

Ab initio study of lithium and sodium in diamondE. B. Lombardi,¹ Alison Mainwood,² and K. Osuch^{1,*}¹*Department of Physics, University of South Africa, P.O. Box 392, UNISA 0003 Pretoria, South Africa*²*Physics Department, King's College London, Strand, London WC2R 2LS, United Kingdom*

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Interstitial lithium and sodium have been suggested as alternatives to phosphorus to achieve shallow n -type doping of diamond. Experimental results have, however, been contradictory. We report *ab initio* density functional theory modeling of lithium and sodium in diamond and show that although interstitial Li and Na are likely to behave as shallow donors, interstitial Li will readily diffuse with a low activation energy and that it is energetically favorable for both species to be trapped at existing vacancies in diamond. The resulting substitutional centers are themselves not only passivated but also induce deep levels in the band gap of diamond, compensating the remaining donors. This explains the high resistivity observed in lithium and sodium doped diamond. This demonstrates that samples should not be exposed to elevated temperatures in order to prevent Li diffusion, while concentrations of vacancies and other defects should be minimized to restrict the formation of compensating substitutional Li acceptors, if n -type doping of diamond is to be achieved with Li. For sodium, we show that it is energetically favorable for Na to be incorporated in diamond as a substitutional acceptor rather than as an interstitial donor. This is consistent with experimental observations of Na diffusing as a negative ion under electric bias in diamond. It is therefore unlikely that diamond will be successfully n -type doped with Na.

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I. INTRODUCTION

Diamond is a wide band gap semiconductor with a high breakdown field, high thermal conductivity, high electron mobility, and other extreme properties which make it suitable for high power, high frequency, and high temperature applications.¹ Although diamond has been successfully n -type doped with phosphorus,² the relatively deep donor level (optical ionization energy of 0.6 eV) and low mobility³ have resulted in the search for other, shallower, n -type dopants.⁴ More recently, shallow n -type conductivity has been observed in B doped diamond with an excess of hydrogen;⁵ although the donor has not been identified,⁶ a mechanism involving B_n-H_m complexes has been suggested.⁷ Nevertheless, the search for other shallow n -type dopants has continued.^{8,9}

Of the alternative dopants, lithium and sodium have been predicted to have shallow donor levels when in interstitial positions in diamond¹⁰ and have been the subject of significant experimental interest.^{8,11–14} However, despite expectations of Li being a shallow donor,¹⁰ most experimental studies have found Li doped samples to be either highly resistive or electrically inactive.

In spite of a significant number of experimental studies, especially for lithium, the results are not always in agreement with each other. For example, the position of the lithium donor level in diamond is unclear, with some studies finding a shallow level,¹⁵ while others find impurity levels at 0.8–0.9 eV (Refs. 11 and 16) and 1.5 eV.^{11,17} Similarly, the observed diffusion properties of lithium in diamond vary widely, with some results showing lithium to be immobile in ion-implanted samples even at high temperatures,¹⁸ while others have reported that it diffuses into single crystal diamond with an activation energy of 0.9 eV (Ref. 12) or 0.26 eV.¹⁴

Due to the interest in these dopants, the uncertainty regarding their characteristics and the inconsistency between existing experimental and theoretical results, in particular, the expectation of shallow donor behavior versus observed high resistivity, we have carefully modeled the properties of lithium and sodium in diamond using *ab initio* density functional theory (DFT) all-electron, full-potential periodic supercell methods, as well as finite nanocluster methods, modeling these dopants both at substitutional as well as various interstitial sites in diamond. We also consider the relative solubilities of interstitial versus substitutional Li and Na, as well as activation energies of diffusion.

After summarizing the relevant experimental results on these impurities and discussing predictions of previous theoretical modeling in Sec. II, we describe our calculations in Sec. III, present the results and relate them to the experimental data in Sec. IV, and draw conclusions from them in Sec. V.

