

Calculation of the band gap for small CdS and ZnS crystallites

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(Received 1 December 1988; revised manuscript received 7 February 1989)

The tight-binding approximation and the recursion method are used to study the size dependence of the band gap for small CdS and ZnS crystallites (20–2500 atoms). Because of the lack of accurate experimental data, a simple model of the crystal is considered; one which has no dangling bonds and a symmetrical shape. It is then possible to have a good evaluation of the band gap, even for the largest crystallites. The optical-absorption spectra exhibit an excitonic peak; we determine the peak position from a simple evaluation of the binding energy. The results are compared with the results of other calculations based upon the effective-mass approximation and some experimental data.

I. INTRODUCTION

Size effects on the electronic properties of semiconductor crystallites is a subject under intense investigation.¹ It is of fundamental interest to understand how these properties vary as the crystallite size grows from the molecule to the bulk material. In addition, new applications of semiconductors, using, for example, unusual catalytic and photochemical phenomena, could be developed.

A lot of experimental difficulties arise from the synthesis and characterization of small crystallites. Among the different methods, synthesis by controlled chemical reactions has been used extensively.^{2–7} Small crystallites of CdS and ZnS of 20–50 Å diameter have been obtained. Strangely, they exhibit the same zinc-blende structure (with the same lattice constant) as the bulk material. Unfortunately, the shape and the surface structure are not well characterized, although it is clear that they strongly depend on the surrounding medium. Interesting features have been pointed out by optical-absorption experiments. For example, the threshold of the optical spectra is blue shifted by several tenths of an electron volt and a peak appears when crystallite size decreases. This peak is assigned to an exciton energy level. Its position depends on the average size of the crystallites in solution and its shape is related to the distribution of the sizes.

Calculations of this energy level based on the effective-mass approximation have been proposed.^{8–11} All the authors have used the same Hamiltonian except Brus,^{8,9} who includes the potential energy due to dielectric polarization. They have solved the Schrödinger equation by variational methods which differ by the choice of the trial wave function. However, similar results are obtained for the smallest crystallites, typically for a radius lower than that of the bulk exciton. In this case, they have shown that the electron and the hole are practically uncorrelated and can be considered to be individual particles. In this range of sizes a good evaluation of the ground state is given by Kayanuma.¹⁰

$$E(d) = \frac{2\hbar^2\pi^2}{d^2} \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right] - \frac{3.572e^2}{\epsilon d} - \frac{0.124e^4}{\hbar^2\epsilon^2} \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right]^{-1}, \quad (1)$$

where m_e^* and m_h^* are, respectively, the effective masses of the electron and the hole, and d and ϵ are the diameter and the dielectric constant of the semiconductor. The first term is the kinetic energy of both the electron and the hole. The second is their Coulomb attraction. The last term corresponds to the correlation between the two particles. For a CdS crystallite of 50 Å diameter these three terms take, respectively, the values 0.42, 0.18, and 0.015 eV. The kinetic energy is dominant but the Coulomb interaction cannot be neglected. The correlation term is about 7% of the total energy, confirming that the two particles can be considered to be independent. The effective-mass approximation apparently gives a good understanding of the blue shift of the optical-absorption threshold. However, this approach fails for the smallest crystallite sizes because of the oversimplified description of the crystal potential as a spherical well of infinite depth. This can be understood from the band-structure scheme. In the effective-mass approximation the highest valence band and the lowest conduction band are assimilated closer to their extrema (at $k=0$) to parabolic curves of the form $\hbar^2k^2/2m^*$, where k is the amplitude of the wave vector. As k increases, this expression varies more steeply than the true dispersion relation. The ground state of the spherical well is given by this dispersion relation with $|k|=2\pi/d$ (quantum size effect). Thus, the first term in Eq. (1) is the difference between the gap of small crystallites and that of infinite semiconductors. Its value and consequently the exciton peak position will be overestimated in comparison with the true value for the small diameters.

A better description of the band structure can be obtained from a tight-binding framework. Since the atomic structure is implicitly considered, this method is more

adequate for small crystallites. In this paper we use it to evaluate the band gap of CdS and ZnS crystallites as a function of their size. The electronic energy levels are the eigenvalues of the Hamiltonian matrix H and the main problem arises in trying to calculate them, because of the matrix size, typically $\approx 10^4$. We use the recursion method,^{12,13} which does not require the storage of all the matrix elements of H . A simple model of the crystallite is developed. We have taken into account the experimental data and the optimization of the precision of the numerical computations. First, we consider crystallites without dangling orbitals. It is well known that these orbitals create localized states in the gap and consequently make its precise determination difficult. For this we work with a basis of sp^3 orbitals and a computer program excludes all such orbitals that are not involved in bonds. In fact, the dangling orbitals are certainly saturated by molecules of the colloid, but the real atomic structure of the surface is not known. We think that our approach is reasonable in the absence of precise experimental information. Second, we build the crystallites by connecting the successive shells of first-nearest neighbors. The crystallites have the symmetry of the T_d group and the precision of the numerical computations is optimized, as will be described later. For a comparison with experiments we have to calculate the lowest exciton state. Since our calculation gives the band gap of small crystallites, an evaluation of the binding energy is required. The first term of Eq. (1) is related to the band gap and the third one can be neglected. Thus, the Coulomb attraction can be assimilated to the binding energy. This term does not depend on the effective masses and a correct value is expected.

