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ORIGINAL PAPER

Optical gap and excitation energies of small Ge nanocrystals

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Abstract Using the density functional theory (DFT) with the hybrid nonlocal exchange correlation functional of Becke and Lee, Yang and Parr (B3LYP), we have calculated the optical gap and the oscillator strengths for several of the lowest, spin and symmetry allowed, electronic transitions of small Ge nanocrystals passivated by hydrogen. The largest nanoparticle has an approximate diameter of 2 nm. Our results show that the optical gap exhibits size dependence (due to quantum confinement) roughly similar to silicon nanoparticles. However, for this range of diameters, there is an indirect-to-direct transition in the spectra of Ge as the size of the nanocrystals decrease. The first allowed excitation (fundamental optical gap) of each germanium nanoparticle has relatively larger oscillator strengths compared to silicon. The diameter of the smallest Ge nanocrystal capable to emit in the visible region of the spectrum, is approximately 1.9 nm, compared to 2.2 nm for silicon nanocrystals.

Keywords Ge nanocrystals · Optical properties · Quantum dots

1 Introduction

The study of the optical properties of semiconductor (IV) nanocrystals, has been a very active field of research over the last decade [1–8] in view of the mediocre optical performance of the corresponding bulk crystals. Furthermore, the optical performance of such nanostructured materials depends strongly on their size, offering thus the possibility of tunable and controlled optical behavior.

The real breakthrough in this field was the observation of intense photoluminescence (PL) from porous silicon [1] and stimulated considerable efforts towards the

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understanding of the key parameters responsible for visible light emission. Because of the large blueshift of the observed radiation with respect to the bulk Si band-gap energy (1.2 eV), it was proposed that the luminescence in the visible was mainly due to quantum confinement. However, several alternative models challenged or complemented this hypothesis in an effort to make diverse experimental and theoretical results consistent with each other. From the theoretical point of view, the experience gained by the investigation of the optical properties of Si nanocrystals [2,3], shows that in order to achieve the accuracy required to resolve the fundamental issues which dominate the emission of light, high level, well tested calculations, which include an accurate account of electron correlation [3,9,10] are needed.

The extension of research interest from Silicon to Germanium nanocrystals is rather straightforward, as both are group IV semiconductors. Furthermore, Ge has a smaller band gap than Si thus making it possible for smaller structures to produce visible PL. Experimentally PL has been observed in the range 350–700 nm from Ge nanocrystals 2–5 nm in size [4], while there are also studies concerning much larger nanoparticles [5].

It should be noted that up to date the optical properties of Ge quantum dots have been studied only in the framework of either semiempirical methods [6], or simple local density (LDA) ground state calculations [7,8].

2 Outline of calculations

In this work we present ab initio calculation of the optical gap of small Ge nanocrystals based on time dependent density functional theory (TDDFT) [11] employing the hybrid nonlocal exchange-correlation functional of Becke and Lee, Yang and Parr (B3LYP) [12]. The accuracy of these calculations (TDDFT/B3LYP) for the optical gap has been tested for the case of Si quantum dots with excellent results [3]. Furthermore, it has been shown that the B3LYP functional can efficiently reproduce the band structure of a wide variety of materials, including crystalline Si, with no need for ad hoc numerical adjustments [13].

The size of the quantum dots considered here ranges from 1 to 99 Ge atoms, with 4 to 100 H atoms (a total of about 199 atoms). The diameter of the larger cluster falls in the range of 2 nm. All dots have Td symmetry and their geometries have been fully optimized within this symmetry constrain using the hybrid nonlocal exchange-correlation functional of Becke and Lee, Yang and Parr (B3LYP) [12]. As we have shown for the case of Si nanocrystals [3,9], the partially exact Hartree-Fock (HF) exchange that is included in the B3LYP method is very important for the correct description of the optical properties. The inclusion of exact HF exchange remedies the well-known deficiency of local-density approximation (LDA) to underestimate the band gap. The DFT and the TDDFT calculations were performed with the TURBOMOLE [14] suite of programs using Gaussian atomic orbital basis sets of split valence [SV(P)]: [4s3p1d]/[2s] [15] quality which involves 3,400 basis functions for the largest system studied. The B3LYP functional has been used for both, the self-consistent solution of the Kohn-Sham equation for the ground state, and the solution of the linear response problem.

