n-type dopants and conduction-band electrons in diamond: Cluster molecular-orbital theory

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A molecular-orbital study has been made of substitutional (s) atomic Li, N, and P and interstitial (i) Li in diamond through the use of cluster models of the diamond lattice. The small binding energy calculated for P(s) indicates extremely small solubility for P in the lattice. Calculated electronic structures, including lattice relaxations, show Li(s) is an acceptor and P(s) is a donor that should fully ionize in bulk diamond. Li(i) is either a shallow donor or fully ionized. N(s) is a deep donor and its thermal excitation energy is significantly lower than the optical energy because of stabilization from relaxation around N^+. In clusters of the size studied, with up to 98 carbon atoms, conduction-band electrons become trapped in donor C-C bond stretch regions, occupying a C-C σ^* orbital. Electron transport in such clusters would be activated by polaron hopping, with local lattice distortions around the localized electron orbital. In the bulk limit this donor level will be stablized slightly but the bottom of the conduction band lowers to the point that free-electron transport should take over.

INTRODUCTION

Natural diamond can occur in nitrogen n-doped and boron p-doped compositions.[1] The nitrogen n-type doping is believed to stem from isolated substitutional nitrogen atoms and the N(s) optical ionization energy is high, with an absorption edge about 2 eV. With a thermal activation energy of 1.6–1.7 eV, N-doped n-type diamond is unsuitable for typical semiconductor device applications. Boron-doped diamond of high room-temperature conductivity is readily prepared during low-pressure growth in the presence of boron.[2,3] Attempts to incorporate the potential n-type dopants Li and P during low-pressure diamond growth to produce high-conductivity n-type diamond have not yet met with any clear success. Upon in-diffusion of Li, photoemission spectroscopy indicated the presence of deep acceptor levels 1.0–1.5 eV above the valence band which became filled and there was only a slight increase in electrical conductivity.[4] Attempts to dope with P by using large phosphine concentrations during low-pressure diamond growth failed to introduce P in the lattice or have any effect on the electrical conductivity.[4] Low-pressure synthesis with P_2O_5 in the reaction yielded n-type diamond with an activation energy for conductivity of 0.05 eV, but no P could be found in the diamond film, making the cause of the n-type conductivity unclear.[5] A theoretical characterization of diamond doped with Li, P, and N would be of interest and is the theme of this paper.

We recently performed a molecular-orbital study of N and B in the center of a C_{70} cluster with its dangling surface orbitals terminated by 60 H atoms.[6] Nitrogen was found to be a deep donor structurally characterized by a single greatly elongated C-N bond with a bond order of $\frac{1}{2}$. The extra electron from N occupies a C-N σ^* orbital and has greater amplitude on C. Due to the bond stretch and nitrogen's greater electronegativity, the doubly occupied σ orbital has greater amplitude on N, so the appropriate electron dot picture is N:—·C. Removal of the extra electron to the conduction band restores the tetrahedral carbon coordination about N^+. The conduction-band electron might be expected to form a trapped deep-donor state by stretching a C-C bond to form the structure $[C:—·C]^-$. Conduction would then proceed by a poloron description rather than the free-electron description. We note that in this case the two carbon atoms are equivalent so if the electron dot picture is used two resonance forms are required, $[C:—·C]^- \leftrightarrow [C·—:C]^-$. The molecular-orbital picture makes them automatically equivalent in terms of the configuration $(\sigma_b)^2(\sigma_a)^1$ where σ_b and σ_a are the bonding and antibonding C-C σ orbitals.

In this paper it is shown that in diamond clusters, such as C_{98}, which have band gaps sufficiently wider than the bulk band gap, electron transport should proceed by the polaron mechanism, with large local lattice distortions, but in the bulk limit free-electron conduction will probably take over. We will also show that N(s) becomes a deep donor approximately matching the Franck-Condon optical measurements when the limiting bulk band gap is taken into consideration. We point out that lattice relaxations about the ionized N donor lead to significant stabilization, so the non-Franck-Condon thermal band gap should be significantly less, though N remains a deep thermal donor. Our calculations indicate that Li(s) is an acceptor and P(s) is expected to be ionized in the bulk, placing an electron in the bulk conduction band. Li(i) is either a shallow donor or fully ionized in the bulk. However, the synthesis of P(s) appears impossible due to its instability in the diamond lattice.

