

## Direct conversion of graphite into diamond through electronic excited states

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## TOPICAL REVIEW

# Direct conversion of graphite into diamond through electronic excited states

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## Abstract

An *ab initio* total energy calculation has been performed for electronic excited states in diamond and rhombohedral graphite by the full-potential linearized augmented plane wave method within the framework of the local density approximation (LDA). First, calculations for the core-excited state in diamond have been performed to show that the *ab initio* calculations based on the LDA describe the wavefunctions in the electronic excited states as well as in the ground state quite well. Fairly good coincidence with both experimental data and theoretical prediction has been obtained for the lattice relaxation of the core exciton state. The results of the core exciton state are compared with nitrogen-doped diamond. Next, the structural stability of rhombohedral graphite has been investigated to examine the possibility of the transition into the diamond structure through electronic excited states. While maintaining the rhombohedral symmetry, rhombohedral graphite can be spontaneously transformed to cubic diamond. Total energy in the rhombohedral structure has been calculated as a function of cell volume  $V$ ,  $c/a$  ratio and bond length between layers  $R$ . The adiabatic potential energy surfaces for the transition from rhombohedral graphite to diamond in the states after core excitation have been investigated. In core exciton state, the graphite structure is more stable than the diamond. In the valence hole state after the Auger decay process, in contrast, the graphite structure is remarkably unstable compared with the diamond. The conversion into diamond from graphite can be induced spontaneously even at room temperatures due to excited holes. The induced holes decrease the stable interlayer bond length, which can lower the activation energy for buckling displacement of the hexagonal bonds, and the activation energy becomes zero by increasing the concentration of holes up to 0.1/C atom. These results predict that diamond synthesis is possible by a core excitation through the Auger decay process.

(Some figures in this article are in colour only in the electronic version)

## Contents

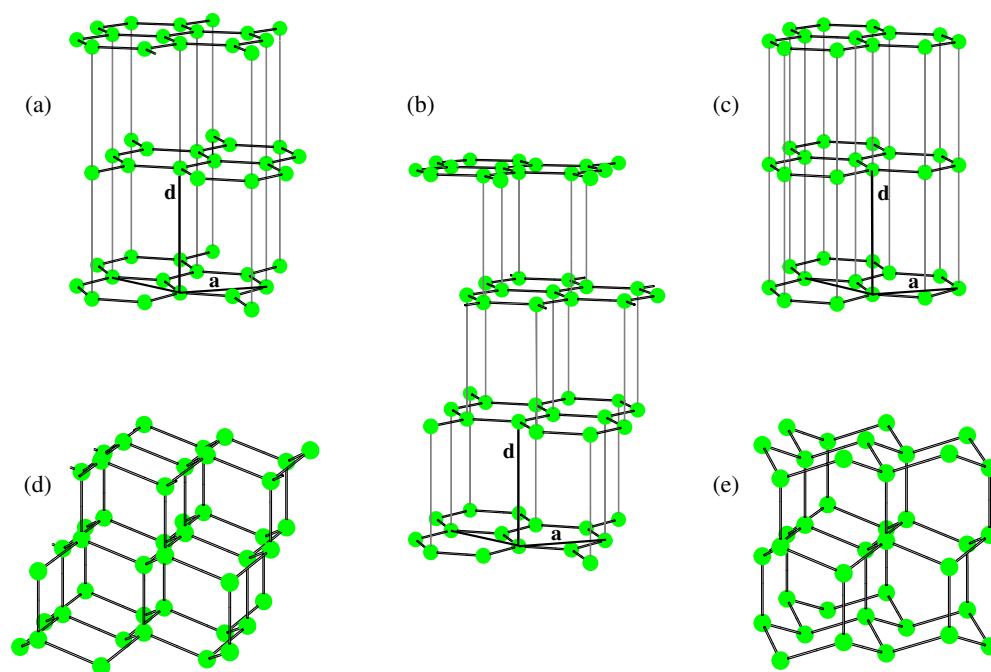
|  |      |
|--|------|
| 1. Introduction  | 1078 |
| 2. Ground state structures   | 1081 |
| 3. Core exciton state in diamond   | 1082 |
| 4. Graphite-to-diamond transition induced by core excitation                     | 1084 |
| 4.1. Dependence on pressure  | 1084 |
| 4.2. Core hole excitation  | 1085 |
| 4.3. Hole excitation in valence band   | 1086 |
| 4.4. Theoretical prediction of a new diamond synthesis method by core excitation | 1089 |
| 5. Concluding remarks  | 1090 |
| Acknowledgments  | 1090 |
| References   | 1090 |

## 1. Introduction

In nature, carbon is stable in two forms, i.e. diamond and graphite. While the graphite phase is slightly more stable, the diamond phase can exist in normal conditions as a metastable state. The total energies of the diamond and graphite structures are almost degenerated and the activation energy for the transition between them is very high. Diamond has been used as a jewel because of its brightness, and it is applicable also for industrial use as semiconductor devices. This is because diamond has a wide variety of extreme physical properties: hardness, large thermal conductivity, wide band-gap semiconductor with high carrier mobility, low dielectric constant, optical transparency for visible light, negative electron affinity, and so on [1]. Diamond has been synthesized artificially from graphite by applying high pressure at high temperatures. However, such industrial diamonds contain many impurities from catalysts.

We will propose here a new method for diamond synthesis by electronic excitation. In the ground state, the positive charge at the nuclei balances the negative charge density from electrons. Thus the crystals are stable against perturbations induced by elementary excitations such as phonons. Once they are in electronic excited states, in contrast, the excited atoms begin to move to a new equilibrium position because the position of the atoms, which was stable in the ground state, becomes stable no longer. There arises a possibility of fabricating new materials by making transitions to a metastable state by way of the electronic excited states from the ground state.

