Probabilities for dopant pair-state formation in a nanocrystal: simulations and theory

J. F. Suyver[a,1], R. Meester[b], J. J. Kelly[a] and A. Meijerink[a]

[a]) *Debye Institute, Physics and Chemistry of Condensed Matter, Utrecht University, P.O. Box 80.000, 3508 TA Utrecht, The Netherlands.*
[b]) *Division of Mathematics and Computer Science, Free University of Amsterdam, De Boelelaan 1081a, 1081 HV Amsterdam, The Netherlands.*

Abstract

For certain dopants, luminescence measurements allow one to distinguish between single-ion and pair-state dopant emission in a (semiconductor) host. In a bulk crystal the concentration of each of these dopant-states can be calculated from the dopant fraction present in the material, and is found to correlate with luminescence measurements. However, for a nanocrystalline host-lattice, these concentrations cannot be calculated due to the difference in coordination numbers for ions at the surface (a substantial fraction in nanocrystals) and in the bulk. Here simulations of dopant pair-state distributions are presented for a zincblende nanocrystal. The probability of finding at least one pair-state in the nanocrystal and the percentage of dopants forming part of a pair-state were calculated on the basis of a statistical average of $1 \cdot 10^5$ simulations for the same crystal size and dopant concentration. Furthermore, the distribution of nanocrystal lattice positions over the surface and the bulk of the crystal are computed from the simulations and found to agree well with a first-order theory. Finally, a closed-form approximation of the probabilities (valid in any crystal lattice) and a rigorous upper bound for the error in the approximation are discussed.

PACS-codes: 61.46, 68.65.-k, 68.66.Hb, 78.67.Hc, 81.07.

1 Introduction

There is a strong current interest in materials with nanometer dimensions [1–5]. This research area is driven not just by scientific curiosity; new applications based on nanosized building blocks are expected [6, 7]. Synthesis procedures to make very small (1−10 nm) nanocrystals are well established and fundamental research on the changing properties as a function of particle size has resulted in fascinating results [1–3, 7, 8]. Applications are suggested in electroluminescent devices, where electrical current can be converted into visible light by generating luminescence from the semiconductor dots or from luminescent ions inside the dots [5, 6].

The most obvious difference between nanometer-sized materials and bulk materials is the much larger surface area of the former. An effect that has not been studied is the influence of the particle size on the formation of pairs of dopant (impurity) ions in nanometer-sized particles. The formation of pairs of dopant-ions can be important for the magnetic and optical properties [9, 10]. For example, the luminescence lifetime of the Mn^{2+} emission in $ZnS:Mn^{2+}$ decreases and the emission shifts to longer wavelengths when Mn^{2+} pairs are formed. This

---

[1]Corresponding author. Tel.: $+31 − 30 − 253\ 2214$; Fax: $+31 − 30 − 253\ 2403$; e-mail: j.f.suyver@phys.uu.nl

is due to magnetic interaction between the ions [11–14]. For studies on a single magnetic quantum dot (containing one magnetic dopant ion) [15] it is also useful to determine the fraction of nanocrystals with one or more magnetic dopant ions. In oxide nanocrystals (e.g. YVO_4 and Y_2O_3) the luminescence properties of rare earth ions like Ce^{3+}, Sm^{3+}, Eu^{3+}, Tb^{3+} and Dy^{3+} have been studied in detail [16–18]. Also here, the luminescence properties are significantly influenced by dopant pair formation. For example, the emission from higher ^5D_J levels of Eu^{3+} or Tb^{3+} is quenched by cross-relaxation processes in pairs, whereas this is not observed for single ions [19].

For bulk crystals the probability for the formation of dopant pairs as a function of the dopant concentration can be analyzed analytically [20–24]. For nanocrystalline semiconductor quantum dots this is not possible. The main problem is that the coordination number (i.e. the number of nearest neighbours with the same valence) of ions at the surface is lower than that of ions in the bulk. The contribution of ions in surface sites becomes increasingly important as the quantum dots decrease in size and this complicates the determination of the number of pairs. As a result, for the same concentration of dopant ions the fraction of pairs will be different for different particle sizes.