In the following section we give more details of our theoretical approach. In Sec. III we give the numerical results for the band gap of CdS and ZnS. Finally, Sec. IV is devoted to a comparison with the experimental data and the results of other calculations.

II. METHOD OF CALCULATION

For a bulk semiconductor, the band gap is the energy difference between the bottom of the conduction band (BCB) and the top of the valence band (TVB). We extend this definition to the crystallites, even though they have a finite number of energy levels. The energy levels are obtained by using a semiempirical tight-binding theory. This method has been extensively used in solid-state physics and is successful in the determination of the electronic properties of semiconductors.^{14,15} It has also been applied to metallic clusters, for which interesting features have been pointed out.¹⁶⁻¹⁸

With this method the energy levels and the wave functions are, respectively, the eigenvalues and the eigenvectors of the Hamiltonian matrix H . The matrix elements of H are expressed in a basis of atomic orbitals or of linear combinations of them (hybridization) in terms of two-center integrals.¹⁴ In a semiempirical approach, these integrals are considered as free parameters and fitted to known band structures. Experimental work has shown that the atomic structure of small crystallites is similar to that of the bulk. Thus, the parameters can be

adjusted in order to reproduce as well as possible the bulk band structure. The conduction band is never fully described by the tight-binding approximation. To obtain a good description of the valence band and of the lowest conduction band it is necessary to consider the interactions up to the second-nearest neighbors with a sp^3 basis or to include the d orbitals. However, we choose, for facility, to limit the interactions to the first-nearest neighbors. In this case, a real improvement of the description of the lowest conduction band is obtained by adding an excited state s^* per atom as was proposed by Vogl *et al.*¹⁹ Only 13 parameters are required and they are calculated in order to obtain a correct band structure compared with those obtained by more elaborate methods or by experiments. Application of this method to CdS and ZnS will be discussed in the next section. Note that the elements of the Hamiltonian matrix can be easily modified if the interatomic distances differ from those of the bulk. We should also take into account the relaxation around a defect or at the surface. For example, the d^{-2} law of the bond-orbital model of Harrison¹⁵ could be used.

Once the tight-binding parameters are known, we can calculate the eigenvalues of H . This matrix is formed by 5×5 block matrices describing the interactions on the same atom (intra-atomic) or between two first-nearest neighbors (interatomic). If N is the number of atoms in the crystallite, the dimension of H is $5N$ and a direct diagonalization becomes impossible for several hundred atoms. To circumvent this problem we use the recursion method. This is an iterative algorithm which does not require the storage of all the elements of H . A lot of papers have been published on this method,^{12,13} and we study its application to crystallites.

The recursion method generates a basis set of vectors $|j\rangle$ from a "starting vector" $|0\rangle$. In this basis the Hamiltonian matrix is reduced to a tridiagonal matrix H_0 of dimension $M \leq 5N$. The basic relations are

$$|1\rangle = (H - a_0)|0\rangle, \quad (2a)$$

$$|j+1\rangle = (H - a_j)|j\rangle - b_j|j-1\rangle, \quad 1 \leq j \leq M. \quad (2b)$$

The diagonal and subdiagonal elements of H_0 are respectively a_j and $(b_j)^{1/2}$. They are obtained by imposing the orthogonality of the $|j\rangle$. Only two vectors occur on the right-hand side of (2b) and the storage of all the elements of H is not required. The relation (2a) shows that only the wave vectors having a projection on $|0\rangle$ are generated. Thus, the eigenvalues related to the eigenvectors which have no projection on $|0\rangle$ are not found from H_0 and we can have $M < 5N$. In other words, the recursion method generates the tridiagonal matrix H_0 in the smallest invariant subspace containing $|0\rangle$. We will see how the choice of the crystallite shape and the starting vector $|0\rangle$ give the smallest M value. This point is important because the finite precision of computers imposes the calculation of the smallest number of recursion coefficients. As j increases, the orthogonality of the $|j\rangle$ deteriorates and the elements of H_0 go away from their exact values. In this case, H_0 must be truncated and only some approximate eigenvalues can be expected. However, because H

is a sparse matrix, its eigenvalues have some remarkable properties. For example, the lowest eigenvalues are obtained very accurately from a small number of iterations. For the band gap the convergence is slower, but correct values are obtained. In practice we calculate all the recursion coefficients a_j and b_j for clusters of less than 100 atoms and we limit their number for larger crystallites. In this latter case the stability of the band edges is verified; in other words, additional coefficients do not modify these levels in a noticeable way. The effect of the truncation of H_0 for a finite system is at the present time not clear and would require a more rigorous study. However, our empirical approach is sufficient for the present purpose. Now, we develop three specific points of our model: the crystallite shape, the starting vector of the recursion method, and the surface atomic structure.

