

Theoretical total-energy study of the transformation of graphite into hexagonal diamond

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Variations in the structural energy of solid carbon along a transformation path from a graphitic structure with $\dots[AA]\dots$ stacking to hexagonal diamond are calculated using the first-principles pseudopotential local-orbital total-energy method. The transformation path is that defined in an earlier study of the transformation of rhombohedral graphite into cubic diamond. The energy barrier along the transformation path is found to be only slightly higher than that of the corresponding path in the earlier study. Thus the major features of the energetics of the transformation are found to be relatively insensitive to the stacking of the graphite. However, it is found that in the region of metastability of graphite, the $\dots[AA]\dots$ stacking never has lower energy than the rhombohedral stacking, and so we do not expect a transition from rhombohedral to $\dots[AA]\dots$ stacking under static pressure. While the energy of hexagonal diamond is higher than that of cubic diamond in their final formation, nevertheless, as the sp^3 bonds are forming during the transition from graphite, it is found that the hexagonal diamond has approximately the same energy as cubic diamond. The implications of these results for the synthesis of diamond from graphite are discussed.

I. INTRODUCTION

The synthesis of diamond from graphite has been a topic of great interest for many years.¹⁻⁶ Although much has been learned empirically about the process, we have relatively little theoretical knowledge of its microscopic details. The roles of temperature, catalysis, and mechanical stress have been investigated experimentally but from the point of view of fundamental theory are still poorly understood. It is in an effort to understand the latter of these ingredients, mechanical stress, in the transformation that we have undertaken the present study. In particular, it has been observed that in shock-wave synthesis of diamond from graphite, a substantial proportion of the diamond so obtained can be of the hexagonal rather than of the cubic variety.^{4,6} The proportions of hexagonal to cubic diamond vary depending on the experimental conditions involved, but the yield of hexagonal diamond can be as high as 50%.⁶ This is somewhat surprising since cubic diamond is clearly the more thermodynamically stable of the two diamond forms, being the form found normally in nature.⁷

In this paper we present the results of a study of the transformation from graphite to hexagonal diamond similar to a recent study⁸ by the present authors of the transformation from rhombohedral graphite to cubic diamond. Here we calculate the energies along an analogous path from graphite with $\dots[AA]\dots$ stacking to hexagonal diamond. The path studied here has high crystallographic symmetry and so it is convenient for the theoretical calculation. However, we do not wish to imply that it is the actual path by which the transformation proceeds in reality. Indeed, at least in the case of the synthesis of hexagonal diamond under static pressure, it is clear that the reaction path studied here cannot be the actual transformation path. This is because the epitaxial relationship be-

tween the parent graphite and the hexagonal diamond product [i.e., parallelism of the (0001) planes in both structures] implied by the path presented here is not in agreement with what is observed experimentally.^{3,9} In the static pressure synthesis of hexagonal diamond the [0001] direction in hexagonal diamond is parallel to the $[10\bar{1}0]$ in graphite and the $[\bar{1}2\bar{1}0]$ direction in hexagonal diamond is parallel to the $[\bar{1}2\bar{1}0]$ direction in graphite.³ Moreover the present analysis does not address the problem of how the stacking of the graphite layers would change from $\dots[AB]\dots$ to $\dots[AA]\dots$, as is presupposed in the present transformation path.

Hexagonal diamond (or lonsdaleite) consists of buckled layers of hexagonal carbon rings.⁷ As is the case in the cubic diamond structure, each atom has perfect tetrahedral coordination. Although the stacking of the double (buckled) layers in hexagonal diamond is in the $\dots[AB]\dots$ sequence, if the buckling of the layers is set to zero (i.e., each double layer becomes a single layer), the A and B layers become the same and we obtain $\dots[AA]\dots$ stacking of hexagonal planes of atoms (see Fig. 1). In this way we can see that hexagonal diamond is most simply related to graphite with $\dots[AA]\dots$ stacking rather than to hexagonal graphite. Thus we can define a general structure with the same crystallographic symmetry as hexagonal diamond, which is parametrized by the bond length R between the double layers, the bond length B within the double layers, and the angle θ between these two bonds.¹⁰ When $R=B=1.54$ Å, and $\theta=109.47^\circ$, we have the ideal hexagonal diamond structure, and when $R=3.35$ Å, $B=1.42$ Å, and $\theta=90^\circ$, we obtain a graphitic structure with the same interlayer separation and intralayer bond length as hexagonal graphite but with $\dots[AA]\dots$ stacking sequence. Throughout the transformation¹¹ the space group is D_{6h}^4 . Using this parametrization we can relate the hexagonal structures in the present

