PHYSICAL REVIEW B VOLUME 41, NUMBER 9 15 MARCH 1990-II

Comparison between calculated and experimental values of the lowest excited electronic state of small CdSe crystallites

P. E. Lippens and M. Lannoo

Laboratoire de Physique des Solides, Institut Supérieur d'Electronique du Nord, 41 boulevard Vauban,
59046 Lille CEDEX, France

(Received 22 September 1989)

The lowest excited electronic state of small CdSe crystallites is calculated within a tight-binding approximation. Two types of crystal shape and a spatially varying dielectric constant are considered. The results are found to compare favorably to recent experiments.

Quantum size effects in small semiconductor crystallites have been widely studied experimentally. Much work has been devoted to the II-VI compounds and recently to CdSe. Quasispherical CdSe crystallites of average radius lower than 30 Å have been synthesized by different methods: by colloidal preparation,[1-4] in glasses,[5] or by chemical deposition.[6] The optical-absorption spectra of these crystallites exhibit a peak near the absorption threshold. This peak is assigned to the creation of electron-hole pairs in the crystallites. Its position is size dependent and shifted to higher energies as the crystallite average radius decreases.

Theoretical predictions of the lowest excited state of the crystallites are generally based on the effective-mass approximation (EMA).[7-9] In the small-size limit, typically for a crystallite radius lower than the exciton Bohr radius ($\simeq 50$ Å for CdSe), this approximation overestimates the real values. In a previous paper[10] we have proposed an empirical tight-binding calculation for CdS and ZnS crystallites. We have shown that large discrepancies exist between the results of this calculation and those obtained with the EMA. However, the comparison with the experimental data was not conclusive.

In this paper we use the same basic approach as in Ref. 10, but for CdSe crystallites which are the object of current interest because of their optical applications. In addition, the experimental preparation of these crystallites seems to be better controlled than in the past, and a comparison with the theoretical results is more meaningful. For example, a very narrow size distribution (± 1.5 Å) has been obtained by Alivisatos *et al.*[2-4] for CdSe crystallites of 22.5 Å radius. In the present calculation we have considered crystallites of spherical shape which are in closer correspondence with the experimental situation than those of Ref. 10. We have also improved the description of the Coulomb energy of the electron-hole pairs in the crystallites. However, we will show that these changes have a small influence on the value of the lowest excited state.

The lowest excited state of a crystallite is assumed to be the ground state of an electron-hole pair. In the small-size limit the two particles can be considered as independent.[9] The energy of the ground state $E(R)$ can be considered as the sum of the crystallite band gap $E_g(R)$, which is the dominant term, and of the Coulomb energy $E_c(R)$ of the electron-hole pair which appears as a small correction.

The band-gap energy $E_g(R)$ is calculated within a tight-binding approximation. The sp^3s^* model proposed by Vogl *et al.*[11] is used. Since the CdSe crystallites have the same zinc-blende structure as the bulk material, the tight-binding parameters are calculated from the energy levels at some symmetry points of a bulk band structure. We use the experimental data compiled by Wang and Duke[12] and the parametrization scheme described in Ref. 10. The resulting tight-binding parameters are given in Table I. A good description of the bulk band structure near the band gap ($\Gamma_{15}^{v} \rightarrow \Gamma_{1}^{c}$) is of importance because it reflects the evolution of the crystallite band gap for large R. A good test is the evaluation of the electron and hole effective masses which are found equal to $m_e^* \simeq 0.13m$ and $m_h^* \simeq 0.41m$, respectively, where m is the free-electron mass, in good agreement with experiments.[13]