In particular, core excitation using x-rays from a synchrotron radiation (SR) light source can induce large displacements of the excited atoms even in covalent crystals like diamond and graphite. This is because the core exciton is well localized due to the essentially infinite effective mass of the core hole and because the excited electron occupies the anti-bonding orbital around the excited atom. Moreover, in the multiple charged state after the Auger decay processes, Coulomb repulsion between the excited atom and its neighbours may induce further large displacements. The core exciton state in diamond [2–9] is a typical example in which the movement of the excited atom is induced by electronic excitation. Instead of a very short lifetime of the core exciton state, a large off-centre relaxation in the [111] direction due to a quasi-Jahn–Teller effect has been observed with x-ray resonant emission spectroscopy. Also in graphite, a strong vibronic coupling has been observed when the core electron is excited to  $\sigma^*$  band threshold [6]. This indicates the existence of atomic displacement along one of the three C–C bonds on the honeycomb plane and that the trigonal symmetry of the ground state is broken. Crystallization of amorphous silicon after SR x-ray irradiation is another example [10], which is applicable to the fabrication of crystalline silicon. In amorphous



**Figure 1.** Crystal structures of solid carbon: (a) hexagonal graphite, (b) rhombohedral graphite, (c) simple hexagonal graphite, (d) cubic diamond, and (e) hexagonal diamond.

carbon, an increase in the  $sp^3$  bond and a decrease in the  $sp^2$  bond after SR x-ray irradiation has been observed [11]. This indicates a structural change to a diamond-like structure induced by the core excitation.

The graphite structures can be classified into three types according to the stacking sequence of the honeycomb planes. The first is the hexagonal or Bernal structure [13] shown in figure 1(a), which has an AB stacking. Half of the atoms are directly located just above each other in adjacent planes and the other half are directly above the centres of the hexagonal rings in the adjacent plane. The space group symmetry of this structure is  $D_{6h}^4$ . The second is the rhombohedral structure shown in figure 1(b), which has an ABC stacking. Half of the atoms are directly above atoms in the adjacent plane and directly below the centres of the hexagonal rings, and the other half are directly below atoms and above the ring centres. The space group symmetry of this structure is  $D_{3d}^5$ . Finally, we can consider the simple hexagonal graphite structure shown in figure 1(c), which has an AA stacking. All atoms are directly above each other in the adjacent planes. The space group symmetry of this structure is  $D_{6h}^1$ . The hexagonal diamond structure, shown in figure 1(e) is obtained from simple hexagonal graphite by decreasing the interlayer distance and by buckling the hexagonal rings. Each plane A (or B or C) can be transformed into each other by slipping the plane by the amount of the intralayer bond length or by  $60^\circ$  rotation around the perpendicular axis for the planes. Natural graphite exists in the hexagonal structure with 5–15% of the rhombohedral structure intermixed in a mosaic combination with the hexagonal form and with disordered graphite. Crystals of almost pure hexagonal graphite can be made by heat treatment and quenching. Although the rhombohedral form is not obtained in isolation, it is suitable for theoretical calculations because, by the simple geometrical relationship, the rhombohedral graphite structure can be continuously transformed into the cubic diamond as a function of the bond length between

layers  $R$ , by decreasing the interlayer distance and by buckling of the hexagonal rings. Thus we can calculate the potential energy surfaces (PESs) for the transition from graphite to diamond by maintaining rhombohedral symmetry. Such calculations have already been shown by several researchers [14–16] in the ground state. However, calculations of the PES in the electronic excited states are also needed in order to investigate the possibility of a graphite-to-diamond transition induced by core excitation.

For this purpose, *ab initio* total energy calculations for the rhombohedral structures in electronic excited states have been performed to compare with the results in the ground state. Remarkable results have been obtained on the theoretical prediction about the direct conversion from the graphite structure into the diamond through electronic excited states [12]. *Ab initio* total energy calculations have been performed for the rhombohedral structure, including the cubic diamond structure and the rhombohedral graphite structure. The adiabatic PES under the transition from the graphite structure to the diamond can be calculated by maintaining the rhombohedral symmetry. We have found that the graphite structure becomes greatly destabilized when holes are excited in the valence  $\pi$  band. The excited holes can cause instability for the plane configuration of graphite and can induce a transition from the graphite into the diamond structure, while changing the bonding character from  $sp^2$  to  $sp^3$ .

Calculations were performed by the full-potential linearized augmented plane wave (FLAPW) method within the framework of the local density approximation (LDA). We have used the KANSAI-99 source code, which was developed by Osaka University. Gunnarsson-Lundqvist's parametrization for the exchange correlation potential [17] was adopted. Although the density functional theory does not guarantee accuracy in expressing the excited states, the self-consistent calculations based on the LDA successfully simulate the PES in the core exciton state of diamond [9] and the desorption process of halogen atoms on silicon surfaces [18]. We have calculated the electronic structure of diamond in the core exciton state in order to check the validity of our calculations. A supercell which contains 31 atoms and a core-excited atom at the body centre site was used for calculations of the core-excited diamond. For the calculation of rhombohedral graphite, a rhombohedral supercell which contains seven carbon atoms and a core-excited atom was used. In both cases, a core-excited atom is treated like an impurity. Unlike calculations using the pseudopotentials [9], the core states are also taken into account as well as valence states in the calculation process of potential generation. The self-consistent calculations were performed under the condition that the electron excited from the C 1s core level occupy the lowest unoccupied state, namely the bottom of the conduction band ( $\pi^*$  state).

The structural stability in the state with holes in the valence band has been investigated as the excited state after the Auger decay process by decreasing virtually the total electron number in the unit cell. The uniform charges that cancel the excited holes are spread over the cell so that charge neutrality for the system is satisfied. In other words, the excited holes are screened by free electrons in the jellium model. Muffin-tin radii were chosen as 0.672 Å (1.27 au) for all the atoms. The plane waves with kinetic energy up to 24.0 Ryd were taken in calculations. The number of plane wave basis functions depends on the cell volume and was typically 170 per constituent atom for the ground state configuration of rhombohedral graphite. To describe the Bloch states, 189  $k$  points in the irreducible Brillouin zone with  $(n_x, n_y, n_z) = (12, 12, 4)$  were sampled for calculations of the rhombohedral structures for the ground state. In the supercell calculation for the core-excited state, the corresponding 60  $k$  points with  $(n_x, n_y, n_z) = (6, 6, 4)$  were required.

