New Theoretical Model for the Diamond 1*s* Core Exciton

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The binding energy of the diamond 1*s* core exciton has a measured value of 0.2 eV, in marked contrast to the 1.7-eV binding energy of the physically similar nitrogen donor in diamond. Using the local-density approximation to study the core exciton, we find the shallow exciton binding energy is explained by dipole selection rules which prohibit occupation of a deep exciton gap state in single-photon excitation. This deep state has not yet been observed experimentally, and the calculation predicts a binding energy in the range of 0.8–1.7 eV.

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The binding energy of the diamond 1*s* core exciton has a measured value of about 0.2 eV [1], in marked contrast to the much larger binding energy of the nitrogen donor in diamond, 1.7 eV [2]. A simple qualitative argument, however, suggests that these two binding energies should be very similar. A core exciton is formed by the excitation of an electron from a tightly bound core state, leaving behind a core hole on one of the atoms in the system. In the process, the effective nuclear charge of this atom seen by the valence and conduction electrons changes from Z to $Z+1$, i.e., to that of the adjacent atom in the periodic table, the principal donor atom. The electronic structure in the vicinity of the fundamental band gap should therefore be quite similar for the core-exciton and donor systems. In this paper we use first-principles, quantum-mechanical calculations based on the Hohenberg-Kohn-Sham local-density approximation (LDA) to study the diamond 1*s* core exciton. We find that the observed difference between the core-exciton and nitrogen-donor binding energies is due to dipole selection rules which prevent a direct transition from the 1*s* core level to a symmetric exciton state lying deep in the diamond band gap. Instead, the observed core exciton corresponds to a shallow, *p*-like state. The symmetric deep state is the analog of the nitrogen donor state in diamond, and the calculation predicts a binding energy in the range $0.8 < E_b < 1.7$ for this level which has not yet been seen experimentally.

The diamond core exciton has an interesting history in the literature. Morar *et al.* [1] measured the binding energy of the diamond core exciton using x rays from a synchrotron source in a high-resolution, secondary-electron partial-yield experiment. The x rays in this experiment directly excite 1*s* core electrons into unoccupied states, and the measured partial yields correspond to the absorption coefficient as a function of x-ray energy. The data span a region stretching from a few eV below the fundamental absorption edge to roughly 50 eV into the conduction band (CB), and yield a binding energy for the core exciton of 0.189 eV.

Two previous theoretical treatments of the diamond core exciton have supported the shallow measured binding energy for the exciton, but neither addressed the qualitative difference between the measured core-exciton and nitrogen-donor binding energies, and neither recognized the importance of dipole selection rules in the creation of the exciton. Morar *et al.* [1] used the hydrogenic effective-mass theory (HEMT) [3] to compare their measurements of the diamond core-exciton binding energy with theory. Using the appropriate parameters for diamond, they obtain an HEMT prediction of 0.191 eV for the core-exciton binding energy. The authors note that the rather precise agreement between the HEMT and experiment is probably fortuitous. Indeed, the HEMT is not expected to work well for diamond, because of its large band gap (5.5 eV) and small dielectric constant ($\epsilon=5.84$). Morar *et al.* [1] point out that while the HEMT appears to correctly describe the diamond core exciton, it fails to describe even qualitatively the core-exciton binding energies in systems such as Si and GaAs, where the theory works well for valence excitons. Furthermore, the exciton state described by the HEMT is the direct analog of the nitrogen-donor state. In fact, the simple HEMT cannot distinguish between the donor and the core exciton, and would give identical shallow binding energies for both systems.

Alves *et al.* [4] used the $X\alpha$ theory in a cluster formulation to study the core exciton. Their results also suggested a shallow exciton binding energy, in apparent agreement with experiment. However, the exciton state they study is again the symmetric deep state, and the technique they use for calculating the exciton binding energy is valid only in the limit of very large clusters, and is probably not converged for the cluster size studied in Ref. [4].

As we show below, the use of dipole selection rules is crucial for understanding the diamond core-exciton system. Hjalmarson, Büttner, and Dow [5] noted the importance of selection rules in their empirical tight-binding model for core excitons. The model successfully predicts trends in core-exciton binding energies for an array of elemental and compound semiconductors. For diamond, however, the model gives a negative binding energy for both the deep, *s*-like exciton state, and the shallow, *p*-like state.

Our calculations are based on the Hohenberg-Kohn-Sham LDA [6]. In the LDA, the total energy of an electronic system is a functional of the electronic density ρ, which can be written as

$$\rho(\mathbf{r}) = \sum_i f_i |\psi_i|^2 ,$$

where the ψ's are one-electron orbitals which are the self-consistent solutions of the Kohn-Sham equations [6] and the f's are occupation numbers. The LDA is, in principle, a ground-state theory, and as such yields ground-state structural properties and charge densities in very good agreement with experiment. For excited states the use of the LDA can be formally justified only for the lowest state of each symmetry different from the ground state. However, the theory is frequently applied in an essentially empirical way to obtain information about higher-lying states. In the present calculation, the LDA is expected to give a qualitatively correct description of the core-exciton states in the diamond band gap.