To calculate $E_g(R)$, the one-electron Schrödinger equation is solved by the recursion method.[14] The Hamiltonian matrix is formed by 5×5 block matrices describing the intra-atomic energies and the interactions between the first-nearest neighbors. We have considered spherical crystallites of radius R, in which all the neighbors of the central site at a distance smaller than R are taken into account. To evaluate the influence of the crystallite shape, we have also considered the crystallites depicted in Ref. 10, which are obtained by connecting the successive shells of first-nearest neighbors. For the two sets of crystallites the symmetry of the T_d group is preserved as the crystallites grow. Thus, the energy levels of each representation of the T_d group can be calculated independently by the recursion method. In the absence of experimental characterization of the surfaces, we have considered crystallites without dangling bond. These orbitals are excluded from the orbital basis by a computer program. As indicated in Ref. 10, this procedure provides an unambiguous determination of the band gap. The variations of the top of the valence band and the bottom of the conduction band as a function of R are plotted in Figs. 1 and 2, respectively. The tight-binding results obtained for the two different shapes of crystallites are very similar. In the two cases, the band edges show successive large and small variations as a function of R, depending on the type of ions which are

©1990 The American Physical Society

TABLE I. Tight-binding parameters (in eV) for CdSe crystals. The notations of Vogl *et al.* (Ref. 11) are used. The indexes *a* and *c* refer to anion and cation, respectively.

	$E(s,a)$	$E(p,a)$	$E(s,c)$	$E(p,c)$	$E(s^*,a)$	$E(s^*,c)$
	−9.63	1.47	0.03	4.73	7.53	5.72
$V(s,s)$	$V(x,x)$	$V(x,y)$	$V(sa,pc)$	$V(sc,pa)$	$V(s^*a,pc)$	$V(s^*c,pa)$
−4.64	2.64	5.36	4.57	5.54	3.05	2.49

connected on the surface. The comparison between these results and those obtained within the EMA, which are of the form $2\hbar^2\pi^2/m^*R^2$, shows large discrepancies in the small-size limit.

The calculation of $E_c(R)$ is not simple because it requires the determination of the eigenfunctions. As noticed below, the value of $E_c(R)$ is small compared to $E_g(R)$, and a correct order of magnitude is sufficient for the evaluation of $E(R)$. Thus, we have just considered the interaction of two charge carriers in a spherical well of infinite depth for which the 1*s* wave functions are easily found. A simple Coulomb law of the form $-e^2/\epsilon r$, where r is the distance between the two particles and ϵ the dielectric constant of the bulk semiconductor, can be used and gives

$$E_c(R)=-\frac{e^2}{\epsilon R}\left\langle\frac{R}{r}\right\rangle , \qquad (1)$$

where the term in large angular brackets denotes the value of R/r averaged over the 1*s* wave functions, and is approximately equal[7] to 1.786. In this calculation ϵ is a constant and the choice of its exact value is a matter of controversy. Some authors[6,7] have used the optical dielectric constant $\epsilon(\infty)$, and others[8,9] the static dielectric constant $\epsilon(0)$. In this work, we have made use of the more accurate expression derived by Haken,[15] which is equivalent to consider a spatially varying dielectric constant

$$\epsilon(r)=\left[\frac{1}{\epsilon(\infty)}-\left[\frac{1}{\epsilon(\infty)}-\frac{1}{\epsilon(0)}\right]\times\left[1-\frac{e^{-r/\rho_e}+e^{-r/\rho_h}}{2}\right]\right]^{-1} , \qquad (2)$$

with

$$\rho_e=\left[\frac{\hbar}{2m_e^*\omega_{\mathrm{LO}}}\right]^{1/2} \text{ and } \rho_h=\left[\frac{\hbar}{2m_h^*\omega_{\mathrm{LO}}}\right]^{1/2} ,$$

where ω_{LO} ($\simeq 4\times10^{13}\ \mathrm{s}^{-1}$ for CdSe), is the longitudinal-optical-phonon frequency. The average value of the Coulomb energy with ϵ defined by (2) has been calculated by expanding the two exponentials in power series. An analytical, but somewhat complicated, expression is obtained which is then computed numerically.

