Phase transition mechanism of hexagonal graphite to hexagonal and cubic diamond: 
*ab initio* simulation

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Abstract

*Ab initio* molecular dynamics simulations are used to elucidate the mechanism of the phase transition in shock experiments from hexagonal graphite (HG) to hexagonal diamond (HD) or to cubic diamond (CD). The transition from HG to HD is found to occur swiftly in very small time of 0.2 ps, with large cooperative displacements of all the atoms. We observe that alternate layers of atoms in HG slide in opposite directions by \(1/6\) along the \([2, 1, 0]\), which is about 0.7 Å, while simultaneously puckering by about \(0.25\) Å perpendicular to the \(a–b\) plane. The transition from HG to CD occurred with more complex cooperative displacements. In this case, six successive HG layers slide in pairs by \(1/3\) along \([0, 1, 0]\), \([-1, -1, 0]\) and \([1, 0, 0]\), respectively along with the puckering as above. We have also performed calculations of the phonon spectrum in HG at high pressure, which reveal soft phonon modes that may facilitate the phase transition involving the sliding and puckering of the HG layers. We have further calculated the Gibbs free energy, including the vibrational energy and entropy, and derived the phase diagram between HG and CD phases.

Keywords: phase transition, *ab initio*, molecular dynamics, Gibbs free energy, soft phonon, carbon

Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)

1. Introduction

The compression of graphite under extreme thermodynamic conditions is subject of intense scientific research\([1–6]\). Cubic diamond (CD) was recovered\([3]\) after explosive shock compression of hexagonal graphite (HG). Synthetic diamond can be obtained by simultaneously applying high pressure and temperatures on graphite\([1, 3, 7]\). Hexagonal form of diamond\([8]\), which was later called lonsdaleite\([4]\), was identified inside fragments of the Canyon Diablo meteorite. Lonsdaleite\([4]\) is believed to be a harder form of carbon than CD\([9, 10]\). Static compression of HG results in transformation to hexagonal diamond (HD)\([8, 11]\) or CD\([2, 12]\) over wide range of pressure and temperature. The melting transition has also been extensively studied\([13, 14]\).

Recent shock studies\([15–18]\) of the transition from HG to HD or CD have created much interest in understanding the mechanism of these transitions. A variety of experiments have been performed, namely, using a laser shock\([15]\), plate impact shock\([16, 17]\), and detonation-induced shock experiments\([18]\), which reveal the transition above 50 GPa.
The thermodynamic behaviour of graphite as well as that of other graphitic materials, such as graphene and carbon nanotubes is of considerable scientific interest [19–33]. Theoretical works have been reported [34–38] to understand the dynamic process for synthesis of CD and HD. Various theoretical studies of the enthalpy in various phases indicated [39, 40] that under compression above a few GPa, both CD and HD are more stable in comparison to HG, while CD is always more stable than HD. However, experimental measurements [8, 11, 15–18] also show transformation from HG to HD.

The unit cell of HG structure (space group $P6_3/mmc$) consists of 4 carbon atoms that occupy two Wycoff sites, namely, $2b$ \{$(0, 0, 1/4), (0, 0, 3/4)$\} and $2c$ \{$(1/3, 2/3, 1/4), (2/3, 1/3, 3/4)$\}. Interestingly, HD also crystallizes in $P6_3/mmc$ space group, but the carbon atoms occupy 4f Wycoff sites \{$1/3, 2/3, z\}, \{(2/3, 1/3, z + 1/2), (2/3, 1/3, −z)\} and \{(1/3, 2/3, −z + 1/2), with $z = 0.0625$. The CD crystallizes in $F\bar{d}-3m$ space group. The structure of CD can also be represented in a hexagonal unit cell containing 6 atoms (see supplementary material (https://stacks.iop.org/JPCM/33/425403/mmedia) [41]).

Despite numerous previous experimental as well as theoretical studies, atomic level understanding of the transformation from HG to HD/CD remains incomplete. The calculations of the energy barrier [18] do not always give the complete picture including correlated dynamics. The nucleation and growth mechanism of these phase transitions has been investigated in detail [34, 37, 38]. However, the transition in shock experiments occurs at a fast time scale of $\sim$ps, and may involve a different mechanism. We have performed ab initio molecular dynamics (AIMD) simulations to understand the mechanism of the transition from HG to HD as well as to CD. Our simulations suggest that, once the lattice is sufficiently compressed, the transition can occur swiftly through cooperative movement of all the atoms, unlike in the nucleation mechanism. The simulations thus seem to provide an alternative mechanism that may be applicable to the shock transitions observed in shock experiments. Such a concerted mechanism has been suggested earlier [42, 43]. However, the present AIMD simulations provide evidence of clear atomic dynamics, the pathways and the time scales.