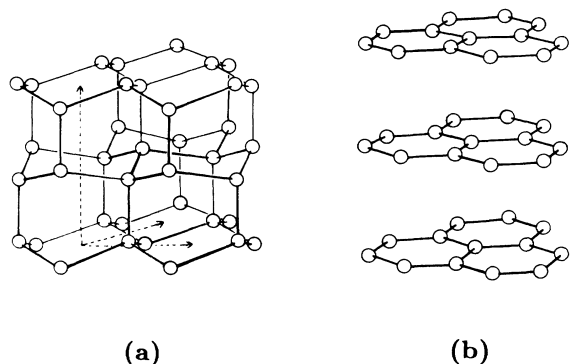


FIG. 1. Three hexagonal ring layers of the (a) hexagonal diamond structure and (b) the corresponding graphite structure with ...[AA]... stacking. The dashed lines indicate the primitive translation vectors of the hexagonal diamond structure.

study to the rhombohedral structures leading from rhombohedral graphite to diamond as parametrized in Ref. 8. Each value of (R, B, θ) defines a hexagonal structure and a rhombohedral structure.

In Ref. 8 two paths from rhombohedral graphite were examined: in one path, the energy of the system was minimized for each value of the interlayer bond length (this path leads to the cubic diamond structure); in the other path, the energy was minimized for each value of the atomic volume (this path is that followed under conditions of hydrostatic pressure and does not lead continuously to the diamond structure). In the present study we have used the same values of the parameters R , B , and θ and calculated the energy of the corresponding hexagonal structure. The results are shown in Figs. 2 and 3.

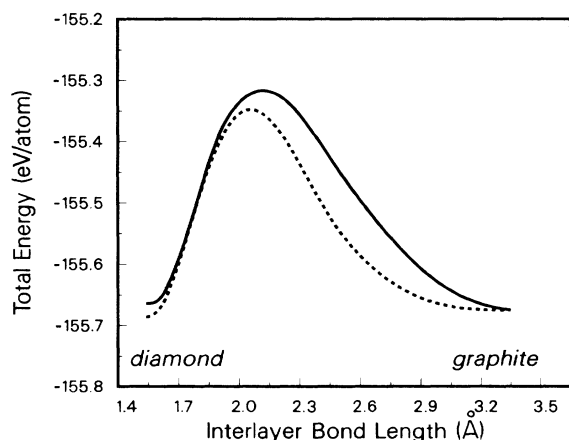


FIG. 2. Energy as a function of interlayer bond length R in the transition from graphite to diamond for the hexagonal (solid curve) and rhombohedral (dashed curve) structures as discussed in the text. The atomic coordinates along the transformation path are those which minimize the total energy of the rhombohedral structure for each value of R , as calculated in Ref. 8. The curves are cubic spline interpolations between 11 calculated points.

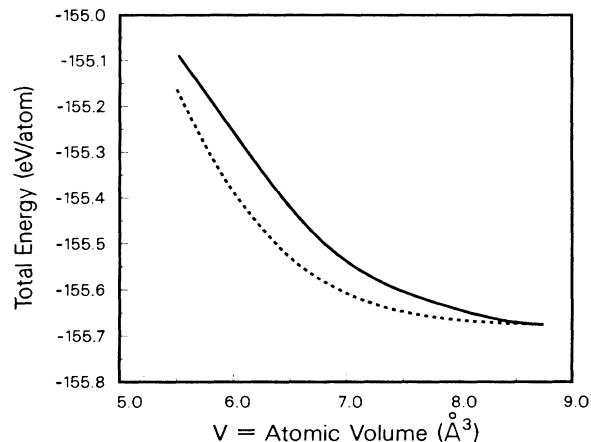


FIG. 3. Energy as a function of the atomic volume for graphite with ...[AA]... stacking (solid curve) and for rhombohedral graphite (dashed curve). The atomic coordinates along the path are those which minimize the total energy of the rhombohedral structure for each value of the atomic volume, as calculated in Ref. 8. The curves are cubic spline interpolations between six calculated points. We terminate the curves at $V = 5.5 \text{ \AA}^3$ because the rhombohedral graphite structure is not metastable for smaller values of V .

