Diamond-Graphene Composite Nanostructures

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ABSTRACT: The search for new nanostructural topologies composed of elemental carbon is driven by technological opportunities as well as the need to understand the structure and evolution of carbon materials formed by planetary shock impact events and in laboratory syntheses. We describe two new families of diamond-graphene (diaphite) phases constructed from layered and bonded sp3 and sp2 nanostructural units and provide a framework for classifying the members of this new class of materials. The nanocomposite structures are identified within both natural impact diamonds and laboratory-shocked samples and possess diffraction features that have previously been assigned to lonsdaleite and postgraphite phases. The diaphite nanocomposites represent a new class of high-performance carbon materials that are predicted to combine the superhard qualities of diamond with high fracture toughness and ductility enabled by the graphitic units and the atomically defined interfaces between the sp3- and sp2-bonded nanodomains.

KEYWORDS: Graphene-diamond nanocomposite, high-resolution TEM, density functional theory calculations, sp2- and sp3-bonded nanomaterials, mechanical properties

Interest in new carbon allotropes is driven by the desire to identify novel materials for advanced technologies as well as to understand the role and fate of carbon phases in planetary processes. The stable form of carbon at ambient conditions is layered hexagonal graphite with sp2 bonding. The nanomaterial graphite, which has remarkable electronic and mechanical properties, consists of single or very few stacked layers of the graphite structure. Following high-pressure (HP) and high-temperature (HT) treatment, graphite and graphitic carbon are transformed to sp3-bonded diamond that forms a superhard material with technological importance. This material has tetrahedrally bonded carbon atoms that are covalently linked to form six-membered rings in a “chair” conformation, and the atoms are stacked into layers according to a cubic (c) close-packing arrangement or the 3C stacking polytype. A metastable sp3-bonded carbon allotrope identified within natural impact diamonds and laboratory samples created under static HP and HT or shock conditions is “lonsdaleite”, a dense crystalline form displaying diffraction features consistent with hexagonal symmetry. Observations of such hexagonal diffraction features provide an important mineralogical marker for the P and T conditions recorded in diamonds from bolide impact sites. Lonsdaleite was interpreted as a 2H polytype with carbon layers stacked in a hexagonal fashion (h), although recent analyses suggest that natural and experimentally produced lonsdaleite samples are more accurately described as nanotwinning and stacking-disordered sequences of c and h units. Density functional theory (DFT) calculations as well as experimental measurements suggest that the hardness and other mechanical properties of lonsdaleite may be superior to that of cubic diamond, thus motivating the search for identifying the sp3-bonded hexagonally stacked polytype among natural materials, or preparing it in the laboratory. Computational studies suggest a wide range of novel carbon polymorphs that might be produced in the laboratory or discovered in natural samples. In particular, several metastable carbon phases have been identified as being associated with the transition between sp2- and sp3-bonded structures.

It was first shown by analysis of high-resolution transmission electron microscopy (HRTEM) images that hexagonal features appearing in the diffraction patterns of impact diamonds could be interpreted as cubic (3C) diamond containing a high density of stacking faults associated with nanoscale twinning. Analysis of the X-ray diffraction profiles...
of natural and laboratory-shocked diamond samples using the MCDIFFaX modeling technique later correlated the appearance of lonsdaleite features with different proportions of \( h \) vs \( c \) layer stacking within diamond polytype structures.16,17,31 The average degree of hexagonality (\( \Phi_h \)) and stacking disorder among the \( c \) and \( h \) layers can be represented on a stackogram plot.16,17,31 These analyses were based on the assumption that the structures contained only sp\(^3\)-bonded carbon atoms.

Introducing hybrid materials with sp\(^2\)- and sp\(^3\)-bonding give rise to additional features into the images and diffraction patterns. From HRTEM studies of an extraterrestrially shocked meteorite, Garvie et al.27 described crystallites composed of few-layered graphene domains embedded within and exhibiting a topotactic relationship to slabs of diamond. Mixed sp\(^2\)- and sp\(^3\)-bonding is also observed in amorphous carbon forms with important technological applications.32 For example, amorphous diamond-like carbons exhibiting a high degree of tetrahedral bonding contained within an sp\(^2\)-bonded graphitic matrix can achieve hardness values approaching that of diamond,33 while “hard carbon” materials with a similar nanocomposite structure are being developed for their reversible Na-ion intercalation properties as battery anodes.34

