Supplemental Material for “Influence of Polytypism on Electronic Structure of CdSe/CdS and CdSe/CdSe Core/Shell Nanocrystals”

Carlos Segarra, Fernando Rajadell, Juan I. Climente, and Josep Planelles*

Departament de Química Física i Analítica, Universitat Jaume I, E-12080, Castelló de la Plana, Spain

E-mail: josep.planelles@uji.es

*To whom correspondence should be addressed

Material parameters

Below we summarize the material parameters used in the calculations. m_0 is the free electron mass and ε_0 the vacuum permitivitty. A relative dielectric constant of 3 and confining potential of 5 eV is taken outside the NC to account for the dielectric environment. For alloyed regions, $CdSe_{1-x}S_x$, we assume exponential evolution of the composition (from $x = 0$ at the CdSe core interface, to $x = 1$ at the CdS shell interface) and interpolate the material parameter.

Hexagonal material parameters

See Supplementary Information of Ref.[1] for a complete list.

Cubic material parameters

Description	Symbol	CdSe ZB	CdS ZB	Units	CdSe Ref.	CdS Ref.
Elastic modulus tensor	C_{11}	$66.7 \cdot 10^9$	$77.0 \cdot 10^9$	Pa	[2] p. 314	[2] p. 258
Elastic modulus tensor	C_{12}	$46.3 \cdot 10^9$	$53.9 \cdot 10^9$	Pa	[2] p. 314	[2] p. 258
Elastic modulus tensor	C_{44}	$22.3 \cdot 10^9$	$23.6 \cdot 10^9$	Pa	[2] p. 314	[2] p. 258
Piezoelectric constant	e_{14}	0.16	0.29	$C \cdot m^2$	[3]	[3]
Dielectric constant	ε	9.6	8.43	ε_0	[4]	[4]
Lattice constant	a	6.077	5.825	Å	[5]	[6]
Spin-orbit matrix element	Δ_{SO}	0.41	0.079	eV	[7]	[8]
Electron mass	m^*	0.12	0.209	m_0	[9]	[10]
Luttinger parameter	γ_1	5.51	4.11	$1/m_0$	[2] p. 323	[2] p. 266
Luttinger parameter	γ_2	1.24	0.77	$1/m_0$	[2] p. 323	[2] p. 266
Luttinger parameter	γ_3	2.14	1.53	$1/m_0$	[2] p. 323	[2] p. 266
CB Deformation pot.	a_c	-3.77	-3.59	eV	[11]	[11]
VB Deformation pot.	a_v	-1.81	-1.51	eV	[11] [12]	[11] [12]
VB Deformation pot.	b	-0.8	-4.7	eV	[15] [12]	[16] [12]

VB Deformation pot.	d	-4.4	-4.4	eV	[12]	[12]

Table S1: Zinc-Blende CdSe and CdS parameters used in the calculations.

Band offsets

All values are derived from Ref.[18]

Material	**CdSe WZ**	**CdSe ZB**	**CdS WZ**	**CdS ZB**
CdSe WZ	0.0	-0.094/-0.035	0.341/-0.409	0.226/-0.455
CdSe ZB		0.0	0.435/-0.374	0.32/-0.42
CdS WZ			0.0	-0.115/-0.046
CdS ZB				0.0

Table S2: Conduction band/valence band offsets listed for different materials and crystal structures. Units are eV.

Strain in polytypes

To estimate the initial strain of a ZB[111] (core) material buried inside a WZ (shell) one, we need to transform the ZB[100] lattice constant a_{ZB} (Table S1) into WZ-like lattice parameters. To this end, we will start from a_{ZB} and calculate the lattice constants a_{WZ}^{id}, c_{WZ}^{id} of an *ideal* WZ structure where the buried ZB[111] material is not stressed, i.e., no strain is present. Comparison of ZB[111] and WZ[0001] lattices, see e.g.,[19] show that under the assumption of an *ideal* tetrahedral coordinations of anions and cations, three times the ideal WZ[0001] unit cell has the same volume than twice the ZB[111] one. Besides, geometrical considerations for ideal WZ crystal implies $c/a = \sqrt{8/3}$ (see e.g. Bimberg et al.[20]). We then reach the following equivalences: $a_{WZ}^{id} = \frac{1}{\sqrt{2}}\, a_{ZB}$ and $c_{WZ}^{id} = \frac{2}{\sqrt{3}}\, a_{ZB}$. For CdSe, we infer $a_{WZ}^{id} = 4.297$ Åand $c_{WZ}^{id} = 7.017$ Å.

