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Quantum size effects on the exciton energy of CdS clusters

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We report an experimental investigation of the dependence of the lowest exciton energy of CdS clusters (quantum dots) on the cluster size. The cluster diameter is varied from 60 to 10 Å. X-ray diffraction provides definitive identification of the cluster phase and permits a determination of the average cluster size. We find that the observed size dependence cannot be explained by models based on the effective-mass approximation, but, for clusters larger than 20 Å in diameter, it is in agreement with a recent tight-binding calculation [P. E. Lippens and M. Lannoo, Phys. Rev. B **39**, 10 935 (1989)]. Below 20 Å, where the cluster deviates from the bulk zinc-blende structure, some discrepancy between the tight-binding calculation and experiments becomes evident.

The syntheses and characterization of semiconductor clusters (or quantum dots) represent areas of intense recent research.[1-3] As the radius of the cluster approaches the Bohr radius of the exciton, quantization of the energy bands becomes apparent and a blue shift in the exciton transition energy can be observed. This quantum size effect can be described qualitatively by models based on the effective-mass approximation.[4-7] However, for a quantitative description of the size dependence of the exciton energy, one has to go beyond this effective-mass approximation since, for small clusters, the dispersion of the energy band in the region of **k** space involved frequently deviates from the ideal parabolic form. In our previous study of the quantum size effect on the optical band gap of PbS clusters, we demonstrated experimentally this breakdown of the effective-mass approximation and developed a simple tight-binding model to explain the data.[8] For II-VI clusters such as CdS, reliable data covering a large enough size range have been difficult to obtain. This is because the shift in the exciton energy becomes pronounced only for CdS clusters smaller than ~60 Å, a region in which the *necessary* characterization by x-ray diffraction becomes difficult unless suitable samples are available. This problem is now alleviated with the recent advances in the syntheses of quantum-confined semiconductor clusters.[9,10] We now report the size dependence of the exciton energy of CdS clusters from 10 to ~60 Å. We show that the data cannot be explained by models based on the effective-mass approximation but are in reasonable agreement with a recent tight-binding calculation.[11]

Several synthetic techniques have to be developed to prepare the proper samples for such a study. Not only does the size of the CdS clusters have to be small and controllable, but the samples have to be characterizable by x-ray diffraction. X-ray diffraction not only provides definitive identification of the clusters, but also gives a reliable method for the determination of their average size. The cluster size can be obtained by either direct computer simulation of the x-ray diffraction pattern or from the measurement of the width of the diffraction peak followed by application of Scherrer's equation.[12] The validity of Scherrer's equation and the effect of defect, shape, and size dispersion on the x-ray diffraction pattern have already been critically examined using direct computer simulation.[13] In the following we will give a brief account of methods for synthesizing the CdS clusters.

