

Optical Properties of Germanium Quantum Dots

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We report a combined theoretical and experimental investigation of quantum confinement effects on the E_1 interband structures in the optical spectra of Ge quantum dots. The experimental average radius goes from ≈ 12 to ≈ 60 Å. A blueshift of the E_1 absorption peak (up to 0.1 eV) and a strong reduction in the oscillator strength, are measured effects of the quantum confinement. The theoretical analysis is performed for nanocrystals up to 15 Å through a semi-empirical tight-binding approach. We overcome the single-particle scheme including, in a perturbative approach, the Coulomb electron–hole interaction which induces a red-shift of the E_1 peak with respect to the one-electron calculation.

1. Introduction The interest in quantum dots is essentially related to the strong modifications of the basic properties of the material induced by space confinement, with remarkable effects on the joint density of states, optical absorption and photoluminescence spectra, nonlinear response, etc. [1, 2]. While the main efforts have been devoted to III–V and II–VI semiconductors (due to the fact that the direct gap allows the observation and measurements of relevant signals), increasing attention is now being paid to Si and Ge quantum dots. This work is based on the study of the optical response in Ge quantum dots above the gap: more specifically on a comparison between experimental data and a theoretical treatment of the E_1 structure.

2. Experimental Section The nanocrystals investigated, grown in ultra high vacuum by an evaporation–condensation self-organized technique described elsewhere [3], are embedded in an amorphous transparent matrix on a sapphire substrate. The average radius R goes from 15 to 60 Å, with a size dispersion $\sigma/R \leq 20\%$. The size distribution for each sample was determined by means of TEM analysis, as illustrated in Ref. [4]. The absorption spectra have been collected at 77 K in an energy range between 0.6 and 6 eV using a spectrophotometer Varian Cary 5 with a spectral resolution better than 0.01 eV in the range of interest; in Fig. 1 we report the spectra (in arb. units) for the dots with 12 and 15 Å of average radius. The spectral feature at about 2.5 eV is related to the E_1 and $E_1 + \Delta_1$ interband transitions between two nearly parallel bands along the Δ direction in the Brillouin zone. The size dependence of its spectral position and the related oscillator strength have been discussed in Ref. [5].

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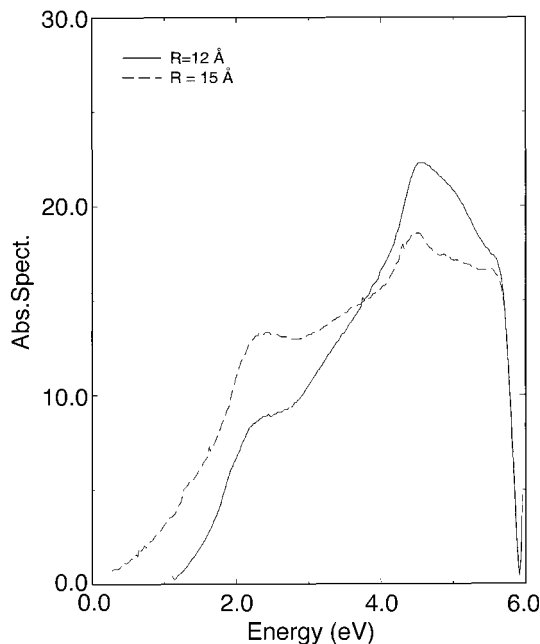


Fig. 1. Measured nanoparticle absorption (in arb. units) obtained by subtracting the spectrum of a sample without Ge from the collected spectra. The cut-off at about 6 eV is due to the sapphire substrate

3. Theoretical Analysis

3.1 One-particle calculations The optical spectra are calculated by modelling the experimental samples with spherical dots, where the atomic positions are fixed at the bulk interatomic distances and hydrogen atoms are used to saturate the dangling bonds.

