Energetical preference of diamond nanoparticles

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The energetical advantage of diamond in comparison with graphite caused by small particle sizes is established by modeling and computation of free energy. The results, obtained for low external pressure, $P \cong 0$, and for temperatures up to 1100 °C, indicate that diamond is the stable modification of carbon, and graphite is the metastable one at small particle sizes which are less than the boundary of stability regions of these phases. The models of crystal charge lattices have been determined to compute lattice energies by summation of pair interaction potentials acting between elements (ions, electrons) of the charge lattices. The diamond charge lattice is presented by an ion-electron lattice of negative bond charges and positive ions. The graphite charge lattice consists of hexagonal ion-electron nets and collectivized conduction electrons located between the nets. The consideration of conduction electrons in the graphite model provides the stable graphite structure because the attraction between the conduction electrons and hexagonal nets compensates for the repulsive forces acting between the nets. Mechanisms of the nucleation of diamond and graphite have been considered to determine the structure of clusters forming these phases. The considered mechanism of nucleation of diamond clusters consists in the forming of octagonal carbon clusters with the following transformation of the octagonal clusters to the ten-atomic-diamond clusters. The octagonal clusters consist of the same fragments of carbon atoms as the fragments forming the graphite nets. But the difference is that diamond crystals are generated from an octagon of atoms and the graphite clusters are formed from hexagons. The intersection of size dependences of free energies of diamond and graphite indicates the size-related stabilization of diamond nanoparticles. The established boundaries of the stability regions of diamond and graphite are 10.2 nm at room temperature, 6.1 nm at 525 °C, 4.8 nm at 800 °C, and 4.3 nm at 1100 °C. [S0163-1829(96)04827-8]

I. INTRODUCTION

The low-pressure synthesis of diamond by chemical vapor deposition (CVD) (Refs. 1 and 2) and by laser decomposition of ethylene[3] and an existence of diamond nanoparticles in meteorites[4] indicates the homogeneous nucleation of diamond. But there is a question of whether the diamond nanoparticles are stable or metastable in comparison with graphite ones since the low-pressure diamond formation occurs in the metastable for the diamond bulk crystal pressure-temperature region.

We can suppose that the stabilization of diamond is caused by the small particle size. The effect of stabilization of a nanosized phase that is unstable in the bulk crystal state has been established experimentally for many substances, and explained by the energy advantage caused by small particle sizes.[5,6]

A similar assumption has been made in a few publications[7–9] to explain the homogeneous nucleation of diamond at low pressure. In Ref. 7 an approximate estimation of the energy was made for graphite and for the hexagonal modification of diamond, lonsdaleite, based on the calculation of the number of bonds in these structures. The energy advantage of lonsdaleite in comparison with graphite was established for very small nanoparticles elongated along the c axis. In Ref. 8 the data for surface energies of diamond and graphite were compared for the investigation of the stability of the phases. But the uncertainty of the surface energies is too large to make a careful conclusion about the phase stabilization. In Ref. 9 the more stable state was indicated for 3-nm diamond particles. But the estimation of diamond and

graphite energies was made not by their structure but through the energies of C-H compounds and therefore could not provide sufficient accuracy. So the estimation of the energies made in Refs. 7–9 is too rough to make a careful conclusion about the stability of the phases, since the models of the computation methods are not sufficiently accurate.

The present work is devoted to a comparison of the crystal energy of diamond and graphite nanoparticles to answer the question about the possibility of stabilization of diamond at low pressure caused by small particle size.

II. METHOD OF CALCULATION

The energetical state of each phase is determined by the Gibbs thermodynamic potential

$$G = E_{at} - TS + PV,$$

where E_{at} is the atomization energy, S is the entropy, and P, T, and V are the external pressure, temperature, and volume, respectively. At low pressure ($P \cong 0$) the energy advantage of a phase is determined by free energy

$$F = E_{at} - TS.$$

The atomization energy is determined by the relation

$$E_{at} = E + E_k + I, \tag{1}$$

where E is the lattice energy per atom depending on the crystal structure and particle sizes, and E_k and I are the kinetic energy and ionization potential of bond charges per atom, respectively.