THEORETICAL METHOD

We employ the atom superposition and electron delocalization molecular-orbital[7] (ASED-MO) and band[8] theories. The ASED-MO theory is based on partitioning

a molecular or infinite crystal electron charge-density distribution function into isolated free atom ρ_a and charge delocalization ρ_d components,

$$\rho = \sum_{i}^{\text{atoms}} \rho_a^i + \rho_d \ . \tag{1}$$

The electrostatic theorem is used to calculate the pairwise atom superposition energies E_r^{ab} by integrating the force on the nucleus of the less electronegative atom of each pair as the atoms are placed in a molecular configuration. Each component is repulsive, hence the subscript. These are summed to give the total atom superposition energy E_R with the formula

$$E_R = \sum_{a < b} E_r^{ab} \ . \tag{2}$$

The electron delocalization energy E_D which is due to the integral of the electrostatic force from each ensuing ρ_d as the atoms are superimposed, is approximated by a molecular-orbital electron delocalization energy ΔE_{MO}. The total energy of the atom system E given by

$$E = E_R + E_D \tag{3}$$

is therefore approximated using the formula

$$E = E_R + \Delta E_{\text{MO}} \ . \tag{4}$$

ΔE_{MO} and the molecular orbitals are calculated using a modified extended Hückel Hamiltonian with diagonal matrix elements for orbitals on the same atom H_{ii}^{aa} equal to the negative of actual or shifted atomic valence state ionization potentials and off-diagonal matrix elements for orbitals on different atoms H_{ij}^{ab} given by the formula

$$H_{ij}^{ab} = 1.125(H_{ii}^{aa} + H_{jj}^{bb})\exp(-0.13R_{ab})S_{ij}^{ab} \ , \tag{5}$$

where R_{ab} is an internuclear distance and S_{ij}^{ab} is the overlap integral between Slater orbital i in atom a and Slater orbital j in atom b. Off-diagonal matrix elements for orbitals in the same atom, H_{ij}^{aa}, are set equal to zero. The band version is a straightforward extension of the model.

Parameters used in this work are in Table I. Carbon parameters are from a band calculation study of diamond and graphite, for which the calculations yielded good (for a semiempirical theory) lattice constants and bulk moduli for these materials.[8] The diamond band gap is underestimated (3.1 versus 5.5 eV from the optical excitation[1]). Li, N, and P valence ionization potential parameters were shifted in 0.5-eV increments so that the diatomic LiC, NC, and PC ionicities, calculated by applying the Mulliken partitioning to the molecular orbitals, were close to those estimated from the electronegativity differences between C and the other atoms. Additional increases in Li valence orbital exponents were made so that the charge calculated on Li(s) decreased to ~ 0.8.

RESULTS AND DISCUSSION

The C_{71} cluster for modeling a substitutional (s) site is in Fig. 1 and the C_{84} cluster modeling the interstitial (i) site is in Fig. 2. The calculated electronic structures for Li(s), Li(i), N(s), and P(s) are in Fig. 3. Nearest- and next-nearest-neighbor atoms around the dopant atoms are fully structurally relaxed to produce the maximum stability. The band gap of this cluster is high, 6.9 eV, compared to the bulk calculated limit of 3.1 eV. It is evident that substitutional Li is an acceptor, substitutional P is predicted to be ionized, placing an electron in the conduction band, and interstitial Li and substitutional N are deep donors in these clusters, provided structure relaxations around $Li^+(i)$ and $N^+(s)$ are not too stabilizing. Structure distortions around the dopant atoms are shown in Fig. 4. The interstitial Li is associated with a greatly elongated C-C bond; elongation is due to electron promotion to a neighboring C-C σ^* orbital, resulting in the structure

$$[\text{C}\!\!:\!\!\underset{\text{Li}^+}{\text{—}}\!\!\cdot\text{C}]^- \ .$$
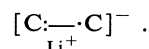
Symmetric relaxations about Li(i) did not bring about the stabilization that occurs when a single C-C bond is stretched, for that allows a σ^* orbital to lower into the band gap, whereas symmetric distortions do not. The resulting electronic stability balances the increase in atom superposition energy E_R at equilibrium. There is a small trigonal distortion around Li(s). The bond stretches

TABLE I. Atomic valence orbital parameters used in the calculations: principal quantum number n, diagonal matrix elements H (eV), and orbital exponents ζ (a.u.). For hydrogen, H is -13.6 and ζ is 1.2.

Atom	n	s H	ζ	n	p H	ζ
C[a]	2	-16.59	1.8174	2	-11.26	1.7717
Li[b]	2	-6.892	1.0896	2	-5.044[c]	1.0896
N[b]	2	-18.33	1.9237	2	-12.53	1.9170
P[b]	3	-17.65	1.8806	3	-11.99	1.6288

[a]Reference 8.