CdS clusters in the ~40–60-Å-size regime were synthesized inside a perfluoroethylenesulfonic acid polymer film (Nafion®). Cadmium ions were first exchanged into the ionic domains of the polymer followed by reaction with H_2S to generate the CdS clusters. The details of this preparative procedure and the x-ray diffraction data have been reported.[14-16] For CdS clusters smaller than 40 Å, good-quality x-ray diffraction spectra cannot be obtained from polymer film samples because of the low concentration of the CdS clusters in the polymer. Instead, "free-standing" (i.e., without a supporting matrix) CdS clusters capped with thiophenolate groups (C_6H_5S—) have been synthesized.[9] The clusters are grown in solution using the reaction $Cd^{2+}+S^{2-}\rightarrow CdS$ and their growth is stopped using the reaction $Cd^{2+}C_6H_5SH\rightarrow CdSC_6H_5{}^{+}+H^{+}$. Using this method, stable clusters whose cores are essentially sphalerite CdS but whose surfaces are covered by phenyl groups can be made. X-ray diffraction data on these clusters can be easily obtained, despite their small size, since they are made of essentially pure CdS with no supporting matrix to act as diluent. Detailed synthetic procedures and x-ray data can be found in Ref. 9. With these samples, the smallest cluster whose size can be determined from the x-ray technique is ~15 Å. Finally, we have recently synthesized monodisperse 10 Å CdS clusters by fusing two $[Cd_{10}S_4(\text{Sphen})_{16}]^{4-}$ molecular clusters[17] together (where "phen" is a phenyl group). The core of this 10 Å cluster is a $Cd_{13}S_{13}$ unit, with the sphalerite-like structure, while the edges consist of $CdSC_6H_5$ units. The cluster has 55 Cd and S atoms and a pyramidal shape. The quoted size refers to that of the crystalline CdS core from the base to the tip of the pyramid, not including the peripheral phenyl groups. Detailed synthetic procedures and complete characterization of this sample, including chemical analysis, x-ray diffraction, nuclear magnetic resonance (NMR), and photoluminescence, will be reported elsewhere.[10] The absorption spectrum of this 10 Å CdS cluster is shown in Fig. 1, along with the spectra of several larger CdS clusters synthesized by the techniques mentioned above. Because of the absence of size dispersion in the 10 Å cluster, a very sharp exciton-absorption band can be clearly observed at 351 nm (3.53 eV). Other larger CdS clusters have ~20% size dispersion and, as a result, show only broad exciton-absorption bands.

With the availability of these well-defined samples, the size dependence of the lowest exciton energy of CdS clusters can be determined down to a cluster diameter of 10 Å. The experimental data are shown in Fig. 2. The exciton energy is determined by locating the peak in the second derivative plot of the absorption spectrum. The uncertainty in the exciton energy is smaller than the size of the symbol in Fig. 2. Major uncertainty comes from the size determination, which is represented by error bars in Fig. 2. For the 10 Å clusters there is no error bar because they are essentially monodisperse.

We now compare the experimental data with available theoretical models. The simplest three-dimensional confinement model based on the effective-mass approximation predicts the energy shift, ΔE, as[4-6]

$$\Delta E=\frac{\hbar^2\pi^2}{2R^2}\left[\frac{1}{m_e}+\frac{1}{m_h}\right]-\frac{1.786e^2}{\epsilon R}-0.248\,E^*_{\mathrm{Ry}}\,, \tag{1}$$

where R is cluster radius, m_e is the electron effective mass, m_h is the hole effective mass, ϵ is the dielectric constant, and E^*_{Ry} is the effective Rydberg energy, $e^4/2\epsilon^2\hbar^2(m_e^{-1}+m_h^{-1})$. The first term in Eq. (1) represents the kinetic energy,[4] the second term the Coulomb energy,[5] and the third term is a result of the correlation effect.[6] The calculated exciton energy based on Eq. (1) is plotted as a dotted line in Fig. 2, using $m_e/m=0.19$, $m_h/m=0.53$, and $\epsilon=5.5$. Clearly, the calculation cannot reproduce the experimental results, indicating the failure of the effective-mass approximation even for a large-band-gap semiconductor such as CdS.

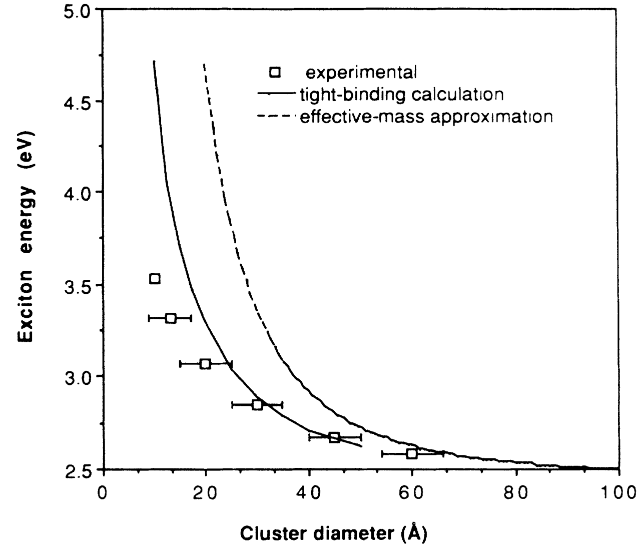

FIG. 2. The exciton transiton energy of CdS clusters plotted as a function of cluster diameter. Dashed line is calculated from Eq. (1). Solid line is the result of a tight-binding calculation taken from Ref. 11.