We now compare the calculated values of $E(R)$ with the experimental values obtained recently.[2–6] We do not compare directly $E(R)$ but the difference $E(R)-E_g(\infty)$, where $E_g(\infty)$ is the bulk band gap of CdSe. We assume that the temperature dependence of $E(R)$ is similar to that of $E_g(\infty)$. Thus, the difference between these two terms does not vary very much with temperature, and it is possible to compare the experimental data obtained at different temperatures. We have plotted in Fig. 3 the variations of $E(R)-E_g(\infty)$ obtained by a smooth extra-

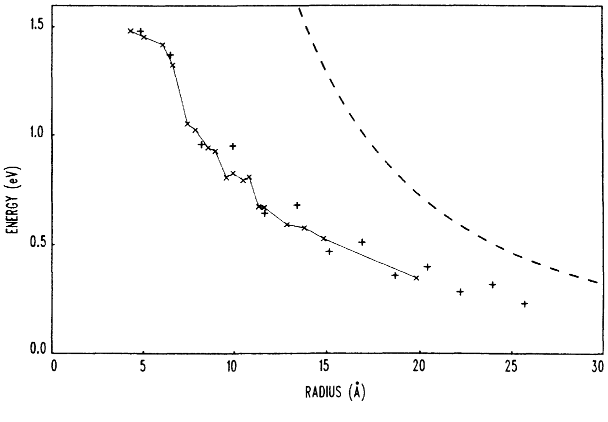

FIG. 1. Variations of the bottom of the conduction band as function of the radius R for CdSe crystallites. The tight-binding results are given for crystallites built by connecting the successive shells of first-nearest neighbors (+) and by connecting the successive neighbors of the central site (×). In the latter case a solid line is drawn as a guide for the eye. The dashed line represents the results of the effective-mass approximation. The origin of energies is taken at the bottom of the conduction band of the bulk material.

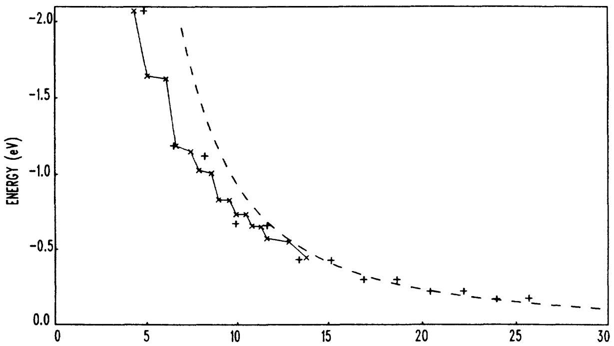

FIG. 2. Same as Fig. 1, but for the top of the valence band. The origin of energies is taken at the top of the valence band of the bulk material.

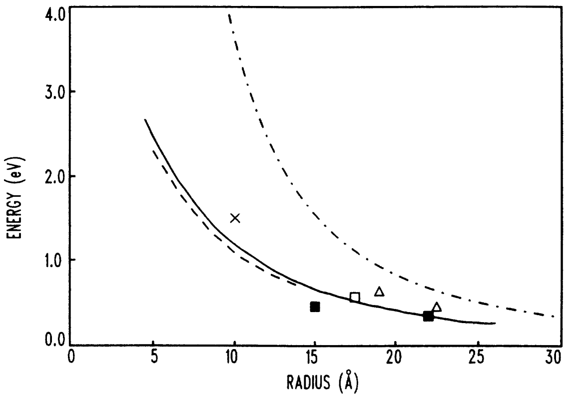

FIG. 3. Variations of the lowest excited state energy as a function of the radius R. The tight-binding results are given for the two crystallite sets obtained by connecting the successive shells of first-nearest neighbors (solid line) and the successive neighbors of the central site (dashed line). The effective-mass results are also plotted (dashed-dotted line). The experimental data are taken from Refs. 1, 2, 5, and 6, as the cross, open triangles, solid squares, and open square, respectively.

polation between the calculated values, and the experimental data. Note that the data point for the smallest crystallite ($E \simeq 1.5$ eV) is given for guidance because the average radius has not been accurately determined. The smallest expected radius has been considered.