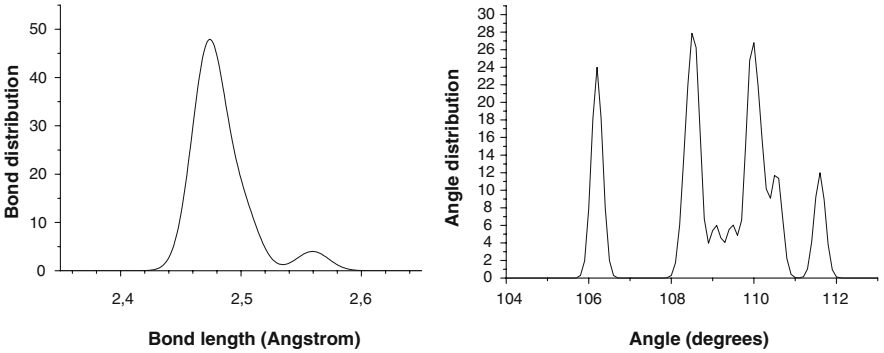

Fig. 1 Bond–length and bond–angle distribution diagram of $Ge_{47}H_{60}$ nanocrystal

We have calculated the fundamental optical gap, which is identified as the energy of the lowest allowed electronic transition (i.e., with nonzero oscillator strength) and its variation as a function of the nanocrystal diameter. Additionally, we have also calculated the 20 lowest allowed electronic transition simulating in this way the lower part of the excitation spectrum.

3 Results and discussion

3.1 Ground state properties

The ground state geometry of the nanocrystals was obtained by geometry optimization, under Td symmetry constrains, of the initial bulk structural parameters (bond lengths and angles).

The optimized structures adopt different values due to the truncated size of the nanocrystals. The correct optimized geometry is very important for the accurate descriptions of the electronic and optical properties. For this reason we have plotted in Fig. 1a representative bond-length and bond-angle distribution diagram for the $Ge_{47}H_{60}$ nanoparticle. The bond lengths appear to be slightly larger in the inner core of the nanoparticle than in the surface. In particular, the largest bond length (2.56 Å) is formed between the central germanium atom and its first neighbours, while the shortest one (2.47 Å) occurs at the surface. In Fig. 1, we can also see a distribution diagram for the corresponding bond angles. The deviations from the ideal value of 109.47° are found to be much larger. The smallest value is found to be around 106°, while the largest one is approximately 117°. It is worth noting that there are only six angles with the ideal value of 109.47°. An analogous dispersion of bond lengths and bond angles is also found for the rest of the nanoparticles. As would be expected, the bond lengths (and the bond angles) should approach their ideal bulk values, as the size of the nanocrystals becomes larger.

In order to facilitate the simple comparison of the ground state electronic structure ("band structure") for nanocrystals of different size, we have plotted in Fig. 2a the Density of States (DOS_) for two nanocrystals of "medium" and "large" sizes (as far

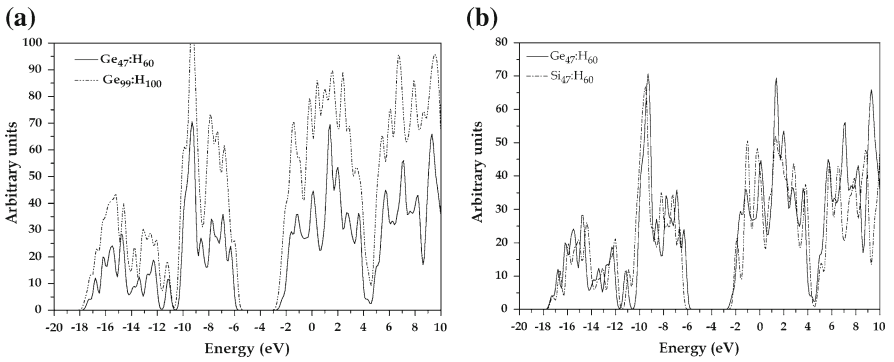

Fig. 2 **a** Comparison of the density of states of Ge_{47}:H_{60} and Ge_{99}:H_{100} nanocrystals. **b** Comparison of the density of states of Ge_{47}:H_{60} and Si_{47}:H_{60} nanocrystals