Our calculations of the lattice energy are based on the method of summation of pair interaction potentials between elements of crystal charge lattices—atoms, ions, and electrons.[6,10] We approximate the pair interaction potential by Born-Lande potential $\varphi_{mn} = (e_m e_n / r_{mn}) + (A/r^q)$, where the first term represents the Coulomb interaction and the second term represents the short-range repulsive forces acting between pairs of atoms; e_m and e_n are the charge values of mth and nth interacting elements in the lattice, r_{mn} is the distance between these elements, q is the power exponent in the repulsive potential, and A is a constant.

In the case of equilibrium positions of atoms in a crystal the Born-Lande potential is known to be $\varphi_{mn} = (e_m e_n / r_{mn})[1 - (1/q)]$. The repulsion power exponent q is determined by compressibility of a crystal.[10] We have calculated the value of q by experimental literature data of compressibilities of diamond and graphite.

The structure of the charge lattices of diamond and graphite is determined by excessive negative covalent charges located on the bond lines between neighboring atoms.[11,12] The charge values in the lattices used for computation of the energy have been calculated from the experimental structural x-ray data and from the literature data of atomization energy.[11]

There are quantum-mechanical calculations of the structure and energy of small carbon clusters.[13,14] The aim of these considerations is to determine the energy as the geometry of the clusters and configuration of atoms in the clusters.

Our approach is based on quantum-mechanical effects: (1) the covalent bond charge is the result of exchange interaction between neighboring atoms, and (2) the short-range repulsive forces are caused by an overlapping of external orbitals of neighboring atoms.

For our calculations we use the known geometry of crystal lattices in clusters, which is determined by structural experimental data. Our approach allows us to calculate crystal energies in the wide range of particle sizes—from one unit cell to bulk crystal, avoiding the difficult calculations peculiar to the quantum-mechanical methods.

Let us remark that the traditional calculation methods for lattice energy[15–17] are useful for 1–2-nm clusters or for massive crystals, and are not able to provide high accuracy by computation of the energy over the wide range of particle sizes and especially for charge lattice structures with a large number of charges in the unit cell. That is why other methods were used,[6,18–20] which contain the approximation of lattice sums by integrals.[20]

The accuracy of this method equals $\sim 1/l_0^4$, where l_0 is the size of the edge (expressed in the number of crystal unit cells) of a particle with a cubic external shape whose lattice energy is included in analytical expressions for calculations by this method. This energy should be computed by sums, not by integrals.[20] Therefore, l_0 determines the computational time of the method, and the accuracy of the method. Larger l_0 gives us better accuracy but requires more time for computations. We used $l_0 = 10$ by our computations. This provides accuracy in the computation of lattice sums $\sim 0.01\%$. By these conditions the time spent for computation of the energy of a crystal of any sizes did not exceed 0.5 h.

Analytical expressions of the lattice energy E for a crystal of the orthorhombic symmetry with the external shape of a rectangular parallelepiped are presented in Refs. 6 and 20 and for a crystal of hexagonal symmetry with the external shape of a hexagonal prism in Ref. 19.

Expressions for atomization energies of diamond $E_{\mathrm{at},d}$ and graphite $E_{\mathrm{at},g}$ obtained from (1) have the following form:

$$E_{\mathrm{at},d} = E_d + E_{k,d} + \rho_d I_1,$$

$$E_{\mathrm{at},g} = E_g + E_{k,g} + \rho_g I_1, \qquad (2)$$

where E_d and E_g are the lattice energies per atom of diamond and graphite particles, respectively; ρ_d and ρ_g are the values of bond charges per atom (expressed in the values of the electron charge) in crystal lattices of diamond and graphite particles, respectively; $E_{k,d}$ and $E_{k,g}$ are the kinetic energies of electron bond charges per atom in diamond and graphite, respectively; and I_1 is the carbon first ionization potential.

Expressions for the kinetic energy of diamond and graphite bond electrons have been derived from the relation

$$F_C = F_{\mathrm{cp}} \qquad (3)$$

between the Coulomb force F_C acting on a bond electron in the crystal charge lattice and the bond electron centripetal force F_{cp} to the nearest atom.

Equation (3) is similar to the principal relation for the derivation of the virial theorem[21] that determines the kinetic energy of an electron belonging to a free atom. The difference is that the centripetal force acting on a crystal bond charge is determined by the force F_C of the interaction of the bond charge not with one atom (as in the case of free atom), but with all the surrounding charged atoms in a crystal.