II. REVIEW OF PREVIOUS THEORY AND EXPERIMENT OF Li AND Na IN DIAMOND**A. Lithium**

Lithium has been incorporated into diamond by doping during chemical vapor deposition (CVD) growth, interdiffusion, ion implantation, and nuclear transmutation using the $^{10}\text{B}+n\rightarrow^7\text{Li}+\alpha$ reaction.^{8,9,19} In different experiments on samples doped during CVD growth, activation energies of 0.8–1.0 eV, (Refs. 11 and 16) and 1.5 eV (Refs. 11, 17, 20, and 21) were observed; however, n -type conductivity was not observed. Photoconduction studies¹¹ on high quality *in situ* lithium doped homoepitaxial CVD diamond samples²² revealed two absorption thresholds at 0.9 and 1.5 eV, which were metastably occupied. In contrast, activation energies of

diamond doped with lithium by ion implantation,^{23–25} in-diffusion of lithium,²⁶ or nuclear transmutation,¹⁹ have generally found low lithium donor activation energies (0.17–0.23 eV), possibly due to variable range hopping.²⁴ It has also been suggested that this conductivity may be attributed to residual damage.^{24,27} In all cases, activation energies in the range of 0.17–0.23 eV were observed in samples that had been exposed to high temperatures^{14,26} or suffered severe damage including amorphization, or both.^{8,19,23–25}

Recent attempts^{8,9} to incorporate Li by nuclear transmutation using mainly lower-energy thermal neutrons resulted in much less damage to the diamond host without the amorphization that was reported in previous¹⁹ high-energy fast neutron flux experiments. These more controlled experiments showed evidence of *n*-type doping, with a possible donor activation energy of 0.143 eV; *n*-type donors were activated at lower temperatures than the remaining unreacted ¹⁰B acceptors. In previous work,¹⁹ compensation of *p*-type carriers due to unreacted ¹⁰B by *n*-type carriers from interstitial Li donors was not observed, while in these new experiments, it was observed.⁹ Importantly, these samples were continuously cooled during irradiation and not annealed after irradiation, which prevented diffusion of vacancies or interstitials,⁸ including diffusion of interstitial Li, in contrast to previous experiments.¹⁹

The results of lithium diffusion in diamond have been inconsistent.^{14,28,29} More recent experiments^{14,26,30} found that lithium diffused partially as a positive ion at temperatures of 770–800 °C, while in ion-implanted samples, lithium diffusion was not observed, possibly since it was trapped by ion implantation damage.^{29,31} In natural single crystal samples, an activation energy for lithium diffusion of 0.9 ± 0.3 eV was found;¹² however, reinterpretation of these results together with new measurements¹⁴ suggested a much lower activation energy of diffusion of 0.26 eV. In contrast, emission channeling studies¹³ indicate a diffusion activation energy $E_d > 1.25$ eV. It has also been pointed out¹⁴ that due to Li accumulation in the subsurface region of diamond during forced in-diffusion,¹² incomplete cleaning of diamond surfaces after Li diffusion could result in secondary-ion-mass spectroscopy profiles that may be erroneously interpreted as real Li diffusion.¹⁴

The solubility of lithium in single crystal diamond was found to be low,^{14,32} while in polycrystalline material, lithium was found to diffuse primarily through grain boundaries.^{30,33} This is in contrast to earlier studies³⁴ which suggested that lithium was readily incorporated into diamond.

Emission channeling studies found that a large proportion [(40±5)%] of lithium atoms occupied tetrahedral interstitial sites.^{13,35} A significant fraction [(17±5)%] occupied substitutional sites, with a possible displacement of up to 0.2 Å from the ideal lattice site.¹³

B. Sodium

CVD diamond films that have been doped with sodium during growth³⁶ exhibited very high resistivity but an activation energy of 0.32 eV could be measured, while in sodium

ion-implanted samples, *n*-type hopping conduction was observed.²⁴ Other sodium ion implantation studies²⁷ found activation energies in the range of 0.4–0.48 eV; however, annealing at high temperatures resulted in an increase in resistivity and activation energies, while implantation with electrically inactive species with an equivalent damage density as Na resulted in similar but higher activation energies and electrical resistance as Na implanted samples.

Optically enhanced diffusion of sodium under an electric bias²⁶ found sodium to behave as a shallow acceptor in diamond, diffusing as a negatively charged ion; an electronic activation energy of 0.2 eV was deduced for the sodium acceptor. On the other hand, sodium ion-implanted samples showed no diffusion³¹ even at 1100 °C, most likely since it was trapped at ion implantation damage. Reference 26 also stated that the solubility of sodium was greater than that of lithium in diamond.