Calculated and experimental values of $E(R)$ differ by less than about 0.2 eV, i.e., they are in fairly good agreement. It is difficult to estimate the accuracy of our model, but at least three limitations can be suggested. At first, the tight-binding parameters are computed from energy levels at special points of the Brillouin zone, which are known with a precision of about a tenth of an electron volt. Second, the sp^3s^* tight-binding model gives a correct description of the valence band and of the lowest conduction band, but not of the upper conduction bands. Finally, the description of the crystallite surface is rather simple in our calculation. A more accurate description requires new experimental data. However, the last two effects should not noticeably modify the values of $E_g(R)$ for crystallites of about one thousand atoms ($R \simeq 20$ Å). Thus, a precision of about 0.2 eV can be expected in this size range.

The agreement between the calculated values of $E(R)$ and the experimental data is better in the present work for CdSe than in our previous paper[10] for CdS. The reason is not clear at the present time and could be attributed to the better accuracy of the experimental data. By comparison with Ref. 10, two changes have been made to improve the calculation of $E(R)$. At first, a more realistic shape of the crystallites has been considered, but no noticeable change in the value of $E(R)$ can be observed (see Fig. 3). We have also used a spatially varying dielectric constant [Eq. (2)]. However, its effect on $E(R)$ is rather small. For example, the values of $E(R)$ for CdS are increased by less than about 40 meV when Eq. (2) is used instead of Eq. (1) with $\epsilon(\infty)$. The differences between the calculated and the experimental values of $E(R)$ in Ref. 10 have been found equal to several tenths of an electron volt. Thus, they cannot be explained from the slight improvement caused by these two modifications.

In conclusion, we have obtained accurate predictions of the lowest excited state for CdSe crystallites with $R \simeq 15-25$ Å. Two crystallite models with different shapes, and a new evaluation of the Coulomb energy of the electron-hole pair have been considered. A comparison between our results and the experimental data for $R \simeq 10-15$ Å would be interesting to check our calculation and evaluate the influence of the surface atoms.

---

[1] N. Chestnoy, R. Hull, and L. E. Brus, J. Chem. Phys. **85**, 2237 (1986).

[2] A. P. Alivisatos, A. L. Harris, N. J. Levinos, M. L. Steigerwald, and L. E. Brus, J. Chem. Phys. **89**, 4001 (1988).

[3] A. P. Alivisatos, T. D. Harris, L. E. Brus, and A. Jayaraman, J. Chem. Phys. **89**, 5979 (1988).

[4] A. P. Alivisatos, T. D. Harris, P. J. Carroll, M. L. Steigerwald, and L. E. Brus, J. Chem. Phys. **90**, 3463 (1989).

[5] N. F. Borrelli, D. W. Hall, H. J. Holland, and D. W. Smith, J. Appl. Phys. **61**, 5399 (1987).

[6] G. Hodes, A. Albu-Yaron, F. Decker, and P. Motisuke, Phys. Rev. B **36**, 4215 (1987).

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

[8] S. V. Nair, S. Sinha, and K. C. Rustagi, Phys. Rev. B **35**, 4098 (1987).

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

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

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

[12] Y. R. Wang and C. B. Duke, Phys. Rev. B **37**, 6417 (1988).

[13] *Physics and Chemistry of II-VI Compounds,* edited by M. Aven and J. S. Prener (North-Holland, Amsterdam, 1967).

[14] *The Recursion Method and Its Applications,* edited by D. G. Pettifor and D. L. Weaire (Springer-Verlag, New York, 1985).

[15] H. Haken, Nuovo Cimento [Ser. 10] **3**, 1230 (1956); see also R. S. Knox, *Theory of Excitons* (Academic, New York, 1963), pp. 50 and 91.