As a result the kinetic energy of diamond bond electrons (per atom) in a crystal equals

$$E_{k,d} = Q \rho_d E_{k,d}^{(1)}, \quad E_{k,d}^{(1)} = \frac{2 r_o (r - r_o)}{r^2} I_1,$$

where Q is the atom charge value in the diamond charge lattice, r is the interatomic distance between neighboring atoms, and r_o is the carbon orbital radius. A similar approach has been used to calculate the kinetic energy of graphite bond electron charges. For instance, the kinetic energy of a bond electron in a bulk crystal, estimated by the suggested method, equals 343.6 kJ/mol (3.5 eV) for diamond and 292.7 kJ/mol (3.0 eV) for graphite.

III. MODELS OF CRYSTAL CHARGE LATTICES

A. Description of the unit cells

Selection of the models has been made in accordance with the structure and interatomic bond types, and to obtain the experimental values of the atomization energies of diamond and graphite bulk crystals in the results of computations. The diamond charge lattice is presented by excessive negative covalent bond charges and positive ions (Fig. 1).[22]

Covalent bond charges are caused by exchange interaction of neighboring atoms. The covalent bonds are formed by pairs of sp^3 (in diamond) and sp^2 (in graphite) electrons with antiparallel spins belonging to neighboring atoms. Ex-
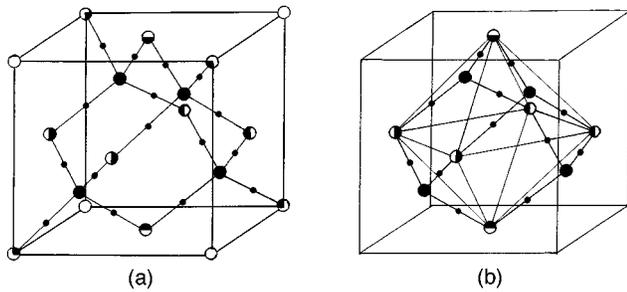
FIG. 1. Charge lattice cells of diamond: (a) The unit cell in the traditional model. (b) The cell in the model without one-bonded atoms. Small black circles are excessive negative charges on the bond line between nearest atoms. The atoms are designated by large circles: the shaded part of a large circle means the part of the absolute value of the electron charge belonging to the unit cell.

istence of the excessive negative bond charges requires the existence of positive carbon ions in the models to provide the neutrality of the unit cells.

We approximate the charge distribution in the crystal charge lattices by the point-charge lattice model,[11,22] where bond charges, distributed in space, are substituted by point charges located in the middle between neighboring carbon atoms. This approximation makes the programs for computation less complex, decreases the computation time, and provides an accuracy of ~0.05%.

Besides the traditional diamond model [Fig. 1(a)], we also consider a model that does not contain atoms with one covalent bond—the atoms are located at crystal apices and edges. We can construct this crystal lattice by cells [Fig. 1(b)] which differ from the traditional diamond unit cells [Fig. 1(a)] by the absence in the cubic cells of atoms with one covalent bond. But in a crystal we have to add the atoms located at apices of the cubic cells when the atoms are not located at apices or edges of the crystal; i.e., we have to add the atoms bonded with at least two neighboring atoms by a covalent bond.

The cell presented in Fig. 1(b) contains ten carbon atoms and we will call it a ''ten-atomic-diamond cluster.'' This nontraditional model seems to be energetically more favorable because of the larger average value of bonds per atom in this model in comparison with the traditional one.

The graphite charge lattice consists of hexagonal ion-electron nets and collectivized conduction electrons located between the nets (Fig. 2). Excessive negative charges causing the covalent bond are located between neighboring atoms in the nets.

Interaction of elements of the hexagonal nets leads to repulsive forces acting between the nets, and results in an unstable graphite structure. This is confirmed by computation of the inner tension, intracrystalline pressure, caused by the interaction between the nets (the determination and the calculation method of the intracrystalline pressure in a hexagonal crystal is described in Ref. 19). In the direction of the c axis, the inner tension is repulsive, and is equal to $P_{m,3} = -0.7$ kbar for the bulk crystal.