C. Previous theoretical studies of Li and Na in diamond

Kajihara *et al.*¹⁰ have found, using plane wave density functional (DFT) methods, that lithium and sodium occupy tetrahedral interstitial sites in diamond. They predict that sodium has a donor level at $E_c - 0.3$ eV (deeper than their phosphorus donor), while interstitial lithium has a donor level at $E_c - 0.1$ eV (shallower than phosphorus). Formation energies were positive and large, indicating that both impurities would be very insoluble in diamond. For lithium, a formation energy of 5.5 eV was found, while for sodium, the formation energy was 15.3 eV. For interstitial sodium, there was a strong outward relaxation, both at tetrahedral (0.19 Å) and hexagonal sites (0.26 Å).

III. METHOD

In order to address the inconsistencies between previous experimental and theoretical results, we have performed *ab initio* spin polarized density functional theory (DFT) calculations for lithium and sodium at various substitutional and interstitial sites in diamond. These dopants were modeled using both finite nanoclusters as well as periodic supercell calculations, in order to take into account the effect of polycrystalline vs single crystal diamond.

Finite nanocrystal calculations were performed using norm-conserving pseudopotentials,³⁷ in neutral, positive, and negative charge states, using the AIMPRO code,³⁸ which has been successfully used in modeling dopants in diamond in the past.^{39,40} Nanoclusters of 165 carbon atoms,⁴¹ bounded by hydrogen terminated <111> surfaces (denoted C₁₆₅), were used, placing substitutional impurities *X* at the center of the cluster (XC₁₆₄) or the interstitial atom *X* close to it (XC₁₆₅). In the initial geometries, the impurity atoms were shifted away from high symmetry sites to ensure that the final structures obtained were not dependent on the initial geometries used.⁴² Geometry optimizations were performed without restricting the cluster to any symmetry.

Periodic supercell calculations were performed using the full-potential, all-electron augmented plane waves with local orbitals (APW+lo) formalism with relativistic treatment of

core⁴³ and valence⁴⁴ electrons, as implemented in the WIEN2k code.⁴⁵ The generalized gradient approximation of Perdew-Burke-Ernzerhof⁴⁶ was used for the exchange-correlation functional. Modified tetrahedron method⁴⁷ of Blöchl *et al.* was employed for integration over the Brillouin zone. In APW+lo calculations,⁴⁸ the value of $R_{mt} \cdot k_{max}$ (smallest muffin tin radius multiplied by the maximum k value in the expansion of plane waves in the basis set) determines the accuracy of the basis set; $R_{mt} \cdot k_{max} = 5.00$ was used in this study. A $3 \times 3 \times 3$ mesh of k points was employed for geometry optimization. Increasing $R_{mt} \cdot k_{max}$ to 6.00 for selected calculations did not result in significant changes; similarly, increasing the number of k points in the irreducible wedge of the Brillouin zone also did not result in any significant changes. For band structure and density-of-states plots, the number of k points was increased to a $7 \times 7 \times 7$ k mesh.

For the APW+lo periodic supercell calculations, the primitive fcc diamond cell was optimized using $R_{mt} \cdot k_{max} = 7.00$ and a $10 \times 10 \times 10$ k point mesh (47 k points in the irreducible wedge of the Brillouin zone). This yielded a lattice constant of 3.576 Å, which is very close to (0.26% larger) the experimental value⁴⁹ of 3.567 Å. For the finite nanocrystal calculations,⁶ a fully relaxed 123-atom cluster was used and the interatomic distance from this cluster was used to create a second 123-atom cluster in which only the central atoms were allowed to relax. The interatomic distance in this cluster was used to calculate the interatomic distance, corresponding to a bulk lattice constant of 3.655 Å, only 2.5% larger than the experimental bulk value.⁴⁹ This lattice constant was used to construct the 165 C atom cluster used in this study.