[b]H based on valence state ionization potentials from W. Lotz, J. Opt. Soc. Am. **60**, 206 (1970), shifted as discussed in the text. Exponents are from E. Clementi and D. L. Raimondi, J. Chem. Phys. **38**, 2686 (1963), with those for Li shifted as discussed in the text.

[c]Based on excitation for Li ground state to the lowest excited state from data reported by C.E. Moore, *Atomic Energy Levels*, Natl. Bur. Stand. Ref. Data Ser., Natl. Bur. Stand. (U.S.) Circ. No. 467 (U.S. GPO, Washington, DC, 1958).
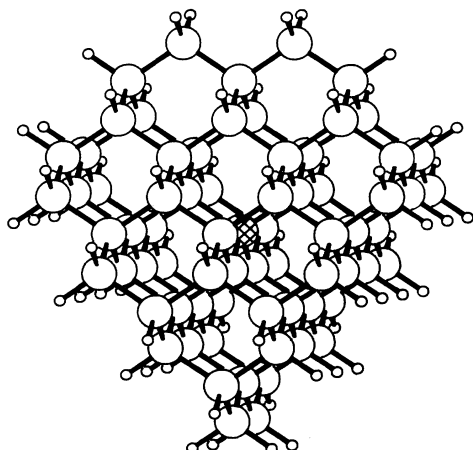
FIG. 1. Bulk superimposable C_{71} model for diamond, with 60 H atoms saturating the dangling radical orbitals on the surface carbon atoms. The hatched atom in the center is on the substitutional site. The nearest-neighbor C-C internuclear distance is taken to be 1.54 Å in this model and the C-H internuclear distance is taken to be 1.10 Å.

FIG. 3. Electronic structures in the band-gap regions for $C_{71}H_{60}$, Li(s) ($LiC_{70}H_{60}$), Li(i) ($LiC_{84}H_{64}$), N(s) ($NC_{70}H_{60}$), and P(s) ($PC_{70}H_{60}$). For the dopants, the local lattice structures are optimized—see Fig. 4.

around substitutional N and P are due to the promoted electrons occupying N-C and P-C σ^* orbitals to give the electronic structures N:—·C and P:—·C. However, in the P case the distortion and σ^* stabilization are smaller, an expected result of the large P atom size, so the P will be ionized, placing an electron in the conduction band and an expanded carbon tetrahedron forms around P^+.

The calculated binding energies for Li, C, N, and P atoms to vacancy sites and for a Li atom to the interstitial site are given in Table II. Given a vacancy formation energy of about 6 eV in diamond[9] and assuming gas-phase atomic standard states for the dopants, it is evident from these binding energies that N and Li but not P will incorporate in the diamond lattice as stable substitutional dopants. This is consistent with observations for at-
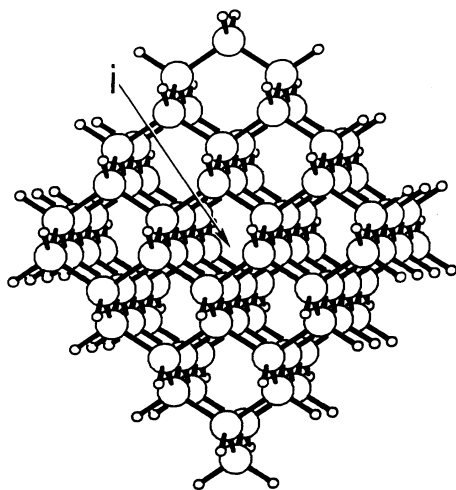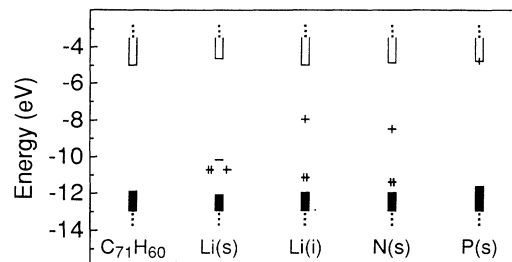
tempts to dope with P (Refs. 4 and 5) and possibly Li.[4] Both interstitial H (Ref. 9) and substitutional Li could provide the acceptor levels that are filled by interstitial Li as noted in Ref. 4. Interstitial Li binds strongly enough to exist in the lattice and is easily ionized (vide infra) so as to compensate the acceptor levels as noted in Ref. 4. In its ionized form, interstitial Li shifts to the tetrahedral interstitial site where it will migrate easily from site to site through the lattice, allowing it to diffuse to the surface to react with oxygen as observed in Ref. 4. To complete the reaction, for each Li^+ that reacts with oxygen an electron will be withdrawn from the Li-compensated acceptor band of levels near the valence band.