If between the neighboring hexagonal nets we arrange a small value (in comparison with the electron charge value e_0) of the conduction-electron charge (and we can do this since graphite is a conductor), the repulsive tension along the
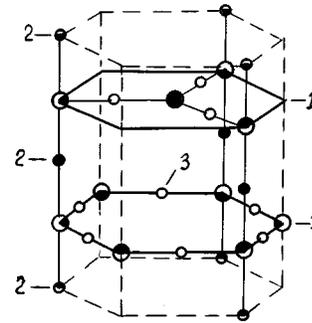
FIG. 2. Charge unit cell of graphite; atoms are designated by larger circles; the partly shaded circles mean that a part of an atom belongs to the unit cell. (1) Ion-electron net. (2) Collectivized conduction electrons. (3) Excessive negative charges located between neighboring atoms in the hexagonal nets.

c axis ($P_{m,3} < 0$) switches to attractive tension ($P_{m,3} > 0$) because of the attractive forces acting along the c axis between the hexagonal nets and conduction electrons. For instance, at a conduction-electron charge value per atom equal to $0.09e_0$, $P_{m,3} = 54$ kbar. So we obtain a model describing a stable graphite structure.

B. Models of octagonal clusters of carbon atoms and a mechanism of nucleation of diamond

Now we will consider the structure of clusters of carbon atoms forming the structure of diamond and graphite. This will allow us to investigate similar and different configurations of atoms in these structures to determine charges in the models, and to investigate a possible mechanism of nucleation of diamond and graphite.

Let us consider the model of a cluster of covalent bonded carbon atoms forming an octagon with atoms joined to all or some of the atoms located at apices. A model of such a cluster with atoms of type 3 joined to four atoms of type 1 located at apices of the octagon is presented in Fig. 3(a). This cluster contains fragments consisting of four atoms—''quartets'' of atoms where each atom of type 1 is surrounded by three atoms of types 2 and 3 [Fig. 3(a)].
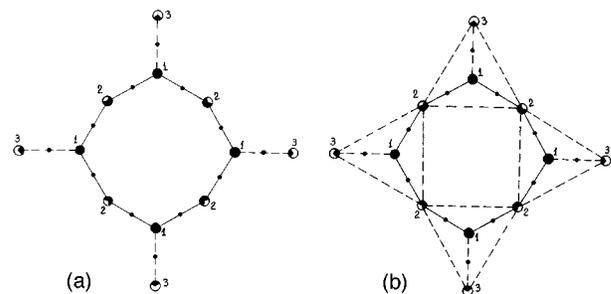
FIG. 3. Models of octagonal carbon clusters containing quartets of atoms with threefold symmetry at positions 1; small black circles are the covalent bond charges. Atoms are designated by large circles; the shaded part of the circle means the part of the absolute value of the electron charge given up by the atom for the bond. The dashed bond lines mean that position 3 may be occupied or not occupied by an atom. (a) Flat cluster. (b) Cluster containing space quartets of atoms designated by triangles.
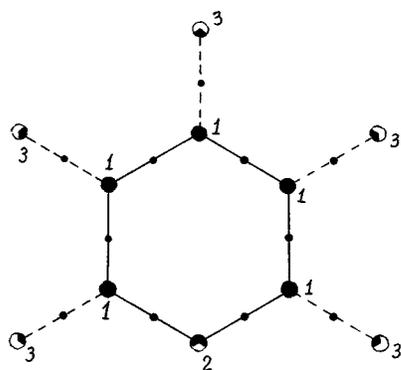
FIG. 4. Model of a hexagonal carbon cluster. Small black circles are the covalent bond charges. Atoms are designated by large circles; the shaded part of the circle means the part of the absolute value of the electron charge given up by the atom for the bond. The dashed bond lines mean that position 3 may be occupied or not occupied by an atom.

Each quartet of atoms has threefold symmetry if the three angles at apices 1 equal 120°. These quartets of octagonal clusters are similar to quartets of carbon atoms forming graphite hexagonal nets (Fig. 4), but the difference is that in the first case [Fig. 3(a)] carbon atoms form the octagonal cluster, and the quartets in graphite nets (Fig. 4) form the hexagons.

The octagonal cluster presented in Fig. 3(a) contains two atoms of type 3 which can occupy any two of four possible neighboring positions. Such a cluster contains ten carbon atoms and we will call it an ''octagonal ten-atomic-carbon cluster.''

