Luminescence and absorption in germanium and silicon nanocrystals: The influence of compression, surface reconstruction, optical excitation, and spin-orbit splitting

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Germanium nanostructures have been predicted to exhibit very strong HOMO-LUMO transitions, contrary to the respective silicon structures. However, few experiments have found luminescence that can clearly be attributed to quantum-confined electron-hole pairs. We resolve this apparent contradiction by identifying four effects that strongly reduce the luminescence intensity in clean, hydrogenated Ge nanocrystals: compression, surface reconstruction, optical excitation, and spin-orbit splitting. The pressure dependence of the HOMO-LUMO gaps and of the radiative lifetimes is explained in terms of the mixing of bulk optical transitions. The localization of electronic states due to a surface reconstruction, and the effect of the optical excitation reduce the luminescence intensity by creating weak transitions below the onset of the absorption spectrum. Spin-orbit coupling reduces the luminescence intensity in a $Ge_{41}H_{60}$ nanocrystal by a factor of about 5 compared to calculations where it is neglected. Throughout the paper, the results are compared with those of equivalent silicon nanocrystals.

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I. INTRODUCTION

Germanium and silicon nanostructures are of great interest for applications in photovoltaics and optoelectronics, in light-emitting devices, and as biomarkers. The two materials, despite their chemical similarity, are optically very different. While quantum-confined Si nanocrystals (NCs) retain the indirect character of the bulk material, several groups predicted very strong HOMO-LUMO transitions (transitions between the highest occupied molecular orbital and the lowest unoccupied molecular orbital) in different Ge nanostructures, rendering these structures quasidirect.[1–5] Moreover, alloying with Ge decreases the radiative lifetimes in Si nanocrystals.[6–9] However, few experiments have demonstrated luminescence clearly originating from quantum-confined excitons in Ge nanostructures. Luminescence is suppressed when the radiative lifetimes of the lowest transitions become longer than the lifetimes connected with nonradiative recombination channels, mostly connected with phonons or defects. In this case, the excited electron-hole pair recombines without luminescence. The general experimental finding therefore stands in apparent contradiction to the prediction of strong HOMO-LUMO transitions. Most luminescence found has been related to defect or interface states[10,11] just as in the case of oxidized Si nanostructures.[12–14] This is due to the fact that in many experimental situations, the Ge NCs are oxidized.

By contrast, in clean, hydrogenated nanocrystals the intrinsic properties are expected to determine the optical properties. Examples are nanocrystals produced by laser pyrolysis[15] and in PECVD under certain conditions,[16] as well as NCs produced by ion implantation in SiC with subsequent annealing.[17] This raises the question as to which effects reduce the transition probabilities and, therefore, the luminescence intensity in these systems in the absence of oxygen. In the present paper, we study four effects that strongly reduce the transition probabilities around the fundamental gap in clean, hydrogenated Ge NCs depending on the experimental situation: compression, surface reconstruction, and the relaxation following an optical excitation. Spin-orbit coupling reduces luminescence compared to calculations where it is neglected. The calculations for Ge are compared with Si NCs throughout the article.

(1) Compression: The Ge nanocrystals prepared in a variety of experiments are compressively strained,[18] e.g., by 3% for ion-implanted Ge in SiC.[17] For bulk Ge, compressive strain changes the character of the band structure and the energetic order of optical transitions decisively.[19] This leads to the question as to what this means for the electronic states and in particular the strength of the optical transitions in the respective NCs. Studying the pressure dependence of the HOMO-LUMO gaps we show that quantum-confined Ge and Si NCs behave as expected in view of the respective bulk band structures. This study has a twofold aim: to investigate the relation with the bulk band structures, and to treat the physical effect in its own right.

(2) Surface reconstruction: In most of the simulations cited above, relatively simple model structures have been used. In particular, a hydrogen passivation is customarily applied to the surface to avoid dangling bonds in the calculations that would prevent luminescence in the physical system. Moreover, the structures are usually constructed as pieces cut from the bulk. In the case of Ge nanocrystals, this leads to HOMO and LUMO wave functions which are well distributed over the whole volume of the nanocrystal.[20] On the other hand, in analogy with the situation at semiconductor surfaces, surface reconstructions are to be expected. These have been investigated for silicon clusters in view of the changes they induce, in particular, of the gaps.[21,22] In the present work, we investigate the influence of a surface reconstruction on the radiative lifetimes in particular of the Ge nanocrystals.

