Self-Purification in Semiconductor Nanocrystals

Gustavo M. Dalpian and James R. Chelikowsky
Center for Computational Materials, Institute for Computational Engineering and Sciences, Departments of Physics and Chemical Engineering, University of Texas, Austin, Texas 78712, USA

(Received 15 February 2006; published 6 June 2006)

Doping of nanocrystals is an important and very difficult task. "Self-purification" mechanisms are often claimed to make this task even more difficult, as the distance a defect or impurity must move to reach the surface of a nanocrystal is very small. We show that self-purification can be explained through energetic arguments and is an intrinsic property of defects in semiconductor nanocrystals. We find the formation energies of defects increases as the size of the nanocrystal decreases. We analyze the case of Mn-doped CdSe nanocrystals and compare our results to experimental findings.

DOI: 10.1103/PhysRevLett.96.226802 PACS numbers: 73.22.−f, 61.72.−y, 71.70.−d, 75.50.Pp

The properties of impurities in nanostructures can be very different from the precursor materials, sometimes even leading to novel phenomena. This usually is due to quantum confinement effects and to the reduced size of the system. In pure semiconductor nanocrystals, the most remarkable change is in their energy gap, which is blueshifted from the bulk value as the size of the nanocrystal decreases. This leads to the possibility of tuning the band gap of the material in order to satisfy specific needs, providing a wide spread of applications such as solar cells [1], electroluminescent devices [2], and possible electronic devices. Bulk semiconductors need to be doped to build functional devices. In order to develop functional devices with semiconductor *nanocrystals*, they should also be doped. Although this is a formidable task [3], recent work has demonstrated the feasibility of doping nanocrystals [4–10].

Understanding the role of impurities and defects is fundamental in explaining some properties of nanocrystals, such as melting [11] and phase transitions [12]. The melting temperature and the transition pressure in nanocrystals are known to be different from the bulk materials. One of the reasons why this happens is their high crystal quality. In 1950, Turnbull was probably the first to propose that small crystals will contain fewer defects [13]. Defects are easily annealed out owing to the material's limited size: the distance the defect must move to be ejected from the nanocrystal is much smaller than in bulk materials. Kinetic arguments like this are usually invoked to explain most observed processes in nanostructures. The problem with kinetic arguments is that they are usually not well posed, leading to assumptions and speculations. Energetics or thermodynamics would lead us to a much more well-defined problem, if the system of interest is under equilibrium. The answer to such problems often lies in between kinetics and thermodynamics. In order to understand doping in nanocrystals, one needs to consider both kinetic and thermodynamic properties of the system.

Here, we focus on the process of doping nanocrystals. From a kinetics perspective, self-purification mechanisms are claimed to make doping more difficult [6,7,14]. Despite these difficulties, several improvements have been made regarding the nature of dopants in semiconductor nanocrystals and on how to dope them [4–7]. Erwin *et al.* [7] proposed the limiting factor to be the binding energy of the impurity to the surface of the nanocrystal. They show that the zinc-blende (100) face is the one that shows highest binding energy, and a change in the anion:cation concentration is suggested for increasing the adsorption of Mn into ZnSe. For small nanocrystals, as no specific surface is observed, doping is very difficult, while for larger nanocrystals, grown in the Se-rich limit, more impurities are incorporated into the nanocrystal. We will demonstrate that *most* of these conclusions can be obtained using energetic arguments.

We examine the stability of magnetic impurities in CdSe nanocrystals as a function of size, and show that the formation energy of magnetic impurities *increases* as the size of the nanocrystal *decreases*, making doping more difficult. This is partly reflected by the creation of a deep impurity level in the gap of the nanocrystals. The level is deeper for smaller quantum dots [10]. We will also perform an analysis of the thermodynamic limits for the elemental chemical potentials, and show that more Mn atoms should be incorporated into CdSe in the anion-rich regime, since its formation energy decreases in this regime. All these results are in agreement with experimental evidence. We believe the increase in the formation energy should be a *general* property of defects and impurities in nanocrystals. This should explain why it is so easy to anneal these impurities away from the nanocrystal and also help find new ways to increase the dopability of these materials.