To study the core exciton, the occupations are constrained so that $f_{1s}=0$ and $f_{\text{ex}}=1$, for a given core state and the exciton level, respectively. Within this constraint, full electronic relaxation is allowed around the core hole. By directly including the core hole in the calculation, the Coulomb interaction of the core hole and the excited electron is treated exactly, and the quantum-mechanical exchange and correlation interactions are treated approximately through the LDA. Because of the point-defect nature of the core hole, the calculations are carried out in a finite cluster geometry, with the core hole located on the central atom in the cluster. The extremely accurate computational method used in this work is based on the linear-combinations-of-atomic-orbitals framework, using Gaussian orbitals. The details of our approach can be found in Ref. [7].

To test our results for cluster size effects, we have performed systematic calculations on the C_5H_{12}, $C_{17}H_{36}$, and $C_{29}H_{36}$ clusters, consisting of one, two, and three near-neighbor shells of carbon atoms around a central carbon. The carbon atoms in these clusters are placed at their ideal, bulk-diamond positions, and hydrogen atoms are used to tie off dangling bonds on the cluster surfaces. One measure of the convergence of the electronic environment in the cluster interiors is to compare the eigenvalues of the 1*s* core states on the central and first-neighbor atoms in clusters without a core hole. In an infinite crystal, the core eigenvalue associated with each atom is identical to all the others. In the clusters, however, the presence of the cluster surface introduces chemical shifts of the core levels near the surface. Comparing the core eigenvalues of the central and first-neighbor atoms in the smallest cluster, in which the first-neighbor atoms make up the cluster surface, we find a substantial difference of 6.0 eV. This difference drops to 0.5 eV for the C_{17} cluster, and to only 0.05 eV for the C_{29} cluster, suggesting that the interior of the largest cluster is quite bulklike.

A second, complementary measure of convergence is the gap between the highest occupied and lowest unoccupied electron states in the pure cluster. This cluster band gap should converge to the bulk band gap in the large cluster limit. For the three clusters studied here, the calculated gaps are 7.6, 4.4, and 4.5 eV, showing good convergence for the largest clusters. The corresponding LDA bulk band gap for diamond is 4.1 eV [8]. Note that a part of the difference between the bulk and cluster gaps is likely due to the fact that the CH bond is slightly stronger than the CC bond. This should have the effect of lowering the energy of the states at the valence-band maximum, which are concentrated at the cluster surface, thereby increasing the cluster gap.

When a core electron is removed from the central carbon atom to form the exciton, two defect states appear in the cluster band gap, as shown schematically in Fig. 1. The state a_1 in Fig. 1 has an antibonding character and transforms in the totally symmetric (*s*-like) A_1 representation of the T_d point group, in complete analogy to the nitrogen-donor state [9]. The upper state t is *p*-like, transforming in the T_2 representation. Since the core excitons are created experimentally via one-photon excita-

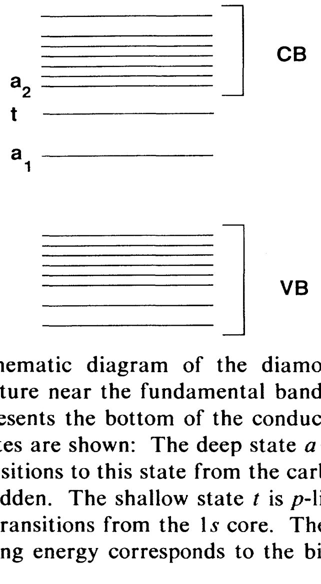

FIG. 1. Schematic diagram of the diamond core-exciton electronic structure near the fundamental band gap. The state labeled a_2 represents the bottom of the conduction band. Two exciton gap states are shown: The deep state a_1 has *s*-like symmetry, and transitions to this state from the carbon 1*s* core level are dipole forbidden. The shallow state t is *p*-like, and is occupied by direct transitions from the 1*s* core. The experimentally measured binding energy corresponds to the binding energy of this state.

tion, a transition to the a_1 state from the 1s core is dipole forbidden. The lowest allowed transition is to the p-like state t and the experimental core-exciton binding energy thus measures the depth of the t state with respect to the bottom of the CB. By contrast, in the donor system the a_1 level is occupied in the ground state, and the donor binding energy measures the depth of the a_1 state.