Since the value of M must be as small as possible to obtain an accurate band gap, we consider crystallites having the symmetry of the T_d group. In this case, H can be diagonalized into block matrices related to the irreducible representations A_1 , A_2 , E , T_1 , and T_2 . Each block matrix can be obtained independently in tridiagonal form with the recursion method. This is the best way to generate the smallest number of recursions. The crystals are built by connecting the successive shells of first-nearest neighbors. They have two distinct shapes as a function of the parity of the number of shells n_s . It can be shown that the number of atoms N is related to n_s by the relations

$$N = \frac{1}{12}(10n_s^3 - 15n_s^2 + 26n_s - 9) \text{ for odd } n_s, \quad (3a)$$

$$N = \frac{1}{12}(10n_s^3 - 15n_s^2 + 26n_s - 12) \text{ for even } n_s. \quad (3b)$$

This approach can appear somewhat arbitrary, but in fact no specific shape has emerged from experiments. The important feature of our model is that the crystallites grow in three dimensions. However, more realistic shapes could be easily included in our computer program.

The five irreducible representations of the T_d group are obtained from an adequate choice of the starting vector $|0\rangle$. There is no single set to generate them and we give one possible choice. The A_1 and T_2 representations are generated, respectively, by the s and p orbitals on the central atom of the crystallite. Since the T_2 levels are triply degenerate, the three components of the p orbital give the same energy levels and only one is necessary. The E and

T_1 representations are obtained from a combination of p orbitals on the four first-nearest neighbors of the central atom. This combination must have a d -like character. The A_2 representation is generated by a combination of p orbitals on the 12 second-nearest neighbors of the central atom. The starting vectors are given in Table I.

Finally, the atomic structure of the crystallite surface must be considered. Experimentally this structure is not well characterized. In fact, it depends on the experimental conditions. The molecules of the colloid react with the crystallite surface and form a complex structure. It may seem that the dangling bonds are saturated and no corresponding state appears in the gap. However, the lack of experimental data precludes an accurate modeling of the crystallite surface. We have, therefore, chosen to exclude the dangling bonds from the orbital basis. The elements of the Hamiltonian matrix are expressed in the basis of sp^3 hybridized orbitals. A computer program detects the sp^3 dangling bonds and sets to zero their intra-atomic energy and their interactions with the other orbitals. It is the simplest solution and we do not introduce any arbitrary interaction as would be the case if, for example, we were to saturate the dangling bonds with s -type orbitals.

III. NUMERICAL RESULTS

The tight-binding parameters of the sp^3s^* model can be obtained in different ways. We follow the approach of Vogl *et al.*¹⁹ by fitting them on nine points of a band structure and on atomic levels (see Appendix). We have taken the atomic levels of Ref. 19 and the energy levels at the Γ and X points from the experimental and theoretical work²⁰⁻²⁶ (Table II). The origin of energies is taken at the top of the valence band. The values of the bulk band gap of CdS and ZnS are, respectively, 2.5 and 3.7 eV.

The parameters are given in Table III. An accurate determination of the crystallite band gap involves a good description of the highest valence band and of the lowest conduction band. The comparison with more elaborated calculations²³⁻²⁶ shows that the valence band is correctly described except near the states denoted by Σ_1^{min} (along the line $K_1^v \rightarrow \Gamma_{15}^v$). This discrepancy is typical of the first-nearest-neighbor approximation, as previously noticed by Chadi and Cohen.²⁷ A better description requires second-nearest-neighbor interactions. Wang and

TABLE I. Components of the starting vectors of the recursion method which generate the irreducible representations of the T_d group. The s , x , y , and z are the orbital notations. The (α, β, γ) give the reduced positions of the sites. They must be multiplied by $a/4$, where a is the lattice constant, for the real positions.