To study doped nanocrystals, we use first principles methods based on the density functional theory and using norm-conserving pseudopotentials [10]. The Kohn-Sham equations are solved on a real space grid using higher-order finite difference method [15]. We use a grid spacing of 0.4 a.u. (1 a.u. = 0.529 Å) and at least 5 a.u. between the outermost passivating atoms and the spherical boundary. Our nanocrystals are saturated with pseudohydrogen atoms [16], in order to remove states related to dangling bonds from the gap. All atoms are allowed to relax to their minimum energy position. One advantage of real space methods in comparison to plane wave methodologies for the study of nanocrystals is that one does not have to utilize supercells. We studied zinc-blende spherical CdSe nanocrystals with up to 293 Cd and Se atoms, that is equivalent to a diameter of 2.6 nm. All the studied nanocrystals are spherical and centered in a Cd atom, and this is the atom that is replaced by the Mn impurity. We do this in order to retain the T_d symmetry [17].

As reported previously [10], quantum confinement of magnetic impurities in quantum dots leads to the creation of a deep level in the gap with d character. This level is deeper for smaller nanocrystals. In order to understand better the nature of this level, we have studied it through partial densities of states. We project the radial wave function onto spherical harmonics inside a sphere of radius 2.4 a.u., centered at the atom position. In Fig. 1(a) we plot the partial density of states of Mn_d levels in bulk CdSe for the spin-up and spin-down channels. We can clearly observe a peak resonant in the valence band (~ -2.5 eV), that is, a convolution of the peaks related to the t_2 and e levels. It is also possible to observe some spectral weight at higher energies, below the Fermi energy. This appears due to the hybridization between the resonant t_{2d} levels and the top of the valence band, since they have the same t_2 symmetry. The hybrid level, with mixed d and p character, will be the highest occupied orbital in this case. In the spin-down channel, it is possible to observe a similar pattern, but the Mn_d levels are empty, above the conduction band minimum.

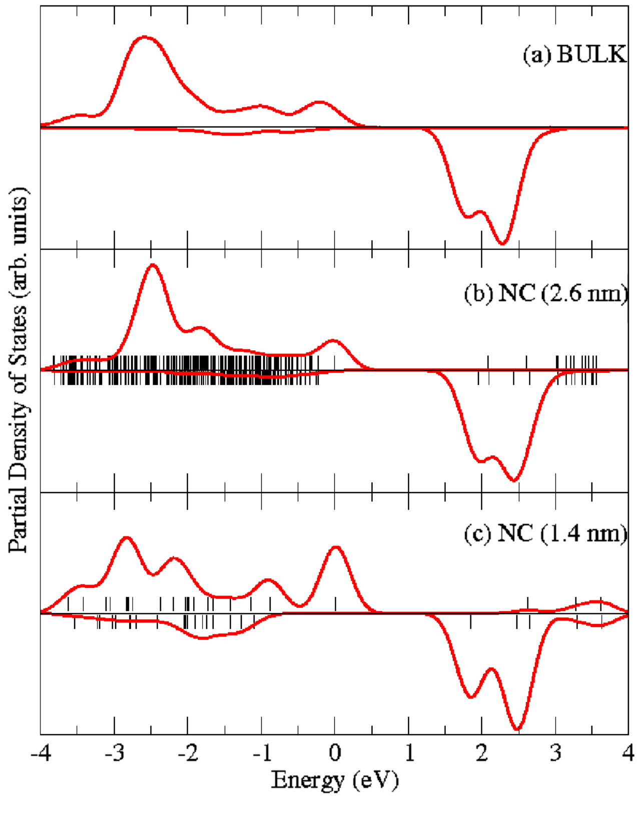

FIG. 1 (color online). Partial density of states projected into Mn_d orbitals for Mn-doped (a) bulk CdSe and nanocrystals with (b) 2.6 nm and (c) 1.4 nm diameter. Each figure is split into spin-up (above) and spin-down (below) channels. The dashes in (b) and (c) are the eigenvalues for the nanocrystals. The zero of energy is set to the highest occupied orbital.

When nanocrystals are formed, it is well-known that quantum confinement effects shift the valence band maximum down, to lower energies, and the conduction band minimum to higher energies. This increases the band gap of the nanocrystal; the increase of the band gap should be proportional to the effective masses of the conduction and valence bands. This means that localized deep impurity levels, such as the Mn_d levels, should not be affected as much by quantum confinement. The final effect of quantum confinement in this system will be an increase of the Mn d character of the hybrid level (highest occupied) [18] that also makes the level deeper for smaller nanocrystals [10]. These effects can be observed in Figs. 1(b) and 1(c), where we show the projected density of states (into Mn_d levels) for doped nanocrystals with 2.6 and 1.4 nm.