The ab initio enthalpy calculations [18, 39] based on the density-functional theory indicated the transition from HG to HD/CD at a rather low pressure of $\sim$1 to 6 GPa depending on the choice of the density functional. The phonon spectra have important role in determining the phase stability, through the vibrational energy including the zero-point vibrational energy, and the vibrational entropy. We have calculated the equation of state and the phonon spectra at high pressures using ab initio methods, and used these to calculate the Gibbs free energies in all the three phases to understand the role of atomic dynamics in phase transitions. We find that many of the phonon modes in HG occur at rather low energies than those in HD/CD. Such low-energy modes in HG contribute to increase in the vibrational entropy, thereby favoring the stability of HG over HD/CD. We have further identified soft phonon modes in HG at high pressures which could be related to the phase transition mechanism.

### Table 1. Comparison between the calculated and experimental [52] structural parameters of the HG.

|          | $a (=b)$ (Å) | $c$ (Å) |
|----------|--------------|---------|
| Experimental (300 K) | 2.456 | 6.696 |
| Calculated (0 K) | 2.465 | 6.693 |

2. Computational details

The first-principles density functional theory (DFT) calculations were performed using the Vienna ab initio simulation package (VASP) [44, 45]. The generalized gradient approximation with Perdew, Becke, and Ernzerhof [46, 47] functional implemented in VASP has been used for exchange-correlation energy. The projector augmented wave method was used to incorporate the interaction between valance and core electrons. The plane-wave basis set with maximum kinetic energy cutoff of 820 eV was used. The Brillouin zone integration was performed on $20 \times 20 \times 2$, $20 \times 20 \times 10$ and $14 \times 14 \times 14$ mesh generated using the Monkhorst–Pack method [48] for HG, HD and CD respectively. The convergence criteria for total energy and forces were set $10^{-8}$ eV and $10^{-7}$ eV Å$^{-1}$, respectively. The relaxation of the graphite structure was performed with including various vdW-DF non-local correlation functional [49–51]. We find that the relaxation performed using the optB88-vdW [51] (BO) functional scheme of the vdw-DFT method produces the best match with the experimental structure. The dispersive potential is chosen so as to reproduce the c-lattice parameter of HG close to the known experimental value. This potential is the same as used in our previous paper [30] on study of defects in graphite. The comparison between the calculated and experimental [52] structural parameters of HG is given in table 1. The PHONOPY software [53] has been used to generate the supercell and displaced configuration for phonon calculations. The partial density of states (DOS) of individual atom has been calculated by projecting the individual atomic eigenvectors on the total eigenvector.

AIMD simulations were performed to understand the phase transition from HG to hexagonal and CD. All three structures can be represented by hexagonal unit cells, although the primitive cell of CD is smaller. The hexagonal unit cells of HG and HD comprise of two layers (ABAB...), while that of CD comprises of three layers (ABCABC...). We used $4 \times 4 \times 1$ and $3 \times 3 \times 3$ supercells of HG unit cell to simulate the transition from HG to HD and CD, respectively. The two supercells for the simulations are chosen such that the length of the supercell along the c-axis is compatible with the periodicity of the HD and CD structures, respectively. The AIMD simulations were initiated with the HG structure with fixed values of the lattice parameters corresponding to hexagonal/CD at a given pressure. The simulations were performed in NVT ensemble at several temperatures from 300 K to 6000 K. The desired temperature in NVT simulations is achieved with Nose thermostat [54]. We used an energy convergence of $10^{-6}$ eV and zone-centre point for Brillouin zone integration. The simulations were performed for $\sim$20 ps with 2 fs step size at each temperature.
3. Equation of state

The equation of state refers to the plot of the pressure dependence of the unit cell volume. This has been calculated at absolute zero temperature by minimizing the enthalpy, which does not include the contribution from vibrational modes. The experimental data of structural parameters for HG [55, 56], HD [16, 18], and CD [57] are available in the literature. The calculated structural parameters are compared with the experimental data in figure 1(c). The calculated volume drop of about 13% at 49 GPa on transition from HG to HD is in agreement with the experimental data from literature [16, 18]. The calculated bulk modulus values for HG and CD/HD are 38 GPa and 437 GPa, respectively, which are in good agreement with the available experimental data of 35.8 for HG [58] and 443 GPa for CD [59].