We can consider a more general model of a cluster with the octagonal configuration that contains space quartets of atoms, instead of the flat ones, forming pyramids with equal flat angles at apices 1 [Fig. 3(b)]. The surrounding of atoms of type 1 by atoms of types 2 and 3 becomes the tetrahedral diamondlike one when the flat angles in the quartets become equal to 109.47°.

The octagonal ten-atomic-carbon cluster with tetrahedral quartets of atoms can be transformed into the ten-atomic-diamond cluster [Fig. 1(b)] by a turn of the quartets of atoms relative to the sides of the square presented in Fig. 3, so that each atom of type 3 becomes the common atom of two opposite quartets and is bonded with two atoms of type 1. This transition seems to be energetically favorable because of the two additional covalent bonds in the ten-atomic-diamond cluster in comparison with the octagonal one at the same number of atoms in the clusters.

It is natural to expect that the octagonal clusters, like the hexagonal ones, can be generated from unclosed elements consisting of carbon atoms: dimers—pairs; trimers—three; and quartets—four of covalent bonded atoms; and single carbon atoms [Fig. 5(a)]. For instance, the octagonal ten-atomic-carbon cluster (Fig. 3) can be formed from two trimers and two dimers.

So we can suppose a possible mechanism of the nucleation of diamond by a joining of the unclosed elements [Fig. 5(a)] in the octagon clusters with the subsequent transformation to ten-atomic-diamond clusters [Fig. 5(b)].
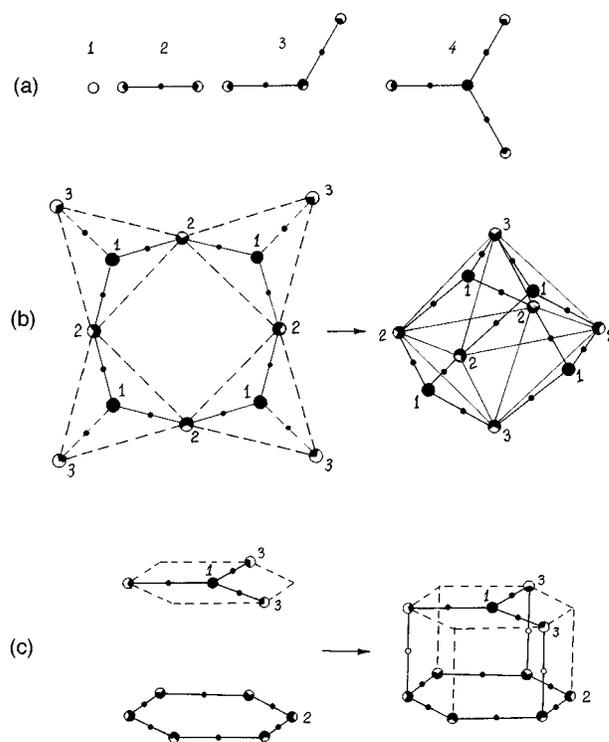
FIG. 5. Mechanism of nucleation of diamond and graphite. (a) Fragments forming diamond and graphite clusters: (1) single atom, (2) dimer, (3) trimer, and (4) quartet. (b) Transformation of the octagonal carbon cluster (left) to the ten-atomic-diamond cluster (right). (c) Transformation of elements of hexagonal carbon nets (left) to the graphite unit cell cluster (right). Small black circles are the covalent bond charges. Atoms are designated by large circles; the shaded part of the circle means the part of the absolute value of the electron charge given up by the atom for the bond. The dashed bond lines mean that position 3 may be occupied or not occupied by an atom. The unshaded small circles in the graphite unit cell cluster designate the conduction electrons.

Similarly, the nucleation of graphite can be considered a result of joining the same unclosed elements of carbon atoms [Fig. 5(a)] in hexagonal nets with the following joining of the nets in a graphite nucleus by conduction electrons [Fig. 5(c)].

The 14-atomic-diamond cluster realizing the diamond unit cell in the traditional model [Fig. 1(a)] can also be generated by transformation of an octagonal carbon cluster containing an additional four carbon atoms joined to the apices of the octagon in comparison with the octagonal ten-atomic-carbon cluster. But the 14-atomic-diamond cluster seems to be energetically less favorable than the ten-atomic-diamond cluster because of the lower value of the covalent bonds per atom in the 14-atomic-diamond cluster.