HRTEM images of impact diamonds and laboratory-shocked graphite reveal the intrinsic structural complexity of these crystalline carbon materials. Nanostructures that exhibit lattice fringe spacings of both \( \sim 3.4 \) Å (closely matching the \{001\} reflection of graphite) and \( \sim 2.1 \) Å (consistent with both \{111\} diamond and \{100\} graphite) have been observed in both natural and synthetic samples (Figures 1, 2, and S1–S3). However, instead of suggesting the presence of independent graphite, lonsdaleite, or diamond within...
samples, the ∼3.4 Å fringes appear as domains consisting of few-layered graphene to graphitic domains contiguous with the {111} diamond layers (Figures 1, S1, and S2). Their lateral extent normal to the layer stacking direction ranges up to a few nanometers, and they terminate within the sp3-bonded lattice. We refer to this as a type 1 diaphite nanostructure.

A TEM image of diaphite is a 2D projection of superimposed nanodomains. As a result, the graphitic and diamond regions are observed most clearly in thin (<20 nm) sections (Figure 1a). The DFT structure model of few-layered graphene sandwiched between {111} diamond slabs (Figure 1b) not only reproduces the image contrasts consistent with type 1 diaphite but also reveals the interface corresponding to the Pandey (2 × 1) reconstructed surface. In thicker (<50 nm) samples, the graphene and {111} diamond fringes are less visible, but their contributions can be detected in fast Fourier transforms (FFT) of the HRTEM data (Figures 1c,d and S1). Our electron energy-loss (EELS) spectra show the presence of both sp2- and sp3-bonded carbon coexisting within the type 1 diaphite materials (Figure 1e). The peak near 285 eV represents electronic transitions from 1s core states to unoccupied π* (2pπ) states of sp2-bonded carbon. This peak is most intense in those regions where graphitic domains are clearly visible in the HRTEM images (Figure S2).

A second diaphite nanostructure, which we call type 2 diaphite, consists of hexagonally arranged graphitic carbon layers inserted within and bonded at high angles to the sp3-bonded diamond surfaces (Figures 2 and S3). HRTEM images of this diaphite are characterized by (121) diamond domains and subnanometer-sized regions containing ∼2.1 Å fringes arranged in a hexagonal pattern (Figures 2a,b and S3). Both the HRTEM images and the FFT indicate a topotaxial relationship between the two domain types (Figure 2b). A similar image from the Canyon Diablo meteorite had previously been interpreted as two- and four-layer-thick {113} diamond twins. However, our DFT calculations described below and further comparison with the simulated HRTEM images indicate that this nanostructure corresponds to a nanocomposite consisting of sp2- and sp3-bonded carbon regions (Figure 2c–e).

We performed DFT calculations on atomic models of type 1 and 2 diaphite structures (see Supporting Information for details) to reveal the structural relationships between the sp2- and sp3-bonded nanodomains and the stability of our diaphite structures relative to other carbon allotropes (Figure 3). In both structure types, the models were constructed to include varying amounts of diamond (d) vs graphene (g) content (Figure 3a,b). The relative proportion of interface regions between the two structural units was varied by modifying the size of the unit cell, with increasingly large cells producing a

![Figure 1](image1.png)

**Figure 1.** HRTEM images and DFT modeling of a type 1 diaphite nanocomposite containing graphitic layers inserted at high angles within {113} diamond. (a) HRTEM image from a Popigai diamond shows perpendicular 2.1 and 1.26 Å (contoured by a black circle) as well as hexagonally arranged 2.1 Å fringes (contoured by a white circle). (b) Background filtered image calculated from the area marked by white corners of (a). The FFT in the inset shows (001) graphene hhk reflections. (c) Structure model of type 1 diaphite and its characteristic d spacings obtained from DFT calculations. (d) The simulated HRTEM image calculated from the structure shown in (c) using the experimental microscopy conditions successfully reproduces the image contrast of the observed features (e) from the area marked by white corners of (b).
lower density of interfaces. The two types of diaphite nanostructures give rise to the range of image and diffraction features observed experimentally in natural and laboratory-shocked samples (Figures 1, 2, and S1–S3).

