

**Dopants in Diamond Nanoparticles and Bulk.  
Density Functional Study of Substitutional  
B, N, P, SB, S, PN, O, NN, and Interstitial H**

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We show how the electronic structure of doped diamond nanoparticles can be used to predict the donor and acceptor excitation energies of doped n-type and p-type semiconducting bulk diamond. By the same token, electronic structures of doped diamond nanoparticles may be estimated from the bulk properties. The method uses good quality quantum chemical calculations on small clusters of diamond and doped diamond. Excitation energies are calculated based on differences in total energies of neutral and positively or negatively charged clusters. When charges are free in the bulk, as for an electron in the conduction band or a hole in the valence band, and the weakly bonded electron associated with substitutional B, a simple particle in a box kinetic energy of cluster confinement is taken into account.

The B3LYP density functional theory with 6-31G atomic basis functions is used on the diamond cluster model C<sub>44</sub>H<sub>42</sub> and diamond defect cluster models XC<sub>43</sub>H<sub>42</sub>, XYC<sub>42</sub>H<sub>42</sub>, and C<sub>44</sub>H<sub>42</sub> with an interstitial H at the midpoint of the central C-C bond. The two central atoms, C-C, C-X, X-Y, and the C atoms in C-H-C are allowed to relax along the [111] directions as are the six C atoms that are nearest neighbors to the defects.

The diamond band gap is calculated from the C<sub>44</sub>H<sub>42</sub> cluster as follows. First, the cluster model's ionization potential, IP<sub>cm</sub>, is calculated as the energy for the process



where the electron is at the vacuum level. The cluster harbors an electron hole at the top of its valence band with confinement energy E<sub>ch</sub>. The predicted energy level for a bulk valence band hole is then

$$E(h) = -\text{IP}_{\text{cm}} + E_{\text{ch}} \quad (2)$$

The cluster model electron affinity, EA<sub>cm</sub>, is the calculated energy for the process



The electron at the bottom of the conduction band has confinement energy E<sub>ce</sub> so that the predicted energy level for a bulk conduction band electron is then

$$E(e) = -\text{EA}_{\text{cm}} - E_{\text{ce}} \quad (4)$$

The predicted bulk band gap is then

$$E_g = E(e) - E(h) \quad (5)$$

E<sub>g</sub> equals the cluster band gap reduced by E<sub>ch</sub> + E<sub>ce</sub>. Earlier work has discussed the relationship between nanoparticle and bulk band gaps in semiconductors using Eqs. (2), (4), and (5) and a bulk effective mass approximation for the charge carriers.<sup>1-3</sup> The bulk effective mass approximation breaks down for very small nanoparticles<sup>2,3</sup>, no doubt including our clusters. Simply using the electron mass for the electron and the

hole and using the particle-in-a-box energy for E<sub>ch</sub> and E<sub>ce</sub> in our clusters, which measure 0.92nm by 0.68nm by 0.68nm yields a band gap of 5.61eV, which compares well with the 5.49eV measured value.

No charge confinement energy is used for the positively charged donor cluster models with X = P, N, S, and O, and XY = SB, PN, and NN, and for H(i) because the positive charge is associated with the defect. For the negatively charged acceptor cluster model with X = B, the confinement energy is used because the electron is bonded only weakly to the substitutional boron atom by a weak electron pairing energy, and so it has an orbit much larger than the cluster.

Predicted bulk excitation energies based on our model are in the Table below. The optical results are vertical

Defect	Excitation Energy (eV)	
	Optical	Thermal
B acceptor	0.99	0.37 (0.37)
P donor	1.02	1.02 (0.46)
SB donor	1.79	1.49
N donor	2.77 (>2.2) <sup>a</sup>	1.53 (1.60)
S donor	1.93	1.53
PN donor	2.58	1.77
O donor	3.11	3.10
NN donor	4.00 (3.8)	3.54
H(i) donor	3.84 (4.1)	3.82

a. Experimental literature results are in parentheses.

excitation energies and the thermal results include relaxation of atoms in the ionized clusters. The boron acceptor level is in agreement with experiment and most of the predictions are close the experimental results. None of these donors are predicted to be shallow.

The confinement energy used above is based on an approximate estimate of the cluster size and on the simple particle-in-a-box model. The size is particularly difficult to determine but nevertheless these results indicate that a single parameter exists, at least for this cluster, that allows fitting of the diamond band gap and six known donor and acceptor excitation energies to good accuracy. The current model apparently has predictive value with errors of about 0.5 eV or less. Calculations at this level allow theoretical screening for potential shallow donor and shallow acceptor defects.

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