In the nanocluster calculations, the impurity atoms were initially shifted away from high symmetry sites to ensure that the final structures obtained were not dependent on the initial geometries used.⁴² Geometry optimizations were performed without restricting the cluster to any symmetry. The outer layer of atoms were kept fixed at their lattice sites during geometry optimization. These optimized finite cluster geometries were used as initial geometries for the all-electron periodic supercell calculations. In the latter case, the geometries were restricted to C_{3v} , C_{2v} , or T_d symmetry, allowing positions of all atoms to be optimized, based on the results of the nanocluster calculations.

The formation energy E_f of a neutral system X is given by

$$E_f(X) = E^{tot}(X) - \sum_i^{atoms} \mu_i, \quad (1)$$

where $E^{tot}(X)$ is the calculated total energy of the system in diamond, μ_i is the chemical potential of each atomic species, and the sum is over all atoms in the system.

The relative formation energies of interstitial versus substitutional dopants can be determined by comparing the energy gain of trapping an interstitial dopant at a vacancy, with the formation energy of a vacancy in diamond. The formation energy of a neutral vacancy in diamond is given by⁵⁰

$$E_f(\text{vac}) = E_{N-1}^{tot} - \frac{N-1}{N} E_{\text{bulk}}^{tot}, \quad (2)$$

where $E_{N-1}^{tot}(g)$ is the calculated total energy of a vacancy in diamond and E_{bulk}^{tot} is the calculated total energy of a pure diamond supercell.

Several approaches have been suggested for the determination of defect energy levels in the band gap.^{6,51} For full-potential, all-electron periodic supercell calculations, we use the calculated density of states as well as band structure plots, while for nanocrystal calculations, we quote the thermodynamic transition levels as calculated using the marker method. This approach, described elsewhere,⁶ has had considerable success in estimating the position of thermodynamic transition levels in the band gap.^{52,53} Impurity levels are quoted relative to the respective band edges and are not tied to the vacuum level.

IV. RESULTS AND DISCUSSION

A. Lithium in diamond

1. Interstitial lithium

After geometry optimization, we find the tetrahedral interstitial site (T_d symmetry) to be the most stable form of interstitial lithium (Li_i). Using all-electron periodic supercell calculations, we find that the neighboring C atoms relax away from Li_i , increasing the Li_i -C distance by 5.9% to 1.64 Å. Nanocrystal calculations yield a very similar geometry, with a Li_i -C distance of 1.63 Å.

We have also considered lithium at the hexagonal, anti-bonding, and bond-centered interstitial sites in addition to the tetrahedral interstitial site using nanocluster calculations. Only the bond-centered site was metastable (5.75 eV higher in energy), while the other interstitial configurations relaxed to the tetrahedral interstitial configuration.

Positively ionized interstitial lithium also occupies the tetrahedral interstitial site, with a structure nearly identical to that of neutral interstitial lithium.

From periodic supercell calculations, we find that interstitial lithium induces a very shallow donor level in diamond, similar to previous predictions.¹⁰ The band structure of Li_i is illustrated in Fig. 1. It is evident that the Li impurity band merges with the diamond conduction band, with the Fermi level lying within and close to the bottom of the conduction band. The system is therefore metallic, as may be expected based on high shallow donor concentrations in these supercell calculations (impurity concentration in the 64-atom $2 \times 2 \times 2$ fcc supercells employed here corresponds to 0.016 at. %); the calculated metallicity is therefore wholly a predicted property and would not be observed for lower, experimentally realistic dopant concentrations, where shallow donor activity would be observed.

In contrast, determining thermodynamic transition levels using the nanocrystal approach, we find that Li_i induces a deeper (0/+) donor level at $E_c - 0.63$ eV. We ascribe this difference in donor levels to the well known effect that impurity levels are shifted deeper in the band gap in nanocrystals than in bulk due to quantum confinement effects.⁵⁴ This