The calculated results for the ground state energetic stability between diamond and graphite are shown in the next section. The results for the core exciton state in diamond are shown in section 3. Fairly good coincidence with experiment or other calculations has been obtained

**Table 1.** The ground state results for lattice parameter  $a$ , interlayer distance  $d$  and total energy difference  $\Delta E$ . In cubic diamond,  $a$  and  $d$  for the rhombohedral unit cell are shown. The lattice constant  $a_{cub}$  for the conventional cubic cell of diamond is shown with  $a$  and  $d$  as  $a_{cub} = \sqrt{2}a$  and  $d/a = \sqrt{2/3}$ .

|                             | Stacking sequence | Lattice parameters |        | Total energy $\Delta E$ (eV/atom) | $k$ points ( $n_x, n_y, n_z$ ) |
|-----------------------------|-------------------|--------------------|--------|-----------------------------------|--------------------------------|
|                             |                   | $a$ (Å)            | $d/a$  |                                   |                                |
| <i>Graphite</i>             |                   |                    |        |                                   |                                |
| Simple hexagonal            | AA                | 2.445              | 1.447  | 0.075                             | 133 (12, 12, 12)               |
| Hexagonal (exp.)            | AB                | 2.446              | 1.328  | 0.061                             | 76 (12, 12, 6)                 |
| Rhombohedral                | ABC               | 2.446              | 1.324  | 0.059                             | 189 (12, 12, 4)                |
| <i>Cubic diamond</i> (exp.) | ABC               | 2.493              | 0.8165 | 0.000                             | 189 (12, 12, 4)                |
|                             |                   | 2.522              |        |                                   |                                |

for the lattice displacement induced in the core exciton state. Section 4 is devoted to our main prediction of the graphite-to-diamond transition induced by the core excitation. A new method of diamond synthesis by core excitation is presented and discussed. Finally, our results are summarized in section 5.

## 2. Ground state structures

Table 1 shows calculated results of the lattice parameter  $a$ , the interlayer distance  $d$  and the total energy difference relative to that of diamond for the ground state configuration of each crystal structure. In order to compare the results for the graphite structures, calculations for the cubic diamond structure were performed by using the rhombohedral primitive cell. The calculated lattice parameters  $a$  and  $d$  for the hexagonal graphite and the cubic diamond are in good agreement with experimental data. Although they are smaller by  $\sim 1\%$ , this is characteristic of calculations using the LDA. In these three different graphite structures,  $a$  are almost the same. This indicates that in-plane  $\sigma$  bonding is almost unchanged for the different stacking sequences of the planes. The interlayer distance  $d$  changes slightly with a change in stacking. However, the interlayer distance for rhombohedral graphite is almost the same as that for hexagonal graphite. In contrast, the change of the stacking sequence greatly affects the electronic structure at the Fermi level through a decrease/increase of the transfer integral between the  $\pi$  orbitals [19]. Our calculations tell us the rhombohedral graphite is a semiconductor with a band-gap of 0.8 eV, while the others are semi-metallic.

Rather contradictory results have been obtained for the stability between the graphite structure and the diamond in the ground state. In our calculations, the cubic diamond structure is stabilized too much. The calculations were checked by increasing the plane waves with cut-off energy from 20.0 to 40.0 Ryd, but the stability remains unchanged within the differences of 2 meV. This result contradicts experiments [20] or other calculations using the LDA [16, 21, 22]. Experimentally, the enthalpy difference between diamond and graphite measured from heat combustion is about  $-19$  meV/atom [20]. After taking into account the correction for vibrational zero-point energy between the two structures [21], the estimated total energy difference should be  $-40$  meV/atom. On the other hand, previous LDA calculations have shown that the total energies for these two structures are nearly equal, except for computational uncertainties. Recent calculations using the generalized-gradient approximation (GGA) [22–24] succeed in predicting the stability between the two structures with high accuracy. The GGA lowers the total energy of the less dense graphite structure by more than that of

the diamond structure. However, the calculated  $c/a$  ratio using the GGA tends to be too large [22].

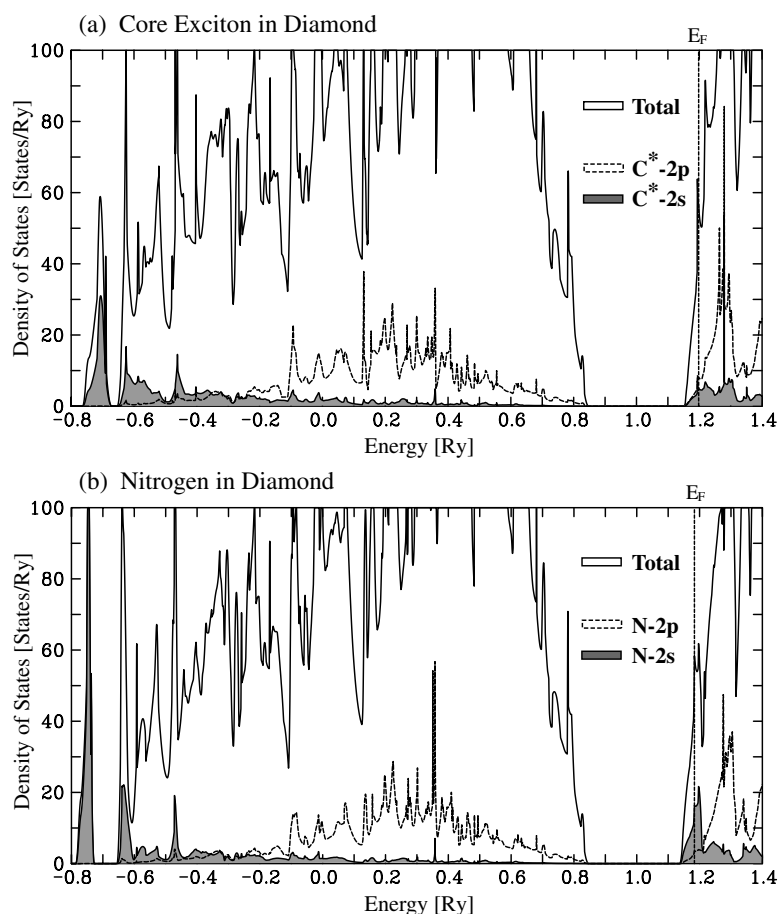
Although our calculations fail to predict the stability between the diamond and the graphite structures in the ground state quantitatively, this does not affect our conclusions on the stability in the excited states, since the total energy differences in the excited state become much larger than that in the ground state. As shown in section 4, they are typically of the order of 1 eV/atom. Therefore the calculated energy difference of about 60 meV/atom in the ground state is negligibly small compared with that in the excited states. In contrast to the ground state, where the total energies of diamond and graphite are almost degenerate, their energetic stability changes drastically in the excited states. On the other hand, our calculations may underestimate the activation energy for the graphite–diamond transition and its dependence on pressure.

