

Possible domain-type collective dimerization of graphite induced by interlayer charge transfer excitations in the visible region

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(Received 14 August 2009; revised manuscript received 22 October 2009; published 20 January 2010)

We theoretically study possible domain-type collective dimerizations of graphite induced by interlayer charge transfer excitations in the visible region. Using the semiempirical Brenner's model, we have calculated the adiabatic energy along the path that starts from original two distant graphite layers and finally reaches the dimerized domain which consists of about 100 carbons with interlayer σ bonds. The energy barrier between this new domain and the starting graphite is shown to be on the order of 1 eV, being easily overcome by applying a few visible photons. The early stage dynamics is also studied in the model that a photogenerated electron-hole pair spanning two layers, locally contracts the interlayer distance through the Coulomb attraction, and results in the σ -bond formation. Our considerations are aimed at clarifying mechanisms of interlayer dimerization recently observed experimentally.

DOI: [10.1103/PhysRevB.81.035417](https://doi.org/10.1103/PhysRevB.81.035417)

PACS number(s): 81.30.Hd, 61.66.-f

I. INTRODUCTION

There is considerable interest to form variety of nanostructures from the graphite crystal. Specific structures such as fullerenes and nanotubes are expected to lead to important applications for medicine, electronics, and nanoengineering.^{1,2} Meanwhile, recent experimental investigations suggest a possibility to photogenerate a novel non-equilibrium phase with interlayer σ bonds between two distorted graphite layers. In the experiment,^{3,4} graphite layers were illuminated by laser light polarized perpendicular to the layers. After this illumination, the STM analysis has revealed that a new buckling domain appeared, wherein four carbon atoms within a six-membered ring extruded out of the layer, whereas remaining two intruded inside of the layered crystal. The essential points of experiment^{3,4} are as follows. (1) The laser light with the energy 1.57 eV has to be polarized perpendicularly to graphite layers, while the parallel polarization gives no effect. This feature means that only an interlayer charge transfer excitation can trigger the transformation. (2) The exciting light should be a femtosecond pulse rather than picoseconds one. (3) The transformation is highly nonlinear multiphoton process, but less than ten-photon one. (4) The resulting domain consists more than 1000 atoms, being stable for several days at room temperature. (5) The surface-structural changes are not simply governed by excitation density, but are specifically triggered by p -polarized light that has an electric vector component parallel to the c axis, showing the electronic origin of the transformation.⁴

On the other hand, Raman *et al.*⁵ reported another interesting structural change in the graphite induced also by a femtosecond laser-pulse irradiation. Following an initial contraction of the interlayer spacing by less than 6%, the graphite is driven nonthermally into a transient new state with sp^3 -like interlayer bonds. The electron-diffraction investigations revealed that the newly contracted interlayer distance is about 1.9 Å.

The results of these experiments in Refs. 3–5 may be connected with the idea of the so-called photoinduced phase transition (PIPT),^{6–10} which has attracted great interests in recent years. As it is widely known, a photoexcited electron in an insulating crystal induces a local lattice distortion around itself. A sudden change in the charge distribution leads to motion of the surrounding crystal lattice, resulting in new equilibrium position within the excited state. This idea behind the PIPT may be associated with the hidden multistability: material besides its true ground state, also possesses a false one.^{1,6} These two stable states, the ground state and a metastable one, are often separated by a high-energy barrier, which is inaccessible by thermal fluctuations. However due to aforementioned photoexcitation and lattice relaxation, the system may jump from ground state to the metastable one, resulting in a new electronic and structural orders. This type of nonequilibrium phase transition has already been observed recently in many organic molecular solids, organic metal-complexes crystals, and in the Perovskite type compounds.⁶

In this paper, we will theoretically clarify a possibility of photogeneration of a graphite domain which consists of locally dimerized graphite layers with σ -type interlayer bonds. At first, we will examine possible candidates for this new domain structure. Next we will propose a simple electronic mechanism for the dynamics of this conversion. The whole process may be a very complicated, multistage phenomenon. Henceforth, in this paper, we will deal with its early stage dynamics. In a proposed scenario, a photoexcitation leads to a charge transfer from one graphite layer to its neighboring one, resulting in an electron-hole pair generation. Since graphite is a good electric conductor, this excitonlike electron-hole pair will mostly be dissipated as free carriers. However, as will be shown, there is a small but finite probability that the excitonlike state will remain at a same lattice site; this results in the graphite dimerization and may lead to a stable interlayer domain formation.