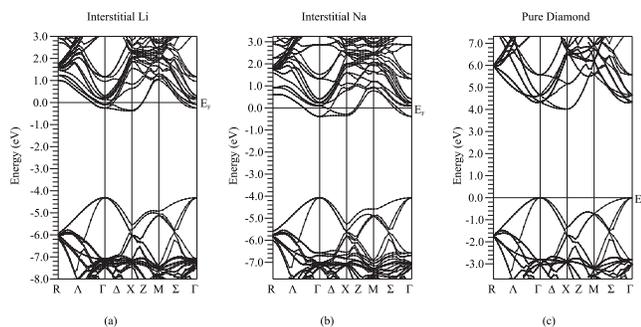


FIG. 1. Band structure of (a) interstitial Li and (b) interstitial Na in diamond, together with (c) the band structure of a similar pure diamond periodic $2 \times 2 \times 2$ fcc supercell, for comparison. Path in Brillouin zone is as for a simple cubic structure. All energies are relative to the respective Fermi energies. The band structures have been aligned so that the valence band maxima coincide. The band structures plotted in (a) and (b) correspond to the majority spin components, respectively; the band structures of the respective minority spin components are identical. Dots correspond to data points; lines guide the eye.

is directly related to the self-purification and higher formation energies observed for dopants in nanocrystals.⁵⁴ Indeed, we find that interstitial lithium close to the surface of a diamond nanocrystal is 0.96 eV more stable than at a tetrahedral interstitial site close to the center of the nanocrystal. This also explains, together with the low solubility of Li in diamond,¹⁰ why Li diffuses primarily through grain boundaries in polycrystalline diamond,^{30,33} as well as the clustering of Li in the subsurface region during in-diffusion in single crystal diamond.^{12,14}

We also consider the diffusion of interstitial Li. For Li_i to migrate from a tetrahedral interstitial site, it must pass through a saddle point site at the center of the buckled hexagon of C atoms (hexagonal interstitial site) or via one of the other unstable interstitial sites calculated earlier. The lowest saddle point occurs via the relaxed hexagonal site¹⁰ and corresponds to an activation energy of diffusion of 1.3 eV (from nanocluster calculations), in acceptable agreement with an experimentally observed¹² activation energy of 0.9 ± 0.3 eV and previous theoretical predictions.¹⁰ However, all these values are substantially larger than the more recently established experimental value of 0.26 eV.¹⁴ Despite the relatively wide range of experimentally determined activation energies of diffusion of Li in diamond, all results agree that the activation energy of diffusion of Li in diamond is low.

Significantly, these low activation energies of diffusion show that interstitial Li will be mobile under processing or CVD growth conditions. It is therefore likely that interstitial Li donors will be trapped at other defects or grain boundaries where they will be passivated.¹⁰

2. Substitutional lithium

Due to the high mobility of interstitial Li and the substantial concentrations of vacancies that exist in ion-implanted,^{23–25} neutron irradiated,⁸ and polycrystalline CVD diamond films,⁵⁵ together with the observation of sig-

nificant fractions of substitutional Li in ion implantation emission channeling studies,^{13,35} we consider the possibility of interstitial Li being trapped at a vacancy and the properties of the resulting substitutional lithium (Li_s).

Using all-electron periodic supercell calculations, we find substitutional lithium (Li_s) with T_d symmetry to be the most stable structure. In this configuration, the C neighbors of Li relax away from Li, elongating the Li-C distance by 14.5% to 1.77 Å; the Li atom remains at the lattice site. We find that Li_s with T_d symmetry possesses a net spin of $3.0 \mu_B$ per supercell.

Li_s also possesses a metastable structure with C_{3v} symmetry and net spin of $1.0 \mu_B$ per supercell. This configuration is only very slightly (+0.02 eV) higher in energy than the T_d configuration.

This geometry of Li_s is in agreement with the results of emission channeling studies, where Li_s with no static displacements was found to be in best agreement with the data, but with indications of Li_s with increased vibration amplitudes or static displacements up to 0.2 Å.^{13,35}

We find that the geometry of Li_s is sensitive to the lattice constant used. Performing a geometry optimization with identical calculation parameters, but a lattice constant 2.3% smaller than the optimized lattice constant, it is found that Li_s with C_{3v} symmetry becomes the most stable configuration. Similarly, finite nanocluster calculations also find a geometry with approximate C_{3v} symmetry to be the most stable.

The density of states (DOS) of Li_s in diamond is illustrated in Fig. 2. It is seen that Li_s induces deep partially occupied levels in the diamond band gap; levels closest to the Fermi level are spin polarized by 0.9–1.14 eV. Importantly, it is evident from these deep levels that lithium trapped at a vacancy is not only itself passivated but will also compensate other interstitial Li donors.