It is the aim of this paper to provide a better understanding of the probability of pair formation as a function of particle size in nanocrystalline particles. To this end an algorithm has been developed which allows numerical simulations to be made to determine both the probability of finding at least one pair-state in the nanocrystal, and the percentage of dopants that are part of a pair-state in the quantum dot as a function of the particle size. In addition, the fraction of bulk and surface sites is also determined as a function of particle size. Furthermore, a mathematical probabilistic theory (Stein-Chen Poisson approximation) is presented which yields a closed-form approximation of these probabilities which is valid in any crystal structure, thus obviating the need for further numerical simulations.

The simulations are performed assuming a random distribution of the dopant ions, i.e. it is assumed that there is no preferential pair formation or preference of dopant ions over host lattice ions for surface or bulk sites. In the case of the rare earth oxide nanocrystals this assumption is expected to be valid: the rare earth ions are chemically quite equivalent and a random distribution is expected. For $3d$ transition metal ions a random distribution is not expected and the results of the model will give a lower limit for the fraction of pairs.

2 Simulations and numerical results

2.1 Definition of the algorithm

Through the introduction of the dimensionless parameter $\rho \equiv (r/a)$ a formalism is described that does not depend on the lattice parameter a and holds for any crystal with the same crystallographic structure. The method presented here is generally applicable to every nanocrystalline system. In the remainder of this section, the zincblende structure (space group $F\ \bar{4}\ 3m - T_d^2$) is chosen, as an example. This crystal structure is found in a wide range of semiconductors that are also interesting as nanocrystalline materials, such as CdSe, ZnS, HgTe, InP and GaAs.

The number of available lattice positions in a spherically chosen crystal of radius ρ is denoted by n. The value of n is determined by analysis of the overlap of the zincblende crystal with a sphere of radius ρ centered at a lattice position. The complete lattice of the nanocrystal is defined by the set of n vectors $\{\mathbf{p}_i\}$ that point to each of the lattice positions. The nearest-neighbour distance ζ is the smallest (non-zero) distance between any two vectors in this set. For the zincblende crystal structure, $\zeta = a/\sqrt{2}$.

The complete crystal consists of n lattice positions. The situation in which a fraction f of these lattice positions is filled with dopant ions, is simulated by choosing a random subset $\{\mathbf{q}_b\}$ of $k = fn$ different vectors from the complete set $\{\mathbf{p}_a\}$. A pair-state in this crystal configuration is now defined to occur if and only if

$$\exists \lambda > \sigma \in \mathbb{Z} : |\mathbf{q}_\lambda - \mathbf{q}_\sigma| = \zeta . \tag{1}$$

Note that the set $\{\mathbf{q}_b\}$ does not contain duplicate vectors and because of the symmetry only the $\lambda > \sigma$ part needs to be evaluated. By choosing the random subset $\{\mathbf{q}_b\} \subset \{\mathbf{p}_a\}$ a very large number of times, one approximates the actual probability for pair-state formation. Let $\Phi(n,k)$ and $\Psi(n,k)$ represent the probability for at least one pair-state, and the percentage of positions that are part of a pair-state (relative to the number of dopants present in the nanocrystal), respectively.

To find the probability for the presence of at least one pair-state in the nanocrystal, a set of $1 \cdot 10^5$ nanocrystals of identical size and number of dopants is simulated and $\Phi(n,k)$ is identified with the fraction of all the nanocrystals that contained at least one pair-state (i.e. a valid solution to equation (1)). The algorithm replaces in each nanocrystal a fixed fraction f of the n lattice positions with dopant ions. However, a realistic procedure would be to replace each lattice position with a dopant ion with a probability f because a random distribution of dopants in the nanocrystal is assumed, as was explained in the Introduction. This will result in a binomial distribution of the number of dopant ions present in the nanocrystal with expectation value k. Using this fact, combined with the knowledge of $\rho(n)$, the expression for finding at least one pair-state in the nanocrystal is given by [25]

$$\mathcal{P}(\rho, f) = \sum_{i=2}^{n} \left(\begin{array}{c} n \\ i \end{array} \right) f^i (1-f)^{n-i} \Phi(n,i) , \tag{2}$$

where the summation begins with $i = 2$, because at least two dopant ions are required to form a pair-state. The percentage of dopants forming part of a pair-state in the nanocrystal is found through a similar argument as was used for equation (2). For small f, the percentage of dopants that are part of a pair-state is given by the sum over the binomial coefficients times $2\Psi(n,i)/k \cdot 100[\%]$. The factor 2 is due to symmetry.