as the present investigation is concerned). The DOS curves were generated from the eigenstates of the ground state calculations with a suitable gaussian broadening. As we can see, the decrease of the gap with increasing size of the nanocrystals is practically "symmetrical" with respect to the conduction and valence band edges. This can also be seen in Fig. 3c, where we have separately plotted the variation of the HOMO and LUMO orbital energies. It should be noted that although the energy of the HOMO orbitals exhibits a smooth increase as a function of the nanoparticle size, the LUMO orbital energies exhibit a significant dispersion. The LUMO energies of $Ge_{29}H_{36}$ and $Ge_{35}H_{36}$ seem to deviate from the trend observed for the other nanoparticles. Since, this strange behaviour also affects the calculated values of the optical gap it will be further discussed in a next paragraph.

The similarity of the electronic structure of Si and Ge nanocrystals becomes evident in Fig. 2b, where, we have plotted the density of states for Ge_{47}:H_{60} and Si_{47}:H_{60}. As we can clearly see, the two structures are fully homologous. In general the electronic structure of Si and Ge nanocrystals is homologous, and the same is more or less true for the optical properties. However, due to the smaller energy gap of Ge, the diameter of the smallest Ge nanoparticle which could emit in the visible region of the spectrum is expected to be smaller than the corresponding "critical" diameter of Si nanocrystals (2.2 nm).

3.2 Excited state properties: absorption spectrum

In Fig. 3a, we have plotted the variation of both HOMO–LUMO gap and the fundamental optical gap as a function of the diameter of the Ge nanocrystals. The two curves are shifted to lower energies compared to the corresponding of Si nanocrystals but they reveal almost the same size dependence. The diameter of the smallest Ge quantum dot for which the fundamental optical gap lies in the visible area of the spectrum is in the range of 1.9–2.0 nm. The corresponding critical diameter for the case of Si quantum dots is approximately 2.2 nm [3,9,10]. At this point, it should be noted that although the calculated HOMO–LUMO and optical gap shown in Fig. 3a

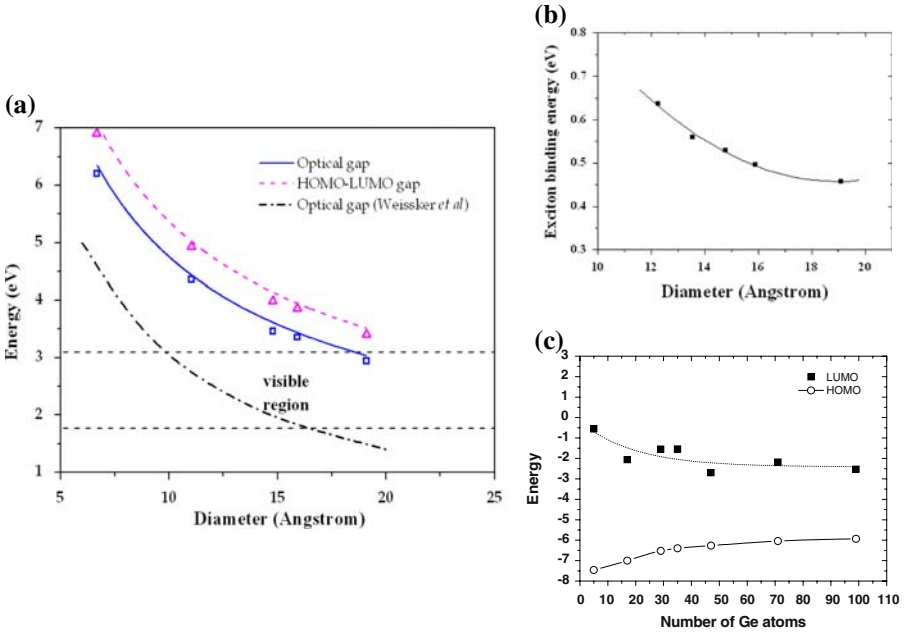

Fig. 3 **a** Variation of the fundamental optical gap and the HOMO–LUMO gap as a function of the nanocrystal's diameter. **b** Variation of the exciton binding energy E_B. **c** Variation of the HOMO and LUMO energies