Let us remark that quantum-mechanical calculations of the structure and energy of small carbon clusters, containing 2–10 atoms, indicate stable cyclic hexagonal and octagonal clusters[13] with small differences in the atomization energy of these clusters. These results indicate the possibility of forming hexagonal as well as octagonal clusters for nucleation graphite clusters as diamond clusters by the mechanisms described above (Fig. 5).
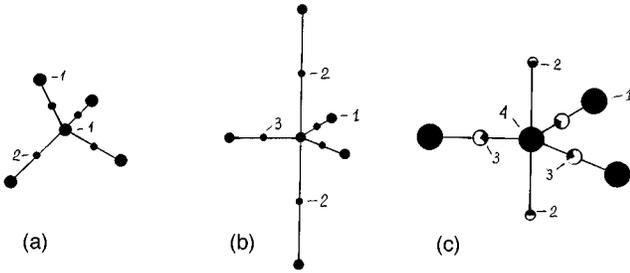
FIG. 6. Distribution of bond electron charges in diamond and graphite. (a) Tetrahedral configuration of atoms of type 1 in diamond bonded by sp^3 bond electrons 2. (b) sp^2 covalent electron bond charges 3 in graphite hexagonal nets of atoms of type 1 and conduction electron bond charges 2. (c) Bond charge values given up by one atom 4 in graphite for the five directions: (3) for covalent bond with atoms of type 1 in hexagonal nets, and (2) for conduction electron bond between the nets. The shaded part of circles 3 and 2 refers to the part of charges Q_0 and ε_0 given up by the atom of type 4 for covalent bond and conduction electron bond, respectively.

The question about the preference of the transformation of hexagonal clusters in graphite clusters or octagonal clusters in diamond clusters should be answered by computations of the energies of diamond and graphite clusters. Results of these computations are presented below in Sec. IV.

C. Determination of charges in the models

Let us determine the charge values of elements of the charge lattices which are necessary for a calculation of the energy. For the determination we use the following postulate: each inner atom of a crystal gives up one electron charge value for the bond. This postulate has been confirmed by a computation of the crystal energy and size-related changes of lattice parameters for many substances: platinum, palladium, nickel, diamond, silicon, germanium, etc.[22–24,11]

For diamond the bond charge value is one electron per atom distributed over all the bond directions. For each inner atom the one-electron-bond charge is distributed over four directions corresponding to the tetrahedral surrounding by sp^3 bond electrons [Fig. 6(a)].

For graphite the bond charge value is one electron per atom distributed over three covalent bonds of sp^2 electrons located in the hexagonal nets, and over two bonds of conduction electrons in the perpendicular direction [Fig. 6(b)]. Let us designate the covalent bond charge value per atom by Q_0 and the conduction electron charge value per atom by ε_0.

We have estimated Q_0 and ε_0 from the experimental data—structural x-ray data of the size-related change of the lattice parameter c in small graphite particles. Precise measurements indicate the increase of the lattice parameter c and the decrease of the lattice parameter a in highly disperse samples.[12] For instance, the relative increase of parameter c in the soot sample with an average size of crystallites of $\sim$5 nm in comparison with the bulk crystal equals $(2.5\pm0.07)\times10^{-2}$. By a comparison of the experimental data with the computation of the size-related change of lattice parameters by the same model of the crystal charge lattice (Fig. 2) that was used for the computation of crystal energy,

the following charge values were established: $Q_0=0.7813e_0$ and $\varepsilon_0=0.2187e_0$ [$(Q_0+\varepsilon_0)/e_0=1$, in accordance with the above mentioned postulate].

The bond charges in the graphite charge lattice corresponding to the experimental literature data of the bulk crystal atomization energy equal $Q_0=0.8051e_0$ and $\varepsilon_0=0.1949e_0$. The good coincidence of the charge values Q_0 and ε_0 calculated from the size-related change of lattice parameters in small graphite particles and from the bulk crystal atomization energy of graphite shows that the suggested models and methods are correct, and may be used for computations.