### 3. Core exciton state in diamond

Extensive studies have been made on the core exciton state of diamond since the first observation by Morar *et al* [2]. Controversial results were obtained about whether the wavefunction of the C 1s core exciton is diffused [2, 3], like an effective-mass donor, or is strongly localized [4, 5], until Tanaka and Kayanuma had clarified the lattice relaxation dynamics of the core exciton in diamond [8]. Ma *et al* [6] observed a broad phonon sideband in the x-ray emission spectrum for the resonant excitation of the core exciton in diamond, while in the absorption spectrum they observed just a sharp peak structure. They attributed this broad structure in the emission spectrum to the Jahn–Teller distortion. In contrast, Mainwood and Stoneham [7] showed, with a self-consistent molecular dynamics simulation, that the excited C atom undergoes a substitutional displacement in the [111] direction with a relaxation energy of 1.12 eV, but they attributed the origin of the off-centre instability to the population of an anti-bonding orbital, not a Jahn–Teller effect. Finally, Tanaka and Kayanuma [8] succeeded in reproducing the unique feature of both the absorption and emission spectra observed by Ma. They mentioned the lattice instability is caused mainly by a quasi-Jahn–Teller effect. The electron excited to the shallow p-like state with  $T_2$  symmetry undergoes nonradiative transitions to the deep s-like state with  $A_1$  symmetry, to which the transition from the C 1s core level is dipole-forbidden [4]. This  $A_1$  state makes an instability for the lattice through the quasi-Jahn–Teller effect, resulting in the large off-centre displacement along the [111] direction.

Mauri and Car have already calculated the relaxed configuration for the lattice and PES in the core exciton state by an *ab initio* pseudopotential approach using the LDA [9]. In the relaxed configuration, the excited atom and one of its nearest neighbours move away from each other along the [111] direction. They have found that the corresponding displacements from the ideal lattice are 13.8% for the excited atom and 14.5% for the nearest neighbour, and the bond is stretched by 28.3% with a relaxation energy of 0.86 eV. On the other hand, our calculations give the corresponding displacements as 13.8 and 14.0% of the bond length, respectively. The other three nearest neighbour atoms also move away from the excited atom slightly by 1.8%. The relaxation energy is calculated to be 0.82 eV, while the binding energy for the core exciton, which was calculated in the manner of Mainwood and Stoneham [7], is 1.31 eV. Consequently, our results are in good agreement with experiment and other *ab initio* calculations.

This problem is also of special interest because the core exciton in diamond is related to the substitutional nitrogen impurity problem [25–28] in diamond; the potential of the excited core seen by the valence and conduction electrons is equivalent to that of a  $Z + 1$  atom, i.e. nitrogen.



**Figure 2.** The DOS for the calculated (a) core exciton in diamond and (b) nitrogen in diamond. The contributions of 2s and 2p electrons at the impurity site (magnified 5 times) are also shown in the figures.

However, this approximation is inappropriate for the 2s electrons. Figure 2 shows the density of states (DOS) for the core exciton in diamond and for the nitrogen impurity in diamond, for the unrelaxed configuration with  $T_d$  symmetry. The contributions of the 2p electrons to the total DOS, which are plotted by a broken curve, are almost the same between the core exciton and the nitrogen. In contrast, the differences can be recognized in the 2s contributions shown as grey; the 2s states of the core exciton are somewhat shallower than that of nitrogen.

In general, the point charge at the nucleus seen by the valence electrons is screened by the core electrons. After the excitation of the core electron, the valence electrons see additional charges from the core hole. Because the core hole is strongly localized at the nucleus, the approximation that the charge from the core hole can be regarded as a point charge at the nucleus is, in most cases, appropriate. However, the spreading of the wavefunction of the C 1s core hole cannot be neglected for the valence 2s electrons. As a result, the potential of the excited core seen by the 2s electrons becomes less attractive than that of the nitrogen.

The energy gain in the  $A_1$  core exciton state by the lattice displacement  $Q$  through the quasi-Jahn–Teller effect,  $\Delta E_{JT}$ , can be described by the following equation using the second-



order perturbation formula:

$$\Delta E_{JT} = - \sum_i \frac{|\langle \psi_s | \partial H / \partial Q | \psi_i \rangle|^2}{\epsilon_i - \epsilon_s} Q^2, \quad (1)$$

where the summation for  $i$  runs over all unoccupied states with energy  $\epsilon_i$ . In the core exciton state of diamond, the energy of the occupied s-like  $A_1$  state,  $\epsilon_s$ , is relatively larger than that in the nitrogen impurity state of diamond. Therefore the energy gain by the quasi-Jahn–Teller effect will be enhanced due to the increase in the reciprocal energy differences. In fact, the smaller relaxation energy has been obtained for calculation of the nitrogen in diamond; the calculated lattice displacements of the nitrogen atom and one of its nearest neighbour atoms are 10.7 and 13.7 % of the bond length, respectively, and the relaxation energy is calculated to only 0.29 eV.

