

Comment on "Size Dependence of Excitons in Silicon Nanocrystals"

In a recent Letter [1] Hill and Whaley present a tight binding calculation of excitons in silicon crystallites and conclude that their results agree quantitatively with photoluminescence data, proving that the photoluminescence mechanism is dominated by radiative recombination across the gap. They note, however, that their prediction is in contradiction with those of two previous calculations, a tight binding [2] and a pseudopotential one [3], which give practically identical results. Their explanation for this difference is that their improved agreement is due to the superiority of their tight binding prediction using an expanded basis. In this Comment we want to express some warning against the confusion which might arise from such oversimplified statements.

The basic point is that all three calculations are of semiempirical nature. This means that they are based on the postulate of "transferability" of the parameters from the known bulk band structure (to which they are fitted) to the unknown crystallite case. If this is accepted, then an essential criterion by which a particular semiempirical model can be judged is how well it describes the bulk band structure. In this regard the models of Refs. [2] and [3] both give extremely good fits to the silicon bulk band structure over a large energy interval (18 eV for Ref. [2] with a rms error of 0.1 eV [4]) containing the valence band as well as the conduction band. It is thus not surprising that they produce identical results for the crystallites. On the contrary, the sp_3s^* model of Ref. [1] gives in comparison a very poor description of the conduction band, which is much too flat, and consequently must underestimate the band gap, as it indeed does. This can be judged by the conduction band effective masses, practically exact for Ref. [2] ($m_l = 1.09, m_t = 0.2$) but much too large for Ref. [1] ($m_l = 1.62, m_t = 0.74$). Thus, from the point of view of semiempirical theory, the calculation of Ref. [1] is much less accurate than those of [2] and [3]. The point that it uses a larger basis set than Ref. [2] is not a good argument since it does not apply with respect to the plane wave calculation of Ref. [3] which produces the same results as [2]. The fact that Ref. [1] gets quantitative agreement with luminescence is obviously not a proof of the accuracy of this particular calculation.

The previous criterion for "transferability" only strictly applies to clusters which are large enough for the Hamiltonian in the interior to become identical to the

bulk one (i.e., roughly speaking, with diameter larger than 1 nm). Then the solution of the problem at energy E can be obtained as a combination of the bulk solutions at this energy plus the appropriate boundary conditions. This means that a second criterion must be that these are correctly simulated in the model. In Ref. [2], we have used Si-H terminations with coupling parameters large enough to avoid Si-H states in the gap in order to simulate an interface with a material with a large band gap (like SiO_2). This approach is justified by the agreement with pseudopotential [3] and local density (LDA) [5] calculations treating real Si-H bonds.

Finally, our point of view is completely supported by a quite recent compilation [5] of *ab initio* LDA calculations for Si crystallites, wires and slabs in which the predicted gap is shifted by +0.6 eV to account for the well-known underestimation of the bulk band gap by this method. The corresponding predictions are in quantitative agreement with our values (including crystallites [2] and wires [6]) and, of course, with those of empirical pseudopotential calculations.

In conclusion, we have shown that the agreement between the predictions of Ref. [1] and photoluminescence cannot be taken as convincing evidence that luminescence is due to transitions across the fundamental gap of the crystallite.

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