We have been using the two last values of Q_0 and ε_0, presented above, for a computation of the size dependences of the atomization energy to provide literature data of the bulk crystal atomization energy. It is important, by the determination of the point of intersection of the energy size dependences (that is, the boundary of the stability regions of the phases), because the bulk crystal atomization energies determine the mutual positions of the atomization energy size dependences of diamond and graphite.

The bond charge of a surface atom has been determined by the number of bonds of the atom with surrounding neighboring atoms. The bond charge values of an atom in graphite corresponding to one neighboring atom in the hexagonal net are $Q_0/3=(e_0-\varepsilon_0)/3$ for each (of three) covalent bond in the net, and $\varepsilon_0/6$ for each (of two) conduction electron charge located between the hexagonal nets [Fig. 6(c)]. So we can determine the bond charge values given up by an inner atom or a surface atom depending on the number of its neighboring atoms n,

$$q_g = n\,\frac{Q_0}{3} = n\,\frac{e_0-\varepsilon_0}{3},$$

(4)

$$\varepsilon = nk\,\frac{\varepsilon_0}{6},$$

where q_g and ε are the total charges given up by each graphite atom for the bond in the hexagonal nets (covalent bond), and in interplanar spacings between the hexagonal nets (conduction-electron charge), respectively; k is the number of interplanar spacings between the nets neighboring to the atom: $k=2$ for the atom located in an inner hexagonal net, and $k=1$ for the atom located in a surface hexagonal net.

Diamond surface atoms with one, two, or three neighboring atoms are surrounded similarly by other carbon atoms as in graphite, since the clusters forming diamond (Fig. 3) and graphite (Fig. 4) consist of similar quartets of atoms; atoms of type 3 are joined with the nearest atoms by one covalent bond, atoms of type 2 are joined with the cluster atoms by two bonds, and atoms of type 1 are joined with the nearest atoms by three bonds.

The difference is that in diamond there are no conduction electrons. That is why for the bond charges given up by diamond surface atoms expression (4) has been used at $\varepsilon_0=0$. So for a diamond surface atom the bond charge

$$q_d = \frac{ne_0}{3},$$

(5)

TABLE I. Atomization energy per atom E_{at} of diamond and graphite clusters; N is the number of atoms in a cluster.

Type of a cluster	N	E_{at} (kJ/mol)
Ten-atomic-diamond cluster which does not contain one-bonded atoms	10	-370.1
Diamond unit-cell cluster in the traditional model	14	-204.8
Graphite unit-cell cluster	10	-31.3

where n is the number of neighboring atoms. It follows from (5) that, for a one-bonded atom, an atom located at an apex or an edge $n=1$, that $q_d=e_0/3$, for a face atom $n=2$, that $q_d=2e_0/3$, and for surface atoms bonded with three atoms that $n=3$, and this results in $q_d=e_0$.

IV. SPECIFIC ENERGY OF DIAMOND AND GRAPHITE NANOPARTICLES

The preference for the nucleation of diamond or graphite, and especially the preference of the type of diamond clusters forming the nucleus—with one-bonded atoms [Fig. 1(a)] or without them [Fig. 1(b)]—has been determined by a computation of the energies of diamond and graphite nanoparticles.