These deep partially occupied levels may be compared with the metastably occupied level observed at 1.5 eV in Li doped homoepitaxial CVD diamond.^{11,17,20,21}

To establish whether diffusing Li_i will be trapped at a vacancy, we consider interstitial Li removed as far away from a vacancy as possible, compared to Li_s trapped at a vacancy in an identical supercell. Using this approach, we establish a reduction in energy of 4.12 eV for the trapping of interstitial Li at a vacancy.

The relative formation energies of Li_i versus Li_s can be determined by comparing the stability gain of Li_i trapped at a vacancy, with the formation energy of a vacancy in diamond. Using Eq. (2) with identical parameters as the defect supercell calculations, we find a neutral vacancy formation energy of 5.86 eV, very close to other recent studies.⁵⁶ This results in the relative formation energy of Li_i being 1.74 eV larger than that of neutral Li_s , as expected, and in agreement with emission channeling studies.¹³

In the same way, since Li will primarily diffuse as an interstitial species, the rate-limiting step in the diffusion of substitutional Li will be by the detrapping of Li_s , with the formation of Li_i , leaving a vacancy. Since this process is the reverse of the trapping of Li_i at an existing vacancy, the activation energy of this rate-limiting step will be equal to the 4.12 eV stability gain for the trapping of Li_i at a vacancy.

