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Confinement and shape effects on the optical spectra of small CdSe nanocrystals

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A tight-binding model is used to investigate confinement and shape effects on the optical absorption spectrum of CdSe nanocrystals up to 5 nm diam. The effects of size dispersion are studied and we show that to simulate the spectrum of a collection of nanocrystals it is not always sufficient to broaden inhomogeneously the mean diameter cluster spectrum. Our results are compared with calculations based on other methods and show good agreement with experimental data. We have also calculated the absorption spectra of CdSe crystallites with different morphologies: spherical clusters and oblate and prolate elliptic nanocrystals. We have performed a comparison of the energies and absorption bands as a function of the morphological changes and we present a detailed study of the modifications in the features of the optical spectra. [S0163-1829(98)03932-0]

I. INTRODUCTION

In recent years, the study of ultrasmall systems on the 1–10 nm length scale have stimulated intense investigation. Semiconductor nanocrystals have focused great interest[1] and diverse methods have been developed to elaborate crystallites. Among them, growth in glass matrix and synthesis in colloids[2–6] have been used to obtain II-VI nanocrystals with diameters ranging from 1 to 11.5 nm. Whatever the elaboration processes are,[7] the crystallites show a high-quality bulk crystalline structure, with few exceptional defaults and no change in the first-neighbor interatomic distances.[8] On the other hand, the fabrication techniques strongly influence the shape and surface structure. In the small size range, where quantum confinement effects arise, nanocrystallites appear to be spherical.[7] Nevertheless, nanocrystals can show a facetting aspect[9] beyond a critical diameter (7–10 nm for CdS_xSe_{1-x} crystallites[10]) or ellipsoidal shapes.[11] A slight ellipticity[12] has been observed on CdSe nanocrystals by high-resolution transmission electron microscopy.

Semiconductor nanocrystals exhibit modified electronic and optical properties due to quantum confinement. All optical absorption experiments indicate a blueshift of the absorption edge when the crystallite size decreases.[13] The presence of discrete absorption bands is also clearly evidenced. Assigned to excitonic transitions, the position and the shape of the bands are strongly dependent on cluster sizes. To compare theoretical results with experiments, the knowledge of the confinement energies is not sufficient and it is necessary to obtain the optical transitions, which requires the calculation of oscillator strengths. Up to now, such a calculation has been achieved only for few CdSe samples.[14] Therefore, in order to make a systematic study, we have investigated, in the tight-binding approximation, the optical absorption spectra in function of nanocrystals diameter. Moreover, nanocrystals are not monodisperse but samples contain different size clusters. They present a distribution of size that can appreciably influence the optical spectra of the samples. That masks information about a single-size nanocrystal and perturbs the study of size dependence of crystallites properties. Particularly, the observed blueshift of the absorption threshold, due to confinement effects when the crystallite diameter diminishes, is reduced by a redshift due to size fluctuations. Size dispersion also perturbs the comparison of experimental data with theoretical results. We therefore have included size dispersion effects in our calculation. Our method takes into account the structural characteristics of the clusters: size, surface passivation, and size fluctuations of the samples. It allows the comparison with previous theoretical studies of CdSe nanocrystals and with recent and accurate experimental data.

In addition, morphological influence has only been examined, up to now, for silicium crystallites. Wang and Zunger[15] have established that the gap variation with cluster size is almost identical for spheres, rectangular boxes, and cubes. The calculation of a low-energy excitonic spectrum has been achieved only for a single deformed ellipsoid by Delerue and co-workers[16,17] showing that the lowest-energy state presents a longer lifetime than the first higher state. The present development of nanocrystals, widely elaborated from II-VI materials, makes interesting the study of shape effects for these systems. We have calculated the excitonic transitions on a large energy range for ZnS faceted crystallites[18] and we will focus in this paper on CdSe elliptic crystallites.

The paper is organized as follows: after a description of the model in Sec. II, we present in Sec. III the confinement effects on CdSe nanocrystals and we discuss the optical properties in comparison with other previous calculations and experimental data. In Sec. IV, we study nonspherical nanocrystals. Section V is devoted to our conclusions.

II. MODEL

We have developed a realistic model taking into account the spin-orbit interactions and the real arrangement of the atoms in the nanocrystal. We have considered spherical crystallites obtained by connecting the successive neighbors of the central site. Dangling bonds of surface atoms are saturated by hydrogen atoms that simulate the bonds at the cluster surface, occurring with the glass matrix or with molecules of the colloid, and clear the band gap from surface states. In our tight-binding approach, the cadmium and selenium atoms are described by a sp^3s^* basis and the hydrogen atoms by a single s orbital, both including spin. This is necessary to

TABLE I. Tight-binding parameters (in eV) for CdSe in the sp^3s^* basis including spin-orbit interactions. a and c stand, respectively, for anion and cation.