Two typical simulations are shown in figure 1. These examples were calculated using $\rho = 4$ (i.e. $n = 1048$) and $f = 0.01$ (i.e. $k = 10$). In the simulation on the left, a pair-state has formed as can be seen in the top right part of the simulated crystal. The simulation on the right did not result in a pair-state. For this specific case, values were found of $\mathcal{P}(4, 0.01) = 0.3921$ and $\mathcal{Q}(4, 0.01) = 10.80\,\%$.

The calculations were performed using the bare 4.0.1 *Mathematica* kernel on
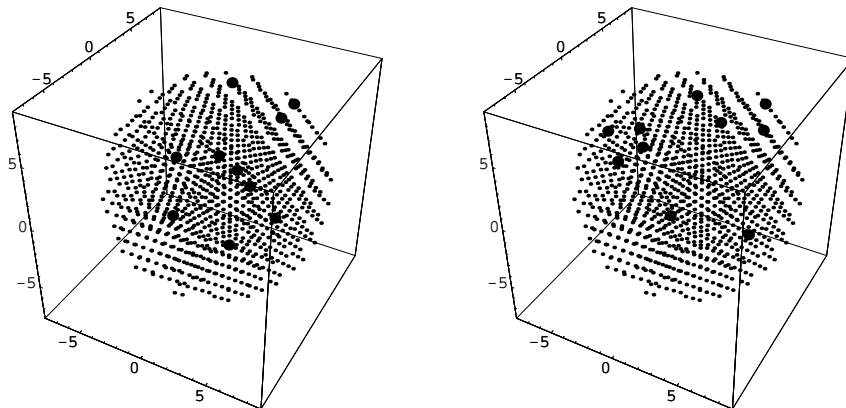
Figure 1: Two typical simulations obtained for $\rho = 4$ and $f = 0.01$. The small dots ($\cdot$) represent the lattice and the large dots ($\bullet$) indicate the dopants present in this lattice. The figure is discussed further in the text.

a Compaq ES40 Alpha (Tru64 Unix 4.0d) system. The stepsize in the calculations was $\Delta k = 0.001n$ and $\Delta \rho = 0.5$.

2.2 Probability for at least one pair-state

The results of the calculations for $0.5 \leq \rho \leq 8.5$ are shown in figure 2. Note that for large ρ the probability distribution converges to a step function. This result is straightforward, since $\mathcal{P}(\rho, f)$ denotes the probability of finding *at least one* pair-state in the crystal.

Upon close inspection of figure 2, it is noted that for small particles (i.e. $\rho < 5$) the surface contribution to the probability distribution is very large. The fact that lattice positions on the surface have only 8 neighbours, instead of the usual 12 for bulk lattice positions, results in a drastic increase of the probability for pair-state formation compared to larger crystals. This is seen clearly from the following argument: For $\rho = 7$ the surface contribution will be relatively small and the simulation shows $\mathcal{P}(7, 0.0052) = 0.57$. If the surface did not influence the probability distribution, then $\mathcal{P}(2, f) = 0.57$ can be solved easily through $f = (7/2)^3 \cdot 0.0052 = 0.22$ because of the cubic dependence of n on ρ. However, the simulations show that $\mathcal{P}(2, 0.043) = 0.57$. The much smaller (about 5 times) dopant-fraction required is a direct result of the larger surface contribution to the probability distribution.

2.3 Pair-state concentration

In this section the results obtained from the simulations of $\mathcal{Q}(\rho, f)$ in the low-dopant concentration regime are described. It is important to stay roughly in the $0 < f < 0.1$ range, because for larger f triple-states (i.e. one dopant that has at least two nearest neighbour dopants) need to be taken into account. For these states the symmetry of the problem can no longer be exploited because a triple-state in the zincblende structure can be three particles on a line (which would count as four dopants forming part of a pair-state in the algorithm presented
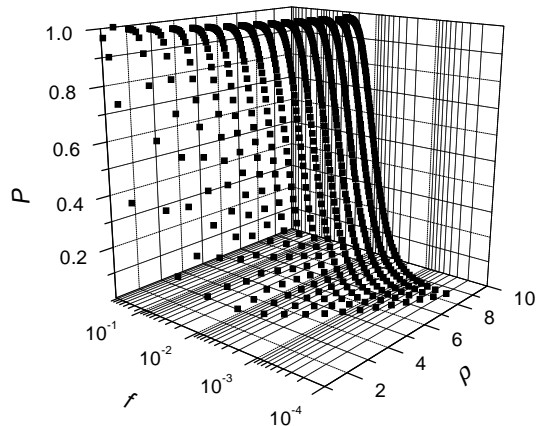
4