The interaction of the conduction-band electron with the diamond lattice is of interest. On allowing a C-C bond near the middle of the C_{71} cluster to stretch, and optimizing the positions of the three nearest neighbors to each of these carbon atoms, a C-C stretch to 1.97 Å occurs and a singly occupied σ^* orbital appears 2.7 eV below the conduction-band edge. Thus, the electron is, in a Franck-Condon optical sense, deeply trapped in a stretched cluster C-C bond. However, a transition state, C:—C·—C, for e^- migration to the next bond is calculated to have an activation energy of only 0.9 eV. Nevertheless, conductivity by such "conduction-band" electrons would be very low and such electrons could not be described as "free." We note that the bulk band calculation yields a conduction-band edge 2.4 eV below the C_{71} conduction-band edge. Consequently, we carried out calculations to estimate by extrapolation the likely properties of a conduction-band electron in the infinite crystal. To do this we used the surface H saturated C_8 and C_{98}
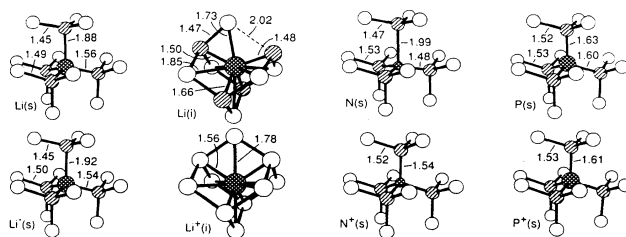

FIG. 2. As in Fig. 1, but this $C_{84}H_{64}$ cluster models the tetrahedral interstitial site in which Li is placed.

FIG. 4. Local structures around Li(s), Li(i), N(s), P(s), $Li^-(s)$, $Li^+(i)$, $N^+(s)$, $P^+(s)$.

TABLE II. Calculated binding energies (BE) for dopant atoms in vacancy (V) and interstitial (i) sites in the diamond lattice.

Atom and site	BE (eV)
Li(V)	9.7
C(V)	14.4
N(V)	10.5
P(V)	4.6
Li(i)	2.8

models of Figs. 5 and 6. These are symmetric about the stretched C-C bond containing the conduction-band electron. Next-neighbor C-C bonds were not relaxed since the additional stabilization is minor, as was shown for N:—·C.[6] For the C_8 and C_{98} clusters the conduction-band edges are at -2.3 and -5.4 eV, respectively, and, with the stretched C:—·C$^-$ bond lengths calculated to be 1.98 Å in both cases, the band-gap level drops to -7.3 and -7.7 eV. These levels are shown in Fig. 7. Thus the electron orbital stabilizations are 5.0 and 2.3 eV for the C_8 and C_{98} clusters, respectively. However, due to changes in E_R and ΔE_{MO} the total-energy stabilizations are, respectively, only 2.9 and 0.9 eV. E_R is destabilized by 0.8 eV for C_8 and 0.9 eV for C_{98}. The remaining valence-band energies are destabilized by 1.3 eV for C_8 and 0.5 eV for C_{98}. Since the stretched bond band-gap state is not strongly cluster size dependent and is likely to be close to -7.7 eV in the bulk and since this is just 0.4 eV beneath the bulk conduction-band edge, it is unlikely that, when the other energy components are considered, this large or possibly even a small bond stretching distortion will be stabilizing in the bulk. For example, for C:—·C$^-$ in the bulk limit, if the E_R and valence-band destabilizations of the C_{98} cluster for the 1.98-Å C-C dis-
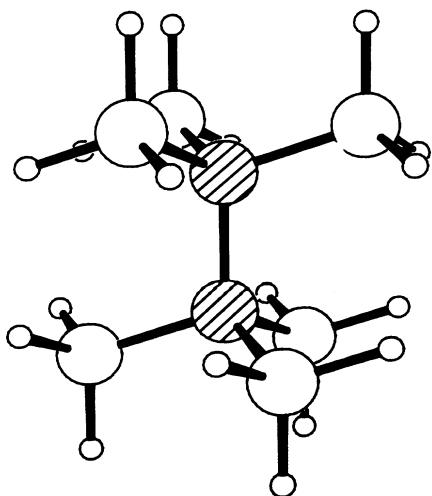