Figure 2 compares the calculated cluster density of states (DOS) in the CB region for the C_{29} cluster with the measured photoabsorption data of Ref. [1]. The upper theoretical curve shows the full DOS for the exciton calculation, while the middle curve is the DOS weighted by the calculated dipole matrix element connecting the upper state with the 1s core level. In both curves a 0.5-eV Lorentzian broadening was used for the discrete cluster eigenvalues for the CB states, while the experimental width of the exciton peak (0.25 eV) was used to broaden the exciton states. The position of the t peak was used to align the theoretical curves with the experimental data, shown at the bottom. Whereas the unweighted DOS curve shows little similarity to the experimental data, the similarity between the weighted DOS curve and experiment is striking. Note that the a_1 state, which appears as a shoulder on the leading edge of the top curve in Fig. 2, is clearly missing from the experimental data. Figure 2 demonstrates both the importance of dipole selection rules in the core-exciton problem, and the usefulness of the LDA for interpreting the experimental data.

While the LDA cannot be expected to give precise predictions for the exciton-state binding energies, it remains interesting to calculate them nonetheless. We define the LDA binding energies of the gap states as $a_2 - a_1$ and $a_2 - t$, respectively, in the limit of infinite cluster size. Here a_2 is the lowest unoccupied state above a_1 and t, and represents the CB minimum. While other definitions of the exciton binding energy are possible, for example, using the ionization energy of the 1s core level and the electron affinity of the cluster to define the CB minimum [10], we find the definition given above to be the best converged as a function of cluster size. We note that this definition based on eigenvalue differences corresponds very closely to total-energy differences between clusters with $f_{\text{exc}} = 1, f_{a2} = 0$ and $f_{\text{exc}} = 0, f_{a2} = 1$. For C_{17}, for example, the total-energy-based binding energies differ from the eigenvalue-based values by less than 0.05 eV in all cases.

Table I presents the LDA binding energies for the three clusters studied. While neither binding energy is completely converged as a function of cluster size, the results clearly indicate a_1 to be a deep state, and t to be considerably shallower. Note that the analogous calculation for the nitrogen-donor level in the C_{17} cluster yields 0.78 eV [9], very close to the 0.82 eV found here for the a_1 level. The first-principles calculations thus confirm the qualitative picture that the core-exciton electronic structure should be very similar to that of C:N near the funda-