A_1	T_2	E	T_1	A_2
$s(0,0,0)$	$x(0,0,0)$	$xz(1, \bar{1}, \bar{1}) \quad x\bar{z}(1, 1, 1)$ $\bar{x}z(\bar{1}, 1, \bar{1}) \quad \bar{x}\bar{z}(\bar{1}, \bar{1}, 1)$	$xy(\bar{1}, 1, \bar{1}) \quad x\bar{y}(1, 1, 1)$ $\bar{x}y(\bar{1}, \bar{1}, 1) \quad \bar{x}\bar{y}(1, \bar{1}, \bar{1})$	$xy(\bar{2}, 2, 0) \quad x\bar{y}(\bar{2}, \bar{2}, 0)$ $\bar{x}y(2, 2, 0) \quad \bar{x}\bar{y}(2, \bar{2}, 0)$ $xz(2, 0, \bar{2}) \quad x\bar{z}(2, 0, 2)$ $\bar{x}z(\bar{2}, 0, \bar{2}) \quad \bar{x}\bar{z}(\bar{2}, 0, 2)$ $yz(0, \bar{2}, 2) \quad y\bar{z}(0, \bar{2}, \bar{2})$ $\bar{y}z(0, 2, 2) \quad \bar{y}\bar{z}(0, 2, \bar{2})$

TABLE II. Band-structure energies in eV at the symmetry points, used for the calculation of the tight-binding parameters (from Refs. 20–26).

	Γ_1^v	Γ_1^c	Γ_{15}^c	X_1^v	X_3^v	X_5^v	X_1^c	X_3^c
CdS	-12.2	2.5	6.4	-11.8	-4.8	-1.8	4.6	5.0
ZnS	-14.2	3.7	8.0	-13.0	-4.0	-1.6	5.2	5.8

Duke^{28,29} have calculated the band structures of CdS and ZnS with an sp^3 model. They have used another parameterization scheme but similar energy values to fit their parameters except for ZnS. They have considered $E(X_3^v) = -5.9$ eV in good agreement with the experimental data but not with the pseudopotential calculations. However, this point is not of real importance for our calculation because of its large negative value compared with the variations of the crystallite gap. Except for this point, the general shape of their valence bands for the two materials is similar to ours.

The lowest conduction band is better described with the sp^3s^* model than with the sp^3 model.¹⁹ However, this band is still less accurate than in other calculations which use, for example, the pseudopotentials^{23,25} or the local-density-functional formalism.²⁶ With the tight-binding model, the lowest conduction band of ZnS and CdS varies less steeply along the direction Δ ($\Gamma_1^c \rightarrow X_1^c$). By comparison with more accurate results, a maximum underestimation of about 1 eV is observed. Thus, the band gap of small crystallites at a given diameter $d \sim k^{-1}$ will be also underestimated.

All the eigenvalues are computed for crystallites with less than five shells (83 atoms). In this case we have verified that the results of the recursion method are exactly the same as those obtained by a direct diagonalization. For bigger crystals the number of recursion coefficients is limited to 60 per starting orbital. We think that this number is sufficient for at least two reasons. First, the band gap is hardly modified by additional itera-

tions. Second, as we will see at the end of this section, the variations of the gap show a correct decrease with growing size. From a number of numerical tests we have verified that a precision of a few percent can be expected for the values of the band edges.

The TVB and the BCB are related to the ionization potential and the electronic affinity, respectively. Their variations as a function of the crystallite diameter are plotted in Fig. 1 for CdS and Fig. 2 for ZnS. Note that we have taken for these figures the origin of the energies at the bulk band edges. The diameter is defined by

$$d = a \left[\frac{3N}{4\pi} \right]^{1/3}, \quad (4)$$

where a is the lattice constant: $a \simeq 5.82 \text{ \AA}$ for CdS and

TABLE III. Tight-binding parameters in eV for CdS and ZnS. The notations of Vogl *et al.* (Ref. 19) are used. The index a (c) refers to anion (cation) and s , p , s^* , x , and y are the orbital notations.

	CdS	ZnS
$E(s,a)$	-11.53	-11.61
$E(p,a)$	0.53	1.48
$E(s,c)$	1.83	1.11
$E(p,c)$	5.87	6.52
$E(s^*,a)$	7.13	8.08
$E(s^*,c)$	6.87	8.02
$V(s,s)$	-3.07	-6.30
$V(x,x)$	1.76	3.11
$V(x,y)$	4.23	5.00
$V(sa,pc)$	2.17	5.16
$V(sc,pa)$	5.48	5.17
$V(s^*a,pc)$	1.99	2.89
$V(s^*c,pa)$	3.06	1.75