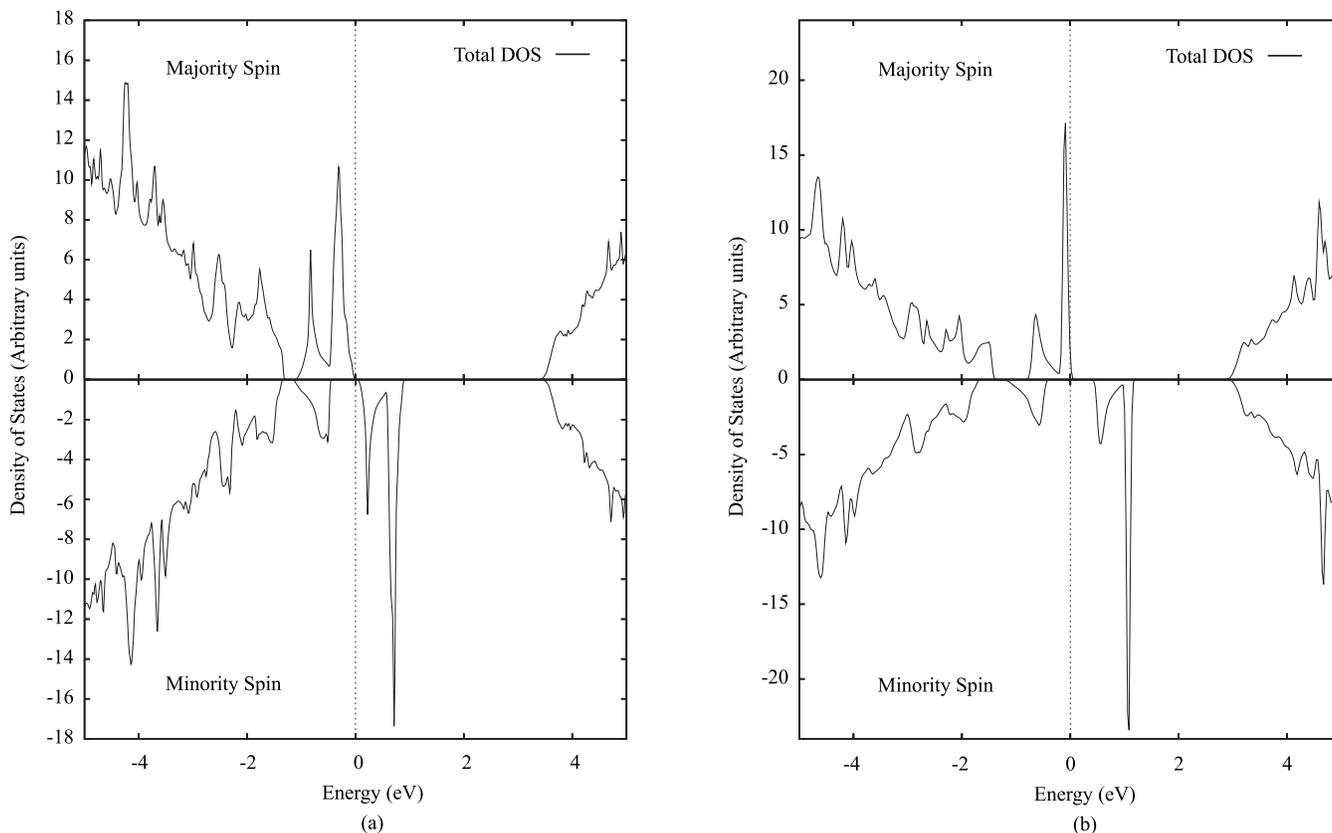


FIG. 2. Density of states of (a) substitutional Li and (b) substitutional Na in diamond. All energies are relative to the respective Fermi energies.

This large energy implies that Li_i captured at a vacancy is likely to remain trapped in the form of substitutional Li. This explains the observed lack of diffusion of Li in ion-implanted diamond, even at elevated temperatures.^{18,29,31}

Therefore, interstitial Li donors in diamond subjected to elevated temperatures will diffuse and be trapped at existing vacancies where they will themselves not only be passivated but will also compensate other remaining interstitial Li donors.

This explains why in all cases where Li diffusion occurs or where Li doped diamond is subjected to elevated temperatures, either during or after Li incorporation, highly resistive samples result.^{8,11,14,19,22–26}

In contrast, when the amount of damage to the host lattice was reduced and the samples were not exposed to elevated temperatures,^{8,9} evidence of *n*-type doping was found.

We therefore suggest that in order to achieve successful *n*-type doping using Li_i , samples should not be exposed to elevated temperatures in order to prevent the diffusion of interstitial Li, while the concentrations of vacancies and other lattice damage should be minimized.

B. Sodium in diamond

1. Interstitial sodium

For interstitial sodium (Na_i), we find the tetrahedral interstitial site to be the most stable (T_d symmetry), similar to Li_i .

From periodic supercell calculations, we find that the neighboring C atoms relax away from Na_i , increasing the Na_i -C distance by 12.6% to 1.74 Å. The distortion of C atoms surrounding Na_i is larger than that about Li_i , which is expected due to the larger ionic radius of Na (Ref. 57) (0.73 Å compared to 1.13 Å).

Nanocrystal calculations yield a smaller distortion, closer to that of interstitial Li, with a Li_i -C distance of 1.63 Å, most likely due to the larger lattice constant of the nanocrystal.

From periodic supercell calculations, we find that interstitial sodium induces a shallow donor level in diamond, similar to previous predictions,¹⁰ but 0.2 eV deeper than the Li_i donor level and slightly deeper than the phosphorus donor level calculated using the same method. The band structure is illustrated in Fig. 1. As for lithium, it is evident that the Na impurity band merges with the diamond conduction band, with the Fermi level lying within and close to the bottom of the conduction band.

Determining thermodynamic transition levels using the nanocrystal approach, we find that Na_i induces a deeper (0/+) donor level at $E_c - 0.63$ eV, similar to interstitial lithium, due to quantum confinement effects.⁵⁴

Establishing the activation energy of diffusion in the same way as for Li_i , we find a value of 3.5 eV for the activation energy of diffusion of sodium. This is larger than has been predicted previously.¹⁰ To the best of our knowledge, the activation energy of diffusion of Na in diamond has not been determined experimentally.

This relatively high activation energy of diffusion of Na, implies that sodium is less likely to diffuse under processing conditions than interstitial Li.

2. Substitutional sodium

Considering the formation of substitutional Na (Na_s) in the same way as for substitutional Li, we find from all-electron periodic supercell calculations that Na_s assumes a structure with T_d symmetry, the Na_s -C distance increasing by 22.8% to 1.90 Å. This configuration possesses a net spin of $3.0 \mu_B$ per supercell, similar to Li_s . In contrast to Li_s , no metastable configurations were found for Na_s .

Nanocrystal calculations, on the other hand, predict a distorted C_{2v} geometry to be the most stable. As for Li_s , this difference is most likely due to the larger lattice constant in the nanocrystal calculations.

