS versus CdSe) between different systems,
for example the report on CdS in glass by Ekimov et
al.[14] shows a large size effect whereas the report on
CdSe in glass[17] shows small changes with size. We
would expect CdSe to exhibit a larger size effect because
the effective mass of both electron and hole are smaller
in CdSe but this is not the case.
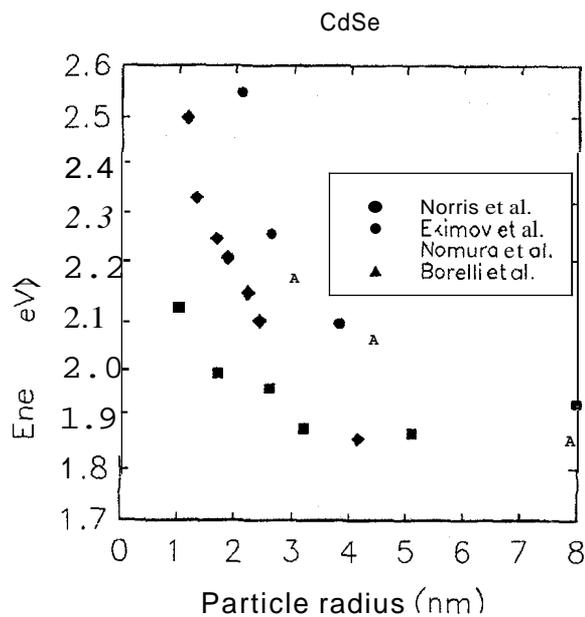
CdSe

Figure 8: Energy of the first excited state of CdSe in glass. References are marked in the figure.

VI. Overview of Current Theories

During the first years of research on 11-VI semiconductor clusters, the effective mass approximation was employed to explain the observed blueshift of the absorption edge[7,32]. In these calculations the electron and hole wavefunctions are described by the single-band effective mass at $k=0$. The effect of Coulomb interactions between electron and hole wavefunctions and surface polarization are treated in perturbation theory and relative simple expressions for the size shift have been deduced. In particular, perturbation theory should be most useful to deduce the limiting behavior of confined excitons when the particle diameter is much smaller and much larger than the exciton radius[6,7,32,33]. All of the early theoretical attempts assumed that the confining barrier was infinite. Comparison of the results of the effective mass approximation with infinite barriers to measurements indicated that the simplest effective mass approximation was qualitatively correct but that it fails quantitatively, especially for smaller particles.

Several solutions to the mismatch between theory and experiment have been suggested. Several studies focus on improving theoretical approximations beyond the first order effective mass approximation with Coulomb terms. The empirical pseudopotential method[34] gives good agreement to the data in reference 1. The empirical tight binding approximation[35] also yields good agreement with the data in reference 1. Jian-Bai Xia[36] considered the effect of mixing of heavy

and light hole states within the effect mass approximation. The effective bond orbital model[37], which includes the effects of multiple valence bands, also compares favorably to experimental data when tlie effect of finite barrier heights are included. Nomura and Kobayashi[20] take the nonparabolicity of the conduction band states into account as well as the fact that the dielectric constant of the material in the particle changes with particle radius.

While it is likely that improvements in approximations are part of the solution to disagreement between theory and experiment, there are also some important system-dependent effects which must be included in any quantitative theory. Finite barrier height for the electron potential may be important. A barrier height of 1 eV leads to wavefunction penetration of tlie barrier of several angstroms when the excited state shift is only 0.5 eV[23]. Also, recent luminescence[38] and electromodulation[39] experiments suggest that the first excited state is polarized, indicating that one of the carriers is excited directly into a surface state or band. Calculations of surface state energies for cleavage faces of CdSe and CdS indicate that there are surface bands near tlie bulk band edges in these systems[40]. Both surface states and finite barrier height will affect the quantum size shifts significantly.

Other effects which may play a role are: surface-induced strain, strain-induced phase differences (i.e.-wurtzite versus zincblende), stacking fault defects, impurities, surface states, charging-induced shifts in tlie band offset.

We must also point out that while the fact that the largest experimental disagreements are observed for the smallest particles implies that there are problems with theory, it also may implicate the experimental size measurements. All size measurements (x-ray Debye, small angle x-ray, TEM, Raman scattering) require some assumptions, either about contrast or size averaging. The relative error will be greatest for small particles. It is important for us to carefully assess the capabilities and systematic errors in tlie various size measurement techniques before theoretical approximations are pushed much further.

VII. Summary and Conclusions

We have reviewed the experimental and theoretical literature on the size dependence of the lowest excited state in nanoparticle 11-VI semiconductors. While there is qualitative agreement that the excited state energy increases dramatically with decreasing size below 5 nm diameter, the experimental studies are in quantitative disagreement in this size range. For example, CdS particles with 3 nm diameter have excited state energy of

2.9 eV aiid 3.25 eV (sliifts of 0.35 eV and 0.7 eV) as interpolated from references 1 and 15 respectively. Tliis is a factor cf two discrepancy.

Many researchers now use tlie excited state energy to *estimate* particle size using an effective mass approxiination rather than rneasure particle size directly. This review suggests that we are not yet at the point where such assumptions can be made. More extensive and careful studies of tlie effects particle size and preparation history on quantum states are indicated. We also suggest that a systematic study of systematics of particle size measurements should be undertaken.