E_{sa}	E_{sc}	E_{pa}	E_{pc}	E_{s^*a}	E_{s^*c}	λ_a	λ_c
−9.63	0.03	1.326	4.73	7.53	5.72	0.1434	0.0591
V_{ss}	V_{xx}	V_{xy}	V_{sapc}	V_{scpa}	V_{s^*cpa}	V_{s^*apc}	
−4.64	2.64	5.36	4.57	5.54	2.49	3.05	

TABLE II. Bulk CdSe parameters.

		CdSe	Reference
Exciton Bohr radius	a_B (nm)	5.4	23
Spin-orbit splitting	Δ_o (eV)	0.4	23
Gap	E_g (eV)	1.8	23
Dielectric constant	ε	6.23	23
Lattice constant	a (nm)	0.67	23
Hydrogen-cadmium bond length	$d_{\text{H-Cd}}$ (nm)	0.176	38
Hydrogen-selenium bond length	$d_{\text{H-Se}}$ (nm)	0.147	38

take into account spin-orbit splitting, as its contribution is not negligible for CdSe, ($\Delta_o = 0.4$ eV). The excited state s^* is used to obtain a correct description of the lowest conduction band with interactions limited to first-nearest neighbors. It avoids the addition of d orbitals and, consequently, allows the restriction of the Hamiltonian matrix to a computable dimension.

Expressed in the sp^3s^* orbital basis, the Hamiltonian elements are fitted to reproduce the band structure of bulk CdSe, known from experiments and other theoretical methods. Only on-site and nearest-neighbor matrix elements are allowed to be nonzero. The 15 parameters are those of Refs. 19 and 20, modified in order to take into account the spin-orbit interaction. They are given in Table I, expressed with the notations of Vogl, Hjalmarson, and Dow.[21] The band structure of bulk CdSe obtained within this parametrization process is in good agreement with results of other calculations and optical measurements.[22] A test for its reliability is the evaluation of the effective mass of electron and holes. The effective masses obtained ($m_e^* \simeq 0.13\ m_o$ and $m_{hh}^* \simeq 0.45\ m_o$, where m_o is the free electron mass) are in good agreement with other published values and experience.[23]

In nanocrystals, the first-neighbor matrix elements between the hydrogen atoms and cations or anions, $V_{\text{H-Cd}}$, $V_{\text{H-Se}}$ are analogous to interatomic elements but are distinguished by a renormalization term. According to Harrison's law,[24] it takes into account the relaxation effect around a defect or at the surface. The Hamiltonian matrix reproduces the physical properties of the bulk material in the limit of the infinite-size cluster. Its dimension for a crystallite is $10\ N_{at} + 2N_{\text{H}}$ where N_{at} represents the total number of atoms in the nanocrystal and N_{H} the number of hydrogen atoms.

The direct diagonalization of the Hamiltonian matrix provides the energy levels, wave functions and fundamental energy gap $E_g(d)$. In order to compare our results with optical-absorption data, it is necessary to take into account the Coulomb attraction between electrons and holes. In the small-size range considered in this work, nanocrystals are strongly confined and the Coulomb attraction is treated as a perturbation. We assume that the energy of the first optical transition $E(d)$ can be evaluated by adding a perturbation term at the energy gap:[25] $E(d) = E_g(d) - (3.572e^2/\varepsilon d)$, where d and ε stand for the diameter and dielectric constant of the semiconductor. Known for bulk materials, the value of the dielectric constant for nanocrystals is still under debate. The constant may be different in the strong- and weak-confinement regimes. In the case of nanoscopic spheres dispersed in a glass matrix or in a colloid, the lack of experimental characterization prevents us from evaluating the best value for ε. Calculations with a varying dielectric constant[19] have shown for CdS crystallites that its effect is rather small, enhancing the energy of the first transition by less than 40 meV. This change is not significant in the comparison between calculated and experimental values and in this framework, we have considered the nanocrystals as continuous, isotropic materials with a bulk dielectric constant (Table II).

While the positions of the excitonic peaks are deduced from the eigenvalues of the Hamiltonian, the intensities of the optical transitions are described by the oscillator strengths related to the eigenvectors. The nanocrystals being optically isotropic, the oscillator strength is independent of polarization and can be described by $f_{nm} = 2/m_o|\langle n|\vec{P}|m\rangle|^2/(E_m - E_n)$ for a transition from a valence state n to a conduction state m. Within the tight-binding framework, the momentum matrix elements between atomic orbitals are calculated according to $\vec{P} = (im_o/\hbar)[H,\vec{r}]$ with the commutator between the Hamiltonian H and position operator $\vec{r}$ expanded on the sp3s* basis.[26]

We have made calculations for crystallites containing 10–2000 atoms, corresponding to increasing diameter up to 5 nm, which is an adequate size range for the study of strong confinement.