For small nanocrystals, both the resonant and the hybrid levels have similar d components, such as observed in Fig. 1(c). If holes were inserted into this system, ferromagnetism should be mediated by double exchange instead of the usual Zener mechanism, as reported previously [10]. This happens because the level where the holes would be localized is very deep, while the Zener model should work for more delocalized carriers [19]. In Figs. 2(a) and 2(b), we show the localization of the resonant (~ -2.5 eV) and the hybrid (0 eV) levels for a small nanocrystal. We observe that both levels have a similar spatial extent, supporting our argument. The increase in the localization of the d levels in the nanocrystals should make the observation of ferromagnetism more difficult. In order to reach the percolation limit [20], a higher concentration of impurities should be necessary. This is in agreement with experimental observations which show that an InAs nanocrystal doped with 5% of Mn does not exhibit ferromagnetism [4].

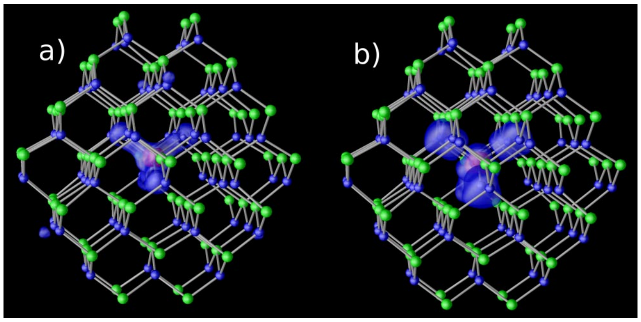

FIG. 2 (color online). Charge density plot of the impurity d levels in a Mn-doped CdSe nanocrystal with 1.7 nm of diameter. (a) is for the level resonant in the valence band, and (b) is for the hybrid level.

Besides the change in the mechanism responsible for the stabilization of ferromagnetism (if holes are present), the localization of the *d* levels leads to another important finding: as it costs more energy to populate deep levels than shallow ones, we expect that this will lead to an increase in the energetic cost to insert Mn atoms into small nanocrystals. As the levels are deeper for smaller nanocrystals, it should cost more energy to insert Mn atoms into the small nanocrystals than the larger ones.

In order to quantify this decrease in the stability for smaller nanocrystals, we will calculate the formation energy of these defects. The calculation of defect formation energies is a very well established concept in semiconductor physics [21], although it has not been widely applied to semiconductor nanocrystals [9,22]. The stability and population of these defects under equilibrium can be elucidated by the defect formation energy. The formation energy (ΔH_F) of a Mn atom replacing a Cd atom in a CdSe nanocrystal is given by

$$\Delta H_F = E_T^{\mathrm{Mn}} - E_T + (E_{\mathrm{Cd}} + \mu_{\mathrm{Cd}}) - (E_{\mathrm{Mn}} + \mu_{\mathrm{Mn}}), \quad (1)$$

where E_T^{Mn} is the total energy of the nanocrystal with the impurity, E_T is the total energy of the nanocrystal without the impurity, E_{Cd} and E_{Mn} are the elemental energies of Cd and Mn, respectively, and μ_i is related to the range of the chemical potentials in different thermodynamic limits. ΔH_F can be interpreted as the energy required to replace a Cd atom by an Mn atom in the nanocrystal. In this equation we are not taking into account the dependence of the formation energy on the Fermi energy, since we want to focus on neutral defects.

We will simplify Eq. (1) by removing its dependency on the chemical potentials. The resulting equation will be rewritten as $\Delta H_F = E_T^{\mathrm{Mn}} - E_T$, and can be understood as a relative formation energy. As we are interested in comparing formation energies for different sizes of nanocrystals, this should be sufficient. The calculated relative formation energy as a function of size is shown in Fig. 3. The zero of the formation energy is set to the formation energy of a substitutional impurity in bulk. As the nanocrystal size decreases, the formation energy increases, showing that it will cost more energy to insert impurities into small nanocrystals than the larger ones; i.e., the impurity will be less stable in the small nanocrystals. In the limit of large nanocrystals, the formation energy will approach asymptotically the value for bulk. This is partially due to the fact that it costs more energy to populate deeper levels than shallower ones, in agreement with our previous discussion. Structural differences such as relaxation effects are not expected to be important, since the difference in the bond-length between the Mn and Se atoms in different nanocrystals is less than 0.01 Å. These results are in agreement with experimental observations that show the exclusion of dopants from small nanocrystals [6]. As their energy is very high, the impurity will be expelled from the cluster and incorporation should be expected just for larger nanocrystals [7]. This should help explain the difficulties found in experiments when inserting impurities into nanocrystals [3]. Although the calculated energy difference from bulk to a medium-size nanocrystal (~5 nm) should be small (~0.2 eV), this is enough to reduce the equilibrium population of defects by 2 orders of magnitude at usual growth temperatures.