One striking aspect of the model structures is the significantly smaller interlayer distances observed for the few-layered graphene domains within type 2 diaphites (∼3 Å). This spacing indicates that the graphene layers are compressed within the nanocomposite structure (Figure 3b), and their bonding, stacking, and electronic properties may be altered from those of bulk graphite or graphene. Although a similar interlayer contraction appears to be predicted for type
1 diaphite (Figure 3a), this arises since the dispersion correction used in our DFT calculations overestimates the attractive forces between sp² layers. However, that phenomenon does not affect the type 2 structures. The {100} spacings of the graphene layers (2.14 Å) in type 2 diaphites are also expanded relative to those of free-standing graphene (2.12 Å). This lattice spacing closely matches the {100} reflection (2.18 Å) that has been assigned to lonsdaleite.11,13

The relative energies of type 1 and 2 diaphite nanostructures were plotted on an energy (E)–volume (V) chart (Figure 3c) and compared with 2H graphite, cubic (3C) and hexagonal (2H) diamond, a range of \( \cdots \text{c}_{\text{nv}}, \cdots \) stacking disordered diamond polytypes, and >200 other metastable carbon structures reported in the SACADA database.23 The diagram also plots estimated pressures as the size of the unit cell, which has the effect of lowering the density of interface regions resulting in a lower overall energy. Extrapolating calculated results for type 1 and 2 structures with fixed \( d \) or \( g \) components toward infinitely large cells (i.e., \( d = 1, g = 1, 2, 3, \ldots \rightarrow \infty \)), allows the prediction of the E–V limits in which the different structures may be produced under equilibrium conditions (Figures S5 and S8). In the limit of \( d = 1 \) and \( g = \infty \), the type 1 structures attain the same energy and volume as 2H graphite. However, our type 2 structures always have a lower volume than 2H graphite due to the contracted interlayer distance between graphitic planes, and the locus of points for \( d = n, g = \infty \) structures does not extrapolate to bulk 2H graphite. Our models are constrained by size and three-dimensional periodicity, so different structural behavior might be observed in real materials.

The range of type 1 diaphite structures depicted as orange squares in Figure 3c spans a locus of points that could be accessed by compression of graphite to between approximately 10 and 40 GPa, neglecting finite temperature effects and activation energy barriers. Large cells containing low densities of interfaces can achieve energy values that are competitive with the transition pressures from 2H graphite to diamond polytypes with a high degree of hexagonality (Figure 3c). We demonstrate this by calculating the type 2 \( (g = 1, d = 41) \) structure (Figures S5–S8), which has a lower energy (in eV atom\(^{-1}\)) than 2H diamond and falls below the transition pressure from 2H graphite to 2H diamond (expanded region of Figure 3c). This plot reveals that the formation of diaphite nanocomposite structures could provide low-energy solutions existing between fully sp²- or sp³-bonded cubic-hexagonal diamond and graphite phases, while maintaining fully saturated C–C linkages. These diaphite nanostructures might also be encountered during recovery to ambient pressure of sp³-bonded cubic-hexagonal diamond polytypes or by heating metastable sp³ carbon phases at ambient pressure, as they return toward the thermodynamically stable graphitic phase. These structures might also form during diamond surface graphitization according to the ab initio theoretical prediction of De Vita et al.43

The question arises as to whether the diaphite structures can be revealed from X-ray diffraction and Raman data. Figure 4a shows the diffraction patterns of several Popigai diamonds previously fitted using h/c diamond stacking disorder models.27 This approach enabled us to reproduce the diffraction pattern including the diffuse diffraction features at \( \sim 20 \) and 35° 20 MoKα. From these fits, hexagonality indices (i.e., percentages of hexagonal diamond stacking) were obtained (Figure 4a). The only diffraction features that were previously not included in our fits were the sharp, but fairly weak peaks at \( \sim 12° \) 20 MoKα, which were observed for the two samples with highest hexagonal index. These peaks are commonly attributed to the 00l peaks of graphite. To test if this peak and perhaps the other diffuse features could arise from diaphite structures, we extended our DIFFAx model to contain type 1 diaphite structures, which were found to be most abundant in our samples. This new DIFFAx model includes c/h diamond stacking, the hexagonal/rhombohedral stacking of graphite, and the mixing of diamond and graphite sequences within the structure (Figures S9–S11). Figure 4b shows calculated diffraction patterns obtained by mixing different stacking-disordered graphite and cubic diamond sequences. The top diffraction pattern is that of stacking-disordered graphite showing that the feature at \( \sim 12° \) 20 MoKα remains sharp despite the disorder in the sp³-bonded layered material. Upon mixing into cubic diamond sequences in a random fashion, this feature is predicted to broaden and shift toward higher angles as increasing amounts of diaphite sequences are created within the diamond lattice. The sharp peak at \( \sim 12° \) 20 MoKα that is most clearly observed in the experimental data sets is thus thought to originate mainly from extended (potentially stacking disordered) graphitic regions included within the sample or from separate graphite inclusions. Diffraction intensity to the low-angle side of the main peak (\( \sim 20° \) 20 MoKα) occurs for the cubic diamond containing even relatively small amounts of graphitic diaphite sequences. The appearance of this shoulder is typically interpreted as c/h stacking-disordered diamond or “lonsdaleite” (Figure 4c). However, the diffraction intensity appearing on the high angle side of the main peak (\( \sim 20° \) 20 MoKα) and that occurring at \( \sim 34° \) 20 MoKα cannot be reproduced by mixing graphitic sequences with diamond, and so these features are likely to be characteristic of the sp³-bonded, c/h stacking-disordered, structures. We conclude that although some contribution from type 1 diaphite nanostructures may be present in those samples that we and others have investigated to date, its quantification using X-ray diffraction is challenging. The type 1 diaphite structures observed in the HRTEM images of Figure 1 are only a few nm in width, which explains why they might be difficult to capture in X-ray diffraction studies of the bulk materials.