Figure 2: The probability distribution $\mathcal{P}(\rho, f)$, which describes the probability of finding at least one pair-state in a zincblende nanocrystal with expanded radius ρ and dopant fraction f. Note the logarithmic scale for the f-axis.

in section 2.1), or three particles in a triangle shape (counting as six dopants forming part of a pair-state). The combinatorial problems associated with these "higher-order" corrections become increasingly more difficult and require much more computer-time to be correctly evaluated. Therefore, the remainder of this analysis will only focus on the low dopant range ($0 < f < 0.1$), and triple-states will be ignored.

Figure 3 shows the resulting $\mathcal{Q}(\rho, f)$ for $1 \leq \rho \leq 7$. The influence of the surface can be seen clearly in the data, just as in the previous section. If the surface did not influence the results, then one would expect $\mathcal{Q}(2, f) = \mathcal{Q}(7, f)$ for all f. However, the data show that $\mathcal{Q}(2, 0.04) = 1.73\%$, while $\mathcal{Q}(7, 0.04) = 0.77\%$. This difference is explained by the increased probability for pair-state formation of a dopant at the surface of the nanocrystal with respect to a bulk dopant (due to the difference in coordination number). All data presented in this figure could be fitted well using a linear relation of $\mathcal{Q}(\rho, f)$ as a function of f, which is also expected. For low-dopant fractions, there are almost no triple-states, and this is the reason that the definition of $\mathcal{Q}(\rho, f)$ has the factor 2 (ascribed to symmetry, shown below equation (2)). In other words, for small f, if no triple-state is present in the nanocrystal, then addition of one more dopant pair-state will most likely also not result in a triple-state. This means that the concentration of pair-states increases linearly with the number of dopants.

3   General formulation of the problem

This section is devoted to deriving closed-form approximations of $\mathcal{P}(\rho, f)$ and $\mathcal{Q}(\rho, f)$ as well as a measure of the uncertainty in the approximation. The results have general applicability and therefore involve a description of the crystal structure. This is done by making the results dependent on the number of neighbours of a bulk lattice position (the bulk connectivity, C_b), the number of
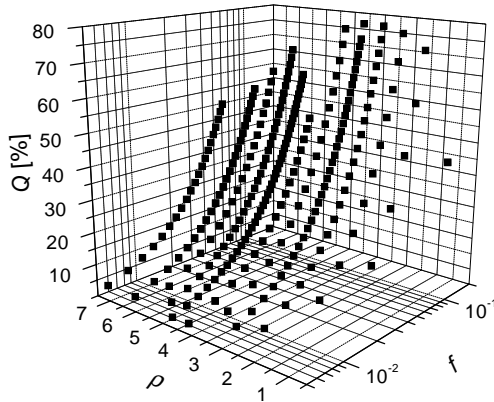
Figure 3: The probability distribution $\mathcal{Q}(\rho, f)$, which describes the expected percentage of dopants part of a pair-state in a zincblende nanocrystal. Note the logarithmic scale for the f-axis.

neighbours of a surface lattice position (the surface connectivity, C_s) and the number of lattice positions present in the unit-cell (ψ).

3.1 Lattice position configuration

The number of bulk and surface lattice positions, denoted as $n_b(\rho)$ and $n_s(\rho)$ respectively, can be found from the simulations. A lattice position is defined to be a surface position if it contributes to $n(\rho)$ but not to $n(\rho - 1)$. The total number of lattice positions in the zincblende crystal structure can be generally defined as

$$n(\rho) \;=\; \sum_{\forall \mathbf{p}} 1 \;\approx\; 4\pi\psi\rho^3/3 \;, \tag{3}$$

where ψ represents the number of lattice positions in the crystal unit cell. The evaluation of the summation was used in section 2.1 and gives an exact value for $n(\rho)$.

When the assumption indicated in the second part of equation (3) is made, then the number of surface lattice positions $n_s(\rho) = n(\rho) - n(\rho - 1)$ and the number of bulk lattice positions $n_b(\rho) = n(\rho-1)$ can be found analytically. The fraction of lattice positions that are located on the surface of the nanocrystal is expressed as $\delta n(\rho) \equiv n_s(\rho)/n(\rho)$, which no longer depends on ψ.