(3) Influence of the optical excitation: The optical properties have mostly been calculated for the ground state. The effects of the excitation of the electronic system on the transition energies and spectra have been introduced, mostly for Si nanostructures, either in the framework of

the *GW* approximation and the Bethe-Salpeter equation of many-body perturbation theory[23–27] or using quantum Monte Carlo calculations[28] or time-dependent density-functional theory (TDDFT).[9,23,29] In addition, the presence of an excited electron-hole pair leads to a structural relaxation producing the Stokes shift, a redshift between the absorption and the emission energy.[1,28,30] The customary way to calculate this effect is to use an occupation constraint in order to create an electron-hole pair. The approximation, sometimes referred to as constrained DFT,[31,32] has been widely used for the calculation of Stokes shifts in nanocrystals.[1,28,30] However, apart from the change of the excitation energies and spectra, the question arises as to what effect the structural changes can have on the radiative lifetimes and, therefore, the luminescence intensity. In the present paper, we show that the structural relaxation following the excitation can indeed strongly change the radiative lifetimes compared to those calculated for the ground-state geometry.

(4) Spin-orbit coupling: Most calculations to date have neglected the spin-orbit coupling. While its effect is small in Si, it is well known that in bulk germanium it induces a rather large splitting in the valence bands. Its effect on the spectra in Ge nanocrystals does not appear to have been studied to date.

The paper is organized as follows. In Sec. II, we detail the models used in the calculation as well as the theoretical methods. After that, we describe in Sec. III the influence of the four aforementioned effects on the optical properties of Ge and Si nanocrystals, before conclusions are drawn at the end.

II. MODELS AND METHODS

We study two different types of structural models. The first one, called "bulklike" in the following, is constructed starting from one Ge or Si atom and adding nearest neighbors shell by shell, in bulklike coordination. All dangling bonds are saturated by hydrogen atoms, which results in $Ge_{41}H_{60}$, $Ge_{83}H_{108}$, $Ge_{147}H_{148}\ldots$ and their Si counterparts. These completely saturated NCs, which are of T_d symmetry, have been studied in the past.[1,9,20] Their HOMO and LUMO wave functions are distributed over the entire NC,[20] and the size dependence of their HOMO-LUMO gaps clearly follows the quantum confinement model.[1] The Ge NCs show strong HOMO-LUMO transitions, while for Si the transitions around the gap are weak.[1,7] However, in tests using molecular dynamics calculations on the Si NCs, these model structures have been found to be unstable under heating.[33]

Therefore, we study a second type of structures, in the following called "reconstructed." First, a spherical structure is cut from the bulk using a given radius and centered at an atom. Then, one-fold coordinated atoms are removed and two-fold coordinated atoms are bonded to form 2×1 dimers. The rest of the dangling bonds are saturated by hydrogen. The resulting structures $Ge_{29}H_{24}$, $Ge_{59}H_{48}$, $Ge_{147}H_{76}$, and their Si counterparts turn out to be very stable. The Si NCs have been heated up to 1500 K in molecular-dynamics calculations without breaking.[33] However, the gaps in these structures do not follow the monotonous decrease with increasing size of the confinement model. We note that NCs of 147 Ge or Si atoms exist for both model types, enabling direct comparison for equal sizes.

The ground-state electronic structure calculations and the ionic relaxation were done by means of the VASP code[34–36] using density-functional theory (DFT) in the local-density approximation (LDA) and with the projector-augmented wave method.[36]

Calculations of the spectra and excitation energies have been carried out by means of the real-space code OCTOPUS[37,38] using time-dependent density-functional theory (TDDFT) in the adiabatic local-density approximation (ALDA), also known as the time-dependent local-density approximation (TDLDA). Following a ground-state calculation, spectra are calculated using the time-evolution formalism. Norm-conserving pseudopotentials have been used. In order to analyze the character of the lowest transitions, calculations using Casida's formalism[39,40] have likewise been carried out.