II. ADIABATIC POTENTIAL-ENERGY SURFACE

A. Model and method

In our model, we consider two, initially noninteracting graphite layers with the *ABAB*-type stacking. In this type of configuration half of the atoms are directly located just above each other in adjacent planes and the other half are above the centers of the hexagonal rings in the adjacent plane. New domain, whatever it may be, is immersed in the semimetallic graphite, and hence all the carbons are expected to be always almost neutral. To handle a great number ($\approx 10\,000$) of atoms with no translational symmetry, methods such as the local-density functional (LDF) approximation are no longer realistic, and in fact, prohibitively difficult. Henceforth we employ the semiempirical Brenner's potential approach.¹¹ The parameters of the potential are determined semiempirically, taking into account most of experimental and theoretical data of carbon clusters.¹¹

1. Brenner's potential

The cohesive energy of material is represented as a sum over the bonds which, following Brenner,¹¹ can be expressed as

$$E = \sum_i \sum_{j(<i)} [V_R(r_{ij}) - \bar{B}_{ij}V_A(r_{ij})], \quad (1)$$

i.e., it is taken over the bonds, of length r_{ij} between atoms j and i . $V_A(r_{ij})$ and $V_R(r_{ij})$ represent an attractive and a repulsive coupling within the bond, respectively, and they are given as

$$V_A(r_{ij}) = \lambda f_{CC}(r_{ij}) D_{CC}^e S_{CC} / (S_{CC} - 1) \times \exp \left[- \sqrt{\frac{2}{S_{CC}}} \beta_{CC} (r_{ij} - R_{CC}^e) \right], \quad (2)$$

$$V_R(r_{ij}) = \lambda f_{CC}(r_{ij}) D_{CC}^e / (S_{CC} - 1) \exp \left[- \sqrt{2 S_{CC}} \beta_{CC} (r_{ij} - R_{CC}^e) \right]. \quad (3)$$

After¹¹ the following parameters values are taken: $R_{CC}^{(e)} = 1.315$ Å, $D_{CC}^{(e)} = 6.325$ eV, $\beta_{CC} = 1.5$ Å⁻¹, $S_{CC} = 1.29$, $\delta_{CC} = 0.80469$, $R_{CC}^{(1)} = 1.7$ Å, $R_{CC}^{(2)} = 2.0$ Å, $\alpha_0 = 0.011304$, $c_0^2 = 381$, and $d_0^2 = 6.25$. Parameter λ was fitted to be $\lambda = 0.49$, so that it reproduces the energy barrier (0.33 eV/atom) obtained by the LDF calculation of Cohen and co-workers,¹² for the ordinary uniform graphite-diamond transition without changing the bond equilibrium distance. Thus, our approach is consistent with the LDF result,¹² if it is used for the uniform phase transition of an infinite carbon system with the translational symmetry. Although Brenner's potential does not take into account long-range (> 2 Å) interactions it does not cause serious mismatch. The transformation occurs only in limited volume (2 layers, 200 atoms each) and the energy difference due to long-range interactions is minor. In such a case energy contribution due to long-range interactions is several orders smaller than due to interlayer bond formation. Hence in the calculations we will focus our attention on predominant process governing the transformation and in this context use of Brenner's potential seems appropriate.

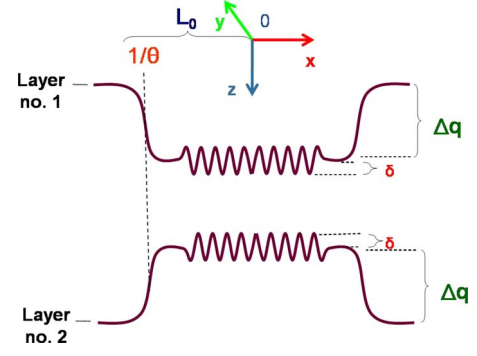


FIG. 1. (Color online) The distortion pattern used in the calculations: Δq —the planar intrusion amplitude, δ —the buckling amplitude, L_0 —the system size, and θ —the shape coefficient.