The squares in figure 4(a)−(d) show the values that were found for $n(\rho)$, $n_s(\rho)$, $n_b(\rho)$ and $\delta n(\rho)$ respectively. For these values the exact crystal configuration was used by means of the simulation-data presented in section 2 (i.e. the complete sum in equation (3) was evaluated). The lines through the data, resulting from the approximation in equation (3) with $\psi = 4$, show a good agreement. From the data in figure 4 it is concluded that the approximation in equation (3) works very well in the zincblende case, even for very small nanocrystals (such as $\rho = 2$).
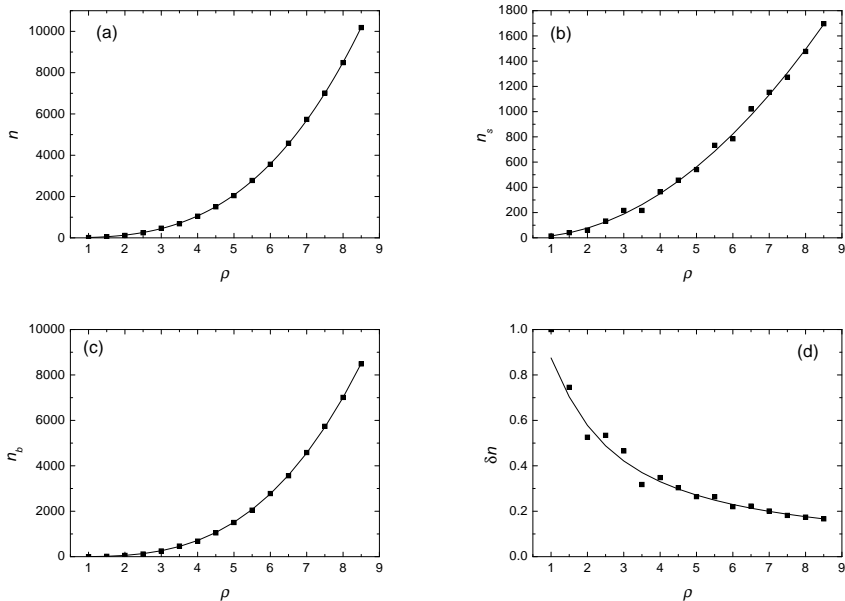
Figure 4: Comparison between the exact summation and the approximation presented in equation (3). The squares in (a) through (d) represent the values found for $n(\rho)$, $n_s(\rho)$, $n_b(\rho)$ and $\delta n(\rho)$ from the simulations presented in section 2 (i.e. the evaluation of the sum in equation (3)). The lines through the data are predictions from the approximation in equation (3), using $\psi = 4$.

3.2 Poisson approximation

In this section, an approach is discussed which enables the computation of approximations of $\mathcal{P}(\rho, f)$ and $\mathcal{Q}(\rho, f)$ for any given crystal, without any simulations. In addition, a rigorous upper bound of the error in the approximation of $\mathcal{P}(\rho, f)$ is provided. The method used is a special case of the Stein-Chen Poisson approximation method [27]. The main idea is that the number of pair-states is close in distribution to a Poisson random variable. This is due to the fact that the pair-states are almost independent. If the pair-states were completely independent, then the total number of pair-states would have a binomial distribution. The binomial distribution is, under the circumstances that are relevant to this paper, very close to a Poisson distribution [25].

The number of nearest neighbour lattice positions in the crystal is denoted by $N = (n_s C_s + n_b C_b)/2$. The probability that a lattice position contains a dopant is denoted by f. Therefore, the expected number of dopant pair-states will simply be given by $N f^2 \equiv \lambda$. The number of pair-states in the nanocrystal will have approximately a Poisson distribution with expectation value λ. This implies that the probability of finding x pair-states in the nanocrystal will be approximated by $P(x) \equiv e^{-\lambda} \lambda^x (x!)^{-1}$. Therefore, the probability of finding at least one pair-state in the nanocrystal will be approximately $\mathcal{P} = 1 - P(0) = 1 - e^{-\lambda}$. Because λ represents the (expected) number of dopant pair-states,

the percentage of dopants that are part of a pair-state is approximated by $\mathcal{Q} = 2\lambda/k \cdot 100[\%]$. Using the approximation of $n(\rho)$ shown in the previous section, $\mathcal{P}$ and $\mathcal{Q}$ can be written as

$$\mathcal{P} = 1 - \exp\left[-\frac{2\pi\psi f^2}{3} \left\{ C_b(\rho - 1)^3 + C_s(3\rho(\rho - 1) + 1) \right\} \right] , \qquad (4)$$

and

$$\mathcal{Q} = \frac{[1 + 3\rho(\rho - 1)]C_s + [\rho - 1]^3 C_b}{\rho^3} f \cdot 100[\%] . \qquad (5)$$