As a result of the lattice displacement in the core exciton state, the local structure around the excited atom after lattice relaxation becomes totally graphitic. This may suggest that, in the core exciton state, the graphite structure is more stable than the diamond structure. The structural stability between diamond and graphite in the core exciton state is discussed in detail in the next section.

#### 4. Graphite-to-diamond transition induced by core excitation

##### 4.1. Dependence on pressure

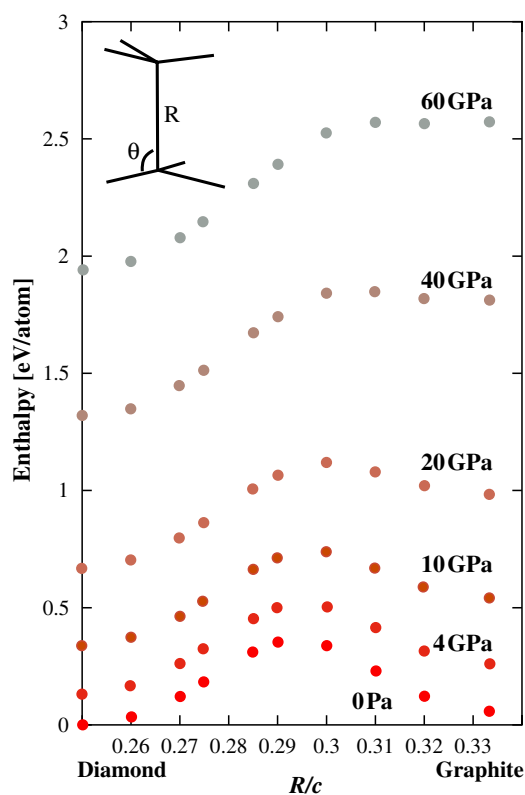
The rhombohedral structure is specified by three parameters: cell volume  $V$ ,  $c/a$  ratio and bond length between layers  $R$ . The rhombohedral graphite structure is realized when  $R = \frac{1}{3}c$ ; the six atoms which construct the hexagonal ring are in the same plane. The perfect cubic diamond structure is realized when  $R = \frac{1}{4}c$  and  $c/a = \sqrt{6}$ . We treat  $R/c$  ( $\equiv r$ ) as the independent variable in transforming the graphite structure into the diamond structure. The PES for the transition from rhombohedral graphite to cubic diamond can be investigated by calculating the total energy  $E(V, \beta, r)$  as a function of  $V$ ,  $\beta$  ( $\equiv c/a$ ) and  $r$  ( $\equiv R/c$ ).

The hydrostatic pressure  $p$  is defined as

$$p = - \frac{dE_{min}(V)}{dV} \quad (2)$$

where  $E_{min}(V)$  is the minimum value of  $E(V, \beta, r)$  for each  $V$ , that is,  $E(V, \beta, r)$  when  $\partial E / \partial \beta = 0$  and  $\partial E / \partial r = 0$  for each  $V$ . If  $\partial E / \partial \beta \neq 0$  or  $\partial E / \partial r \neq 0$ , the pressure cannot be a well defined variable because the internal force or the stress is not zero. However, the definition of pressure can be extended for each given  $r$  as  $p = -\partial E(V, \beta, r) / \partial V$ , in order to investigate the transition path under pressure. The free energy (enthalpy) is calculated as  $H = E + pV$ . For each given  $r$ , a set of  $V$  and  $\beta$  which optimize the total energy under the condition that  $\partial E / \partial V = -p$  and  $\partial E / \partial \beta = 0$  is determined from the cubic spline fit of the calculated data, in order to find the PES for the transition from graphite to diamond.

PES for the ground state and its dependence on the applied pressure are shown in figure 3. See how the graphite phase becomes unstable with an increase of the applied pressure. In the ground state, the activation energy from the rhombohedral graphite structure to the diamond structure is found to be 0.29 eV/atom when the pressure is not applied. Compared with similar calculations by Fahy *et al* [15] or Furthmüller *et al* [16], our result slightly underestimates the activation energy. It decreases with increasing the applied pressure and is roughly estimated to be 0.2 eV at 10 GPa, and 0.1 eV at 20 GPa. Therefore high temperatures and high pressures are necessary in order to cause the transition into the diamond structure thermally in the ground state.

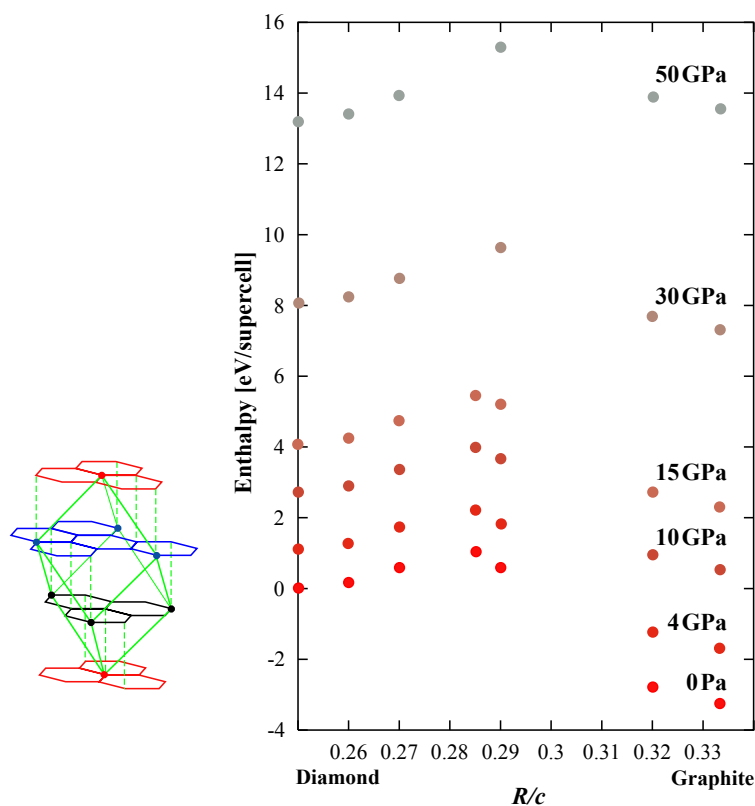


**Figure 3.** The PES in the ground state under the transition from the graphite structure to the cubic diamond and its dependence on the applied pressure.