2. Model

Let us consider initially noninteracting, two graphite layers (200×200 neutral carbon atoms), whose each end is connected by the periodic boundary condition. In Eq. (2), the distance r_{ij}

$$r_{ij} \equiv |\bar{\mathbf{r}}_i - \bar{\mathbf{r}}_j| \quad (4)$$

is expressed in terms of $\bar{\mathbf{r}}_i$, defined as a shift from its original position ($\equiv \bar{\mathbf{r}}_{i0}$) in the graphite as

$$\bar{\mathbf{r}}_i \equiv \bar{\mathbf{r}}_{i0} + E_n(\bar{\mathbf{r}}_{i0}) \{ [\Delta q + \delta B_d(\bar{\mathbf{r}}_{i0})] \bar{\mathbf{e}}_z + \Delta X \bar{\mathbf{e}}_x \}, \quad (5)$$

where, $E_n(\bar{\mathbf{r}}_{i0})$ is the envelope of the new displacement

$$E_n(\bar{\mathbf{r}}_{i0}) = 0.5 \{ \tanh[\theta |\bar{\mathbf{r}}_{i0} - \bar{\mathbf{e}}_z(\bar{\mathbf{e}}_z \cdot \bar{\mathbf{r}}_{i0})| - L_0] - 1 \}. \quad (6)$$

$\bar{\mathbf{e}}_x$ and $\bar{\mathbf{e}}_z$ are the unit vectors in the x and z axes, respectively. As shown in Fig. 1, the parameters introduced in Eq. (5) are as follows: Δq —the amplitude of the planar deflation, L_0 —the size of the intruded domain, θ —the domain boundary width, and ΔX —the magnitude of the shear displacement. While $B_d(\bar{\mathbf{r}}_{i0})$ in Eq. (5) denotes the buckling pattern within the six-membered ring, and it will be defined in detail in the text later. In Fig. 1, this buckling is symbolically denoted by a zigzag line.

Inside of the intruded domain we introduce a buckling, perpendicular to the layer, with an amplitude δ . We will also assume that the center of mass of the six-membered ring is preserved. The deformation of the second layer is assumed to be symmetric as shown in Fig. 1. Using this method, one can calculate the adiabatic energy of the domain formation for selected values of parameters. The key feature is the top of the barrier or the stable point. The stable point formation is a result of competition of two processes: the σ -type interlayer bond formation resulting in an energy gain and the sp^2 -type intralayer bond tension resulting in an energy loss.

Using the above described pattern, we have performed the total cohesive-energy calculations. By varying values of selected parameters ($\Delta q, \delta, \theta, L_0$) we have obtained a potential-energy surface (PES) of the conversion, with some extremal points indicating stable configurations of distorted structures. Our goal is to find such values of parameters ($\Delta q, \delta, \theta, L_0$)

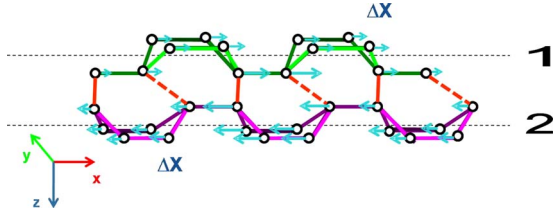


FIG. 2. (Color online) The trial pattern applied in calculations with the additional shear displacement; two atoms forming regular line along the x -axis direction are intruded with an amplitude δ , remaining atoms are extruded with the amplitude 0.5δ . In order to optimize interlayer bond angles, both deflated domains are shifted relatively in the x direction, as denoted $\Delta X(>0)$.

which minimize the energy barrier between the initial graphite structure and a new structure corresponding to a new stable point.

B. Results

Due to a large number of degrees of freedom in the system, there are various possible buckling patterns. Hence one can consider those reflecting the experiment results: four of carbon atoms in the six-membered ring are extruded and remaining two are intruded along the z axis (see Fig. 2) and in order to preserve center of mass, the amplitude of the buckling of extruded atoms is one half of intruded one. The buckling function $B_d(\vec{r}_{i0})$ of this case is also determined; furthermore we apply additional shear displacement ΔX along the x axis (Fig. 2).