III. CONFINEMENT EFFECTS

The first transition energies calculated within our model are shown in Fig. 1 for various crystallite sizes. We have also plotted the results obtained by different theoretical approaches: by the effective-mass approximation,[19] in the tight-binding framework,[19] within the effective bond orbital model[14] (EBOM) and with the pseudopotential method[27] in order to compare with numerous experimental data, CdSe nanocrystals being under intense investigation.

Our results are represented by the solid line. Due to quantum confinement effects, the first transition energy is strongly enhanced compared to the bulk material (1.8 eV). When the crystallite diameter d increases, the confinement energy decreases and follows approximately the law $d^{-1.3}$. Our results in the tight-binding model show that the first transition energy exhibits an oscillatory behavior in function of the nanocrystal size. This discontinued evolution can be interpreted as the effect of the ionic character of CdSe crystallites. Let us examine three nanocrystals of increasing diameter. By construction, the atomic clusters considered in this work are spherical and have a cation on the central site. A crystallite of 1.16 nm diam has 29 atoms and its surface is composed by anions. The connection to this cluster of a shell of cations leads to the formation of a nanocrystal with 35 atoms and 1.23 nm diam. The highest valence state is in-

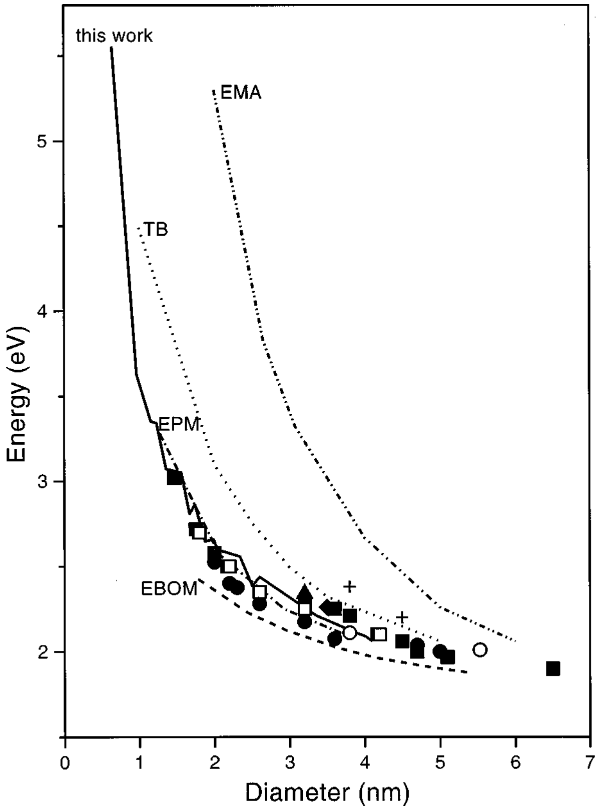

FIG. 1. Variations of the first transition energy as a function of the nanocrystal diameter. The solid line represents the results of this paper and the dotted line the tight-binding calculation of Ref. 19. The EBOM (Ref. 14) and pseudopotential (Ref. 27) results are represented by the dashed line and dashed-dotted line. The effective-mass (Ref. 19) energies are also reported (dashed-double-dotted line). The experimental data are taken from Refs. 28–34 and represented by the solid squares, solid triangles, open squares, black dots, open dots, black diamonds, and crosses, respectively.

creased by 0.09 eV and the lowest conduction state is only weakly modified (enhancement of 0.003 eV). This is related to the ionic composition of the highest valence state, mainly formed by the anion states of p symmetry and lowest conduction state, mainly composed of the cation states of s symmetry. As the interatomic interactions are restricted to first-nearest neighbors, connecting a shell of cations leads to a significant increase of the highest valence-state energy and a slight enhancement of the lowest conduction-state energy. By contrast, the addition of a shell of anions strongly modifies the lowest conduction-state energy and leaves the highest valence state practically unchanged. By consequence, the first transition energy shows an oscillatory evolution as a function of the nanocrystal diameter. Taking into account atomic interactions beyond first neighbors should attenuate the amplitude of these oscillations. When the diameter increases, the ratio of surface atoms to volume atoms diminishes and the connection of one atomic shell to a cluster composed by a great number of atoms only slightly modifies the electronic states. Consequently, related to the ionic character of surface atoms, the discontinued behavior of the first transition energy lessens with increasing size (Fig. 1).