4. Phonon spectra

The calculated phonon spectra figures 1(a) and (b) show significant difference among HG, HD and CD, which mainly arises from the difference in nature of atomic bonding. The HG exhibits large anisotropy with strong sp2 covalent bonding in the a–b plane, and van der Waals interactions between the graphite layers along c-axis. The covalent bonding in the a–b plane results in peaks in the phonon spectrum at about 58, 78, 108 and 170 meV. The low energy modes below about 20 meV occur due to the van der Waals interactions, which are of particular interest as these modes give rise to large vibrational entropy. The calculated peaks positions in the phonon spectrum for HG are in very good agreement with the experimental data [60] from neutron inelastic scattering.

The HD and CD involve isotropic sp3 bonding. The broad peak in the phonon spectrum (figure 1(b)) of CD at around 80 meV and peaks at around 122 meV and 147 are in good agreement with the available experimental data [61]. The calculated phonon spectrum of HD is close to that of CD (figure 1(b)).

5. Calculated Gibbs free energy in various polymorphs

At high temperatures, the contribution due to entropy (S) becomes important, and so, one should calculate the Gibbs free energies (G) in the different phases to identify the stable phase at any pressure and temperature. $G = E + PV − TS$, where E is crystal potential energy and vibrational energy, S is entropy, T is temperature, P and V are pressure and unit cell volume respectively. We have calculated the phonon spectra at several pressures in all the three phases and for calculation of the Gibbs free energy as a function of pressure and temperature. The results of the calculated Gibbs free energy curves, as shown in figures 1(d) and S2 (see supplementary material [41]) for different temperatures, reveal the relative stability of the phases. The phase transition points are gathered into a phase diagram and compared with available experimental data [2, 62] in figure 2. We note that, while the transition pressures are overestimated by ~6 GPa in the ab initio calculations, the slope of the phase boundary is in excellent agreement with experiments. The lateral shift in the figure 2 indicates overestimation of the HG to CD transition pressure values. This means that the potential energy difference between the two phases is overestimated. This is a limitation due to the DFT functional.
The enthalpy and free energy calculations show that CD is always more stable in comparison to HD. It may be noted that the unit cell volume of CD is slightly smaller than that of HD. For example, at 49 GPa the volumes of CD and HD per atom are 5.19 Å³ and 5.20 Å³, respectively; the essential difference is that while all the C–C bonds in CD are of 1.50 Å, in HD three C–C bonds are of 1.50 Å, while the fourth C–C bond along the c-axis is of 1.52 Å. The slightly smaller volume for CD may occur due to the different layer sequence along the hexagonal-axis and favourable long-range van der Waals attraction for CD.

6. Phase transition mechanism of hexagonal graphite to hexagonal and cubic diamond

The AIMD simulations are performed on the $4 \times 4 \times 1$ supercell of HG at various temperatures from 300 K to 6000 K at constant volume and temperature using NVT ensemble. The volume chosen is that of HD at 49 GPa. In the simulations at temperatures up to 5000 K, we observe fairly large shifts of atoms from their reference positions in HG, which indicate a tendency towards the transition to HD, but the transition did not complete at a time scale of 20 ps. However, at 5500 K, the calculated time dependence of fractional coordinates of the carbon atoms clearly shows (figure 3) the HG to HD transition. The transition of HG to HD at 5500 K occurs in very short times of less than 1 ps. As shown in figure 3, during the transition there is cooperative motion of all the four carbon atoms in the unit cell.

The calculated snapshots of atomic coordinates at various times are shown in figure 4 (for more details see figure S3 see supplementary material [41]). The structure of HG has two layers of carbon atoms. The time evolution of the coordinates as well as snapshots of atoms at various time steps show that all the atoms in both the layers move simultaneously. We find that there is large displacement of all the atoms (figure 3) along all the three axes ($x$, $y$ and $z$) in first 200 fs. As shown in figure 4, for the transitions from HG to HD and CD, the coordinates of the 4 and 6 atoms are plotted respectively, which form the hexagonal unit cell of the transformed phase. These coordinates are obtained from average over equivalent atoms in supercells of HG of size $4 \times 4 \times 1$ and $3 \times 3 \times 3$ respectively.

![Figure 2](image-url)  
**Figure 2.** The phase boundary (solid blue line) between HG and CD from Gibbs free energy calculations. Reproduced from reference [2,62]: experimental phase boundary (solid black line), region 'A' of catalytic transformation of HG to CD, region 'B' of spontaneous slow martensitic transformation of HG to HD, black solid symbols of spontaneous fast transformation of HG to CD, and black open circles of spontaneous fast transformation of CD to HG.