Using the energy-barrier minimization technique described in the last section, we have performed large scale (80 000 atoms) calculations and calculated PES is shown in Fig. 3. The intrusion amplitude has the value $\Delta q=0.67 \text{ \AA}$ and buckling amplitude, $\delta=0.24 \text{ \AA}$. Corresponding energy

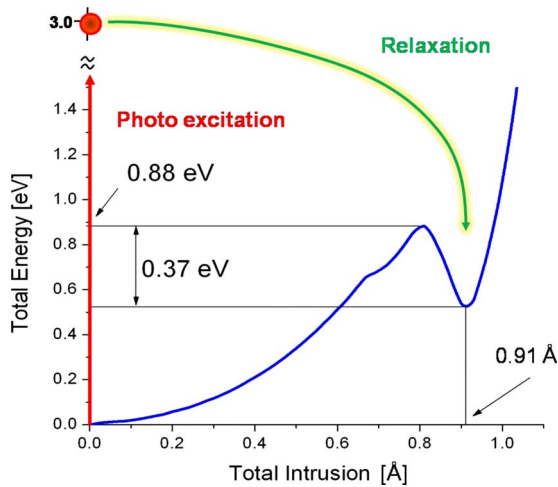


FIG. 3. (Color online) The PES of the transformation with the analyzed pattern. The horizontal axis indicates the total intrusion ($\delta+\Delta q$) of the domain. The second minimum occurs when the total intrusion $\delta+\Delta q=0.91 \text{ \AA}$ with the energy barrier 0.88 eV. This energy barrier may be easily overcome by visible excitations ($\approx 3 \text{ eV}$) and the system may reach the second minimum.

barrier is found to be $E_b=0.88 \text{ eV}$. Shifting the layers in the opposite directions by $\Delta X=0.35 \text{ \AA}$, we obtain a quite stable phase with the nearly 0.4 eV depth. In Fig. 4, we have shown the total energy in a two-dimensional space, as a function of Δq and $(\delta+\Delta q)$. One finds that $\Delta q \approx 0.6 \text{ \AA}$ and $\delta+\Delta q \approx 0.7 \text{ \AA} \sim 0.8 \text{ \AA}$ corresponds to the barrier top, and for $\delta+\Delta q=0.91 \text{ \AA}$, a stable domain is formed with σ -type interlayer bonds. In Fig. 5, the structure corresponding to the new minimum is shown.

Obviously this pattern do not exhaust all the possible buckling patterns. So, we have examined various other buckling patterns. Though variety of (meta) stable phases would be observed with respective different depths of potential well, the lowest energy barrier occurs in aforementioned one. Moreover, if we take the average over the buckling within each layer, the new interlayer distance is about 2 \AA , and the resultant structure (see Figs. 3 and 4), which is referred to as a “diaphite,”^{4,14} agrees well with the experiment.^{4,5}

III. EARLY STAGE DYNAMICS

Although we have calculated the adiabatic energy, the real process starts not from the ground state of graphite, but from the Franck-Condon-type excited state of the graphite as schematically shown in Fig. 3. One can expect that the whole system will relax down to the new minimum from Franck-Condon state. To discuss the early stage dynamics of this transition we consider two, initially undistorted, graphite layers. After the photoexcitation an electron from the bottom layer in Fig. 1 is transferred to the top one and a hole in a bottom layer is created. Such an excitonlike state is formed across the layers but since the graphite is a conductor, most probably electron and hole will soon disappear as free carriers. However, one can ask whether there is finite, though small, probability that electron-hole pair will remain at the same lattice site, since electron-hole Coulomb interaction would enable the layers to contract. When the distance between layers become close enough, σ -type bonds are created resulting in the stable domain formation. The basic question then is: what is the probability that electron-hole pair will remain at the same site, as compared to the free-carrier relaxation process? In this section we will estimate this probability.

A. Model

To estimate the aforementioned probability we propose a simple model in two square lattices with $N(\gg 1)$ lattice sites, containing an electron-hole pair, their Coulomb coupling and a phonon system. Hamiltonian of the model is given as

$$H = H_{eh} + H_{ph} + H_c, \quad \mathbf{h} = 1. \tag{7}$$

The first term of this Hamiltonian is the energy band of electrons and holes,

$$H_{eh} = \sum_{i=1,2} \sum_{j=1,2} \sum_k E(k) a_{kij}^+ a_{kij}, \tag{8}$$

where a_{kij}^+ is a usual electron ($i=1$) and the hole ($i=2$) creation operator and index $j(=1, 2)$ is a layer number with two-