#### 4.2. Core hole excitation

Calculations in the core excited state were performed by using the same value for the parameters  $V$ ,  $\beta$ ,  $r$  and  $p$  ( $= -\partial E/\partial V$ ) as in the ground state. The effect of the local lattice relaxation of the excited atom and its neighbours is not taken into account. PES in the core excited state and its dependence on the applied pressure are shown in figure 4. In the core-excited state, the graphite structure is stabilized in energy, while the diamond structure is still metastable. The reason why the graphite structure becomes more stable than the diamond structure in the core-excited state is attributed to the difference in the band-gap energy. In our calculations, the excited electron from the core level occupy the lowest unoccupied state, which lies at the bottom of the conduction band. The excited electron in the diamond structure has a much larger kinetic energy than that in the graphite structure, owing to the larger band-gap energy of about 5 eV.

As shown in the previous section, the local lattice displacement around the excited atom is induced in the core exciton state in diamond. This local lattice relaxation can lower the total energy in the core-excited state in the diamond structure. However, the energy difference between the diamond and the graphite structure is about 3.4 eV from figure 4, while the relaxation energy of the core exciton in diamond is calculated to be 0.82 eV. Therefore, the graphite structure is still more stable than the diamond, even if the local lattice relaxation around the core-excited atom is taken into account. The activation energy in the core exciton



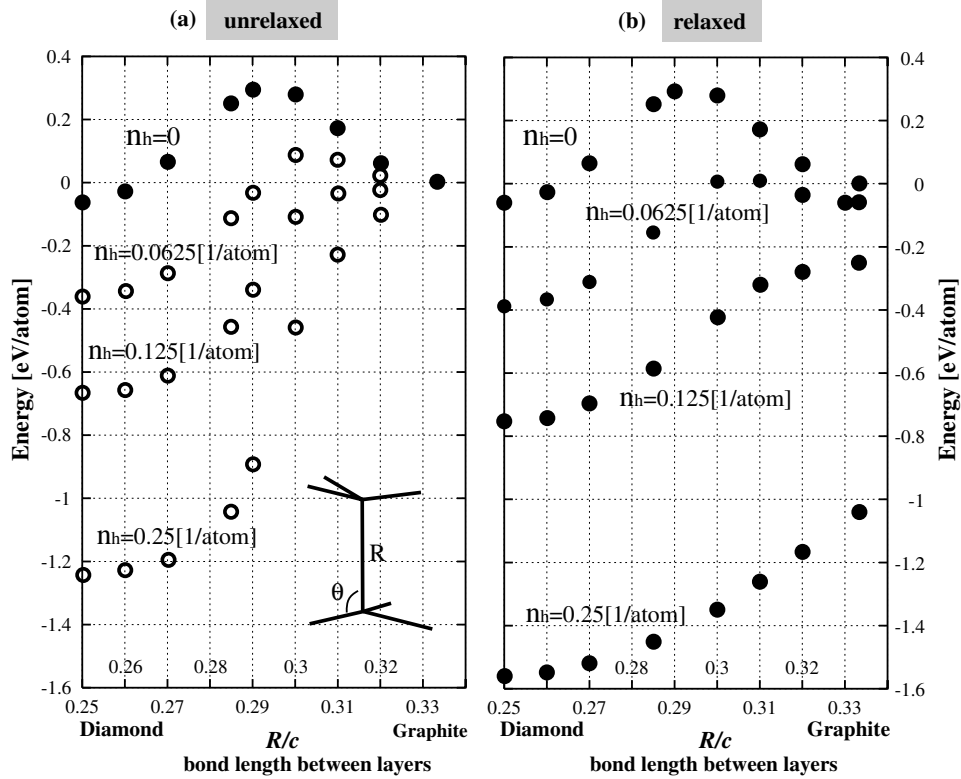
**Figure 4.** The PESs in the core excited state. The supercell used in the calculations is shown on the left side.

state decreases by increasing the applied pressure, but it is relatively larger than that in the ground state. The graphite-to-diamond transition is unlikely to occur in the core-excited state.

#### 4.3. Hole excitation in valence band

Finally, the structural stability in the excited state after the Auger decay process is investigated by introducing holes into the valence band. As seen in figure 5, the graphite structure becomes markedly unstable by the doped holes in the valence  $\pi$  band. The total energy was at first calculated as a function of  $r$  by using the same parameters  $V$ ,  $\beta$  and  $r$  as in the ground state. This result for the unrelaxed configuration is plotted by open circles in the left side of figure 5. Next, the total energy was minimized for each given  $r$  in order to consider the effect of the relaxation of the lattice parameters  $V$  and  $\beta$  induced by doped valence holes. This result is plotted by full circles in the right side of figure 5. The activation energy for the transition into diamond exists for a hole concentration of  $n_h = 0.0625/\text{atom}$ . For higher concentrations of  $n_h = 0.0125$  and  $0.025/\text{atom}$ , however, it vanishes and the graphite structure becomes completely unstable.