The one-electron states of the considered Ge nanocrystals are obtained in a semi-empirical tight-binding (TB) approach, and the matrix elements of the momentum operator between valence and conduction states are

computed as described elsewhere [6]. In order to have a good description also of the E_2 peak in the optical spectrum (and not only of the E_1 peak) it is necessary to go beyond the first-neighbor parametrization proposed by Vogl et al. [7], and consider interactions up to second neighbors. The set of TB parameters (obtained by fitting the band structure calculated from first-principles in Density Functional Theory-Local Density Approximation + Scissor operator) is the following (in eV):

$$\begin{aligned}
 E_s &= -6.0054, & E_p &= 2.5102, & E_{s^*} &= 12.5083; \\
 1ss\sigma &= -1.7433, & 1sp\sigma &= 2.2960, & 1pp\sigma &= 3.1950, & 1pp\pi &= -0.9692, \\
 1s^*p &= 3.3935; \\
 2pp\sigma &= -0.1999, & 2s^*p &= -0.1959.
 \end{aligned}$$

The first eight parameters (on site and first-neighbour ones) are close to those of Ref. [7]; the last two (second-neighbour interactions) are included here for the first time together with the s^* orbitals, and allow a better description of the conduction bands.

Figure 2 shows the bulk dielectric function obtained using this tight-binding parametrization, compared with that elaborated by Vogl et al. The experimental spectrum [8] and the theoretical spectrum obtained by a first-principle calculation (Density-Functional-Theory, DFT) are also reported in the same figure. The experimental curve shows the E_1 peak at 2.5 eV, a well pronounced peak E_2 at 4.26 eV, and a shoulder at 3.5 eV. The first-principle spectrum is almost rigidly redshifted of about 0.3 eV with respect to the experimental result while the intensity of the E_1 peak is underestimated, due to the neglect of the excitonic effect. In the theoretical spectrum obtained with Vogl et al.'s sps^* first-neighbours tight-binding Hamiltonian the situation is reversed: a large peak at 3.5 eV is present, while the structure at 4.26 eV appears just as a shoulder.

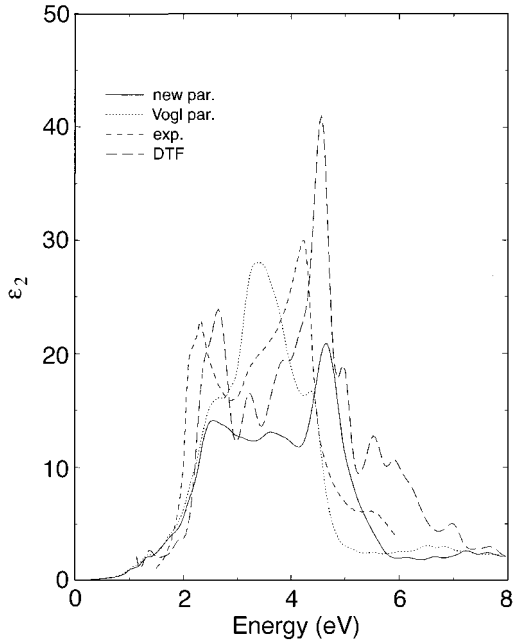


Fig. 2. Theoretical absorption spectra of bulk Ge versus the experimental one [8]. We report the one-particle tight-binding results obtained with Vogl et al.'s (dotted line) and our parametrization (solid line), as well as the spectrum obtained by a first-principle approach within Density Functional Theory in the Local Density Approximation (long dashed line)

This error, which is due to the poor description of the second conduction band, is clearly removed in the spectrum obtained with the new tight-binding parametrization. For this reason, differently from a previous work [9] where Vogl et al.'s parametrization was used, we can analyze now also the energy position of the E_2 peak in the optical spectra as a function of the dot radius.

The imaginary part of the dielectric function of the nanocrystals is calculated following the same approach used for the bulk, but using the dot volume to normalize the result. The $\epsilon_2(\omega)$ of three spherical dots ($\text{Ge}_{87}\text{H}_{76}$, $\text{Ge}_{293}\text{H}_{172}$ and $\text{Ge}_{633}\text{H}_{300}$ with radii of 8, 12, 15 Å, respectively; here the notation Ge_xH_y indicates a dot with x Ge atoms surrounded by y H atoms used to saturate the dangling bonds) are shown in Fig. 3. The structures appearing above 6 eV are essentially due to the presence of the surface hydrogens.