Next, by assuming for the ideal WZ phase the same elastic constant as its ZB partner, we may consider that the strain of either phase buried in a given matrix is the same. Then, if the matrix

is a hexagonal WZ material we can calculate the initial strain as that of the ideal buried WZ. For CdSe(ZB[111]) inside CdS(WZ) we obtain an initial strain of 3.92% (3.97%) in the direction orthogonal (parallel) to the *c* axis. These values are almost identical to those of WZ/WZ CdSe/CdS.

Even after minimizing elastic energy, relaxed strain remains very similar for pure WZ and polytype CdSe/CdS structures, as shown in Figure S1, where we compare the hydrostatic strain for the three model NCs investigated in the main paper.

Figure S1: Strain profile along *c* axis, for CdSe/CdS NCs with WZ/WZ core/shell, ZB/WZ core/shell and ZB/WZ core/shell including and alloyed CdSeS interlayer.

References

(1) J. Planelles, F. Rajadell, and J.I. Climente *J. Phys. Chem. C* 120, 27724-27730 (2016).

(2) Sadao, A. *Handbook of Physical Properties of Semiconductors*; Kluwert Academic Group, 2004.

(3) Jun Xin, Yanqing Zheng and Erwei Shi *Appl. Phys. Lett.* 91, 112902 (2007).

(4) The dielectric constant of cubic CdSe and CdS is reported as the geometric average of the hexagonal $\varepsilon_{\perp}$ and ε_z dielectric constants, see e.g..[2] The values in Table S1 are the the geometric average of dielectric constant used for hexagonal materials.

(5) N. Samarth, H. Luo, J. K. Furdyna, S. B. Qadri, Y. R. Lee, A. K. Ramdas, and N. Otsuka, *Appl. Phys. Lett.* 54, 2680 (1989).
Cited in Ref.[2] p. 312.

(6) W. R. Cook, Jr., *J. Am. Ceram. Soc.* 51, 518 (1968).
Cited in Ref.[2] p. 256.

(7) C. Janowitz, O. GÃijnther, G. Jungk, R. L. Johnson, P. V. Santos, M. Cardona, W. Faschinger,

and H. Sitter, Phys. Rev. B 50, 2181 (1994).
Cited in Ref.[2] p. 319.

(8) M. Willatzen, M. Cardona, and N. E. Christensen, *Phys. Rev. B* 51, 17992 (1995).
Cited in Ref.[2] p. 264.

(9) Y. D. Kim, M. V. Klein, S. F .Ren, Y. C. Chang, H. Luo, N. Samarth, and J. K. Furdyna, *Phys. Rev. B* 49, 7262 (1994).
Cited in Ref.[2] p. 322.

(10) M.-Z. Huang and W. Y. Ching, *J. Phys. Chem. Solids* 46, 977 (1985).
Cited in Ref.[2] p. 265.

(11) Su-Huai Wei and Alex Zunger *Phys. Rev. B* 60 (1999) 5404

(12) There is a scatter of data in the literature on valence deformation potentials for cubic CdSe, CdS compounds. For example, A. Sadao[2] reports three sources for cubic CdSe. Namely, A. Blacha et al.,[13] T. Nakayama[14] and H. J. Lozykowski et al.[15] None of them report a proposal for the deformation potential d, and the different b-values reported change even the sign, this last deformation potential being crucial to determine the heavy hole/light hole strain-driven splitting. Then, we employ here the experimental b-values reported for CdS[16] and CdSe.[15] As for a_c, we employ the a_v parameters also calculated by Wei and Zunger.[11] Finally, since no d values are reported for CdS and CdSe, we employ the value $d = -4.4$ eV that correspond to CdTe, this value being close to that reported for many semiconductors.[17]

(13) A. Blacha, H. Presting, and M. Cardona, *Phys. Status Solidi B*126, 11 (1984).
Cited in Ref.[2] p. 324 (CdSe), p. 267 (CdS).

(14) T. Nakayama, *Solid-State Electron.* 37, 1077 (1994).

(15) H. J. Lozykowski and V. K. Shastri, *J. Appl. Phys.* 69, 3235 (1991).

(16) D. W. Niles and H. Höchst, Phys. Rev. B 44, 10965 (1991).

(17) See e.g. Table 8.4 in Sadao Adachi, *Properties of Group - IV, III - V and II - VI Semiconductors* John Wiley and Sons, Chichester, 2005

(18) Calculated from data in: Wei S.H. and Zhang S. B.; *Phys. Rev. B* 62 (2000) 6944; Wei S.H., Zhang S. B. and Zunger A. *J. Appl. Phys.* 87 (2000) 1304.

(19) P.E. Farias Junior and G.M. Sipahi, J. Appl. Phys. 112 (2012) 103716

(20) Andrei Schliwa, Gerald Hönig, and Dieter Bimberg, in Multi-Band Effective Mass Approximations, Matthias Ehrhardt and Thomas Koprucki Eds. (Springer, Heidelberg , 2014).