We discuss the optical gap in terms of the DFT-LDA HOMO-LUMO gap. This approximation neglects both the electron-hole interaction and the "self-energy effects" which describe the excitation of electron and hole due to an optical excitation. However, for the nanocrystals in the size range that we consider, the two quantities cancel rather precisely.[27] Although the question as to what is the correct theoretical description of the gaps is still not conclusively answered (cf. Ref. 1 and references therein) we expect the *change* of the DFT-LDA gap to represent the pressure dependence well. Moreover, for pure Ge NCs, the absorption onset is already well represented, up to a normalization factor describing depolarization effects, by independent-particle spectra as compared to TDLDA calculations.[9]

III. RESULTS

A. Compression and surface reconstruction

Starting from the relaxed NC geometries, compressive strain is modeled by a proportional reduction of all bond lengths d in the nanocrystals. The pressure-dependence of the gaps contains two main effects: the change due to the bond-length reduction, comparable to the same effect in the bulk, and that due to the volume change of the NCs upon compression. To discuss the pure effect of the bond-length reduction, we subtract the part that corresponds to the change of the electronic confinement due to the volume decrease. To this end, we use a fit of the size dependence of nonstrained Ge and Si NCs[1] and subtract the energy difference between the gap energy at the unstrained radius and at the radius reduced by the compression. We thus assume that the two effects act approximately independently.

In Fig. 1, the pressure dependence of the NC gaps shows the qualitative difference between the Si and the Ge NCs. Upon compression, the gap in the Si NCs *decreases*, while it *increases* for the Ge NCs. This is especially clear for the "bulklike" nanocrystals. In Ge, the gaps reach a maximum at between 3% and 5% compression, then they decrease. Comparison with the gaps in the Ge bulk band structure,[19] shown in the inset, shows that the gap in the NCs follows the behavior of the minimum bulk gap. At the beginning, the Γ-L and Γ-Γ gaps are lowest, and both increase with pressure. At about 3% compression, the Γ-X gap, which decreases with compression, becomes lowest. The gaps of the Si NCs show

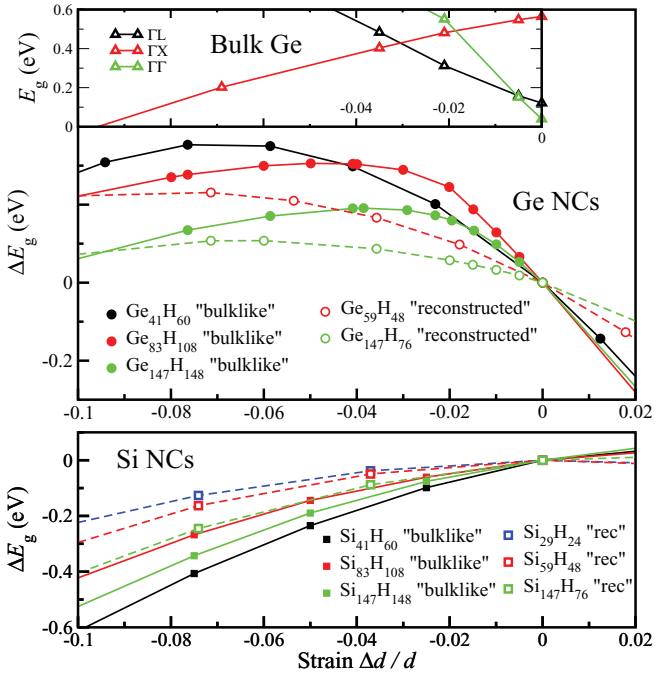

FIG. 1. (Color online) Change ΔE_g of HOMO-LUMO gaps *corrected for the quantum confinement effect* (see text) of Ge and Si nanocrystals as a function of compression. The "bulklike" NCs are given by full symbols and solid lines, their "reconstructed" counterparts by hollow symbols and dashed lines. Inset: Band gaps in bulk Ge as a function of compression, taken from Ref. 19.

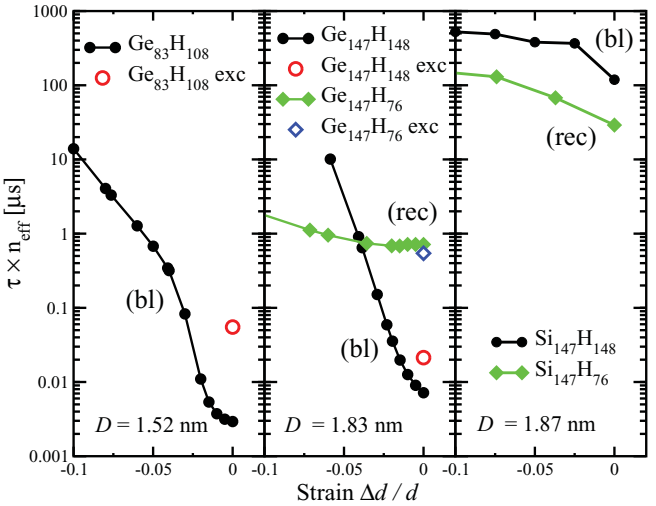

FIG. 2. (Color online) Radiative lifetimes of "bulklike" (bl) and "reconstructed" (rec) Ge and Si NCs of diameter d. The refractive index n_{eff} remains unspecified.

the same correspondence with the bulk bands. Here, the bulk Γ-X gap is lowest in the whole pressure range, and its pressure dependence is negative[19] (not shown).