The evolution of energy versus crystallite size is similar with the tight-binding results of Lippens and Lannoo,[19] where spin-orbit interaction was not included. Nevertheless, our calculated energies have lower values than those of Ref. 19 (Table III). This is mainly due to the spin-orbit interaction taken into account in our model. We have calculated that for a 2-nm-diam cluster, the energy obtained taking spin-orbit coupling into account is 0.28 eV lower than the value obtained without spin. In addition, the use of a varying dielectric constant in Ref. 19 leads to a slight enhancement of the energies. The Coulomb energy calculated with $\varepsilon(d)$ is, for $d=2$ nm, 0.18 eV higher than the value calculated using $\varepsilon(\infty)$. When the diameter increases, the Coulomb part of the total energy diminishes and the energy difference between the two models decreases. The combined effects of spin-orbit interaction and use of bulk dielectric constant $\varepsilon(\infty)$ can explain the differences between the calculated values within tight-binding models.

TABLE III. First transition energies of CdSe nanocrystals, expressed in eV.

Diameter (nm)	This work	Pseudopotential [a]	TB [b]	EBOM [c]	EMA [b]
1.27	3.24	3.28	4.09		
2.06	2.59	2.57	3.01	2.39	5.14
2.92	2.33	2.25	2.53	2.12	3.47
3.84	2.11	2.08	2.25	1.99	2.77

[a] Reference 27.
[b] Reference 19.
[c] Reference 14.

Secondly, we compare our results with the calculation made in the EBOM by Ramaniah and Nair[14] for nanocrystals 1.7 nm to 5.4 nm diam. The first transition energies are lower than within tight-binding calculations, whereas their evolution versus crystallite size is similar (Table III). The energy difference increases for small nanocrystals and bulk CdSe parametrization in the approximation of a cubic face-centered lattice[14] seems to lead to significantly lower energies than in the tight-binding model, which takes into account the arrangement of the atoms in the zinc-blende structure.

We next compare our calculation with the recent results of Wang and Zunger[27] by the pseudopotential method. As shown in Table III, the first transition energies calculated within the pseudopotential method are in excellent agreement with our tight-binding results, the maximum energy difference being 0.08 eV.

Lastly, we compare our results with the effective-mass approximation[19] where $m_e^* \simeq 0.13 m_o$ and $m_h^* \simeq 0.41 m_o$ for electron and hole. We can note that the single-band approximation is reasonable for CdSe because the valence-band splitoff, due to the spin-orbit effect, is sufficiently large ($\Delta = 420$ meV) so that these bands can be considered as decoupled. The calculated energies reveal large discrepancies with other calculations (Table III). The shift between the EMA and other results shows that size estimation by the effective mass model leads to a large overestimation of the nanocrystal diameter. When the crystallite size increases, the strong overestimation of energies in the EMA diminishes. Beyond 5 nm, the various models provide converging results. The EMA is then valid and the energy follows a d^{-2} scaling law.

We conclude from comparison of the first transition ener-

TABLE IV. Comparison of the first transition energies (in eV) of CdSe nanocrystals, obtained by experiments and various calculations.

Diameter (nm)	Experiment	This work	TB [a]	Pseudopotential [b]	EBOM [c]	EMA [d]
2	2.52,[e] 2.58[f]	2.65	3.11	2.63	2.36	5.28
3.2	2.17,[e] 2.25,[g] 2.28,[f] 2.34[h]	2.26	2.4	2.19	2.08	3.21
3.8	2.11,[i] 2.21,[f] 2.38[j]	2.12	2.26	2.09	2	2.79

[a] Reference 19.

[b] Reference 27.

[c] Reference 14.

[d] Reference 19.

[e] Reference 31.

[f] Reference 28.

[g] Reference 30.

[h] Reference 29.

[i] Reference 32.

[j] Reference 34.

gies calculated within various models that confinement effects are clearly evidenced by all formalisms with a strong enhancement on bulk energy for small crystallites. When the diameter increases, results converge and calculated energies come close to the bulk band gap. Quantitatively, by contrast, the results provided by the models differ. (i) The EMA considerably overestimates the energies of small nanocrystals and this clearly shows the inadequacy of the model in predicting first transition energies from the knowledge of the diameter, just as it was not possible to deduce this diameter by comparing the energies to the experimental data. (ii) Our tight-binding results, including spin-orbit interactions, are in excellent agreement with the experimental ones and those obtained by Wang and Zunger[27] with a totally different method using a semiempirical pseudopotential. That shows the necessity to take spin into account in the calculation as well as the adequacy of the tight-binding model in calculating the nanocrystal electronic states.