appear to vary quite smooth, we have found that for some of the nanoparticles the calculations reveal some 'irregularities' (not shown in Fig. 3a). In particular, both the HOMO–LUMO and optical gap of $Ge_{29}H_{36}$ and $Ge_{35}H_{36}$ nanoparticles appear not to vary in accordance with the trend found for the rest of the nanoparticles. For example, since the optical gap of $Ge_{17}H_{36}$ and $Ge_{47}H_{60}$ is 4.36 and 3.46 eV, respectively, it would be expected that the gap of the intermediate $Ge_{29}H_{36}$ and $Ge_{35}H_{36}$ nanoparticles should be smaller than 4.36 eV and larger than 3.46 eV. However, the calculations revealed that the optical gap of $Ge_{29}H_{36}$ and $Ge_{35}H_{36}$ is 4.34 and 4.3 eV, respectively'. It becomes clear that for these three nanoparticles ($Ge_{17}H_{36}$, $Ge_{29}H_{36}$ and $Ge_{35}H_{36}$) the optical (and HOMO–LUMO) gap appear to be practically the same. A similar behaviour was also observed in recent calculations by Tsolakidis and Martin [16], while an analogous but less pronounced behaviour was also observed in earlier studies on silicon nanocrystals [3,10,17]. Since the most striking similarity of these tree nanoparticles ($Ge_{17}H_{36}$, $Ge_{29}H_{36}$ and $Ge_{35}H_{36}$), is that they are all passivated by the same number of hydrogen atoms (36), it seems reasonable to assume that this 'irregularity' may be associated with the passivation of the nanoparticles.

In the same Fig. 3a we can also see the LDA/ΔSCF results of Weissker et al. [7], which successfully describe in a qualitative manner the effect of quantum confinement on the fundamental optical gap. However, their absolute values are significantly shifted to smaller gap energies. This is not surprising since it is well known that simple LDA calculations, seriously underestimates the value of the HOMO–LUMO gap.

Moreover, as it has been shown elsewhere [9,10], the ΔSCF approximation, even when used with the B3LYP functional tends to underestimate the value of the optical gap. Consequently, the combination of the two approximations adopted by Weissker et al. unavoidably leads to a serious underestimation of the optical gap. Additionally, the conclusion that the fundamental optical gap of a 2 nm Ge nanocrystal lies below the lowest end of the visible area of the spectrum is in clear conflict with the experimental results of Wilcoxon et al. [4].

Our results seem to be in a better agreement with the LDA ground state calculations of Melnikov and Chelikowsky [8]. This can be attributed to the fact that, the underestimation of single particle excitation energies derived by ground state LDA calculations is of the same order with the exciton binding energy in our calculations. The agreement deteriorates when the authors subtract from their single particle energies the electron-hole (exciton) Coulomb interaction energy. Although this is physically correct, the LDA single particle transition energies are already underestimated and further subtraction of the exciton binding energy makes them worse. This conclusion is in agreement with the observation made by Vasiliev, Öğüt and Chelikowsky [2], that the corrections incorporated by TDLDA lead to an optical gap which is slightly larger than the LDA single particle HOMO–LUMO gap.

The difference between the HOMO–LUMO gap and the fundamental optical gap can be considered to approximate the binding energy E_B of the exciton formed due to the electronic excitation. As expected by the quantum confinement hypothesis, E_B must decrease as the diameter of the dot increases (Fig. 3b). For diameters around 2 nm, the value of E_B is found to be approximately 0.45 eV. Compared to the case of Si quantum dots, we see that although the Si and Ge nanoparticles with $d \approx 2$ nm contain different number of electrons, the values of E_B practically coincide.