The correspondence with the bulk pressure dependence can be explained as follows. The electronic states in the NCs can be thought of as constructed from the bulk electronic states. This is intuitively clear within the picture of band folding in the supercell approach. Upon construction of a large supercell, the Brillouin zone (BZ) of this supercell system becomes very small, and the bands are repeatedly folded into this smaller BZ. If we remove material such as to leave a nanocrystal surrounded by vacuum in the cell, the electronic states in the NC can be described as expanded in terms of the bulk electronic states. The confinement will change the states and their energies, and potentially mix them in order to form the electronic states of the NC.[41] Due to this parentage of the bulk states, the pressure dependence of the NC gaps reflects the pressure dependence of the bulk band structures. In Ge, the conduction band minima at Γ and L are very close in energy. The LUMO of the corresponding NCs will therefore be composed of states from these two points. In Si NCs, the LUMO consists of states representing the conduction band minimum close to the X point. In the NCs, this behavior is only modulated by the confinement and the relaxation of the surfaces of the NCs. Thus the deviation from the bulk behavior is strongest for the smallest NC, although the qualitative behavior remains the same.

This explanation confirms the interpretation given earlier[1,9] of the very strong HOMO-LUMO transitions in "bulklike" Ge NCs and the weak ones in Si NCs. As the LUMO of the Ge NCs reflects the states from the Γ and the L points, the direct bulk Γ-Γ transition is strongly present in the HOMO-LUMO transition, which is consequently strong. In Si NCs, by contrast, the transitions around the gap reflect the indirect bulk Γ-X gap and are correspondingly weak.

This, in turn, explains the pressure dependence of the radiative lifetimes τ of the "bulklike" NCs, shown in Fig. 2. To quantify this statement, we calculate τ from the transition energies and transition matrix elements from the DFT calculation,[1] assuming completely thermalized electron-hole pairs following Ref. 42. The lifetimes of the Si NC are not strongly influenced by the compression because the composition of the HOMO-LUMO transition does not strongly change; it remains Γ-X-like, which is reflected in the long radiative lifetimes.

By contrast, the lifetimes in "bulklike" Ge NCs are very strongly increased by the compression because the contribution of the direct Γ-Γ transition to the HOMO-LUMO transition gets weaker. Compression of the order found in many experiments increases the radiative lifetimes of the "bulklike" Ge NCs very strongly, reducing the luminescence intensity accordingly.

These results for the free-standing hydrogen-saturated NCs are coherent with results that have been obtained previously for Ge NCs embedded in a crystalline SiC matrix.[43–45] In these calculations, which use model structures that are strongly compressed, no strong transitions between the HOMO and the LUMO states (or the valence band maximum and the conduction band minimum of the supercell system) have been found, the transitions from NC states in the gap of the matrix go into higher states. This is influenced on the one hand by the pressure effects as studied above, and on the other hand by the type-II heterostructure band line-up of the supercell system.[44,45]

A second effect of similar importance for the lifetimes is the surface reconstruction introduced in the "reconstructed" NCs. The gaps of these NCs follow roughly the same pressure dependence as the "bulklike" structures, but the change with

compression is weaker due to the reconstruction. Inspection of the HOMO and the LUMO wave functions (not shown) of the two Ge_{147} NCs illustrates the difference. While in the "bulklike" structure both states are distributed over the entire NC, they are weakly localized on the surface in the "reconstructed" NC. This results in a weaker pressure dependence. Especially close to the equilibrium, the slope is smaller. Interestingly, this holds for both Si and Ge, with their opposite behaviors.

However, the surface reconstruction has a huge effect on the radiative lifetimes, shown in Fig. 2. Similarly strong effects have been found for different surface passivations.[46] We compare the lifetimes of $Ge_{147}H_{148}$ ("bulklike") and $Ge_{147}H_{76}$ ("reconstructed") in Fig. 2. The reconstruction increases the radiative lifetimes of the unstrained Ge_{147} NC by about two orders of magnitude, reflecting the decrease of the contribution of the bulklike direct Γ-Γ transition in a similar way as compression does. Hereafter, the lifetimes are only weakly pressure dependent.