A better description of the band structure can be obtained within the tight-binding framework. In this ap-

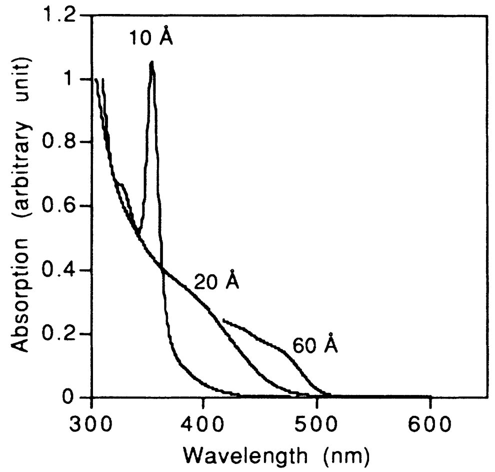

FIG. 1. Absorption spectra of several representative CdS cluster samples. The 60 Å CdS is made inside an ionic polymer film. The 20 Å CdS is a free-standing cluster capped with thiophenolate on the surfaces. The 10 Å sample is a monodisperse 55-atom CdS cluster (not counting the peripheral phenyl groups). The spectra are scaled arbitrarily.

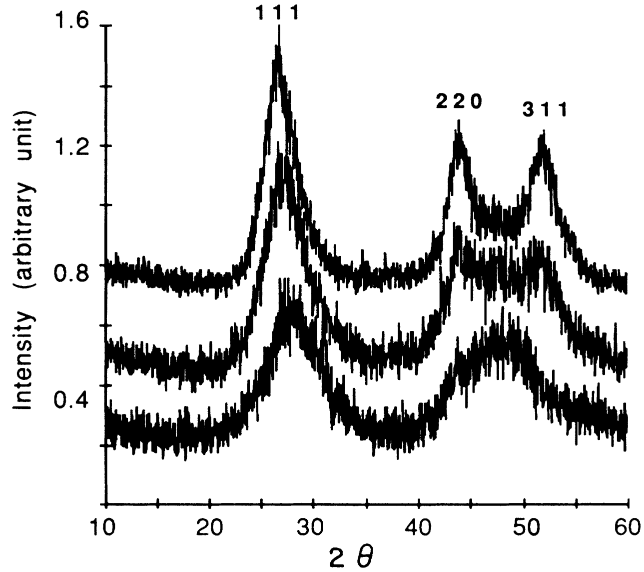

FIG. 3. X-ray diffraction spectra of ~30, ~20, and ~15 Å thiophenolate-capped CdS clusters (top to bottom, respectively). Cu$K\alpha$ radiation was used. Notice the gradual shift of the (111) peak from 26.9° to 27.7°.

proach, one optimizes the tight-binding parameters to obtain a fit with the known bulk band structure, obtained either experimentally or with more-elaborate theoretical methods. Once these tight-binding parameters are known, one can use them to calculate the cluster properties provided the cluster structure remains unchanged from the bulk structure. This tight-binding method has been used successfully to calculate the size-dependent optical band gap of PbS clusters.[8] Because of the well-isolated conduction and valence band of PbS and the simplicity of the rock-salt structure, only three tight-binding parameters were needed to give a satisfactory explanation of the experimental data. For CdS, a 13-parameter tight-binding model has been developed before to give a satisfactory account of the band structure.[18] Recently, Lippens *et al.*[11] used this tight-binding Hamiltonian to calculate the exciton energy of CdS clusters as a function of the cluster size. The result of this tight-binding calculation is displayed as the solid curve in Fig. 2. The agreement with the experimental data is quite good for clusters larger than ~20 Å. Below 20 Å, the tight-binding calculation starts to deviate from the experimental value.