In addition to the fundamental optical gap, we have calculated several low lying (spin and symmetry allowed) electronic transition along with their oscillator strengths. The results for the $Ge_{47}H_{60}$, $Ge_{71}H_{84}$ and $Ge_{99}H_{100}$ nanoparticle are shown in Fig. 4. The first allowed transition of each nanostructure (fundamental optical gap) is found to have a comparably large oscillator strength, which is consistent with the indirect to direct transition in spectra of Ge nanostructures as their sizes decrease. The direct nature of the fundamental optical gap becomes evident in Fig. 5, where we show the major contributions to the lowest allowed transitions for the nanoparticles $Ge_{47}H_{60}$, $Ge_{71}H_{84}$ and $Ge_{99}H_{100}$. The oscillator strengths of the absorption thresholds for all nanocrystals are found to be significantly larger than the corresponding ones of Si nanocrystals, in full agreement with the ground state LDA calculations of Yu et al. [18]. In all cases the HOMO orbitals have t_2 symmetry while the LUMO orbitals have a_1 symmetry. For the case of the $Ge_{71}H_{84}$ nanoparticle, where the LUMO (a_1) and LUMO+1 (t_2) orbitals are almost isoenergetic, the lowest allowed transition (with comparably small oscillator strength) corresponds to the HOMO → LUMO+1 excitation, while the HOMO → LUMO transition is the second one (with large oscillator strength).

The optical gap of the largest nanocrystal in this work ($Ge_{99}H_{100}$) has an approximate diameter of 1.9 nm (including the surface hydrogen atoms) and its fundamental optical gap is at 2.95 eV (420 nm). Although the size of this nanoparticle is still too small to compare directly with existing experiments, the value of 2.95 eV is

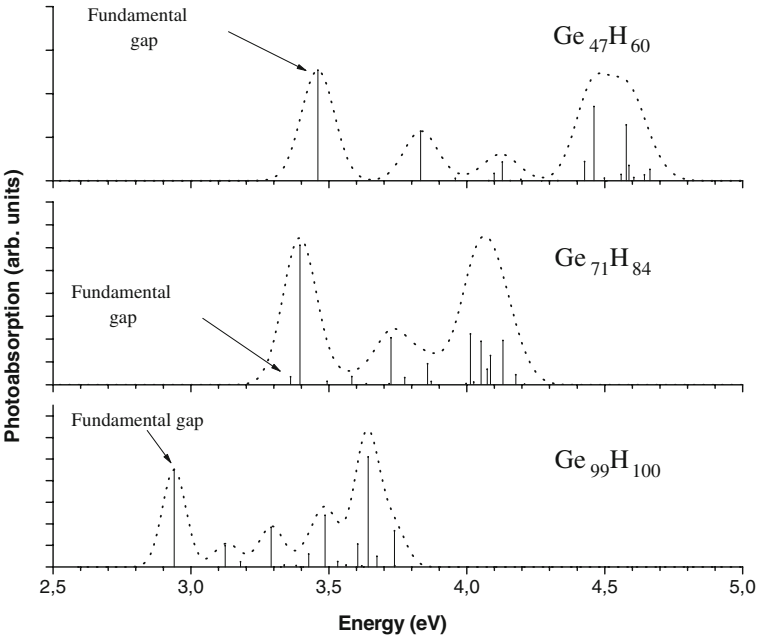

Fig. 4 The 20 lowest allowed transitions of $Ge_{47}H_{60}$, $Ge_{71}H_{84}$, and $Ge_{99}H_{100}$. The *dotted line* is produced by a Gaussian broadening of the *spectral lines*

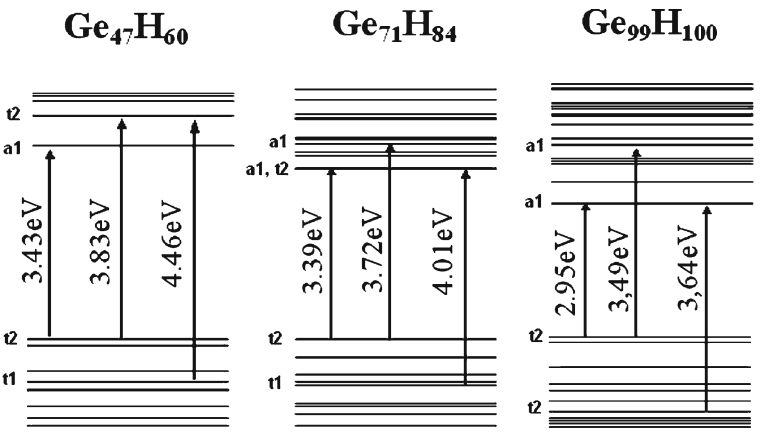

Fig. 5 Energy level diagrams showing the major contributions to the excitation spectrum