In the Si NCs, the effect of the reconstruction is weak. The reordering and modification of the many weak Γ-X-like transitions around the gap do not cause major effects. Finally, it is important to note that even after the reduction of the transition probabilities in the Ge NCs following the reconstruction, the radiative lifetimes in Ge NC are about two orders of magnitude shorter than in Si.

The compression and the surface reconstruction have consequences for the full optical spectrum. In Fig. 3, we show the TDLDA absorption spectra of the two 147-Ge-atom NCs, calculated by means of the code OCTOPUS.[38] In the non-compressed "bulklike" NC, an analysis using TDLDA within Casida's formalism[39,40] reveals a strong peak *at* the absorption onset, as it had been predicted earlier by independent-particle results.[1] These strong transitions are responsible for the short radiative lifetime in Fig. 2. Upon compression, this peak is diminished. Already at about 3% compression, it has almost completely vanished. Apart from that, the peak follows the blueshift corresponding to the increase of the gap shown in Fig. 1.

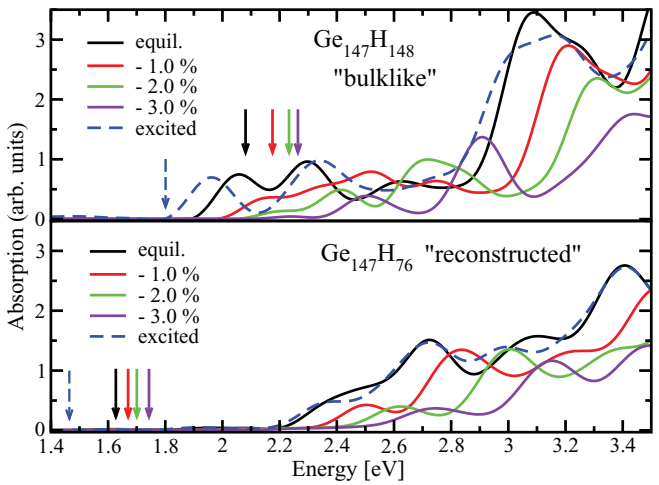

FIG. 3. (Color online) TDLDA absorption spectra of the two directly comparable Ge_{147} nanocrystals for different values of compression and for the excited-state geometry. The "reconstructed" $Ge_{147}H_{76}$ has 18 dimers on its surface. The arrows indicate the lowest excitations from the TDLDA Casida analysis.

For the "reconstructed" NC, the change with pressure is less drastic as far as the intensity is concerned. However, the Casida analysis shows that there are very weak transitions *below* the first peak visible in the spectra. They belong to the weakly localized states at the surface discussed above. Their presence results in the longer radiative lifetimes compared to the "bulklike" NCs. Compression does not change this situation. However, the lowest peak visible in the spectrum is blueshifted. It probably corresponds to the strong first peak in the "bulklike" NC.

B. Effect of optical excitation

A third effect that can substantially change the radiative lifetimes is the optical excitation connected with the luminescence. Emission follows the recombination of an electron-hole pair. The geometry of the NCs changes in the presence of the electron-hole pair, causing a red shift of the emission as compared to the absorption (Stokes shift). We model the excited electronic configuration for the unstrained NCs by transferring an electron from the HOMO to the LUMO Kohn-Sham orbital. With this occupation constraint discussed in the introduction, we determine the relaxed geometry. For the Ge NCs, this procedure finds its justification in the fact that the Casida analysis in TDLDA shows that both the excited- and the ground-state geometry have a lowest transition corresponding to an almost pure transition between Kohn-Sham states.

The excitation of the electron-hole pair may break the symmetry of the system.[28,30] In the case of the "bulklike" T_d NCs, this results in the lifting of the threefold degeneracy of the HOMO. The gap is reduced, and the lowest transition is now much weaker than before. The interesting result is that not only the degeneracy is lifted, but the lowest transition is now much weaker than each of the previously degenerate transitions. This results in a strong increase of the radiative lifetimes included in Fig. 2, more than one order of magnitude for the "bulklike" $Ge_{83}H_{108}$, slightly less in the bigger $Ge_{147}H_{148}$. On the other hand, the "reconstructed" $Ge_{147}H_{76}$ is less sensitive to the excitation because weak transitions below the absorption onset are already present, and due to its larger stability. The radiative lifetime remains almost unchanged, as does the overall spectrum shown in Fig. 3.