II. CALCULATION AND RESULTS

The method of calculation used in the local-orbital calculation is outlined in detail elsewhere^{12,13} so we will give only a brief summary here. The local-density approximation within density-function theory is used,¹⁴ and we employ the Hedin-Lundqvist form¹⁵ of the exchange-correlation energy. The interaction between the ion cores and the valence electrons is treated by the *ab initio* pseudopotential method.¹⁶ The wave functions are expanded in a basis of Bloch sums of Gaussian orbitals centered on the atom sites, of the form

$$f(\mathbf{r}) = e^{-\alpha r^2} r^l Y_{lm}(\theta, \phi).$$

Four values of α and values of $l = 0, 1$ are included, so that there are 16 basis functions per atom (or 64 basis functions at each \mathbf{k} point). In order to make direct comparison with the results of Ref. 8, we have used the same values of α as were used for the corresponding structures in that work. The crystal potential is iterated to full self-consistency using the scheme of Ref. 13, using a uniform grid of 25 \mathbf{k} points in the irreducible Brillouin zone.

As can be seen from Fig. 2, the energetics of the transformation are fairly insensitive to the stacking sequence of the double layers. The peak of the energy occurs at approximately the same place along the transformation path in both cases presented in Fig. 2 and the height of the barrier is not strongly dependent on the stacking sequence. Thus we see that the local bonding properties essentially govern the course of the transformation. This gives additional support to the conclusions drawn in Ref. 8 concerning the conditions for cross link-

ing of hexagonal-ring carbon compounds¹⁷ leading to local tetrahedral coordination.

In Ref. 8 it was shown that the sp^3 bonds start to form between the double layers when the interlayer bond length is approximately 1.8 Å. In its final form cubic diamond has lower structural energy than hexagonal diamond. However, just as the bonds are forming we see from Fig. 2 that the energies of the two structures are equal. At that point along the transformation path cubic diamond is not energetically favored over the hexagonal form. While the interlayer bond length is greater than 1.8 Å, we would expect interlayer bond breaking to be relatively easy and the stacking of the double layers to be not yet "frozen in." However, after the sp^3 bonds form between the double layers, changes in the stacking sequence of the double layers is relatively difficult. If the thermal energy is rapidly quenched in the system^{4,5} (as is the case in those shock-wave processes which produce hexagonal diamond), the proportion of hexagonal diamond which was produced as the sp^3 bonds were forming does not anneal into the cubic form. Thus it is possible that this equality of the hexagonal and cubic diamond energies at the sp^3 bonds are forming is what gives rise to the formation of significant quantities of hexagonal diamond in certain transformation processes.

Finally the following result is clear from Fig. 3: at no point during the "graphitic" phase of the transformation (i.e., on the graphite side of the energy barrier) is the energy of graphite with . . . [AA] . . . stacking lower than the corresponding structure with . . . [ABC] . . . stacking.¹⁸ Because the number of bonds between the layers is the same in rhombohedral graphite and in hexagonal graphite we expect their behavior under compression to be very similar. Thus it is clear from the present calculation that graphite with . . . [AA] . . . stacking will never have lower enthalpy than hexagonal graphite. This is an important conclusion which is by no means obvious without an accurate total-energy calculation. We can therefore conclude that the following transformation path will *not*

occur under static pressure: hexagonal graphite → . . . [AA] . . . stacking graphite → hexagonal diamond.

III. CONCLUSIONS

In conclusion, we have studied the variation of the structural energy of solid carbon along a transition path from graphite with . . . [AA] . . . stacking to hexagonal diamond using the *ab initio* pseudopotential local-orbital total-energy method. We find the salient features of the energy variation to be the same as in a similar study of the transformation of rhombohedral graphite to cubic diamond, thus demonstrating that the main properties of the transformation are determined by the local bonding and are relatively insensitive to the stacking of the carbon double layers. As the sp^3 bonds are starting to form between the buckled layers, the energies of hexagonal and cubic diamond are found to be equal although cubic diamond in its final form is lower in energy than hexagonal diamond. The transformation path studied here is not the path followed in the static pressure transformation of hexagonal graphite into hexagonal diamond. Nevertheless it provides qualitative insight into some aspects of the real transformation and gives a basis for further microscopic analysis of the synthesis of diamond from graphite. In the region of metastability of the graphitic phase under static pressure, the . . . [AA] . . . stacking is found always to lie higher in energy than the . . . [ABC] . . . stacking of rhombohedral graphite.

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¹¹At the graphite end point, where $\theta=90^\circ$, there is additional translational symmetry (because the *A* and *B* double layers become equivalent) and the primitive unit cell has two atoms rather than four as for hexagonal diamond.

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ergy for the hexagonal structure in the present study. However, we expect the error involved to be small relative to the energy differences between the different stackings of the double layers, especially in the high-pressure region.