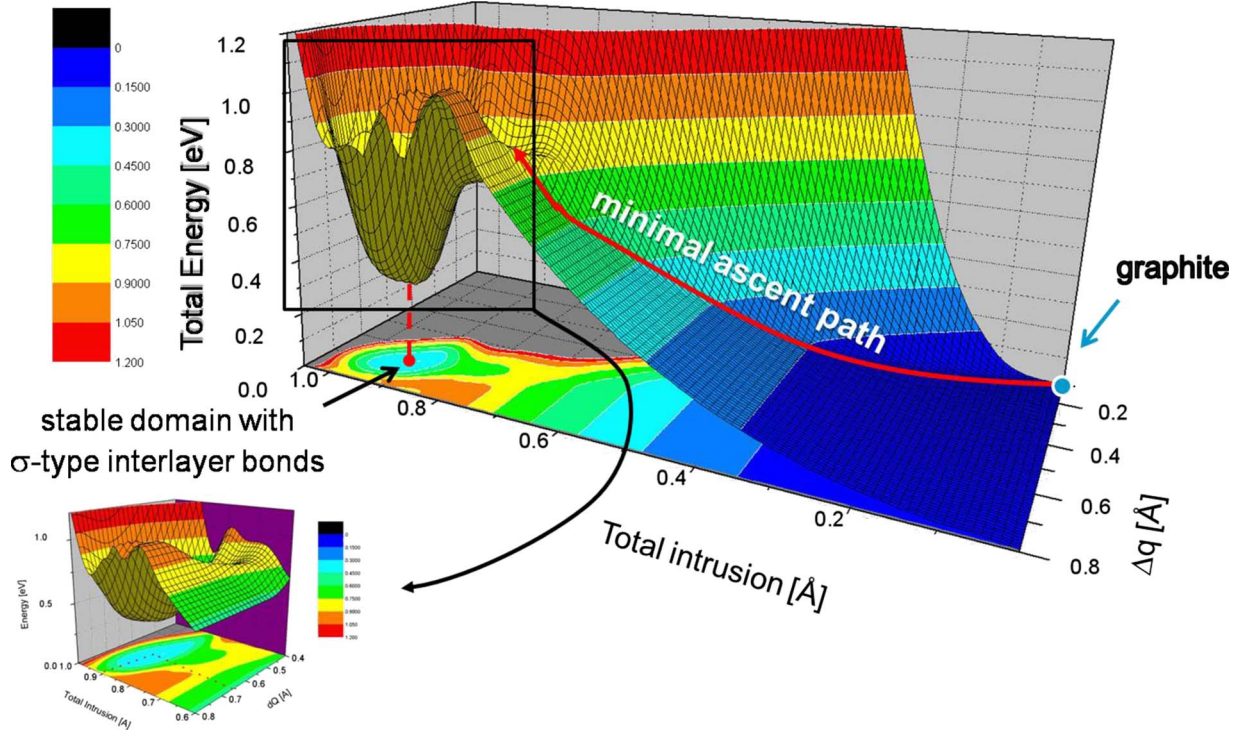


FIG. 4. (Color online) The detailed PES of the structure with the analyzed pattern. The total energy is plotted versus the total intrusion ($\delta + \Delta q$) and intrusion amplitude Δq . When $\Delta q \approx 0.6 \text{ \AA}$ and $\delta + \Delta q \approx 0.8 \text{ \AA}$ a stable domain with σ -type interlayer bonds is formed. Climbing line on the PES indicates the minimal ascent path from the starting graphite to the new domain structure.

dimensional wave vector $k=(k_x, k_y)$, and energy $E(k)$ in a square lattice (spin is neglected). We are interested in visible excitations region with an energy $\approx 4 \text{ eV}$ around the Fermi level whose energy is just zero. This band width is determined from the LDF calculation around the Fermi level. Hence, in this region, dispersion relation is a V shape, and given by

$$E(k) = \sqrt{k_x^2 + k_y^2}, \quad |k_x| \leq \pi, \quad |k_y| \leq \pi. \quad (9)$$