FIG. 5. C_8H_{18} model used to study C-C bond stretching by a conduction-band electron. The carbon atoms participating in the bond stretching are hatched. Their neighbors were constrained to the original lattice sites.
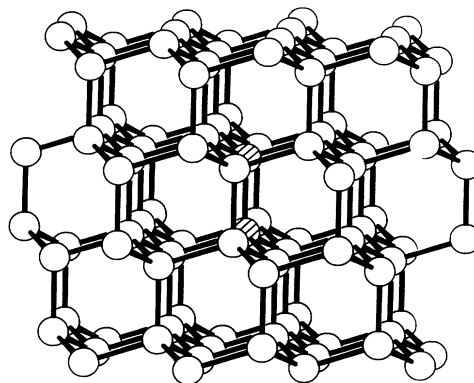

FIG. 6. As in Fig. 5 but for the $C_{98}H_{78}$ model with surface H omitted for clarity.

tance are assumed, then the bond stretch with electron localization would be destabilizing by 1.0 eV. We therefore expect that free-electron conduction will rule in the bulk. For clusters, however, an activated hopping or polaron electron transfer mechanism is inferred from our results.

Returning to substitutional N, which is a deep donor since its stretched N-C bond σ^* donor level lies in the middle of the cluster band gap, it is unlikely to shift significantly in energy in the bulk limit. Its predicted optical excitation energy to the bulk conduction-band edge is then 1.1 eV, about half of the measured optical value of ~ 2 eV. For thermal non-Franck-Condon excitation with relaxation around the positively charged substitutional N that is formed, the calculated energy is reduced to 0.4 eV, rendering substitutional N a deep thermal donor and a poor n-type dopant. The experimental thermal excitation energy of 1.6–1.7 eV indicates the possibility that the relaxation energy about N$^+$ has been overestimated in the calculations, among other uncertainties resulting from the nature of non-self-consistent ASED-MO calculations.

Because of lattice relaxation around Li$^+(i)$, the thermal ionization energy, placing the electron in an isolated stretched C-C bond band-gap orbital of the C_{71}
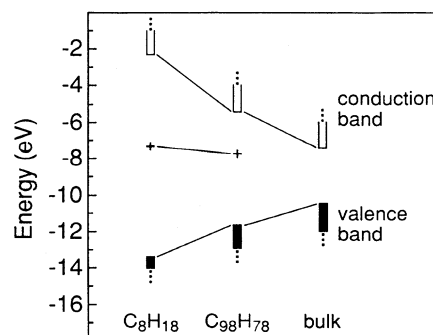

FIG. 7. Conduction- and valence-band edges for C_8H_{18} and $C_{98}H_{78}$ clusters and band-gap states formed by the trapping of a conduction-band electron in a C-C bond stretching σ^* orbital. Also shown are the calculated bulk conduction- and valence-band edges for diamond.

cluster, reduces to 0.4 eV from the optical value of 3.0 eV for the C_{70} cluster. Hence, in the cluster Li(i) is a deep donor but in the bulk limit it will, by the argument given above for band-gap stretched C-C bond electrons, be either a shallow donor or fully ionized. The energy for the process P(s)→P^{+}(s)+C:—·C^{-} is −1.3 eV, so substitutional P will be ionized in the diamond cluster and the bulk lattice.

SUMMARY

Our results indicate substitutional Li is uninteresting as an *n*-type dopant in diamond and will actually behave as an acceptor. In the bulk diamond lattice, substitutional P is predicted to ionize, interstitial Li is either ionized or it is a shallow donor, and substitutional N is a deep donor. Substitutional P will, however, have exceedingly low solubility and so should not contribute significantly to conductivity. Our result for nitrogen is in qualitative accord with experiment (Ref. 1) and the known data for Li[4]- and P[5]-doped diamond. We find that in diamond crystals up to some size greater than 100 atoms, but the upper limit is unknown, electrons injected into the conduction band are not free but are localized into a stretched C-C σ^{*} orbital beneath the conduction-band edge. Electron transport would be by an activated polaron mechanism and the hopping barrier would increase with decreasing diamond particle size. In the bulk limit the free-electron picture is expected to hold. Intrinsic to our conclusions in this paper is the calculation of lattice relaxations around defects, ionized defects, and the electron. This explains why the thermal ionization energy for N(s) is less that the optical one. The fixed band and energy level picture is a good model for optical properties, where the Franck-Condon approximation applies well, but for thermal properties it is a less satisfactory approximation because lattice relaxation can have a significant effect on thermal excitation energies.

ACKNOWLEDGMENT

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