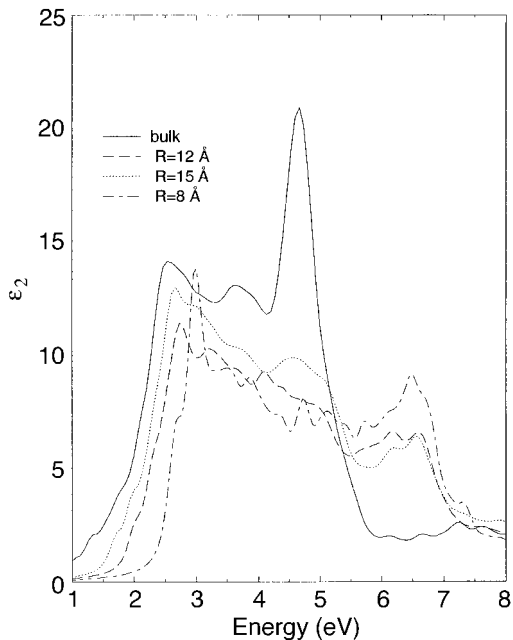


Fig. 3. One-particle tight-binding optical spectra, obtained for three different dot sizes. The tight-binding optical spectrum of bulk Ge is shown for comparison

Table 1
Shifts (in eV) of the E_1 and E_2 peaks with respect to the bulk values for two Ge dots

		exp	TB	TB + exc
$R = 12 \text{ \AA}$	ΔE_1	0.08	0.2	0.1
	ΔE_2	0.12	0.33	
$R = 15 \text{ \AA}$	ΔE_1	0.075	0.11	0.04
	ΔE_2	0.015	0.00	

3.2 Excitonic effects Although Delerue et al. [10] have shown, in a recent paper, that the single-particle calculations give quite accurate values for the excitonic gap of semiconductor nanocrystals, because the self-energy and Coulomb corrections almost exactly cancel each other, the inclusion of the electron–hole Coulomb interaction is necessary here because of the stronger excitonic effects visible in the optical spectra (as on the E_1 peak in the bulk spectrum [11]).

The energy differences between valence and conduction bands in the calculation of $\epsilon_2(\omega)$ are taken including the electron–hole Coulomb attraction within first-order perturbation theory, as described in Ref. [9]. The effect of the inclusion of the Coulomb interactions for the dot of $R = 12 \text{ \AA}$ is shown in Fig. 4. The corresponding values for the peak shifts are reported in the third column of Table 1. The calculations shown here are limited to the energy range up to and around E_1 , leaving out E_2 , for the sake of computational speed. Electron–hole interaction effects around E_2 will be the object of a forthcoming work.

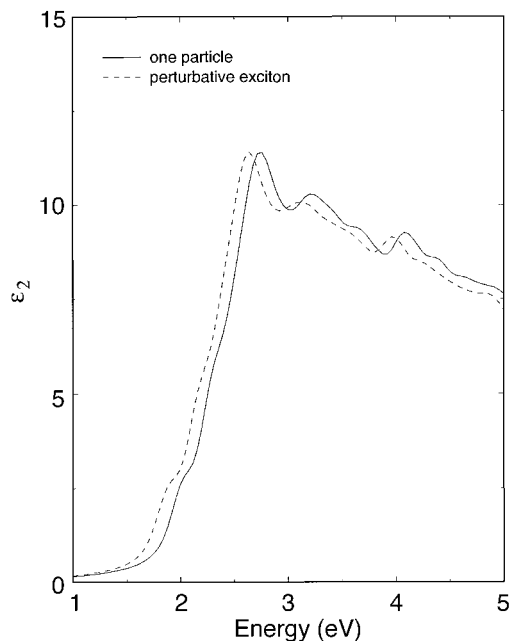


Fig. 4. Tight-binding optical spectra obtained including the diagonal electron–hole interaction, compared with the one-particle result for the dot of $R = 12 \text{ \AA}$ ($\text{Ge}_{293}\text{H}_{172}$)

4. Conclusions In conclusion, we have compared experimental and theoretical spectra of Ge dots. One-electron calculations of the absorption spectrum predict a blueshift of E_1 much larger than observed. The inclusion of the electron–hole interaction at the perturbative level reduces the calculated shifts by a factor of about two and allows a good qualitative comparison with the experiments. A quantitative comparison of theory and experiment requires, in addition to extending the excitonic calculations to the energy range around E_2 , also a thorough treatment of light propagation, including local-field and geometry effects.

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