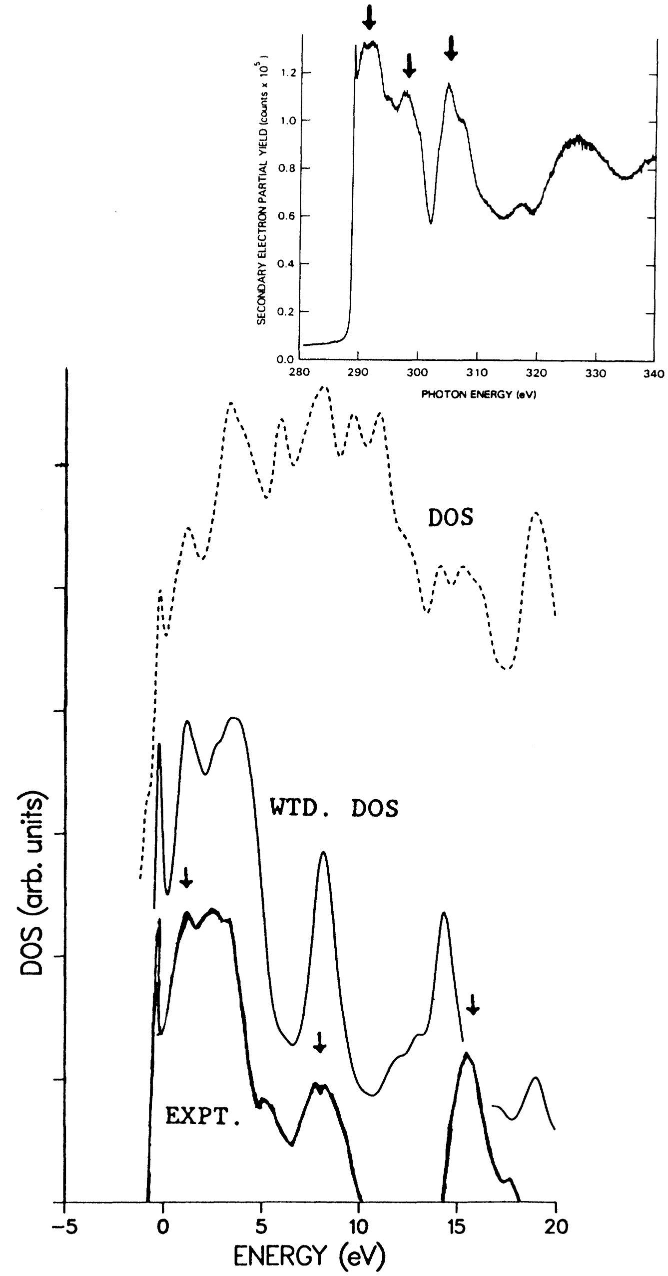

FIG. 2. Calculated conduction-band density of states (DOS) from the C_{29} exciton cluster compared with the experimental photoabsorption data of Ref. [1]. The upper curve shows the full calculated density of states; the middle curve is the calculated DOS weighted by the dipole matrix element for each state with the 1s core level. A 0.5-eV Lorentzian broadening is used for the CB states in these curves, and a separate 0.25-eV broadening is used for the exciton states, reflecting the experimental width of the exciton peak. The bottom curve is the photoabsorption data of Ref. [1]. The original figure from Fig. 1 is reproduced in the inset, with arrows indicating the main features. The position of the exciton peak is used to align the curves. The striking similarity of the weighted DOS with the observed data makes clear the importance of dipole selection rules in interpreting the experimental results.

TABLE I. The calculated binding energies (in eV) of two diamond core-exciton gap states are shown for three clusters. The binding energies are measured with respect to the lowest unoccupied state of A_1 (s-like) symmetry in each cluster. The deep gap state a_1 also has A_1 symmetry, while the state labeled t is p-like.

	a_1 (eV)	t (eV)
C_5	1.30	0.39
C_{17}	0.82	−0.25
C_{29}	0.82	0.16

mental band gap, and support the explanation for the observed shallow binding energy for the diamond core exciton based on dipole selection rules.

It is clear from Table I that the position of the t state is less converged than the a_1 state as a function of cluster size. This can be understood on two grounds. First, since the p-like state has a node at the cluster center, it samples more of the outer region of the cluster and more of the cluster surface than the s-like a_1 state, making the t state more sensitive to cluster size effects. From a more fundamental point of view, it is well known that shallow defect states are difficult to describe in the LDA [11]. These states often appear as resonances in the CB, rather than as shallow gap states. It is possible that this attribute of the LDA accounts for some of the variation in the placement of the t state in the clusters studied here. Although the precise placement of the t state is not clear from Table I (or whether the state is definitely bound in the LDA), the values suggest that 0.39 eV represents an upper bound on the binding energy of the t state, in reasonable agreement with the experimental observation of 0.189 eV [1]. (Note that a value for the exciton binding energy taken from the middle curve of Fig. 2 corresponds to the energy difference $t_2 - t$, where t_2 is the lowest unoccupied p-like state after t. Using this definition, the C_{29} calculation yields a value of 0.49 eV for the binding energy of the t state, in good agreement with the result obtained using a_2 as the CB minimum. We have opted above and in Table I to reference the exciton levels to the a_2 state, in order to make contact with our earlier work on the nitrogen donor, and because the more tightly bound a_2 state is better converged with cluster size. The qualitative results of the calculation are not affected by this choice.)

An important implication of Fig. 1 is the existence of a deep exciton gap state, a_1, which has yet to be seen experimentally. This state should be observable in an experiment using techniques, such as two-photon or electron impact excitation, which circumvent dipole selection rules in creating the exciton. Alternatively, fluorescence from t to a_1 might be used to detect the a_1 state. As shown in Table I, the LDA binding energy for a_1 is in the range 0.82 to 1.02 eV. The actual binding energy is likely to be somewhat greater, however, due to the tendency of the LDA to underestimate the position of deep levels [9,11]. By analogy with the nitrogen donor, this level could be expected to lie as deep as 1.7 eV. We note, however, that the position of the C:N-donor state may be affected somewhat by atomic relaxation known to occur at the nitrogen site. The creation of the exciton state occurs too fast for atomic relaxation to shift the exciton binding energy. Calculations for the C:N system [9,12] suggest that atomic relaxation shifts the donor level downward relative to its value for substitutional N. 1.7 eV should thus be a reasonable upper bound for the a_1 binding energy, and we therefore predict a range of 0.8 to 1.7 eV for the deep gap state.

In summary, we have used the LDA to study the diamond 1s core exciton, and find the electronic structure of the core-exciton system to include a symmetric deep gap state which is the analog of the nitrogen donor. While this state is occupied in the donor ground state, the deep exciton level cannot be reached by one-photon excitation from the 1s core due to dipole selection rules. The measured core-exciton binding energy of 0.189 eV is thus that of a shallow, p-like gap state. The LDA calculation yields an upper bound of 0.39 eV for the binding energy of this state, in reasonable agreement with experiment. The deep s-like exciton state has not yet been observed experimentally, and we use our calculated results to predict a range of 0.8 to 1.7 eV for the binding energy of this state.

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