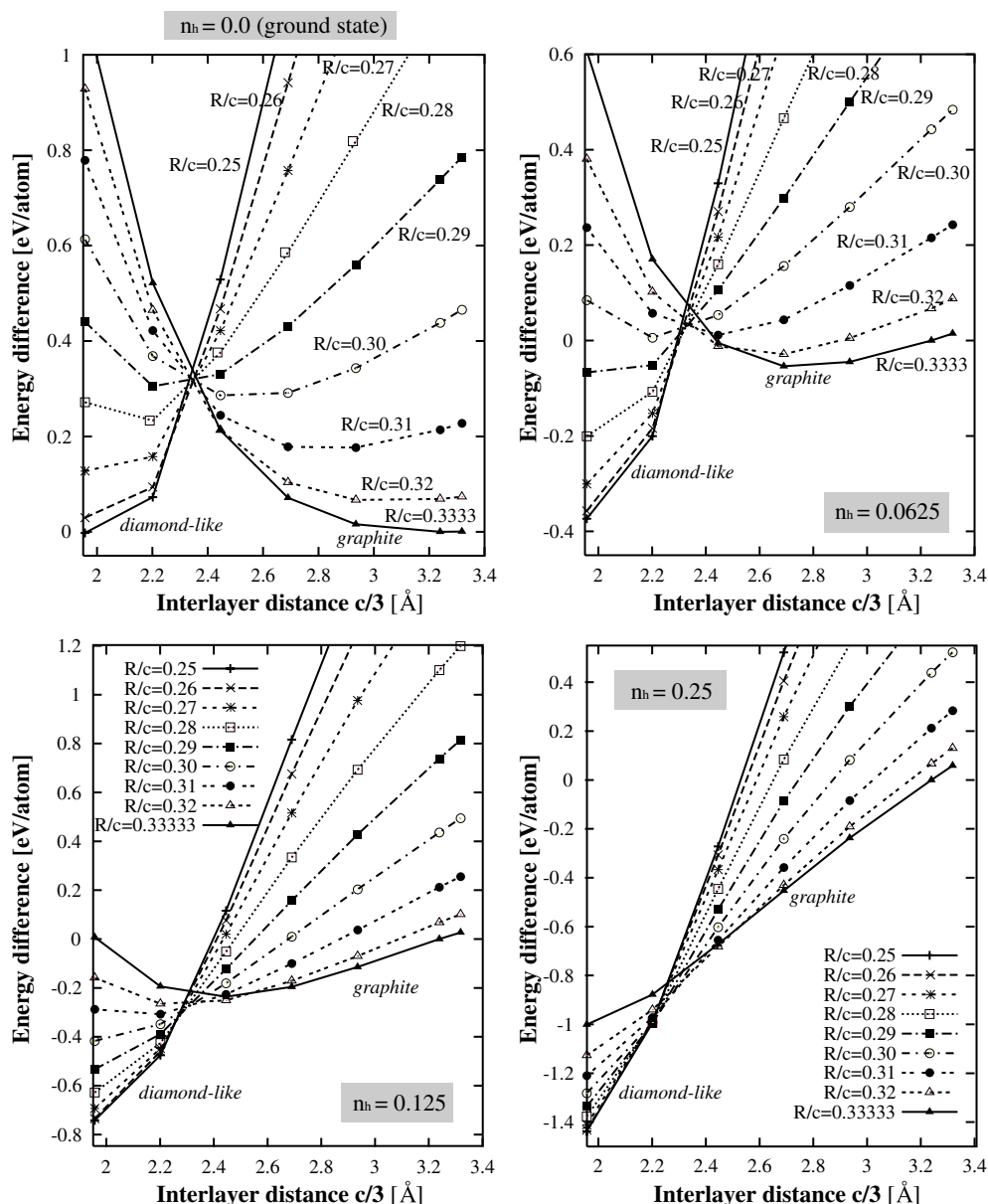
As a result of the lattice relaxation by doped valence holes, a decrease in the bond length between layers,  $R$ , can be induced, which results in shrinkage of the whole lattice. The cell volume of the rhombohedral graphite structure shrinks to 83% and the  $c/a$  ratio decreases from 3.97 to 3.38 when the hole concentration  $n_h$  is 0.0625/atom. When  $n_h$  is 0.125 or 0.25/atom,



**Figure 5.** The PESs for the hole doped state in the valence  $\pi$  band. Total energies relative to that for the ground state rhombohedral graphite structure are plotted for each hole concentration  $n_h$ . The data calculated by using the same lattice parameters as that of the ground state are plotted by open circles in the left figure. After taking into account the lattice relaxation, the diamond structure is markedly stabilized as plotted by full circles in the right figure.

it shrinks further to 72 or 58% and  $c/a$  decreases to 2.99 or 2.45, respectively. This shrinkage of the lattice comes mainly from the decrease of the interlayer distance. The buckling of hexagonal bonds can proceed after the  $c/a$  ratio decreases to less than 3.0 and the interlayer bond length becomes around 2.4 Å (see figure 6). In contrast to the ground state, the excited holes decrease the stable interlayer bond length, which can lower the activation energy for the buckling displacement of the hexagonal bonds. In other words, doping holes in the graphite structure induce a similar effect as applying pressure. Since the lifetime of the valence hole in graphite ( $\sim$ ps) is considerably longer than that of the core hole ( $\sim$ 10 fs), the conversion into the diamond structure is likely to occur through the Auger process.

Recently, Watanabe and his co-worker have performed similar calculations for hole-doped rhombohedral graphite by using *ab initio* pseudopotentials and LDA [29], and reached similar conclusion to our results. They have also commented on the Coulomb interaction between the system and the uniform charge which is introduced virtually in order to keep charge neutrality. Although the energy losses by this Coulomb repulsion is not considered in calculations, they are negligibly small for a hole concentrations less than 0.1/atom and the gains in kinetic energy by doped holes overwhelm them. They have also predicted that the activation energy for the diamond transition vanishes at a hole concentration of  $n_h = 0.09/\text{atom}$ , which is consistent with our results.