Numerous experimental studies have been performed on CdSe nanocrystals synthesized by various methods. Among many experimental data, we have only reported in Fig. 1 the optical measurements concerning crystallites the sizes of which are determined by techniques independent from theoretical models, such as high-resolution transmission electron microscopy (HRTEM) and small-angle x-ray scattering (SAXS).

Bawendi *et al.*[28,29] have fabricated CdSe crystallites with a remarkable narrow size dispersion ($<5\%$). Absorption measurements at 10 K agree well with our results, the maximum-energy difference being 0.09 eV. The first transition energies of crystallites synthesized by Hoheisel *et al.*[30] are similar to those reported in Refs. 28 and 29. Bowen Katari *et al.*[31] have studied colloidal nanocrystals whose sizes measured by SAXS vary from 3 to 9 nm and absorption energies are close to those calculated within the tight-binding and pseudopotential methods. In the same way, experimental data from Nogami, Suzuki, and Nagasaka [32] and Hodes *et al.*,[33] where the crystallite size is determined by HRTEM, agree well with theoretical energies. Finally, Alivisatos *et al.*[34] have investigated spherical nanocrystals. When the diameter is 3.8 nm, the first transition energy is above the values calculated within microscopic approaches, but the energy difference stays reasonably small. The measured values are dispersed (Table IV) and comparison to theoretical results is not easy. The EBOM (Ref. 14) provides energies always lower than experiment. In contrast, the EMA strongly overestimates the first transition energy of crystallites. On the wide size range studied, we conclude that all these experimental data of CdSe nanocrystals are coherent and that our model and the pseudopotential method agree well with experiment. Although the accuracy of our model is difficult to evaluate, it is mainly limited by the parametrization of bulk materials and the knowledge of surface passivation. First of all, the model is fitted to reproduce the bulk band structure and particularly the main energy gaps at the points Γ, X, and L. The parameters are calculated from energy levels of high-symmetry points of the Brillouin zone. They are not always known with great precision, and it can lead to a bulk description that is not in perfect agreement with experience. Moreover, our treatment of nanocrystal surface is simple. A more accurate description, taking into account interface effects needs a better experimental knowledge of its structure. At last, Coulomb interaction is treated as a perturbation in using bulk optical dielectric constant. As the Coulomb energy increases when the nanocrystal diameter decreases, this approximated calculation is critical for small clusters. In the size range where confinement effects arise, our model reproduces the first transition energy with a good agreement with experimental data and a precision of about a few tenths of an electron volt.

Within the tight-binding framework, we have also calculated the optical absorption spectra. Besides the structural properties (size, shape, surface states, lattice structure), it is necessary to take into account the size distribution of the samples to compare theoretical results with experiments. To calculate the absorption spectra of a collection of nanocrystals, Ramaniah and Nair[14] have proposed to introduce an inhomogeneous broadening in the interband transition spectra of the mean diameter nanocrystal. A more realistic way consists of calculating the spectra of all the crystallites with a size distribution, considering that each spectrum undergoes a homogeneous broadening. It needs more calculation and, to our knowledge, optical spectra computed within this method and in the tight-binding framework have not been reported in CdSe nanocrystals of various diameters up to now. Comparison with other calculations allows us to test the validity of the inhomogeneous approximation and comparison to experimental data, the ability of the models in predicting the optical properties of crystallites.

CdSe crystallites have been synthesized by Ekimov[35,36] and we compare our results with the absorption spectra of CdSe nanocrystals in oxide glass at 5 K.[36] Determined by SAXS and HRETM, the average diameters of samples 1, 2, 3, and 4 are, respectively, 3, 3.4, 3.6, and 5.4 nm. They show

