Detonation-induced transformation of graphite to hexagonal diamond.

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We explore the structural evolution of highly oriented pyrolytic graphite (HOPG) under detonation-induced shock conditions using in situ synchrotron X-ray diffraction in the ns time scale. We observe the formation of hexagonal diamond (lonsdaleite) at pressures above 50 GPa, in qualitative agreement with recent gas gun experiments. First-principles density functional calculations reveal that under uniaxial compression the energy barrier for the transition towards hexagonal diamond is lower than cubic diamond. Finally, no indication of cubic diamond formation was observed up to >70 GPa.

The structural evolution of graphite under elevated thermodynamic conditions has been the subject of intense research interest. Under isothermal (room temperature) static compression a pressure-induced phase transition above ≈20 GPa towards a superhard phase with sp3 bonding was reported by Mao et al.10 Among the several predicted high-pressure phases of carbon (see Ref.2 and references therein), M-carbon11 was experimentally identified as the high-pressure phase of carbon by Wang et al.12 According to the later study, the phase transition of H-graphite (HG) to M-carbon appears to be extremely sluggish, underlying a strong kinetic effect. Under simultaneous application of static pressure and high temperature conditions on HG, both the formation of hexagonal diamond (HD, lonsdaleite)2 and cubic diamond (CD)2 were reported depending on the thermodynamic conditions. In general, lower pressures and temperatures seem to favor the formation of HD while higher pressures and temperatures favor CD, see Table S1 of Ref. 7 for a detailed list of previous experimental studies. Moreover, a mixture of CD (predominantly) and HD for samples of meteoritic impact origin was determined.3

In the case of shock compression of HG, early studies, back in 90s, clearly indicate the shock-induced transformation of graphite to a phase with much higher density, presumably a sp3 allotrope, above 20 GPa.13 However, only recently the capability of in-situ X-ray diffraction (XRD) under shock conditions allowed the structural characterization of the relevant phases.141516 The two recent in-situ XRD experimental studies141516 on the shock induced transformation of HG contradict each other. Kraus et al. report a HG→CD transition starting at 50 GPa, while HD was observed at pressure above 170 GPa. By contrast, a HG→HD transition was reported by Turneaure et al. above 50 GPa. Very recently, it was reported that the observed high-pressure crystal structure of shocked graphite depends strongly on the initial crystalline quality of HG, i.e. highly oriented pyrolytic graphite (HOPG) transforms to HD while turbostratic carbon to CD.17 It is noteworthy that the formation of high purity lonsdaleite, starting from glassy carbon, was experimentally reported in a diamond anvil cell at 100 GPa and 400 °C, attributed to a strain induced transformation.17 Interestingly, the reverse transition from Wurtzite (2 elements analogue of HD) to graphite-like was predicted in the case of ZnO Nanowires under tensile loading.17

According to previous theoretical studies under static compression both CD and HD become lower in enthalpy than HG above few GPa. However, HD always has a higher enthalpy than CD and thus, HD never has a region of thermodynamic stability. This clear discrepancy with experimental findings of HD formation was recently explained theoretically by the lower calculated barrier for the HG to HD transition than the corresponding HG to CD.17 The lower barrier also results to a much faster (40X) growth of HD than CD.15 Given that the energy barrier for the HG to HD tradition is pressure dependent, a strong kinetic effect is expected as a function of pressure i.e. the time needed for the growth (and thus the possible observation) of HD and CD is affected by the thermodynamic conditions and the time that HG is “exposed” to such conditions. Indeed, critical pressures above 100 GPa are predicted for the HG→CD transition under few picoseconds shock compression conditions.17

In order to resolve the discrepancy between the previous studies and get further insight on the energetics and kinetics of the HG structural evolution under shock conditions, we have performed a concomitant experimental and computational study. Aiming to probe larger quantities, and thus increase the confidence of the Bragg peaks assignments, of HG under shock conditions we use detonation to shock macroscopic quantities of HOPG in a geometry with X-rays orthogonal to the shock front. This allowed us, for the first time, to directly compare the experimental patterns with the calculated patterns of HD.
and CD and also perform a Le Bail refinement.