The DOS of Na_s from periodic supercell calculations is illustrated in Fig. 2. It is seen that Na_s induces deep partially occupied levels in the diamond band gap; levels closest to the Fermi level are spin polarized by 1.08–1.23 eV. Importantly, it is evident from these deep levels that substitutional Na is not only itself passivated but will also compensate other interstitial donors in the same way as substitutional Li.

Determining the relative formation energy of interstitial Na versus substitutional Na in the same way as for Li, we find a stability gain of 8.73 eV for the trapping of Na_i at a vacancy. Comparing this with the formation energy of a vacancy in diamond of 5.86 eV, we find that the formation energy of substitutional sodium is 2.87 eV lower than that of interstitial sodium.

This leads to the interesting result that sodium will be incorporated in diamond as a substitutional acceptor, rather than as an interstitial donor, in contrast to previous expectations,¹⁰ but consistent with experimental observations of sodium diffusing as a negatively charged acceptor in diamond.²⁶

We therefore conclude that not only will substitutional Na compensate any interstitial Na donors in the same way as Li but substitutional Na will also form in preference to interstitial sodium in diamond, where it will act as a deep acceptor, compensating other interstitial dopants. This explains the high electrical resistance observed for all Na doped diamond samples^{24,36} and is consistent with the experimental observation of Na being more soluble than Li in diamond.²⁶

Further, due the large stability gain for the trapping of Na_i at a vacancy and the fact that it is energetically favorable for substitutional Na to form in preference to interstitial Na, it is evident that Na trapped at a vacancy or other lattice damage is likely to remain trapped in the form of substitutional Na. This explains the lack of diffusion of Na observed in ion-implanted diamond, even at elevated temperatures.³¹

V. CONCLUSIONS

We have demonstrated that although interstitial Li and Na are shallow donors in diamond, interstitial Li will readily

diffuse with a low activation energy of diffusion of 1.3 eV or less.¹⁴ Diffusing interstitial Li is shown to be trapped at existing vacancies in diamond, with a substantial energy gain of 4.12 eV. The resulting substitutional Li and Na impurities are themselves not only passivated but will also induce deep levels in the diamond band gap, compensating other interstitial donors. This explains the electrical inactivity or high resistivity observed experimentally in Li and Na doped diamond.

We suggest that the deep, metastably occupied level at 1.5 eV observed in Li doped diamond¹¹ may be related to substitutional Li, while shallow Li levels of 0.17–0.23 eV with high resistivity have previously been suggested to be due to variable range hopping²⁴ or residual damage.^{24,27}

The large stability gains for the trapping of Li and Na at existing vacancies in diamond (4.12 and 8.73 eV, respectively) show that Li_i and Na_i captured at a vacancy are likely to remain trapped as substitutional impurities, explaining the experimentally observed lack of diffusion of Li and Na in ion-implanted diamond, even at elevated temperatures.^{18,29,31}

We have further shown the geometry of substitutional Li to be in agreement with the results of emission channeling studies.¹³ In addition, emission channeling studies¹³ find a substantial fraction of implanted Li occupied substitutional sites, consistent with our results.

For sodium, on the other hand, we have shown that contrary to previous expectations,¹⁰ it is energetically more favorable for Na to be incorporated in diamond as a substitutional acceptor rather than as an interstitial donor, with the formation energy of substitutional Na found to be 2.87 eV lower than for interstitial Na. This is consistent with experimental results of Na diffusing as a negative ion under electric bias.²⁶

In the search for alternative dopants in diamond, we therefore suggest that interstitial Li is likely to be a more attractive alternative shallow donor than sodium, despite the low activation energy of diffusion of Li_i . We propose that in order to achieve successful *n*-type doping using Li_i , samples should not be exposed to elevated temperatures in order to prevent Li_i diffusion. Simultaneously, concentrations of vacancies and other defects should be minimized to restrict the formation of compensating substitutional Li acceptors. Indeed, recent studies⁸ where the amount of damage to diamond was minimized and samples were not exposed to elevated temperatures during or after doping showed evidence of *n*-type doping.

Note added in proof. Goss *et al.*⁵⁸ have recently published a theoretical study of Li and Na in diamond; their findings are consistent with the results published here.

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