Using the total variation norm d_{TV} [26] and Corollary 2.N.1 in Ref. [27] it can be proven that the error introduced in equations (4) and (5) is bounded by

$$\begin{aligned} |\mathcal{P}(\rho, f) - \mathcal{P}| &\leq \left(1 - e^{-Nf^2}\right)\{ \frac{4\pi\psi(f + f^2)}{3N}[(\rho - 1)^3 C_b(C_b - 1) + \quad (6) \\ &\quad (1 + 3\rho(\rho - 1))C_s(C_s - 1)] + f^2 \} . \end{aligned}$$

The values resulting from equations (4), (5) and (6) can be easily computed, and this means that simulations are no longer needed. As long as the upper bound for the error in $\mathcal{P}$, as found from the evaluation of equation (6), remains small, the Stein-Chen Poisson approximations for $\mathcal{P}$ and $\mathcal{Q}$ can be used directly. However, as can be seen from the example in section 4, a large bound does not necessarily imply a large discrepancy between the Poisson approximation and the simulated data. This is caused by the fact that equation (6) is a 'worst-case' scenario. Apparently, the error introduced by the Poisson approximation is much smaller than this worst-case error.

As an example, consider the zincblende crystal discussed in section 2.1, where $\psi = 4$, $C_b = 12$ and $C_s = 8$. A simple evaluation for $\rho = 4$ and $f = 0.01$ leads to $\mathcal{P} = 0.405$ and $\mathcal{Q} = 10.4\%$. These numbers are in very good agreement with the simulations presented in section 2.1. The upper bound of the error is $|\mathcal{P}(\rho, f) - \mathcal{P}| = 0.074$, which shows that the actual error (0.013) is even much smaller than the theoretical upper bound. Further examples are shown in the next section.

4 An example

As a typical example, the probability for pair formation and the average percentage of pair-states in a ZnSe:Mn^{2+} sample with an average nanocrystal radius of 3.4 nm are calculated. The ZnSe lattice has a zincblende structure ($\psi = 4$, $C_b = 12$ and $C_s = 8$) with a lattice parameter $a = 5.6676$ Å (i.e. $r = 3.4$ nm $\Leftrightarrow$ $\rho = 6$) and the Mn^{2+} dopant ions are located on the Zn^{2+} lattice positions.

The results from the simulations presented in sections 2.2 and 2.3 can be used directly. These nanocrystals contain 3564 lattice positions, 785 (22 %) of which are on the surface of the crystal. Table 1 shows both the simulated result and the results obtained in the Poisson approximation. The expectation value for the total number of dopants present in the lattice, k, is also shown.

The results from the Poisson approximation are in very good agreement with the simulation data. Even for the larger dopant fractions very small differences are observed. This result is important because for this ZnSe nanocrystal the

f	k	Simulations		Poisson theory	
		$\mathcal{P}(6,f)$	$\mathcal{Q}(6,f)$	$\mathcal{P}$	$\mathcal{Q}$
0.002	8	0.073	1.56 %	0.072	2.06 %
0.004	15	0.277	3.82 %	0.258	4.13 %
0.007	26	0.638	6.96 %	0.599	7.22 %
0.009	33	0.789	9.11 %	0.780	9.28 %
0.012	44	0.943	12.3 %	0.932	12.4 %
0.015	55	0.989	15.4 %	0.985	15.5 %
0.02	73	0.999	20.8 %	0.999	20.6 %
0.05	181	1.000	52.9 %	1.000	51.6 %

Table 1: Results based on a ZnSe nanocrystal with a radius of 3.4 nm and a dopant fraction f. Both the results from the simulations (section 2) and from the Poisson approximation (section 3.2) are shown.

upper-bound of the error in the approximation will become large for $f > 0.01$. However, as can be seen from the table, the difference between the Poisson approximation and the simulation data remains small, indicating that the Poisson approximation will continue to yield reliable data for higher dopant fractions.