**Figure 6.** Total energies as functions of the interlayer distance for the fixed lattice constant  $a$  of the ground state graphite structure. The plane structure of graphite is stabilized as long as the interlayer distance is more than 2.4 Å. The buckling of the hexagonal bonds can occur when the interlayer distance decreases to less than 2.4 Å. By hole doping, the stable interlayer distance becomes smaller, which can lower the activation energy for bond buckling and thus for the transition into the diamond structure.

It seems controversial that the structural change that breaks the trigonal  $\sigma$  bond can be induced by a hole doping in the valence  $\pi$  band. However, the  $\pi$  band plays an important role in the stability of the plane structures in graphite. The electron which occupies the bonding  $\pi$  band just below the valence band maximum (VBM) can contribute to stabilize the plane

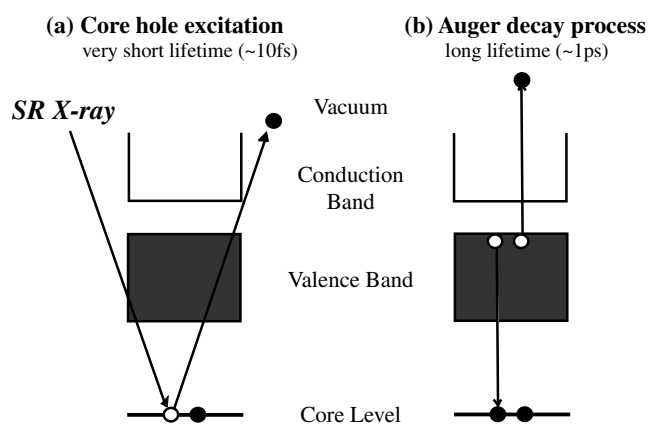


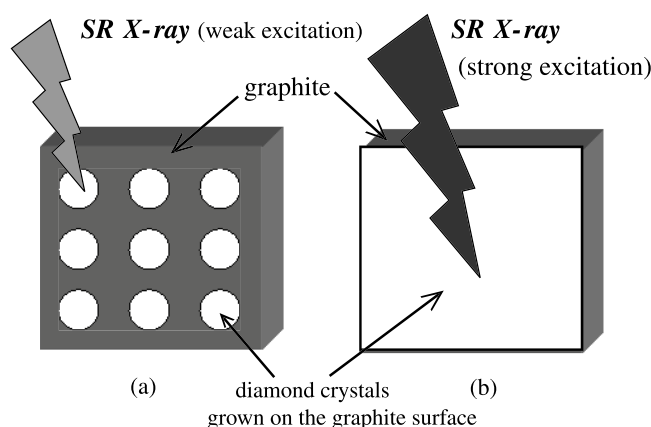
Figure 7. Relaxation process of graphite after SR x-ray irradiation.

configuration by forming the three-fold coordinate bond in the graphite structures. Two holes are doped in the bonding  $\pi$  band just below the VBM through the final states in the Auger decay process. Since the two doped holes make an instability in the plane structure of the graphite, the carbon atoms can migrate in the perpendicular direction by forming the strong covalent bond, changing the local structure gradually from the  $sp^2$  bond in the graphite structure to the  $sp^3$  in the diamond.

#### 4.4. Theoretical prediction of a new diamond synthesis method by core excitation

We have calculated the stability between the diamond structure and the graphite structure in the core excited state and the hole-doped state after the Auger decay process. We have shown that the graphite structure is unstable in the hole-doped state. When graphite is excited with SR x-rays, a hole is created at the C 1s core level. The lifetime of the core hole is about 10 fs and is very short. In this very short lifetime of the core hole, the core-excited graphite relaxes mainly to two hole bound states through the Auger process (see figure 7). In the final state of the Auger decay process, two holes are excited in the valence band. Since the lifetime of the valence hole in graphite is considerably longer and is about 1 ps, we can predict from our calculations that the conversion into diamond can be induced through the Auger decay process.

Diamond has been synthesized from graphite by applying high pressure at high temperatures with the addition of catalysts such as transition metals. However, such synthetic diamond contains many impurities from the catalysts. In contrast to the diamond synthesized under high pressure, the diamond created through core excitation does not contain any impurities. The conversion to diamond can proceed even at room temperature. Moreover, the size of the crystal is controllable at the nanoscale by tuning the irradiated areas and the intensity of the SR x-rays. The concentration of excited holes  $n_h$  can be controlled with the intensity of the SR x-ray. When the intensity of the SR light is low, so that the hole concentration  $n_h$  is less than 0.1/atom, both diamond and graphite can exist in the excited state. In this case, diamond nanocrystals can be created in graphite crystals as shown in figure 8(a). Under irradiation of high intensity SR light, on the other hand, a diamond single crystal can grow on graphite, since the graphite phase becomes completely unstable with increasing concentration of the excited holes up to 0.1/atom.



**Figure 8.** Design of a new diamond synthesis method by core excitation. The size of the diamond crystal can be controlled by tuning the intensity of SR x-rays.

## 5. Concluding remarks

We have performed *ab initio* calculations for excited states in diamond and graphite within the framework of the LDA. Our calculations successfully simulate the lattice displacements induced in the core exciton state in diamond. The stability in the rhombohedral graphite structure under electronic excitations has been investigated to search for the possibility of a transition into the diamond structure. The graphite structure is stable in the ground state and in the core-excited state. When holes are excited in the valence  $\pi$  band, in contrast, the plane configuration in the graphite structure becomes markedly unstable. The conversion into the diamond structure can occur, with a change in the bonding character gradually from the  $sp^2$  to  $sp^3$  by buckling of the hexagonal bonds.

The calculated results for the hole-doped rhombohedral structures indicate that, if one can dope holes in graphite by core excitation or by using other methods, the conversion into the diamond structure can be induced. The formation of nanodiamond on the graphite surface [30] is recently reported by using irradiation by highly charged ions. The high Coulomb potential of the highly charged ions causes multiple electron emissions from the surface atoms, and a considerable number of holes are excited on the graphite surface. This mechanism of nanodiamond formation by irradiation of highly charged ions can be explained theoretically as the structural instability induced by the doped holes in the valence band.

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