We are interested in the energy range around the Fermi level, and we have assumed a V-shaped electron band and the hole one centered at the Γ point ($k=0$) for simplicity (in graphite crystal, the Fermi level is at K point though this difference

may give no effect for our final conclusion). H_{ph} denotes the Einstein phonon localized on a lattice site l with an energy ω and is given as

$$H_{ph} = \omega \sum_l \left(\frac{1}{2} + b_l^+ b_l \right), \quad (10)$$

where b_l^+ denotes the creation phonon operator, and value of $\omega=0.1 \text{ eV}$ is fitted so, to reproduce the energy barrier (0.3 eV/atom) in the global and uniform transition. H_c is the Coulomb interaction Hamiltonian taken as

$$H_c = - \sum_l U(Q_l) n_{l1} n_{l2}, \quad (11)$$

where $n_{li} = a_{li}^+ a_{li}$ denotes the number operator on site l and layer i , Q_l is the phonon coordinate and is defined as

$$Q_l \equiv \frac{b_l^+ + b_l}{\sqrt{2}}. \quad (12)$$

Since Q_l describes the interlayer contractions starting from the original graphite, only one mode per lattice site l is taken into account, although there are two square lattices for the electron and the hole.

We assume a linear relation for the electron-hole coupling strength $U(Q_l)$

$$U(Q_l) = U_0 + U_d Q_l. \quad (13)$$

Its initial value is $U_0 = 1.5 \text{ eV}$. It corresponds to the electron-hole coupling in the undistorted graphite system. The Coulomb attraction energy between the electron and hole was

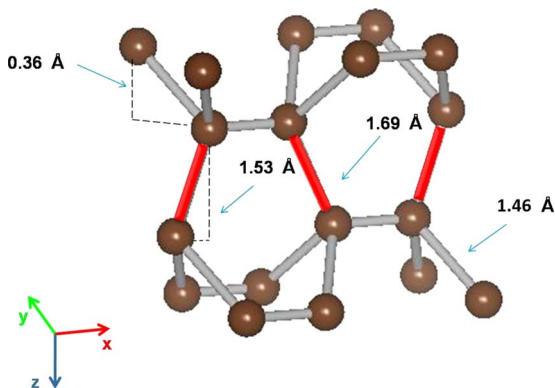


FIG. 5. (Color online) The structure of the analyzed pattern with the additional shear displacement.

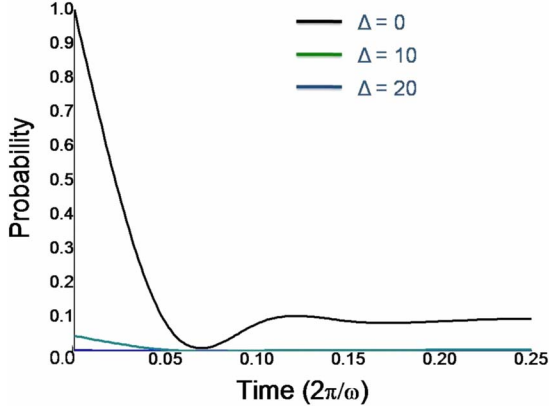


FIG. 6. (Color online) The probability that the exciton remain at the same site with respect to time (in $2\pi/\omega$ units). Different colors indicate different relative electron-hole distances: black (top curve) $\Delta=0$, green (middle curve) $\Delta=10$, and blue (bottom curve) $\Delta=20$.

calculated, by using the Mataga-Nishimoto formula.¹³ The real value of contraction may be derived by relating phonon energy with the energy of the top of the barrier.

B. Calculations

We define Bloch state composed of an electron at site $l+\Delta$ of the first layer, a hole at site l of the second layer, and m phonons at site l , as

$$|\Delta, m\rangle = \frac{1}{\sqrt{N}} \sum_l a_{l+\Delta, 11}^+ a_{l, 22}^+ \frac{(b_l^+)^m}{\sqrt{m!}} |0\rangle, \quad |0\rangle \rightarrow \text{vacuum}. \quad (14)$$

The expression inside the sum over l is an electron-hole phonon state localized at site l . We will assume that there are no phonons ($m=0$), if the electron and the hole are at different sites ($\Delta \neq 0$). The wave vector k_{ph} of a visible photon is almost zero compared to the wave vectors of the electron, hole, or phonons in the first Brillouin zone. Hence, the electron-hole-phonon coupled states which are created by visible photon have the full translation symmetry. We can also see that in Eq. (14), Δ stands for electron-hole distance. This is just the interlayer charge transfer and self-localized exciton.