Our experimental results unequivocally reveal the formation of HD above 50 GPa and 100-200ns after detonation. Although our enthalpy calculations under uniaxial compression (mimicking shock conditions) clearly indicate that the enthalpy of CD is lower than HD, as in the case of static compression, the energy barrier for the transition towards HD is lower than CD.

High purity commercially available HOPG (SPI Supplies Grade-1 5×5×1mm) was used for all XRD experiments. Time-resolved XRD measurements were performed within a Lawrence Livermore National Laboratory (LLNL) detonation tank at the Advanced Photon Source (APS), Argonne National Laboratory, at the Dynamic Compression Sector, within the special purpose hutch (35-IDB) or at 32-IDB. Thin pellets of HOPG were either placed on top of a single high explosive (HE) or sandwiched between two HEs. This way the peak shock pressure was controlled by both the type of HE (30-40 GPa peak pressure) and also by what we will refer to as “single” or “colliding” detonation. Two different polymer bonded explosives were used, one was hexanitrohexaazaaisowurtzitane (CL-20) based, the other pentaerythritol tetranitrate (PETN), to generate different peak pressures. To detonate the HEs, exploding foil initiator (EFI) based detonators were placed underneath or above the HEs forming a colliding detonation geometry, see figure 1. This assembly was placed within a 120L steel vacuum vessel (Teledyne RISI) and pumped down to < 200mTorr. The tank uses upstream and downstream KaptonTM (polyimide) windows to facilitate the X-ray transmission geometry required for XRD and/or radiography under low vacuum conditions. Within the vacuum vessel, LexanTM (polycarbonate) panels were used as shrapnel mitigation. The samples were detonated near the rear window to increase the angular range of the detector; a Tantalum beamstop was placed between two 2mm polycarbonate plates, with an additional 1 mm closest to the sample. These were placed a few cm from the detonation. More details about the LLNL detonation tank and the experimental setup can be found in Refs. 24 and 25.

Detonation is synchronized with the APS bunch clock, thus permitting XRD from discrete 34ps rms X-ray pulses, which arrive every 153.4ns during 24-bunch mode. The sample-detector distance was about 11cm. Scattering intensity was recorded using an array of four identical area detectors (PI-MAX4 1024i ICCD, Princeton Instruments) focused on the output of a scintillator and image intensifier. Si640E and CeO2 were used as calibrants for the XRD sample-detector geometry. Integration of powder diffraction patterns to yield scattering intensity versus 2θ diagrams and initial analysis were performed using the DIOPTAS program. Calculated XRD patterns were produced using the POWDER CELL program for the corresponding crystal structures assuming continuous Debye rings of uniform intensity. Le Bail refinements were performed using the GSAS software. Indexing of XRD patterns was performed using the DICVOL program as implemented in the FullProf Suite.

FIG. 1. a) Schematic diagram of the detonation tank for in situ XRD under detonation conditions and schematic section (not to scale) of the experimental cylindrical setup showing the HOPG rectangle pellet between two cylinders of HEs for the colliding arrangement. The cylindrical setup is aligned in a way that the incident x-ray beam is at the center (vertical and lateral) of the HOPG pellet and perpendicular to the shock front(s). b) A representative pressure distribution from finite element simulations of the colliding shock configuration. c) Pressure histories for the PETN and d) the CL-20 colliding shock simulations.

The shock-induced transformation of HOPG to diamond was modeled by calculating the enthalpy barriers and relative enthalpies of HG to HD and Rhombohedral Graphite (RG) to CD using Density Functional Theory (DFT) as a function of uniaxial static compression up to 40 GPa at 0 K. Minimum energy paths (MEPs) were calculated using the Generalized-Solid State Nudge Elastic Band (G-SSNEB) method. The method is ideal for investigating solid-solid phase transitions where changes in atomic coordinates and lattice vectors describe the phase transition. A Climbing-Image (CI) NEB calculation was performed using the G-SSNEB to obtain the transition state between HG-HD and RG-CD at 40 GPa of static uniaxial stress.