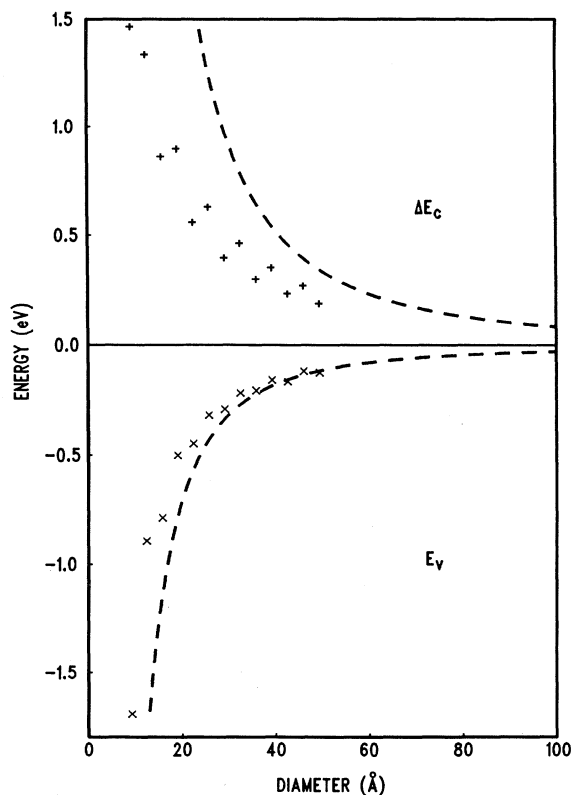


FIG. 1. Variations of the band edges as a function of the diameter for CdS. The origins are taken at the bulk values. The tight-binding results are given for the top of the valence band E_v (\times) and for the bottom of the conduction band $\Delta E_c = E_c - 2.5$ eV ($+$). The dashed curves are the results of the effective-mass approximation.

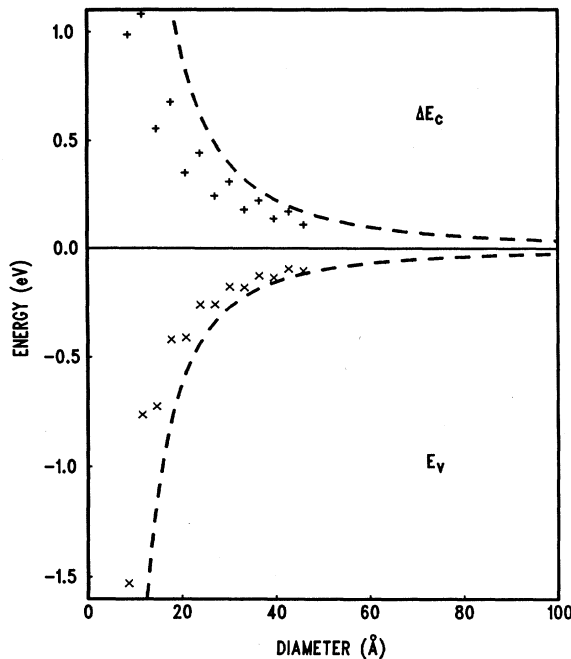


FIG. 2. Variations of the band edges as a function of the diameter for ZnS. The origins are taken at the bulk values. The tight-binding results are given for the top of the valence band E_v (\times) and for the bottom of the conduction band $\Delta E_c = E_c - 3.7$ eV ($+$). The dashed curves are the results of the effective-mass approximation.

$a \simeq 5.41$ Å for ZnS (Ref. 30). We have considered crystallites with the anion S at the central site and sizes increasing from 17 to 2563 atoms. The number of shells, n_s , of atoms N , and the diameter d are given in Table IV.

The tight-binding results (crosses and pluses on the figures) show an oscillatory behavior as the diameter increases. Let us consider, for example, the three smallest crystallites of CdS. The TVB increases first by 0.8 eV

and then by 0.1 eV. At the same time, the BCB decreases by about 0.1 eV and then by 0.5 eV. A simple explanation can be given by realizing that the TVB is of anion type and the BCB of cation type. The surface of the smallest cluster (17 atoms) is formed by anions. The next cluster (41 atoms) is obtained by connecting one shell of cations. Since only the interactions between the first-nearest neighbors are taken into account, the TVB is modified but not the BCB. In fact, the BCB, which is not purely of cation type, is weakly changed. The cluster of 83 atoms is obtained by connecting one shell of anions to the former cluster and the BCB is strongly modified. Two points confirm this interpretation. First, we have calculated the energy levels by changing the type of the central atom to cation instead of anion. We have obtained behavior which is similar but shifted by one shell. For example, the BCB decreases first by 0.7 eV and then by 0.1 eV for the three smallest crystallite sizes considered here. Second, we have calculated the levels for Si, a purely covalent crystal, and no significant discontinuity has been observed. Thus, the oscillations of the band edges are mainly related to the ionic character of the crystals and to the limited extension of the interactions. This effect would be certainly reduced with more distant interactions. The same degeneracy as for the infinite crystal is obtained: nondegenerate for the BCB and triply degenerate for the TVB.