The implementation of type 2 diaphite into a DIFFAx model is difficult since the stacked layers consist of regions of sp²- and sp³-bonded carbon. In Figure S12 the calculated diffraction pattern of a type 2 diaphite unit cell with \( g = 7 \) and \( d = 7 \) is shown. A characteristic feature of a type 2 diaphite is the quite short interlayer distance within the graphitic domains, which results in a Bragg peak at \( \sim 13°40' \) 20 MoKα (corresponding to \( \sim 3 \) Å). The absence of such a feature in our XRD data can be attributed to the overall low concentration of type 2 structures. Furthermore, due to the small domain sizes, any type 2 diaphite diffraction features would be expected to be very broad.

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The Raman spectrum for the sample with the highest hexagonality value reveals a broad and weak feature in the region of the G band, which could imply the occurrence of diaphite domains within the material, although it could also be associated with a bulk disordered graphitic phase (Figure 4d). In summary, analysis of X-ray diffraction and Raman spectral profiles is most sensitive to determining the overall c/h diamond stacking rather than revealing the existence of diaphite $sp^3$-$sp^3$ bonding within the samples.

The presence of diaphite nanostructures can help us to understand the large number of $sp^3$-$sp^1$-bonded phases that are reported to form during the graphite to diamond transition, initiated by static or shock compression or during metastable syntheses from precursor compounds during chemical vapor deposition. Static compression of graphite at room $T$ suggests a sluggish transformation to a metastable phase at $\sim$19 GPa: This material is optically transparent, exhibits superhard properties rivalling diamond, and returns to a mainly $sp^1$-bonded material upon recovery.\textsuperscript{7,37-40}\ Parahydrocarbon diaphite nanostructures during dynamic compression, for example, has been shown to form during high-pressure shock studies, or during their recovery to ambient conditions.\textsuperscript{44} Laser shock experiments combined with in situ X-ray diffraction indicate formation of cubic diamond above 50 GPa and of hexagonal diamond above 170 GPa.\textsuperscript{20} The evidence for the latter has been questioned as the doublet observed in the XRD patterns most likely corresponds to that of type 2 diaphite shown in Figure 2. The projection of these X-ray diffraction data in the angle range of the main diffraction feature show a doublet peak.\textsuperscript{21}\ A further study of graphite-diamond transformation using gas-gun shock experiments combined with synchrotron X-ray diffraction concluded that only elastically strained hexagonal diamond was produced above 50 GPa.\textsuperscript{21} The projection of these X-ray diffraction data most likely corresponds to that of type 2 diaphite shown in Figure 2. The data from these previous studies are consistent with formation of materials containing diaphite nanostructures, both within the compression phase or the rarefaction wave associated with shock studies, or during their recovery to ambient conditions.

Increased hardness and improved mechanical properties have been suggested for lonsdaleite diamond structures containing a high proportion of hexagonal stacking,\textsuperscript{15} consistent with results for cubic-hexagonal cBN/wBN polytype assemblies.\textsuperscript{19} Although our DFT calculations for bulk, shear, and Young’s moduli of different type 1 and 2