The static uniaxial compression is applied in the (001) direction of HG, RG, and HD and in the (111) direction of CD. The (111) direction of CD is chosen because the surface along (111) consists of hexagonal rings commensurate with graphite, while (001) consists of square rings. The surfaces along the (111) and (001) directions are displayed in supplemental Fig. S1(a) and (b) respectively, created using the Generalized Crystal Cutting Method (GCCM) to calculate the barrier, the lattices are rotated so that the compression direction is in the z-direction and so that each h-matrix is a lower-triangular matrix. The simulation cell for HG-HD consists of 8 graphitic layers with 4 atoms in each layer for a total of 32 atoms. The simulations cell for RG-CD consists of 9 graphitic layers with 4 atoms in each layer for a total of 36 atoms. The simulation cell for the RG-CD mechanism...
was doubled in the z direction to investigate system-size effects on the energy barrier. Xiao et al.\(^{13}\) showed that, in the nucleation mechanism, the transformation from HG-HD had a lower energy barrier than RG-CD under hydrostatic compression. So a similar nucleation mechanism was investigated under uniaxial compression in this work. However, the nucleation mechanism is still concerted within the graphitic (xyz) plane. It is computationally prohibitive to consider nucleation mechanisms in the graphitic plane. Khalifullin et al. investigated nucleation mechanisms as a function of nucleus size using neural network potentials under hydrostatic compression.\(^{35}\)

Enthalpy differences under uniaxial compression are defined by the following formula,

\[
\Delta H = \Delta U + V \cdot \sigma_{i,j} \epsilon_{i,j}.
\]  

(1)

\(\sigma_{i,j}\) is the stress tensor, \(\epsilon_{i,j}\) is the strain tensor, \(V\) is the initial volume, and \(\Delta U\) is the change in the potential energy. In this case, the only non-zero component of \(\sigma_{i,j}\) is \(\sigma_{z,z}\) because uniaxial stress is applied perpendicular to the graphitic layers (the z direction). The only relevant strain is therefore \(\epsilon_{z,z}\).

DFT calculations were performed using the Vienna Ab-initio Simulation Package (VASP)\(^{36}\) (VASP) with the Perdew-Burke-Ernzerhof (PBE)\(^{37}\) generalized gradient approximation functional with projector-augmented wave (PAW) pseudopotentials\(^{38,39}\) and Grimme D2 dispersion corrections.\(^{40}\) The wavefunction was calculated with a 700 eV plane wave energy cutoff and kpoint density of 0.05 Å\(^{-1}\). A 5X10X1 kpoint grid is used for RG-CD and 10X5X1 for HG-HD. The self-consistent field accuracy threshold was set to \(10^{-6}\) eV and optimizations of the ionic degrees of freedom were performed with a force-based accuracy threshold of \(3 \times 10^{-2}\) eVÅ\(^{-1}\).

A finite element based approach was employed to estimate the pressure and temperature histories within the explosively loaded HOPG samples. Detonation experiments were simulated using a Jones-Wilkins-Lee (JWL)\(^{41}\) programmed burn. The model uses the JWL equations of state (EOS), for the reaction products to simulate the detonation waves generated in Numerical simulations were performed using the arbitrary Lagrangian-Eulerian hydrocode ALE3D.\(^{42}\) A 2-D axi-symmetric approach has been employed for computational tractability due to the small time step requirements for hydro-thermal coupling. HOPG is modeled with a Steinberg-Guinan EOS and strength model for graphite.

The XRD 2D-images of HOPG at ambient conditions are characteristic of single crystal (SC) HG and in agreement with the results of previous studies.\(^{11}\) See Fig. 2(a). All SC HOPG spots can be indexed with the expected Bragg reflections of HG. For pressures below 40 GPa, achieved by the detonation of a single HE, only a detonation/pressure induced shift of the HOPG SC spots towards higher \(2\theta\) due to compression was observed (see Fig. S2) while, HOPG remains predominantly a SC. For pressure above 40 GPa, archived by a colliding detonation, new Bragg reflections appear, see Fig. 2(b) while the HOPG SC spots practically disappear with the exception of the very intense 002 peak at low \(2\theta\). The pressure shift of the 002 HG peak was estimated to be around 40 GPa, based on the extrapolation (using a third-order Birch-Murnaghan equation of state)\(^{12}\) of the HG EOS under static compression.\(^{43}\) It is plausible to attribute the presence of the 002 peak of untransformed HOPG to the edge regions of the initial HOPG sample that are experience lower pressure, see Fig. 1(b).