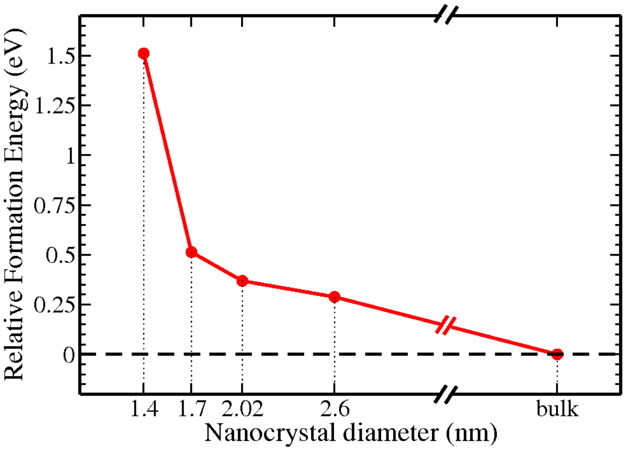

FIG. 3 (color online). Variation of the formation energy of a substitutional Mn impurity in a CdSe nanocrystal as a function of the nanocrystal diameter. The increase in the formation energy is important to explain self-purification in nanocrystals.

The elemental chemical potentials present in Eq. (1) are very important to evaluate the population of each defect in different environments. We discuss qualitatively the influence of the chemical potentials in the formation energy, as shown in Eq. (1), and try to compare with experimental findings. Erwin *et al.* [7] changed the Se:Zn concentration to an Se-rich environment in order to be able to insert more Mn into the nanocrystal. Their argument is that the Se-rich environment changes the structure of the nanocrystal, increasing the probability of the Mn to bind to it. Using Eq. (1), we can reinterpret these experimental results, and propose another mechanism that should be important for this increased incorporation of Mn in the Se-rich environment. We are going to consider that the range of the Cd chemical potentials (μ_{Cd}) for the nanocrystal is the same as in bulk; in this case, under the Se-rich environment, $\mu_{\mathrm{Cd}} = \Delta E_{\mathrm{CdSe}} \sim -1.15$ eV, where ΔE_{CdSe} is the formation energy of bulk CdSe. It is easy to see that inserting a negative μ_{Cd} into Eq. (1) will decrease the formation energy of the impurity, and make its incorporation easier. In the other regime (Cd-rich), $\mu_{\mathrm{Cd}} = 0$, and the formation energy will be larger. This is in agreement with the experimental results and can be considered another explanation for the observed increase in the Mn incorporation into the nanocrystal in Ref. [7] without the need to change its structure. As a general comment for II-VI and III-V binary compounds, the following rule is valid: if the objective is to incorporate cation substitutional impurities, the anion concentration in the solution should be increased in order to reduce the impurity formation energy.

It has already been observed that the cohesive energy of nanostructures decreases as a function of size [23]. Consequently, the formation energy of the bare nanocrystal should be size dependent and higher than that of the bulk material ($\Delta E_{\mathrm{CdSe}} < \Delta E_{\mathrm{CdSe}}^{\mathrm{nano}}$), providing different limits to the chemical potentials, and providing the ability to change the relative stability of different defects. A similar observation was predicted for the behavior of impurities near surfaces during growth [24]. Although this is a more precise approach and deserves further studies, it should not change our conclusions.

We have also performed calculations for other defects, and observed that the formation energy of interstitial Mn impurities increases as the size of the nanocrystal decreases. In this case, the formation energy increased by 0.95 eV when the nanocrystal diameter changes from 2 to 1.4 nm. This is also true for Cd vacancies, and a similar mechanism (creation of deeper levels in the gap of smaller nanocrystals) can be used to explain it. The increase in the formation energies of these impurities is clear evidence that doping of nanocrystals should be more difficult than doping bulk. An increase in the formation energy of DX^- centers [9] in GaAs nanocrystals and shallow donors and acceptors [22] in Si nanocrystals have been also reported. These results support a general conclusion that the formation energy of defects in nanocrystals increases as the nanocrystal size decreases. This is in agreement with the ideas of *self-purification* of nanocrystals and can explain why is it so easy to anneal the defects away from the nanocrystals. Consequently, we can provide another physical interpretation to self-purification: our proposal shows that, besides kinetic factors, self-purification should be an intrinsic property of nanocrystals through the increase of the formation energy of defects and impurities on it.