in general agreement with the results and conclusions of Wilcoxon et al. [4] and Garoufalis and Zdetsis [19]. Moreover, if the Stokes shift between absorption and emission is taken into account (approximately 0.5–0.6 eV for Si nanocrystals), our results appear to be consistent with the experimental photoluminescence energies reported by Katemitsu et al. [20].

In conclusion, we have calculated (in the framework oh the well tested TDDFT/B3LYP approximation) structural and optical properties of Ge nanocrystals with diameters up to approximately 1.9 nm. We provide reliable results for the fundamental optical gap and the lowest part of the absorption spectrum. The diameter of the smallest Ge nanoparticle able to emit in the visible area of the spectrum is found to be around 1.9–2.0 nm. Our results unambiguously verify the indirect to direct transition of Ge nanoparticles as their size decreases, showing that the HOMO–LUMO transitions are both spin and symmetry allowed.

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References

1. L.T. Canham, Appl. Phys. Lett. **57**, 1046 (1990)
2. I. Vasiliev, S. Öğüt, J.R. Chelikowsky, Phys. Rev. Lett. **86**, 1813 (2001)
3. C.S. Garoufalis, A.D. Zdetsis, S. Grimme, Phys. Rev. Lett. **87**, 276402 (2001)
4. J.P. Wilcoxon, P.P. Provencio, G.A. Samara, Phys. Rev. B. **64**, 035417 (2001)
5. J.R. Heath, J.J. Shiang, A.P. Alivisatos, J. Chem. Phys. **101**, 1607 (1994)
6. M. Palummo, G. Onida, R. Del Sole, Phys. Stat. Sol. **175**, 23 (1999)
7. H. Weissker, J. Furthmüller, F. Bechstedt, Phys. Rev. B. **65**, 155328 (2002)
8. D.V. Melnikov, J.R. Chelikowsky, Solid State Commun. **127**, 361 (2003)
9. A.D. Zdetsis, C.S. Garoufalis, S. Grimme, in *NATO Advanced Research Workshop on "Quantum Dots: Fundamentals, Applications, and Frontiers" (Crete 2003)*, ed. by B.A. Joyce et al. (Springer, Heidelberg, 2005), pp. 317–332
10. A.D. Zdetsis, Rev. Adv. Mater. Sci. (RAMS). **11**, 56–78 (2006)
11. M.E. Casida in *Recent Advances in Density Functional Methods*, ed. by D.P. Chong (World Scientific, Singapore, 1995)
12. P.J. Stephens, F.J. Devlin , C.F. Chabalowski, M.J. Frisch, J. Phys. Chem. **98**, 11623 (1994)
13. J. Muscat, A. Wander, N.M. Harrison, Chem. Phys. Lett. **342**, 397 (2001)
14. TURBOMOLE (Version 5.3) Universitat Karlsruhe (2000)
15. A. Schäfer, H. Horn, R. Ahlrichs, J. Chem. Phys. **97**, 2571 (1992)
16. A. Tsolakidis, R.M. Martin, Phys. Rev. B. **71**, 125319 (2005)
17. C.S. Garoufalis, A.D. Zdetsis, Phys. Chem. Chem. Phys. **8**(7), 808 (2006). doi:10.1039/B513184G
18. M. Yu, C.S. Jayanthi, D.A. Drabold, S.Y. Wu, Phys. Rev. B. **68**, 035404 (2003)
19. C.S. Garoufalis, A.D. Zdetsis, J. Phys. Conf. Ser. **10**, 69 (2005)
20. Y. Kanemitsu, H. Uto, Y. Masumoto, Y. Maeda, Appl. Phys. Lett. **61**, 2187 (1992)