One possibility for the discrepancy between the calculation and the experiment for clusters smaller than ~20 Å is the change in crystal structure for small clusters. Figure 3 shows the x-ray diffraction spectra of ~30 Å, ~20 Å, and ~15 Å CdS clusters.[9] Looking at the (111) peak one notices a gradual shift of the peak from 2θ of 26.9° for ~30 Å cluster to 27.7° for ~15 Å cluster, which corresponds to a contraction in lattice constant of ~3%. For the 10 Å cluster, the estimated peak position shifts further to a 2θ value of 28.5°.[10] Since the tight-binding parameters are optimized to the band structure of bulk sphalerite-type CdS, they are not suitable for clusters whose structure deviates from the bulk. Another possible reason for the discrepancy is that in the tight-binding calculation of Ref. 11 the Coulomb interaction was simply taken from that of a spherical cluster in an infinitive potential well (i.e., the effective-mass-approximation model), rather than evaluated properly with the tight-binding Hamiltonian. This could introduce errors in the very small cluster size regime.

Based on this study and previous reports on PbS (Ref. 8) and CdS_xSe_{1-x} clusters,[19] it is clear that one has to go beyond the effective-mass approximation to obtain a quantitative description of the three-dimensional quantum size effect. The semiempirical tight-binding method[8,11] provides an effective tool for calculating the cluster optical band gap if the cluster structure stays the same as that of the bulk. Further improvement requires the consideration of the effects of finite well depth, surfaces,[1,15,16] and defects. The magnitudes of these effects appear to be small compared to the breakdown of the effective-mass approximation.

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[1] Y. Wang, W. Mahler, N. Herron, and A. Suna, J. Opt. Soc. Am. B **6**, 808 (1989).

[2] A. Henglein, Chem. Rev. **89**, 1861 (1989).

[3] L. E. Brus, J. Phys. Chem. **90**, 2555 (1986).

[4] Al. L. Efros and A. L. Efros, Fiz. Tekh. Poluprovodn. **16**, 1209 (1982) [Sov. Phys.—Semicond. **16**, 772 (1982)].

[5] L. E. Brus, J. Chem. Phys. **80**, 4403 (1984).

[6] Y. Kayanuma, Phys. Rev. B **38**, 9797 (1988).

[7] H. Weller, H. M. Schmidt, U. Koch, A. Fojtik, S. Baral, A. Henglein, W. Kunath, K. Weiss, and E. Dieman, Chem. Phys. Lett. **124**, 557 (1986).

[8] Y. Wang, A. Suna, W. Mahler, and R. Kasowski, J. Chem. Phys. **87**, 7315 (1987).

[9] N. Herron, Y. Wang, and H. Eckert, J. Am. Chem. Soc. **112**, 1322 (1990).

[10] N. Herron and Y. Wang, unpublished results.

[11] P. E. Lippens and M. Lannoo, Phys. Rev. B **39**, 10 935 (1989).

[12] A. Taylor, *X-ray Metallography* (Wiley, New York, 1961).

[13] A. Suna and Y. Wang, unpublished results.

[14] Y. Wang and W. Mahler, Opt. Commun. **61**, 233 (1987).

[15] E. Hilinski, P. Lucas, and Y. Wang, J. Chem. Phys. **89**, 3435 (1988).

[16] Y. Wang, A. Suna, J. McHugh, E. Hilinski, P. Lucas, and R. D. Johnson, J. Chem. Phys. **92**, 6927 (1990).

[17] I. G. Dance, A. Choy, and M. L. Scudder, J. Am. Chem. Soc. **106**, 6285 (1984).

[18] P. Vogl, H. P. Hjalmarson, and J. D. Dow, J. Phys. Chem. Solids **44**, 365 (1983).

[19] H. Shinojima, J. Yumoto, N. Uesugi, S. Omi, and Y. Asahara, Appl. Phys. Lett. **55**, 1519 (1989).