Acknowledgements

References

1. Y. Wang aiid N. Herron, Pliys. Rev. B, 42, 7253 (1990).
2. R. Rossrtti, S. Nakahara, and L. Brus, J. Chem. Pliys., '79, 1086 (1983).
3. R. Rossetti, J. L. Ellison, J. M. Gibson, and L.E. Brus, J. Cliein. Phys, 80, 4464 (1984).
4. R. Rossetti, R. Hull, J. M. Gibson, and L. E. Brus, J. Clien . Phys. 82, 552 (1985).
5. Enlian Lu, Ph.D. Thesis, Rensselaer Polytechnic Institute (1993).
6. L. E. Brus, IEEE J. Quantum Electron., 22, 1909 (1986).
7. L. E. Brus, J. Chem. Phys. 79, 5566, (1983); L. E. Brus, J. Chem. Phys., 80, 4403 (1984).
8. A. J. Nozik, F. Williams, M.T. Nenadovic, T. Rajh, ard O. I. Micic, J. Phys. Cliem., 89, 397 (1985).
9. M. G. Bawendi, W. L. Wilson, L. Rotliberg, P. J. Carroll, T. M. Jedju, M. L. Steigerwald, and L. E. Brus, Phys. Rev. Lett, 65, 1623 (1990).
10. M. G. Bawendi, M. L. Steigerwald, and L. E. Brus, Ann. Rev. Phys. Chem., 41, 477 (1990).
11. M. Steigerwald, in "Chemical Processes in Inorganic Materials: Metal and Semiconductor Clusters and Colloids", ed. P. Persans, J. Bradley, R. R. Chiarelli, and G. Schmid (Mat. Res. Soc., Pittsburgh, 1992).
12. M. Steigerwald and L. Brus, Ann. Rev. Mater. Sci., 19, 471 (1989).
13. A. P. Alivisatos, A. L. Harris, N. J. Levinos, M. Steigerwald, L. E. Brus, J. Chem. Pliys., 89, 4001, (1988); M. Steigerwald, A. P. Alivisatos, J. M. Gibson, T. D. Harris, R. Kortan, A. J. Muller, A. M. Thayer, T. M. Duncan, D. C. Douglass and L. E. Brus, J. Am. Chem. Soc. 110, 3046 (1988).
14. A. I. Ekimov, aiid A. A. Onuschchenko, JETP Lett., 34, 345 (1981).
15. A. I. Ekimov, Al. L. Efros, and A. A. Onuschchenko, Sol. State Commun., 56, 921 (1985).
16. P. D. Persans, A. Tu, Y. J. Wu, aiid M. Lewis, J. Opt. Soc. Am. B, 6, 818 (1989).
17. N. F. Borrelli, D. W. Hall. II. J. Holland, and D. W. Smith, J. Appl. Phys., 61, 5399 (1987).
18. F. Hache, M. C. Klein, D. Ricard, and C. Flytzanis, J. Opt. Soc. Am. B, 8, 1802 (1991).
19. B. Potter and J. Simmons, Phys. Rev. B, 37, 10838, (1988); B. G. Potter, E. C. Claussen, C. J. Simmons and J. Simmons, *Ultrastructure Processing*, Uhlinann ed. (Wiley, NY, 1990).
20. S. Nomura and T. Kobayashi, Sol. State Commun., 78, 677 (1991).
21. Y. Kayanuma, Sol. St. Commun., 59, 405, (1986); Y. Kayanuma, Pliys. Rev. B, 38, 9797 (1988); Y. Kayanuma and M. Momji, Phys. Rev. B 41, 10261 (1990).
22. P. Roussignol, D. Ricard, C. Flytzanis, N. Neuroth, Phys. Rev. Lett. 62, 312 (1989).
23. Guang Mei, Ph.D. Thesis, Rensselaer Polytechnic Institute, (1992).
24. M. Ferrari, B. Champagnon, M. Barland, to be published.
25. M. G. Bawendi, A. R. Kortan, M. L. Steigerwald, and L. E. Brus, J. Chem. Phys., 91, 7282 (1989).
26. B. Champagnon, B. Andrianasolo, and E. Duval, J. Cliem. Phys. 94, 5237 (1991).
27. An Tu, Ph.D. Thesis, Rensselaer Polytechnic Institute, (1991).
28. A. P Alivisatos, A. L. Harris, N. J. Levinos, M. L. Steigerwald and L. Brus, J. Phys. Cliem., 89, 4001 (1988).
29. D. J. Norris, M. Nirmai, C. B. Murray, A. Sacra, and M. G. Bawendi, Z. Phys. D., in press.
30. G. Mei, S. Carpenter, L. E. Felton, and P. Persans, J. Opt. Soc. Am. B, 9, 1394 (1992).
31. E. B. Stokes and P. D. Persans, Mat. Res. Soc. Symp. Proc., 283, 865 (1993).
32. Al. Efros and A.L Efros, Sov. Phys. Semicond., 16, 772 (1982).
33. S, V. Nair, S. Sinha, and K. C. Rustagi, Phys. Rev. B, 35, 4098 (1987).
34. M. V. Rama Krishna and R, A. Friesner, Phys. Rev. Lett., 67, 629 (1991).
35. P. E. Lippens and M. Lanoo, Phys. Rev., B 41,

6079 (1990).

36. Jian-Bai Xia, private communication.

37. G. T. Einvoll, Phys. Rev. B, 45, 3410 (1992).

38. M. Nirmai, C. B. Murray, D. J. Norris, and M. G. Bawendi, Z. Phys. D., in press.

39. V. L. Colvin and A. P. Alivisatos, J. Chem. Phys. 97, 730 (1992). S. H. Park, R. A. Morgan, Y. Z. Hu, M. Lindberg, S. W. Koch, and N. Peygambarian, J. Opt. Soc. Ain. B, 7, 2097 (1990).

40. Y. R. Wang and C. Duke, Phys. Rev. B, 37, 6417 (1988).