As mentioned in the Introduction, all the published calculations concerning the electronic properties of small semiconductor crystallites are based upon the effective-mass approximation. In the next section we compare some of their results with ours. But at first, we determine the band edges with the same level of approximation. We consider a spherical well of infinite depth and assimilate the ground state with the band edges. We obtain for the TVB level E_v and the BCB level E_c :

$$E_v(d) = -\frac{2\hbar^2\pi^2}{m_h^*d^2}, \quad (5a)$$

$$E_c(d) = \frac{2\hbar^2\pi^2}{m_e^*d^2} + E_c(\infty). \quad (5b)$$

We have taken the origin of the energies at the TVB and consequently $E_c(\infty)$ is the bulk band gap. In order to be consistent with the tight-binding calculation, the effective masses are deduced from the band structure obtained with the parameters of Table III. Since the BCB of infinite semiconductors is isotropic and nondegenerate, m_e^* is easily found. On the other hand, the TVB is triply degenerate and m_h^* cannot be obtained in the same simple way. In fact, three parameters are required to describe the valence band closer to its top^{31,32} and a single-band model can just give a rough description. However, as for the published calculations, we use it and we take for m_h^* the heavy-hole mass defined by Lawaetz.³³ The results are given in Table V and a reasonably good agreement with other published values is obtained.

The variations of Eqs. (5a) and (5b) are plotted in Figs. 1 and 2 (dashed curves). The BCB obtained with the tight-binding calculation is strongly overestimated. This can be understood from the band-structure scheme. By

TABLE IV. Correspondence between the number of shells, n_s , the number of atoms, N , and the average diameter d in Å for CdS and ZnS crystallites.

n_s	N	$d(\text{CdS})$	$d(\text{ZnS})$
3	17	9.3	8.6
4	41	12.4	11.6
5	83	15.7	14.6
6	147	19.1	17.7
7	239	22.4	20.8
8	363	25.8	23.9
9	525	29.1	27.1
10	729	32.5	30.2
11	981	35.9	33.3
12	1285	39.3	36.5
13	1647	42.6	39.6
14	2071	46.0	42.8
15	2563	49.4	45.9

TABLE V. Values of the effective masses for the electron m_e^* and the hole m_h^* . The values, calculated from the band structures with the tight-binding parameters of Table III, are given in the first row. The other values have been published elsewhere.

Ref.	m_e^* (CdS)	m_h^* (CdS)	m_e^* (ZnS)	m_h^* (ZnS)
this work	0.18	0.53	0.42	0.61
3,8	0.19	0.8	0.25	0.59
30	0.18		0.28	1.76
33	0.20		0.39	

setting $d = 2\pi/k$, Eq. (5b) approximates the lowest conduction band closer to its minimum Γ_1^c by a parabolic curve. As k increases, this curve varies more steeply than the lowest conduction band. An overestimation of 10% is obtained for $ka \simeq 0.19$ (CdS) and $ka \simeq 0.23$ (ZnS). From these values we can deduce a rough evaluation of the diameter for which the effective-mass approximation fails: $d \simeq 190$ Å (CdS) and $d \simeq 150$ Å (ZnS). Thus, quantitative results can be expected with this approximation for large diameters. For $d \simeq 50$ Å the error is about 80% (CdS) and we conclude that, in the size range of interest, inaccurate results will be obtained with the effective-mass approximation. The comparison for the TVB between the two approaches is not easy, since the single-band effective-mass model cannot lead to a good description of the valence band. Thus, the agreement which can be observed in Fig. 1 for CdS and the weak underestimation of the tight-binding results which occurs in Fig. 2 for ZnS are somewhat fortuitous. With a more elaborate effective-mass model, which would describe the three highest valence bands closer to the Γ_{15}^v point, a similar behavior as for the BCB would be observed. In this case, the absolute value of the TVB of small crystallites obtained by the tight-binding calculation would be overestimated by that of the effective-mass calculation.

The band gap is calculated from the previous tight-binding results and plotted as a function of the diameter in Fig. 3 for CdS and Fig. 4 for ZnS (crosses). As for the band edges, an oscillatory behavior is observed. We have also plotted the continuous variations between the computed points in order to evaluate the band gap for all diameters (solid line). The comparison with the results of the effective-mass model obtained from Eqs. (5a) and (5b) (dashed line) reveals large discrepancies, especially for the smallest diameters. For example, a difference of about 0.5 eV is observed for CdS crystallites of 30 Å diameter. In fact, this difference must be larger with a more accurate effective-mass model. It is clear that the results obtained with the two methods must converge as the diameter of the crystallites increases. This behavior is observed for the BCB but not for the TVB because of the inadequacy of the effective-mass model.