5 Conclusions

This paper discusses an algorithm, simulations and a mathematical approximation for determining the probabilities of finding dopant pair-states in a nanocrystal that have general applicability in nanocrystal science. The probability of finding at least one pair state and the percentage of dopants that are part of a pair-state are calculated explicitly for a nanocrystal with the zincblende structure. The results are made independent of the lattice parameter and adaptation of the algorithm to other crystal structures is possible.

The fraction of lattice positions present on the surface of the nanocrystal is simulated and compared with a first-order theory. Very good agreement is reached. Through the Stein-Chen Poisson approximation, the pair-state probabilities are estimated. A closed-form approximation is presented that is applicable to any nanocrystal, regardless of size and crystallographic structure. These results are valid for all dopant fractions for which the density of triple-states is neglibly small.

Acknowledgements

References

[1] R. Rosetti, R. Hull, J. M. Gibson, and L. E. Brus, J. Chem. Phys. **82**, 552 (1985).
[2] L. Brus, J. Phys. Chem. **90**, 2555 (1986).
[3] A. Henglein, Chem. Rev. **89**, 1861 (1989).

[4] Y. Wang, and N. Herron, J. Phys. Chem. **95**, 525 (1991).
[5] B. O. Dabbousi, M. G. Bawendi, O. Onitsuka, and M. F. Rubner, Appl. Phys. Lett. **66**, 1316 (1995).
[6] N. C. Greenham, X. Peng, and A. P. Alivisatos, Phys. Rev. B **54**, 17628 (1996).
[7] R. Bhargava, J. Luminescence **70**, 85 1996.
[8] J. F. Suyver, S. F. Wuister, J. J. Kelly and A. Meijerink. Phys. Chem. Chem. Phys. **2**, 5445 (2000).
[9] D. G. Thomas, J. J. Hopfield, and C. J. Frosch, Phys. Rev. Lett. **15**, 857 (1965).
[10] J. I. Pankove, *Optical Processes in Semiconductors* (Dover Publications, New York, 1971), p. 61.
[11] C. R. Ronda, and T. Amrein, J. Lumin. **69**, 245 (1996).
[12] J. Ferguson, H. J. Guggenheim, and Y. Tanabe, J. Phys. Soc. Jpn. **21**, 692 (1966).
[13] B. C. Barthou, J. Benoit, P. Bennalloul, and A. Morell, J. Electrochem. Soc. **141**, 524 (1994).
[14] A. L. N. Stevels, and A. T. Vink, J. Lumin. **8**, 443 (1974).
[15] A. A. Maksimov, G. Bacher, A. McDonald, V. D. Kulakovskii, A. Forchel C. R. Becker, G. Landwehr, and L. W. Molenkamp, Phys. Rev. B **62**, R7767 (2000).
[16] K. Riwotzki, and M. Haase, J. Phys. Chem. B **102**, 10129 (1998).
[17] H. Eilers, and B. M. Tissue, Chem. Phys. Lett. **251**, 74 (1996).
[18] H. S. Yang, K. S. Hong, S. P. Feofilov, B. M. Tissue, R. S. Meltzer, and W. M. Dennis, J. Lumin. **83-84**, 139 (1999).
[19] G. Blasse, and B. C. Grabmaier, *Luminescent Materials* (Springer-Verlag, Berlin, 1994).

[20] R. E. Behringer, J. Chem. Phys. **29**, 537 (1958).
[21] M. M. Kreitman, and D. L. Barnett, J. Chem. Phys. **43**, 364 (1965).
[22] N. B. Hannay, *Treatise on Solid State Chemistry: Defects in Solids* (Plenum Press, New York, 1975), p. 373.
[23] W. Jones, and N. H. March, *Theoretical Solid State Physics* (John Wiley & Sons, London, 1973), p. 128, 1082
[24] D. Adler, H. Fritzsche, and S. R. Ovshinsky, *Physics of Disordered Materials*, (Plenum Press, New York, 1985), p. 144, 696.
[25] S. Ross, *A first course in probability* (Collier Macmillan, New York, 1976).
[26] This total variation norm measures the distance between two random variables within the Poisson distribution. Details can be found in Ref. [27].
[27] A. D. Barbour, L. Holst, and S. Janson, *Poisson Approximation* (Clarendon Press, Oxford, 1992).