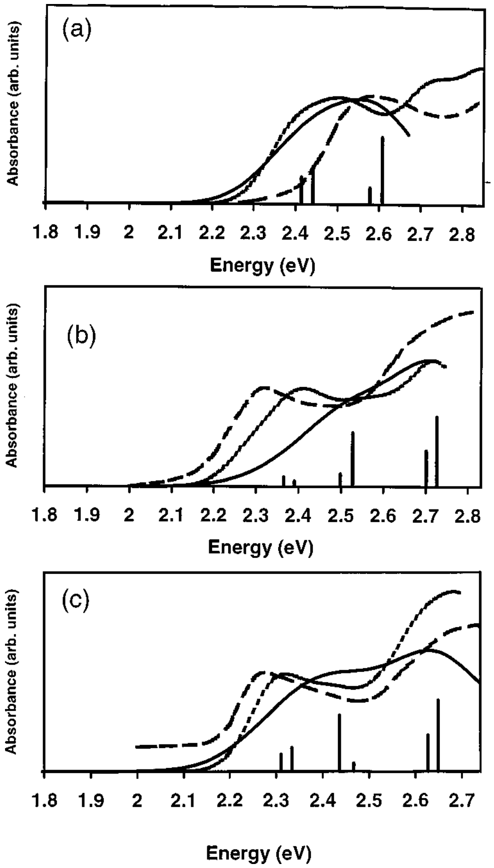

FIG. 2. Variations of the optical spectra for CdSe nanocrystals of 3-, 3.4-, and 3.6-nm diam. The experimental data (dashed lines) are taken from Ref. 36). (a), (b), and (c), respectively, represent the absorption spectra of a collection of clusters (dotted lines) and of a single cluster (solid lines) of 3-nm-, 3.4-nm-, and 3.6-nm-mean-diameter nanocrystals.

a distribution of size of approximately 10%. To evaluate the consequences of size dispersion, we have calculated the contribution to optical absorption of lowest-energy transitions for all the crystallites within the size distribution. So, our results allow to determine precisely which cluster is responsible for a given transition. In the absence of accurate information on the experimental shareout of nanocrystals in the samples, we have considered that each cluster in the distribution participates fairly well for the whole spectrum. Optical spectra of nanocrystals, the sizes of which vary by about 10% around the mean diameter, are convoluted by a Gaussian with a homogeneous broadening of 20 meV (Fig. 2).

The theoretical spectrum of sample 1 [Fig. 2(a)] exhibits a first transition at 2.5 eV, while experimental data[36] show a first absorption band at 2.56 eV. The energy difference is very low and the aspect of the theoretical spectra coincides with experiments. Our calculations indicate excitonic transitions at 2.57 eV and 2.6 eV for the single nanocrystal of 3.04 nm diam, which corresponds to the mean diameter of sample 1. It then becomes apparent that, in that case, the cluster responsible for the absorption band observed is the one that has a diameter equal to the mean diameter. It can be confirmed by the position of the absorption band centered at 2.55 eV, nearly the same value than for the group of crystallites. Size fluctuations of sample 1 do not perturb the optical absorption of the mean nanocrystal.

For sample 2 [Fig. 2(b)] the first absorption band, at 2.41 eV, arises from the crystallite of 3.7 nm diam. The second absorption band, at 2.72 eV, corresponds to the cluster of 3.4 nm. Experiments exhibit a first absorption band at 2.28 eV and a second one near 2.8 eV. Calculated and measured values agree well and our model confirms the importance of size dispersion of nanocrystals in this case. The absorption spectrum of the single cluster of mean diameter 3.4 nm exhibits a small shoulder near 2.52 eV and a clearly resolved band at 2.71 eV. This shows that the convolution of transitions of the mean diameter cluster is insufficient to reproduce experiment and that it is necessary to take into account all nanocrystals within the size distribution.

In the same way, for sample 3 [Fig. 2(c)] we observe three absorption bands at 2.33, 2.4 and 2.68 eV, arising, respectively, from clusters of 3.8, 3.65, and 3.5 nm diameter. The aspect of the spectrum is similar to the experimental one and clearly shows the narrowing of absorption bands when the diameter increases. Experiments show that sample 3 has almost the same spectrum of sample 2 with a more resolved shoulder at 2.4 eV and the last absorption band at 2.74 eV. Theoretical energies agree very well with experimental data. By contrast, the absorption spectrum of the single cluster of 3.6 nm diam exhibits two absorption bands at 2.42 and 2.62 eV and cannot describe experiments.

Our model provides a correct description of the behavior of optical spectra of small CdSe nanocrystals as a function of size and shows the importance of size dispersion. By contrast with the use of an inhomogeneous broadening of excitonic peaks and also the convolution of the mean diameter nanocrystal transitions, considering explicitly the transitions of all the nanocrystals in the size distribution allows us to reproduce the absorption spectra of various crystallites with a good agreement with experiments.

IV. SHAPE EFFECTS

We have modeled elliptic crystallites by the deformation of spheres in one direction. Excluding from a sphere of radius a all the atoms located on surface shells the position vectors of which coordinate along the Oy axis is larger than $b<a$ provides prolate nanocrystals. Ellipsoids can then be described by the equation

$$\left(\frac{x}{a}\right)^2+\left(\frac{y}{b}\right)^2+\left(\frac{z}{a}\right)^2=1, \tag{1}$$

where a is larger than b for the compression along the Oy direction.