IV. DISCUSSION

The band gap of CdS and ZnS crystallites cannot be easily obtained from the optical-absorption spectra since

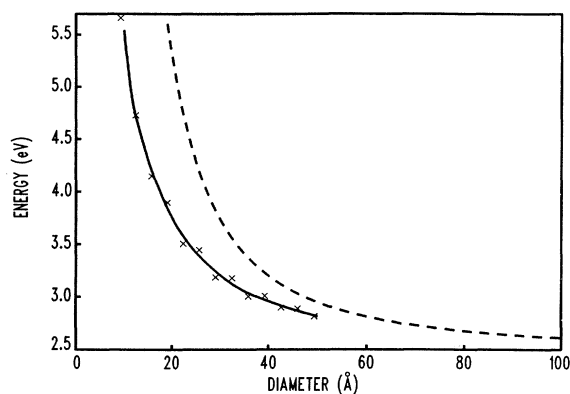


FIG. 3. Variations of the band gap as a function of the diameter for CdS. The solid line represents the expected values obtained from the tight-binding results (\times) and the dashed curve from the effective-mass approximation.

an exciton peak exists at the edge.¹⁻⁷ For a comparison with experiments we have to determine the peak position. This can be obtained by adding the binding energy of the exciton to the energy gap computed in the previous section. A simple evaluation of the binding energy is given by the two last terms of Eq. (1). Since the correlation term is negligible, the binding energy of the exciton is given by the average value of the Coulomb energy for s -type orbitals, which does not depend on the effective masses and varies as d^{-1} .

The variations of the exciton peak position as a function of the diameter are plotted in Fig. 5 for CdS. The results of the tight-binding calculation (solid line) and of the effective-mass model (dashed line) as well as the experimental data points of Refs. 3 and 34 (squares and triangles) are given. The comparison between the two theoretical approaches reveals the same features as for the crystallite band gap. The results of the tight-binding calculation are overestimated by those of the effective-

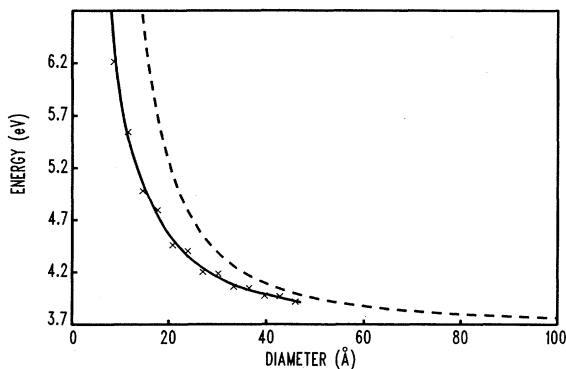


FIG. 4. Variations of the band gap as a function of the diameter for ZnS. The solid line represents the expected values obtained from the tight-binding results (\times) and the dashed curve from the effective-mass approximation.

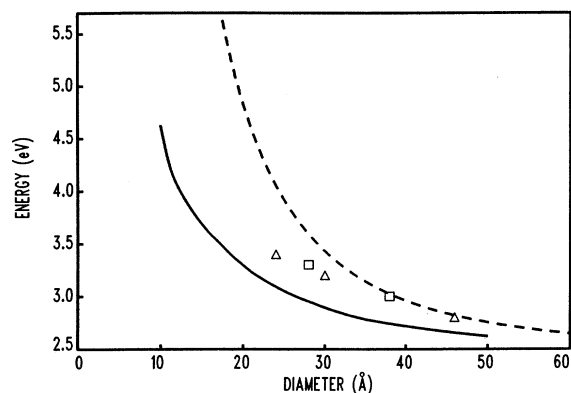


FIG. 5. Comparison with experimental data for CdS. The tight-binding results are given by the solid curve and those of the effective-mass approximation [Eq. (1)] by the dashed curve. The experimental data are the positions of the exciton peak given in Refs. 3 (squares) and 31 (triangles).

mass model, but the two approaches tend to converge as the diameter increases.

The comparison between the experimental data and the effective-mass calculation reveals a good agreement for $d \simeq 40$ Å. It is clear from the previous discussion on the validity of the effective-mass model that this agreement is somewhat fortuitous. In fact, a more accurate model including the three valence bands near the Γ_{15}^v point would provide an overestimation of the experimental data. This agreement fails as the diameter decreases, and the tight-binding calculation gives better results. For the CdS crystallites of 25 Å diameter, the exciton peak is observed at about 3.4 eV, the tight-binding calculation gives 3.1 eV, and the effective-mass model 3.9 eV (see Fig. 5). Smaller sizes have been experimentally obtained for the ZnS crystallites. For 20 Å diameter Rossetti *et al.*⁴ have observed the exciton peak at 4.4 eV and they have evaluated its position from an effective-mass model to 5.5 eV. Our tight-binding calculation gives a value of 4.0 eV, in better agreement with the experimental data. However, for the two materials and for all the diameters, the experimental values of the exciton energy level are always underestimated by the tight-binding model.