In figure 3(a) we compare the XRD pattern acquired at 50 GPa and 200ns after detonation with the calculated patterns of CD and HD at ambient conditions. The calculated pattern of CD cannot explain the doublet observed between 12-16.5 ° 2\(\theta\) or the low intensity peak at 20 °. There is also a clear mismatch with the observed most intense peak (14.2 °) and the 111 peak of CD. A higher cell volume of CD, than the one at ambient conditions, is needed to index the most intense observed Bragg peak. On the other hand, the calculated pattern of HD shows much better agreement and could explain all observed Bragg peaks and the overall “shape” of the experimental pattern. Indeed, close inspection of the 2D images (Fig. 2(b)) reveals three distinct families of XRD patterns, in agreement with the expected 3 Bragg peaks in this 2\(\theta\) range for HD. Thus, it is plausible to conclude that detonation-induced shock compression transforms H-Graphite to Hexagonal Diamond.

Aiming to further justify our conclusions and determine the equation of state (EOS) of HD, the diffraction patterns were analyzed by performing Le Bail refinements as a function of time from detonation and for the two HEs used for the colliding detonation. Using ALE3D calculations the corresponding pressure was determined, see Figs. 1(c)(d). A typical refined profile is shown in Fig. 3(b). From the XRD data we have obtained the volume per carbon atom (\(V_{p}a\)) as functions of pressure. The results are shown in Figure S3.

To gain deeper insight into the HG-HD transformation we have performed first-principles DFT calculations for the relative enthalpies between HG, RG, HD and CD under hydrostatic and uniaxial compression given in Supplemental Fig S4(a) and (b) respectively. The relative enthalpy under uniaxial compression is calculated according to eq. 1. As expected, for hydrostatic compression the enthalpy of HD is always higher than CD in agreement with previous studies.\(^{15,17,46}\) In an apparent contradiction to previous calculations,\(^{45}\) under uniaxial compression CD is still lower in enthalpy than HD up to 40 GPa and the difference between the two appears to increase slightly with pressure. The contradiction may be due to the way the relative enthalpy was defined under uniaxial compression (eq. 1) or the method used\(^{45}\) to optimize the lattice under uniaxial compression. In our case, stresses in the planar direction (\(S_{xx}\) and \(S_{yy}\)) were set to zero. The relative enthalpies under uniaxial compression shows evidence that the transformation from HG to HD is due to the kinetics not the thermo-
FIG. 2. a) 2D X-ray diffraction images in rectangular coordinates (cake) for HOPG at ambient conditions. b) cake and corresponding x-ray diffraction patterns of HD at $\sim 50$ GPa and 200ns. The three distinct families of XRD spots in the 12-16.5° $2\theta$ range corresponding to HD are noted by ovals of different colors: black for 100, red for 002 and blue for 101. The expected $2\theta$ values of the HG and HD Bragg peaks and the corresponding Miller indices are noted with blue vertical ticks. The X-ray wavelength is $\lambda=0.52$Å.

dynamics, i.e. the energy barrier for HG-HD is lower than the energy barrier for HG-CD. The kinetics explanation for the formation of HD was also made in previous studies.$^{18,35}$