We note that the strong effect of the structural relaxation after the electronic excitation will be smaller in the case, for instance, of NCs embedded in a matrix. By contrast, for free-standing NCs, the calculations are expected to give reasonable results.[1,28,30]

C. Influence of spin-orbit coupling

For Ge, we have carried out TDLDA calculations including the spin-orbit coupling, again with the OCTOPUS code using the time evolution formalism. For this, we used the relativistic pseudopotentials of the OCTOPUS distribution. We have used the "bulklike" Ge_{41} cluster which exhibits the general behavior of the nanocrystals[47,48] but is still amenable to a calculation using spin-orbit coupling.

The result is shown in Fig. 4. The two lowest peaks found at about 3.15 and 3.45 eV in the spectrum without spin-orbit

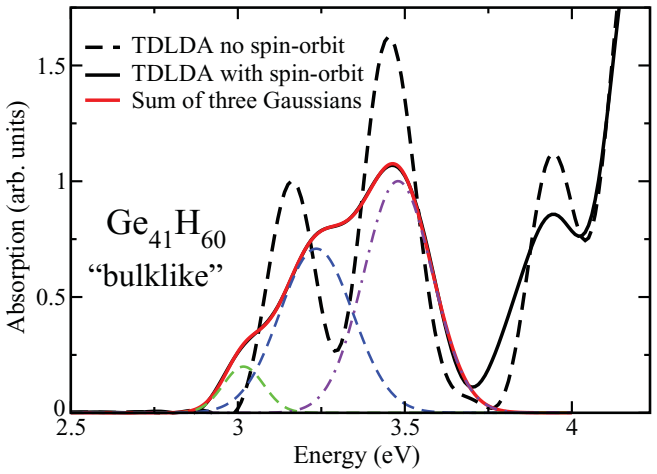

FIG. 4. (Color online) Absorption spectra of the "bulklike" $Ge_{41}H_{60}$. We compare TDLDA calculations without spin-orbit coupling with those where it is included. We also show three Gaussians used to fit the latter result. Between 2.7 and 3.7 eV the sum of the three Gaussians is practically on top of the calculated result.

coupling are split into two peaks each such that the second and the third peaks of the group are roughly at the same energy. In order to estimate the change in the radiative lifetimes, we determine the respective strength of each of the peaks. To this end, we fit three Gaussians to the spectrum (assuming already the same energy for the two middle peaks). This leads to a very good fit of the group of peaks as shown in the result in Fig. 4. We find that roughly one-fifths of the spectral weight of the first peak in the spectrum calculated neglecting the spin-orbit coupling is carried by the small lowest peak calculated including the spin-orbit coupling.

The influence of the splitting on the radiative lifetimes will now depend on the temperature. For $T = 0$, the electron and the hole are in the LUMO and the HOMO, higher or lower states are not involved, and the transition probability would be divided by a factor of 5, corresponding to the ratio between the strength of the lowest peak without and the lowest peak with spin-orbit coupling. However, for higher temperatures, the effect is mitigated by the occupation of the higher (lower) levels, leading to a weaker increase of the radiative lifetimes. The increase of the radiative lifetimes, therefore, lies probably between a factor of 2 and 5, the latter being its upper limit.

IV. CONCLUSION

We have identified four effects that greatly reduce the transition probabilities at the gap of germanium NCs: compression, surface reconstruction, the optical excitation of electron-hole pairs, and spin-orbit coupling. This resolves the apparent contradiction between the theoretical predictions of strong photoluminescence in clean, hydrogenated Ge NCs and the fact that few experiments have found luminescence from confined excitons. Moreover, we have shown for both Ge and Si that in "bulklike" H-saturated nanocrystals the pressure dependence of the HOMO-LUMO gaps can be explained with reference to the bulk band structures. This explains likewise the strong radiative transitions found at the gap in "bulklike" Ge, but not Si, nanocrystals. Surface reconstruction attenuates this behavior. Calculations of radiative lifetimes in the framework of (static) DFT are confirmed by TDDFT calculations of transitions and absorption spectra. It follows from these conclusions that the extreme sensitivity of the Ge NCs to structural changes might be exploited to tune their optical properties in a controlled way. Spin-orbit coupling increases the lifetimes in the $Ge_{41}H_{60}$ NC by less than one order of magnitude compared to calculations where it is neglected.

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