In summary, we find that the formation energy of defects in nanocrystals increases as the size of the nanocrystals decreases. This should explain why it is difficult to dope nanocrystals and also shed some light onto the exclusion of dopants from small clusters. In order to make doping easier, and insert magnetic impurities into the cation substitutional site, we propose that the sample should be grown in an anion-rich environment.

We thank S. Beckman for valuable discussions. This work was supported in part by the National Science Foundation under DMR-0551195 and the US Department of Energy under DE-FG02-89ER45391 and DE-FG02-03ER15491. Calculations were performed at the Texas Advanced Computing Center (TACC) and at the National Energy Research Scientific Computing Center (NERSC).

[1] R. J. Ellingson, M. C. Beard, J. C. Johnson, P. Yu, O. I. Micic, A. J. Nozik, A. Shabaev, and A. L. Efros, Nano Lett. **5**, 865 (2005).

[2] S. Coe, W.-K. Woo, M. G. Bawendi, and V. Bulovic, Nature (London) **420**, 800 (2002).

[3] F. V. Mikulec, M. Kuno, M. Bennati, D. A. Hall, R. G. Griffin, and M. G. Bawendi, J. Am. Chem. Soc. **122**, 2532 (2000).

[4] C. A. Stowell, R. J. Wiacek, A. E. Saunders, and B. A. Korgel, Nano Lett. **3**, 1441 (2003).

[5] S. B. Orlinskii, J. Schmidt, P. G. Baranov, D. M. Hofmann, C. M. Donega, and A. Meijerink, Phys. Rev. Lett. **92**, 047603 (2004).

[6] J. D. Bryan and D. R. Gamelin, in *Progress in Inorganic Chemistry*, edited by K. D. Karlin (Wiley, New York, 2005), Vol. 54.

[7] S. C. Erwin, L. Zu, M. I. Haftel, A. L. Efros, T. A. Kennedy, and D. J. Norris, Nature (London) **436**, 91 (2005).

[8] D. V. Melnikov, and J. R. Chelikowsky, Phys. Rev. Lett. **92**, 046802 (2004).

[9] J. Li, S.-H. Wei, and L. W. Wang, Phys. Rev. Lett. **94**, 185501 (2005).

[10] X. Huang, A. Makmal, J. R. Chelikowsky, and L. Kronik, Phys. Rev. Lett. **94**, 236801 (2005).

[11] A. N. Goldstein, C. M. Echer, and A. P. Alivisatos, Science **256**, 1425 (1992).

[12] C.-C. Chen, A. B. Herhold, C. S. Johnson, and A. P. Alivisatos, Science **276**, 398 (1997).

[13] D. Turnbull, J. Appl. Phys. **21**, 1022 (1950).

[14] Al. L. Efros and M. Rosen, Annu. Rev. Mater. Sci. **30**, 475 (2000).

[15] J. R. Chelikowsky, N. Troullier, and Y. Saad, Phys. Rev. Lett. **72**, 1240 (1994).

[16] X. Huang, E. Lindgren, and J. R. Chelikowsky, Phys. Rev. B **71**, 165328 (2005).

[17] G. M. Dalpian, M. L. Tiago, M. L. del Puerto, and J. R. Chelikowsky, Nano Lett. **6**, 501 (2006).

[18] S. Sapra, D. D. Sarma, S. Sanvito, and N. A. Hill, Nano Lett. **2**, 605 (2002).

[19] G. M. Dalpian, S.-H. Wei, X. G. Gong, A. J. R. da Silva, and A. Fazzio, Solid State Commun. **138**, 353 (2006).

[20] L. Bergqvist, O. Eriksson, J. Kudrnovsky, V. Drchal, P. Korzhavyi, and I. Turek, Phys. Rev. Lett. **93**, 137202 (2004).

[21] S. B. Zhang and J. E. Northrup, Phys. Rev. Lett. **67**, 2339 (1991); S.-H. Wei, Comput. Mater. Sci. **30**, 337 (2004); G. M. Dalpian and S.-H. Wei, Phys. Rev. B **72**, 075208 (2005).

[22] G. Cantele, E. Degoli, E. Luppi, R. Magri, D. Ninno, G. Iadonisi, and S. Ossicini, Phys. Rev. B **72**, 113303 (2005).

[23] T. M. Schmidt, R. H. Miwa, P. Venezuela, and A. Fazzio, Phys. Rev. B **72**, 193404 (2005).

[24] S. B. Zhang and S.-H. Wei, Phys. Rev. Lett. **86**, 1789 (2001).