In the same way, adding to a sphere of radius b atoms occupying zinc-blende lattice sites the position vectors of which are coordinate along the Oy axis is larger than b provides oblate crystallites. The ellipsoids obtained by the dilatation of a sphere along Oy direction can be described by the equation

$$\left(\frac{x}{b}\right)^2+\left(\frac{y}{a}\right)^2+\left(\frac{z}{b}\right)^2=1, \tag{2}$$

where a stands for the long axis and b is the short axis.

In the case of spherical crystallites, the confinement is three dimensional, relative to the characteristic length a. For

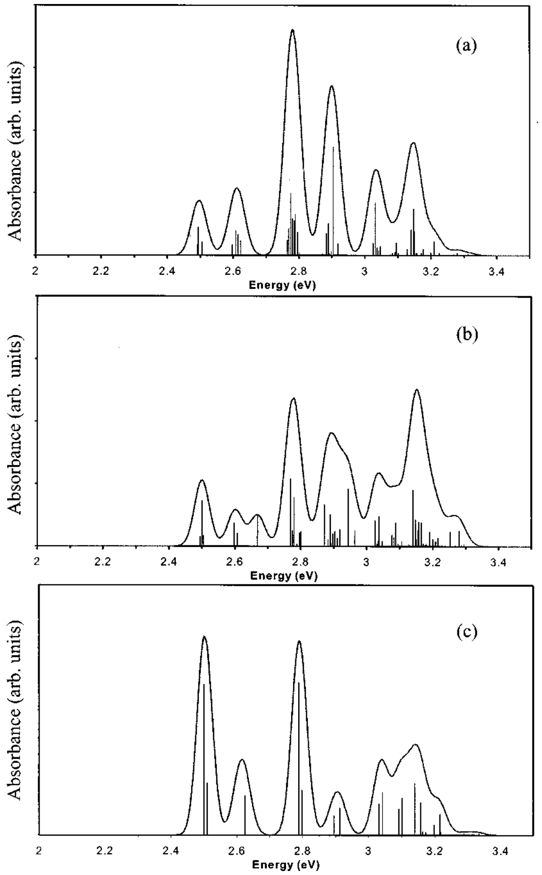

FIG. 3. Optical spectra of a 3.9-nm diam CdSe nanocrystal in the oblate (a) and prolate (b) ellipsoidal shapes and the spherical configuration (c).

prolate nanocrystals, the confinement is determined in two dimensions by the length a and in one dimension by the short axis length b. For oblate nanocrystals, confinement is determined in only one dimension by the characteristic length a and in the other two dimensions by the smaller length b. In this framework, we have studied the effects of morphological changes on optical spectra in function of the characteristic confinement dimensions a and b.

To investigate the features of the optical spectra, we have made a Gaussian convolution with a homogeneous broadening of 10 meV identical for all peaks of the excitonic transitions calculated for CdSe clusters with various shapes (Fig. 3). We have considered a nanocrystal in the oblate type elliptic configuration [Fig. 3(a)] with the characteristic length $a=1.97$ nm in one direction and the short axis dimension $b=1.72$ nm. This cluster corresponds to the deformation of a 3.94-nm-diam sphere along the Oy direction [see Eq. (2)] and contains 1129 atoms. In a similar manner, we have calculated the excitonic transitions of the prolate type nanocrystal [Fig. 3(b)] described by Eq. (1), the confinement of which is determined in two dimensions by the long axis length a. To compare the effects of morphological changes on nanocrystals with a constant number of atoms, we choose identical values of major and minor axes ($a=1.97$ nm and $b=1.72$ nm). The prolate nanocrystal then presents the same degree of ellipticity and the same number of atoms as in the oblate configuration. It is also important to notice that the number of anions located at the crystallite surface is equal for the two elliptic clusters and that the passivation of dangling bonds is identical. Besides, to study the effects of ellipticity, we have represented in Fig. 3(c) the optical spectrum of the corresponding spherical cluster of 1.97 nm radius containing 1147 atoms. The number of atoms for the two types of elliptic crystallites versus the spherical nanocrystal is not identical but the difference is very low (less than 2% of the total number) and allows the comparison of the optical spectra in function of the cluster shape. First, we observe that the first transition energy is only weakly affected by the deformation of the sphere in ellipsoids. Located at 2.49 eV for both the oblate and prolate elliptic clusters, the first excitonic peak is situated at 2.5 eV for the spherical crystallite. In the same way, comparisons of faceted and spherical ZnS clusters have shown[18] that a nanocrystal shape being, strongly dependent on chemical fabrication processes, has rather small effects on the energy gap. By contrast, the calculated energies of other optical transitions are modified by the morphological changes of nanocrystals. The optical anisotropy related to the cluster deformations has lifted the degeneracy of energy levels. This was also observed for wires within the effective-mass approximation.[37] For instance, the highest valence state behaves like a p_y orbital for the prolate elliptic crystallite for which the confinement is stronger along the direction Oy. The energetic value of the splitting between the p_y-like state and the other states originating from the p_x and p_z orbitals is 10 meV. For the oblate nanocrystal, the quantum confinement is stronger in the two directions Ox and Oz. Consequently, the highest valence state behaves like a combination of p_x and p_z orbitals. The splitting energy with the valence state originating from the p_y orbital is of the same order as in the prolate configuration. Nevertheless, the excitonic spectrum remains complex with several transitions the intensities of which strongly depend on the size and shape of the nanocrystals. In spite of the modifications of higher energies transitions, the corresponding peaks exhibit the tendency to regroup in the same way as for spherical clusters and form absorption bands centered around energy values independent of the shape. That is not the case for faceted clusters[18] the relative spacing of which between absorption bands is smaller for the faceted morphology than for the spherical configuration nanocrystals. On the contrary, we observe in this work that the energetic range of the spectra of the clusters with the oblate and prolate elliptic configurations and spherical form is identical. On the other hand, the oscillator strengths are strongly modified by the morphology of nanocrystals. Concerning the first transitions, we observe that the intensity of the first absorption band decreases with the order of confinement of the characteristic length a. For the sphere, the confinement relative to the length a is three dimensional and the first absorption band intensity is maximum. In the case of the prolate-type cluster, the confinement relative to a is only two dimensional and the intensity of the first absorption band has decreased. Finally, when the confinement relative to a is only one dimensional, the first absorption band of the oblate nanocrystal spectrum presents the smallest intensity.