![Figure 3](image-url)  
**Figure 3.** Transformation of HG to HD at 5500 K. and HG to CD at 300 K. The AIMD simulations are performed with NVT ensemble at constant lattice parameters corresponding to that of HD/CD at 49 GPa. The time dependence of the fractional coordinates ($I(x, y, z)$) of the atoms in the hexagonal unit cells, starting with the coordinates in HG. The $x$, $y$ and $z$ are the fractional coordinates along the $a$, $b$- and $c$-axis, respectively, with reference to the HG unit cell. Dashed lines correspond to the fractional coordinates in the transformed phase. For the transitions from HG to HD and CD, the coordinates of the 4 and 6 atoms are plotted respectively, which form the hexagonal unit cell of the transformed phase. These coordinates are obtained from average over equivalent atoms in supercells of HG of size $4 \times 4 \times 1$ and $3 \times 3 \times 3$ respectively.
in agreement with the experimental study [4]. Our AIMD simulation clearly brings out a very swift displacive phase transition at ps time scale at high pressure and temperature akin to that found in shock experiments [17, 18].

In order to simulate the transition from HG to CD, we have performed AIMD simulations on the 3 \( \times \) 3 \( \times \) 3 supercell of HG with NVT ensemble. The volume used is that of CD at 49 GPa. We could observe the transition at 300 K in a fairly short time of less than about 0.5 ps. The transition path involves (figure 3) cooperative movement of all the atoms. The six successive HG layers’ slide in pairs by 1/3 along [1, 0, 0] and equivalent directions, namely, (0, 1/3, 0), (−1/3, −1/3, 0), (−1/3, −1/3, 0), (1/3, 0, 0), (1/3, 0, 0), and (0, 1/3, 0), respectively, while simultaneously puckering by about ±0.25 Å perpendicular to the \( a−b \) plane. We find that each layer of atoms in graphite slides by about 0.8 Å along with puckering by about ±0.25 Å.

It appears that the transition paths of HG to HD and HG to CD are quite similar, both involving swift cooperative movement of all the atoms that includes sliding of the graphite layers by about 0.7 Å with simultaneous puckering of the layers by about ±0.25 Å in a short time of less than 0.5 ps, about 0.2 ps. The direction of the sliding of HG layers is different in the two cases. We observe that in the transition from HG to HD, alternate HG layers slide in opposite directions by about 0.7 Å along \( ±[2, 1, 0] \). The transition from HG to CD involves sliding of six successive HG layers in pairs by ~0.8 Å along \([0, 1, 0], [−1, −1, 0] \) and \([1, 0, 0] \), respectively. The essential difference between HD and CD is the periodicity along the hexagonal direction; it is two puckered layers (ABAB...) in HD and three (ABCABC...) in case of CD. The latter has slightly lower energy, essentially due to favourable long-range van der Waals interaction along the hexagonal direction. This means HD is a metastable structure that may occur if influenced by the kinetics of the shock experiments at certain intermediate pressures and high temperatures.

Figure 4. The snapshots of atoms during transformation of HG to HD (left panel) and CD (right panel). The time after the start of the simulation is indicated below each snapshot.
of the $c$-lattice parameter. Although the lattice dynamics calculations are done at zero temperature, we might expect similar softening of modes also at high temperature at high pressure.

7. Conclusions

In summary, AIMD calculations have provided the mechanism of phase transition of HG to hexagonal or CD. We show that during the phase transition there is large cooperative displacement of atoms in very short time of about 0.2 ps. The transition paths of both HG to HD and HG to CD involve sliding of the graphene layers by about 0.7 Å with simultaneous puckering of the layers by about ±0.25 Å. The pattern of the sliding of the layers is different in case of the transition to HD and CD. The HD transition is achieved by sliding alternate layers in opposite directions along [2, 1, 0], while the CD transition involves sliding of pairs of layers along the [1, 0, 0] or equivalent directions. We find soft phonon modes occur at the Brillouin zone center in HG at high pressure when the $c$-lattice parameter approaches that of the HD/CD phases. These modes involve the sliding and puckering of the layers similar to that found in the AIMD simulations. We have also calculated the Gibbs free energies, which reveal important contributions of phonons, especially the vibrational entropy in stabilizing the HG phase up to higher pressures at high temperatures than the very low values predicted from previous enthalpy calculations.

The CD has slightly lower free energy than the HD, essentially due to the different layer sequence along the hexagonal-axis and favourable long-range van der Waals attraction for CD. However, phase transitions from HG to both HD and CD have been reported in experiments.

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Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

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