To investigate the kinetics of the HG-HD and HG-CD phase transition the enthalpy barriers were calculated at $S_{zz} = 40$ GPa using the G-SSNEB method$^{33}$ similar to the previous calculation under hydrostatic pressure.$^{18}$ The nucleation mechanism for the transformation was investigated since a similar mechanism was shown to have a lower barrier for HG-HD.$^{18}$ The nucleation mechanism is perpendicular to the graphitic planes and also concerted within the plane. The transition from RG to CD was calculated because the lattices of the two are commensurate. The transition from HG to RG is not expected to play much of a role on the energetics because the relative enthalpy difference is small as shown in Supplemental Fig S4(b). The energy barrier for layer sliding is also small.$^{47}$ The calculated enthalpy barriers and snapshots of the crystal structure along the MEP for HG-HD and RG-CD are shown in Fig. 4 and S5 respectively. The total enthalpy barrier for the HG-HD transition was calculated to be 1.987 eV and for RG-CD was calculated to be 2.088 eV, a difference of 0.101 eV. Therefore, the calculations show evidence that the energy barrier for HD is lower than CD under uniaxial compression. While the difference is too small to make a strong conclusion on the kinetic selectivity of HD over CD, previous calculations showed that the difference in the enthalpy barrier increases with nucleation size under hydrostatic pressure.$^{35}$ In addition, when the size of the simulation cell is doubled in the z-direction the enthalpy barrier for RG-CD increases to 2.160 eV (an increase of 0.072 eV) as shown in Fig. S6. This effect may not be as significant for HD because the transition state appears to be more localized, see Fig. 4(e) for the transition state for HG-HD and Fig. 5(c) for the transition state of RG-CD. The calculations therefore provide evidence that the enthalpy barrier for HD is lower than CD indicating kinetic selectivity of HD.

Further insight into the kinetic selectivity of HD can be

FIG. 3. a) Experimental XRD pattern for the HD at 50 GPa and 200ns compared with the calculated XRD patterns of CD$^{45}$ and HD$^{5}$ and b) Le Bail refinement results for the HD pattern of panel (a). Symbols correspond to the measured profile and the red solid lines represent the results of Le Bail refinement. Vertical ticks mark the positions of the Bragg peaks of the HD.
FIG. 4. Enthalpy barrier and minimum energy pathway (MEP) for the HG-HD nucleation mechanism at $S_{zz} = 40 \text{ GPa}$. (a) The MEP and (b-h) snapshots of the crystal structure along the MEP. Yellow arrows show the trajectory of carbon atoms along the MEP to form covalent bonds.

The structural evolution HOPG under detonation-induced shock conditions was studied using in situ synchrotron X-ray diffraction in the ns time scale in a geometry that allowed us, for the first time, to directly compare the experimental patterns with the calculated patterns of HD and CD. This way, the formation of HD at pressures above 50 GPa was unequivocally revealed. According to the calculations in our study, although the enthalpy of CD is lower than HD under uniaxial compression, the energy barrier for the transition towards HD is lower than CD.

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Supplemental Material for “Detonation-induced transformation of graphite to hexagonal diamond”
FIG. S1. The surface of CD along the (a) (111) and (b) (001) direction. The (111) direction consists of hexagons that are commensurate with graphite, while (001) consists of squares that are not commensurate with graphite. The top panel shows a top view looking down along the two directions and the bottom panel shows a side view.

FIG. S2. 2D X-ray diffraction images in rectangular coordinates (cake) of HOPG at a) ambient conditions and b) at \(\sim 20\) GPa and 100ns. The low intensity SC spots of ambient pressure HOPG are due to the edge regions of the sample, see Fig.1.
FIG. S3. Volume-pressure data for carbon under static and shock compression as determined by previous and this study. All volumes are normalized to the ambient volume per carbon atom of HG.
FIG. S4. (a) Relative enthalpy between HG, CD, and HD under static hydrostatic pressure. (b) Relative enthalpy under static uniaxial pressure between RG compressed in the (001) direction and CD compressed in the (111) direction, HG compressed in the (001) direction and HD compressed in the (001) direction, and RG compressed in the (001) direction and HD compressed in the (001) direction.
FIG. S5. Enthalpy barrier and minimum energy pathway (MEP) for the HG-HD nucleation mechanism at $S_{zz} = 40$ GPa. (a) The MEP and (b-h) snapshots of the crystal structure along the MEP. Yellow arrows show the trajectory of carbon atoms along the MEP to form covalent bonds.

FIG. S6. In order to prove that the RG-CD transition is a nucleation mechanism, the RG-CD enthalpy barrier was calculated with a simulation cell doubled in the z-direction (perpendicular to the graphitic plane). The MEP is shown with an enthalpy barrier of 2.160 eV at 40 GPa, only 0.072 eV higher than the mechanism calculated with a smaller cell.