Lifetime transitions are inversely proportional to oscillator strengths, according to the equation

$$\frac{1}{\tau}=\frac{8\pi^2}{3}\frac{ne^2E_o^2}{h^2mc^3}f_{nm}, \qquad (3)$$

where n is the refractive index, E_o the transition energy, and f_{nm} stands for the oscillator strength for a transition from a valence state n to a conduction state m. Therefore, the first excitonic transition presents a longer lifetime in the case of elliptic nanocrystals than that for spherical crystallites.

We also observe in Fig. 3 that the absorption is slightly stronger at the end of the spectrum with the emergence of an intense band in the middle for the oblate ellipsoidal crystallite. Absorption is also more intense at the end of the spectrum in the case of the prolate nanocrystal but the bands exhibit different intensities. Nevertheless, the general feature of the optical spectra for the oblate- and prolate-type crystallites remains similar with a more intense absorption at the end of the spectra. On the other hand, the spherical cluster of 1.97 nm radius presents a strong absorption at the beginning of the spectrum with the presence of two intense equal peaks. This shows the importance of shape effects on the features of the optical spectra of nanocrystals.

V. CONCLUSIONS

The study of the optical properties of small CdSe nanocrystals has allowed us to test the validity of a tight-binding approach taking into account spin-orbit interaction and size dispersion. We have compared our results to numerous experimental data based on a large range of crystallites synthesized by different methods (elaboration in a colloidal solution[28,29] and growth in a glass matrix[36]) and to optical spectra calculated with other methods (pseudopotential,[27] effective bond orbital model,[14] and the effective-mass approximation[19]). The results obtained in the effective-mass approximation confirm the inadequacy of this model in the small-size range. It is of particular interest to compare the methods used to calculate the optical spectrum of a collection of clusters. An approach consists of assuming an inhomogeneous broadening for each transition of the mean diameter cluster. In our other approach, the spectra of the nanocrystals within the size dispersion can be considered as experiencing an homogeneous broadening, estimated to be of the order of 35–50 meV by experiment. Comparison to the experimental data of Chamarro *et al.*[36] for samples with 10% size dispersion, has shown that the first method does not reproduce correctly the position of absorption bands. On the other hand, spectra calculated within our model using a homogeneous broadening are in good agreement with experiment. Absorption experiments reveal the ability of our model to provide a good description of absorption spectra of small spherical CdSe nanocrystals.

The study of spherical and elliptic nanocrystals has shown that the exact shape of nanocrystals has some influence on the confinement energies. We have calculated the first optical transitions for clusters of various shapes and our results indicate that the first transition energy does not vary with the morphological changes of crystallites. On the other hand, the oscillator strengths are strongly modified by the nanocrystal morphology. Shape effects on optical transitions are shown to modify the features of the optical spectra, the first excitonic transition being determined by the smallest cluster dimension.

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