**Figure 4.** X-ray diffraction and Raman spectroscopy of Popigai diamonds. (a) Experimental X-ray diffraction patterns (MoKα: $\lambda = 0.71073$ Å) with different hexagonality indices ($\Phi_{DH}$) as indicated in ref 17. The dashed lines highlight a diffuse diffraction intensity around 35°. (b) Simulated X-ray diffraction patterns of stacking-disordered structures containing cubic diamond ($\Phi_{DC}$), diamond to graphite ($\Phi_{DG}$), graphite to diamond ($\Phi_{GD}$), and stacking-disordered graphite ($\Phi_{GH}$ and $\Phi_{GH}$) sequences with random switching between diamond and graphite. The various stacking probabilities are given for each pattern, and the DIFFaX model developed for this study is described in more detail in the Supporting Information. (c) Simulated diffraction data in the angle range of the main diffraction feature show a doublet peak. (d) Microbeam Raman spectra (adapted with permission from ref 17; 514 nm excitation. Copyright 2019 Springer) of Popigai diamonds with different hexagonality indices. A weak feature due to the G band of graphitic structures contained within the sample is observed at $\sim$1600 cm$^{-1}$ for the sample with $\Phi_{DH} = 0.36$. This is indicative of $sp^3$ carbon associated with either flakes of a separate graphite phase or diaphite nanostructures.
diaphite models show lowered compressibility and tensile strength compared with fully sp³-bonded polymorphs (Table 1), we predict that inclusion of graphitic units within the nanocomposite diaphite nanostructures will result in improved fracture toughness caused by the lateral flexibility afforded by the sp²-bonded domains.

In conclusion, we provide evidence for the existence of novel type 1 and type 2 diamond-graphene nanocomposites within diamond materials recovered from natural impact materials and laboratory-shocked graphite. These nanostructures are characterized by the intimate association of sp³-(diamond) and sp³-bonded (graphene) domains, and the building units have a lateral width of a few nm. Their diffraction signatures exhibit features that are consistent with those previously reported for lonsdaleite as well as the postgraphitic “M-carbon” phase. The calculated E(V) relationships reveal that these nanostructures provide low-energy solutions to structural transformation between fully sp³- and sp³-bonded carbon allotropes that can be sampled under static and dynamic compression, including during the rarefaction wave associated with shock compression and during recovery to ambient conditions. The nanocomposite nature of the diaphite structures is expected to lead to mechanical behavior that preserves the superhard and incompressible properties of the sp²-bonded units, while leading to fracture toughening due to the angular flexibility and tensile resistance of the graphitic domains bonded to them.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.0c00556.

Details of experimental methods include samples; transmission electron microscopy, image processing and image simulation as well as Figures S1–S3; computational methods and Figures S4–S8; DIFFAX modeling and Figures S9–S11 as well as Tables S1–S3; Figure S12; and supplementary references (PDF)

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**Author Contributions**

◆These authors contributed equally. P.N., K.M., P.F.M., and C.G.S. initiated and coordinated different aspects of the project. A.J. and L.A.J.G. provided some of the samples and carried out the initial characterization. B.P., L.A.J.G., and P.N. were involved in the HRTEM investigation, and the data were interpreted by L.A.J.G. and P.N. K.M. and F.C. carried out DFT calculations and modeling. M.M. and M.A. obtained the X-ray data. R.L.S. and C.G.S. carried out the DIFFAX modeling. P.F.M., C.G.S., K.M., P.N., and L.A.J.G. collaborated on writing the manuscript, and figures were prepared by P.N., K.M., and R.L.S. All authors participated in discussion of the results and have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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### Table 1. Calculated Elastic and Mechanical Properties of 3C and 2H Diamonds and Type 2 Diaphite Structures Together with Experimental Data for 3C Diamond

| Method          | Bulk Modulus (GPa) | Shear Modulus (GPa) | Young's Modulus (GPa) | Poisson Ratio | Vickers Hardness (GPa) |
|-----------------|--------------------|---------------------|-----------------------|---------------|------------------------|
| 3C diamond      | 444<sup>47</sup>   | 535<sup>47</sup>    | 1143<sup>47</sup>     | 0.069<sup>47</sup> | 79.7<sup>47</sup>     |
| DFT (this work) | 454                | 558                 | 1184                  | 0.065         | 84.3                   |
| 2H diamond      | 453                | 562                 | 1186                  | 0.064         | 84.8                   |
| (g = 1, d = 1)  | 392                | 376                 | 761                   | 0.171         | 56.8                   |
| (g = 1, d = 3)  | 402                | 407                 | 838                   | 0.149         | 61.5                   |
| (g = 2, d = 2)  | 390                | 349                 | 615                   | 0.230         | 52.8                   |
| (g = 3, d = 1)  | 379                | 300                 | 395                   | 0.321         | 45.7                   |
| (g = 1, d = 5)  | 411                | 429                 | 897                   | 0.134         | 64.8                   |

<sup>*Calculated Vickers hardness (V<sub>H</sub>) values are determined using the relationship proposed by Teter<sup>47</sup> (V<sub>H</sub> = 0.151G, where G is the shear modulus).**</sup>
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