At the present time the discrepancies between our results and the experimental data are not clear. However, our model contains some assumptions which could explain them. First, the shape and the surface structure of the crystallites have been chosen in order to facilitate the determination of the computed values of the gap. These two features are not accurately characterized by experiments. It seems that the shape is quasispherical and that the dangling bonds are saturated by molecules of the colloid. In our calculation the crystallites are built by connecting the successive shells of first-nearest neighbors and the dangling sp^3 orbitals are removed by a computer program. It is difficult to estimate the effect of the shape and of the surface atomic structure on the energy gap. However, we think that our model must give a good approximation of the real crystallites. Second, the binding energy is calculated in a simple way and is certainly overes-

timated. Nevertheless, the error must be lower than a tenth of an electron volt and cannot explain the observed difference. Third, the band gap of the crystallites is strongly dependent on the values of the highest valence band and of the lowest conduction band of the bulk material. By comparison with the band structures obtained by more elaborate calculations,²³⁻²⁶ the sp^3s^* model gives a good description of the highest valence band but underestimates the lowest conduction band in some places. For CdS a difference of about 1.0 eV is found halfway between Γ_{15}^c and X_1^c . If we assume that $k = 2\pi/d$ we obtain in this point $d \simeq 12$ Å. As k decreases this difference also decreases but it is clear that a difference of several tenths of an electron volt can be expected for $d \simeq 30$ Å. We have tried other sets of tight-binding parameters but no real improvement has been obtained. It seems that the sp^3s^* model cannot produce deep curvature in the conduction band. A more elaborate tight-binding model (with more parameters), which would provide a better description of the lowest conduction band, will give more accurate values of the crystallite band gap.

V. CONCLUSIONS

We have used the recursion method and the tight-binding approximation to calculate the band gap of small CdS and ZnS crystals. The position of the exciton peak, which is observed in the optical-absorption spectra, is then determined by adding to this band gap the binding energy evaluated in a simple approximation. It has been shown that the calculations based on the effective-mass approximation strongly overestimate the band gap for the smallest sizes. The discrepancies between our results and some experimental data are attributed to the inability of the sp^3s^* model to give a fully accurate description of the lowest conduction band. However, our approach provides correct semiquantitative results and appears as an appropriate tool to study the size effect on the electronic properties of small semiconductor crystallites.

APPENDIX

The sp^3s^* model has 13 empirical parameters. They can be calculated in different ways, and we describe our approach, which is similar to that of Vogl *et al.*¹⁹ The parameters are fitted on six atomic orbital energies and on the seven points of the band structure given in Table II. The same notations as in Ref. 19 are used. The intra-atomic energies are given by

$$E(s, i) = \frac{1}{2} \{ E(\Gamma_{15}^v) + E(\Gamma_{15}^c) + \beta_{si} [w(s, a) - w(s, c)] \}, \quad (A1)$$

$$E(p, i) = \frac{1}{2} \{ E(\Gamma_{15}^c) + \beta_{pi} [w(p, a) - w(p, c)] \}, \quad (A2)$$

$$E(s^*, i) = E(p, i) - [w(p, i) - w(s^*, i)], \quad (A3)$$

where i stands for a (anion) or c (cation). In the first two expressions we have $\beta_{sa} = -\beta_{sc} = 0.8$ and $\beta_{pa} = -\beta_{pc} = 0.6$. These values as well as the atomic-orbital energies w are taken from Ref. 19. The interatomic energies are given by

$$V(s,s) = -\frac{1}{2} \{ [E(\Gamma_1^c) - E(\Gamma_1^v)]^2 - [E(s,c) - E(s,a)]^2 \}^{1/2}, \quad (\text{A4})$$

$$V(x,x) = [E(p,a)E(p,c)]^{1/2}, \quad (\text{A5})$$

$$V(x,y) = \frac{1}{2} \{ [E(p,a) + E(p,c) - 2E(X_3^v)]^2 - [E(p,c) - E(p,a)]^2 \}^{1/2}, \quad (\text{A6})$$

$$V(sa,pc) = \left[\frac{[E(s,a) - E(X_1^c)][E(s,a) - E(X_1^v)][E(p,c) + E(s^*,a) - E(X_1^c) - E(X_1^v)]}{E(s,a) - E(s^*,a)} \right]^{1/2}, \quad (\text{A7})$$

$$V(sc,pa) = \left[\frac{[E(s,c) - E(X_3^c)][E(s,c) - E(X_3^v)][E(p,a) + E(s^*,c) - E(X_3^c) - E(X_3^v)]}{E(s,c) - E(s^*,c)} \right]^{1/2}. \quad (\text{A8})$$

The parameter $V(s^*,a,pc)$ is obtained from Eq. (A7) by substituting $E(s,a)$ for $E(s^*,a)$ and $E(s^*,a)$ for $E(s,a)$. In the same way, the parameter $V(s^*,c,pa)$ is obtained from Eq. (A8) by inverting $E(s,c)$ and $E(s^*,c)$. Note that our parametrization scheme differs from that of Ref. 19 by the four latter expressions. Other points of the

band structure (as L_3^v) as well as other parametrization schemes can be used (see, for example, Refs. 27–29 for the sp^3 model). We have verified in some cases that other sets of parameters do not noticeably improve the band structures.

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