Results of the computation of the atomization energy of diamond and graphite clusters, containing one cell, are presented in Table I. Computed values of the atomization energy of very small nanoparticles are presented in Fig. 7 for crystals with an equilibrium external shape: cubic for diamond and hexagonal prism for graphite. The equilibrium shape of graphite crystals has been obtained by a minimization of the lattice energy depending on the relation between particle sizes: L_3 along the c axis, and L_1 perpendicular to the c axis. The equilibrium shape is determined by relation $L_1=1.4L_3$. Computation results show that the diamond model that does not contain one-bonded atoms [Fig. 1(b)] is
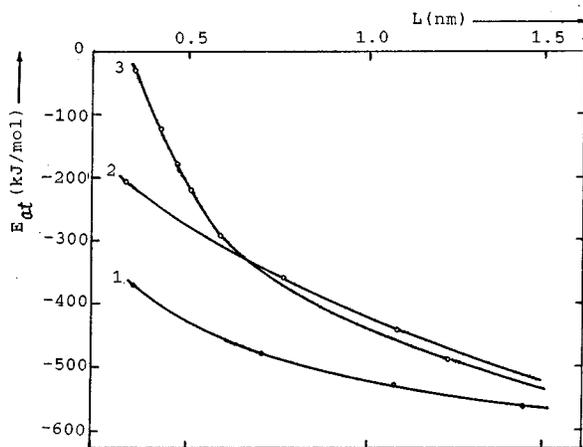
FIG. 7. Atomization energies E_{at} of diamond nanoparticles with cubic external shape: (1) Model of a crystal without one-bonded atoms. (2) Traditional model containing one-bonded atoms and of graphite (3) with the external shape of a hexagonal prism. L is the diamond particle size; each size L corresponds to the same number of atoms in the diamond and graphite particle.
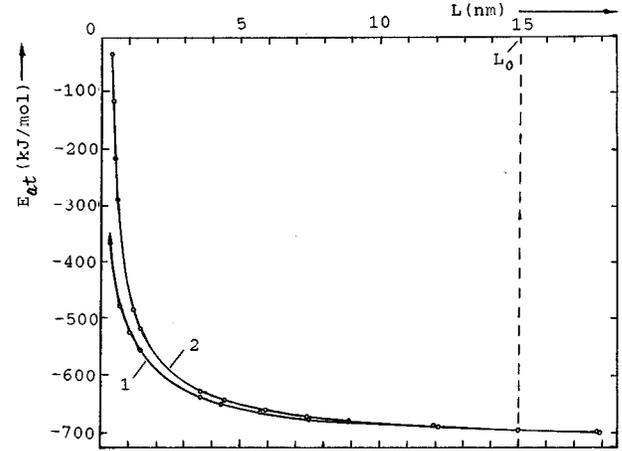
FIG. 8. Atomization energies E_{at} of small particles of diamond (1) and graphite (2) computed for the cubic external shape for diamond and for the hexagonal prism shape for graphite. L is the diamond particle size; each size L corresponds to the same number of atoms in the diamond and graphite particle.

energetically more favorable than the traditional diamond model [Fig. 1(a)].

So we have to compare the energy dependences 1 and 3 of diamond and graphite (Fig. 7), and they show that diamond nanoparticles are energetically more favorable than graphite ones. These two energy dependences, though in a larger range of particle sizes, are presented in Fig. 8, and they show that small diamond particles are more stable than graphite ones until the point of intersection of these dependences, $L=L_0=15$ nm. At sizes larger than L_0 graphite is the more stable modification of carbon. So the size L_0 is the boundary of the stability regions (of sizes) of diamond and graphite. It is valid at temperature $T=0$ K, since the free energy $F=E_{at}-TS$ is equal to the atomization energy at $T=0$.

Let us remark that the atomization energy of graphite crystals without one-bonded atoms has also been computed, and the energy is almost the same as for crystals containing one-bonded atoms (Fig. 2). That is why only one energy size dependence is presented for graphite.

The increase of the temperature T moves the diamond and graphite size dependences of the free energy apart from each other, so that the difference between the bulk crystal energies becomes larger on the value $\delta F=T(S_g-S_d)$, where S_g and S_d are the graphite and diamond entropies, respectively. The nonzero difference δF shifts the point of intersection of the energy size dependences toward smaller values of sizes L,

TABLE II. Boundary of stability regions (of particle sizes) L_0 of diamond and graphite at various temperatures t.

L_0 (nm)	t (°C)	Correspondence to a process
10.2	25	Room temperature
6.1	525	Mean temperature of crystallization by laser decomposition of ethylene
4.8	800	Mean temperature of crystallization by the CVD method
4.3	1100	Upper temperature in the CVD method

and therefore leads to a decrease of the range of stability of diamond. The results of a calculation of the sizes L_0 at various temperatures are presented in Table II. The calculation was made by $\delta S = S_g - S_d = 3.37$ kJ/mol at room temperature, and by $\delta S = 4.59$ kJ/mol at 800–1100 °C. We can see from Table II the boundary of the stability regions of diamond and graphite $L_0 = 10.2$ nm at room temperature, and that it decreases to ~4 nm by an increase of the temperature to 1100 °C.

V. CONCLUSION

Results obtained by the considered models at low external pressure and temperatures up to 1100 °C indicate that diamond is the stable modification of carbon, and that graphite is the metastable one at small particle sizes which are less than a critical size—the boundary of stability regions of diamond and graphite.

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