Using this type of state as a base we can formulate eigenvalue problem of H . Diagonalizing matrix $\langle m, \Delta | H | \Delta', m' \rangle$ one can obtain a set of eigenvalues and eigenfunctions. In our calculations, we have chosen net 50×50 sites with 60 phonons. Having a set of eigenstates $|r\rangle$ and corresponding eigenvalues E_r , one can calculate the temporal evolution of a coupled electron-hole phonon state. Our main interest is to calculate probability that electron-hole will remain at the same site $\Delta=0$. This probability, $D(t)$, is defined as

$$D(t) = \langle W(t) | \left[\sum_m |0, m\rangle \langle 0, m| \right] |W(t)\rangle, \quad (15)$$

where $W(t)$ is $|W(t)\rangle = \sum_r e^{-itE_r} |r\rangle \langle r | \Delta, 0\rangle$.

Numerical results for the initial quarter period are presented in Fig. 6. Time dependence of exciton probability that

it will still remain in the same site is shown. One can notice that even for $\Delta=0$ it decreases rapidly from 1, which reflects the free-carrier relaxation process characteristic of a good conductor. However it does not reach zero but stabilizes at around 0.1, which means a self-localization of the electron and hole pair. Also, the number of phonons rapidly increases. It means that the interlayer contraction has been generated together with this self-localization. We have also calculated largely distant electron-hole evolutions by taking as initial states $|\Delta, 0\rangle$ with $\Delta=10$, and also 20. We can see that these states can never localize.

IV. DISCUSSION AND CONCLUSIONS

In this paper possible scenario of emergent phase in graphite has been discussed. Formation of a photoexcited, nonequilibrium, dimerized domain, with a σ interlayer bonds indicated in recent experimental investigations, has been confirmed. Studies of the adiabatic path, originating at the graphite phase and leading to some (meta) stable phase, have been presented. Applying Brenner's empirical potential, large-scale calculations were performed. We have found several possibilities of *tanh*-like dimerizations with energy barrier of an order of 1 eV. This analysis appears to indicate that the most promising candidate for a new, false ground state of the graphite is the dimerization with the pattern reflecting the experiment,^{3,4} referred to as "diaphite." Although direct conversion via buckling transformation is rather costly, our calculations prove that initial, planar *tanh*-like intrusion drastically lowers the transformation-energy cost. The energy loss due to intralayer bond stress is compensated by radical shrinking the distance between atoms of adjacent planes enhancing the transformation and forming of new, interlayer σ -type bonds. We have shown that energy barrier in this type of conversion is 0.88 eV which is achievable by visible-light excitation. Furthermore we have shown that additional 0.35 Å shear displacement in the x -axis direction repairs the intralayer bond mismatch resulting in material stabilization up to 0.37 eV. It has been mentioned that transformations of other types led to higher energy barriers and less stable phases. The results are with good agreement with experimental results of interlayer bond distance obtained by Raman *et al.*⁵ and shear displacement obtained by Kanasaki *et al.*^{3,4} Recently electronic calculations using *ab initio* method has been performed by Ohnishi and Nasu^{14,15} using 256 carbon atoms system. They have shown that graphite-diaphite transformation is a metal-insulator one. Furthermore they have also clarified structural properties of graphite. Although shear displacement is smaller then in our case by 0.1 Å and the buckling is greater by 0.16 Å the interlayer equilibrium distance is same (1.55 Å).

These types of adiabaticlike considerations have been supported by the studies of early stages dynamics: possible scenario of a graphite conversion has been proposed. Including lattice and electronic degrees of freedom into the Hamiltonian of the system, the evolution of the photoexciton has been investigated. We have shown that there is finite, non-zero probability for self-localization of an electron-hole pair. This opens the way to the possible lattice contraction due to

unbalanced Coulomb interaction between electron and hole possible, aforementioned dimerization may occur.

Let us emphasize that these considerations are in a good agreement with recent experimental observations.³⁻⁵ On the other hand, they should not be regarded as a comprehensive analysis; it is rather a step toward understanding a complex phenomena of transient states occurring in an intriguing class of carbon-based compounds.

ACKNOWLEDGMENTS

This work is supported by the Ministry of Education, Culture, Sports, Science and Technology of Japan, the petacomputing project, and Grant-in-Aid for Scientific Research (S) under Grant No. 19001002, 2007 and by research grant by the Polish Ministry of Science under Grant No. 2290/B/H03/2009/37, 2009-2012.

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