Complex nanostructures in diamond

Meteoritic diamonds formed during bolide impacts on Earth and diamond-related materials synthesized by compressing graphite contain a wide variety of complex nanostructures. This Comment highlights and classifies this structural complexity by a systematic hierarchical approach, and discusses the perspectives on nanostructure and properties engineering of diamond-related materials.

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Elemental carbon continues to surprise by its versatility in bonding resulting in a multitude of structures with markedly different material properties. Graphite and diamond, which are minerals known since antiquity, have been applied and further developed in various applications according to their distinct properties determined by the nature of their interatomic linkages. Graphite is a semimetallic sp^2-bonded layered solid that is widely used as a lubricant and highly absorbent material associated with its weak interlayer bonding. It is the most stable carbon phase at ambient conditions. Varieties of graphitic carbon reversibly intercalate ions and can therefore be used as anodes in energy storage devices. In contrast, diamond is a superhard wide bandgap insulator. It is transparent throughout most of the electromagnetic spectrum and possesses remarkably high thermal conductivity. These properties are the result of its tetrahedrally connected sp^3-bonded network of carbon atoms [1]. First prized as a rare gem mineral with near-mythical properties, its name is derived from the Greek ἀδάμας (the indomitable one) reflecting its extreme resistance to mechanical, heat and chemical stress. Its qualities have been harnessed for cutting and grinding applications. Synthetic diamond production is a multi-billion $/yr worldwide industry estimated at near 4.41 billion carats per year [2]. Nanosized diamonds formed by explosive shock processes are commercially available, whereas highly crystalline diamond films used as protective coatings and in optoelectronic devices are grown by vapour deposition techniques. There is the tantalizing possibility of the existence of other carbon forms with properties that rival those of diamond; search for these materials is under way in laboratories around the world [3,4]. Recent investigations have expanded the list of elemental carbon varieties to include fullerenes, nanotubes, single- to few-layered graphene and new crystalline materials. The menagerie of polymorphic carbon structure types continues to grow as new examples become identified among samples formed naturally within meteorites and by bolide impacts on Earth, produced in the laboratory, or are predicted by theoretical calculations [5-9].

The structures of natural and synthetic carbon materials are typically characterized using X-ray diffraction (XRD) and optical spectroscopic techniques, particularly Raman spectroscopy [10-11]. The nanoscale features present within these materials are increasingly being studied using high-resolution transmission electron microscopy (HRTEM) imaging and diffraction techniques [12-16]. Aberration-corrected HRTEM studies are now revealing unprecedented structural detail and complexity within diamonds and related materials that are recovered from meteorites and impactites as well as laboratory-shocked samples [12, 14, 15]. The results are leading to the discovery of new structural motifs and re-interpretation of previously reported polymorphic forms (Fig. 1). The newly identified features include multiple intergrowths and domains of nanotwinned stacking within sp^3-bonded diamond [10- 12,15], regions with sp^3- and sp^2-structured units coherently bonded to each other [13,14], concentric nanodiamond-containing carbon cages [16], and nanoscale patterns with unusual symmetry within the dense carbon matrix [15]. It is a challenge to unravel the complexity of these nanostructures that are often observed within the same sample and to determine both the relationships between them and how they might arise as a function of the original synthesis and subsequent processing conditions. This Comment aims to present a hierarchical description of these different nanostructured motifs within a range of natural and laboratory-shocked samples and show

how they might be related within a structural map of sp^3- to sp^2-bonded polymorphs sorted as a function of their energy-volume relationships. In addition, we examine how the presence of these varied and complex nanostructures could give rise to potentially useful mechanical, thermal and optoelectronic properties and how these might be engineered to produce new families of next-generation diamond-related materials [14,17,18].

Cubic and hexagonal diamond

Diamond contains tetrahedrally bonded carbon atoms that are covalently linked to form six-membered rings in a "chair" conformation as found in the cyclohexane molecule. The diamond structure is usefully described based on corrugated layers formed from these rings. We refer to these layers as fully saturated "diaphane" units, by extension from the term "graphene" used to describe a single plane of sp^2-bonded carbon atoms [6]. In diamond, identically oriented diaphane layers stack normal to the cubic (111) axis, accompanied by a shift half-way across the diagonal of the six-membered rings. This stacking leads to a cubic (*c*) packing arrangement of the carbon atoms for the cubic diamond polytype.

A metastable sp^3-bonded carbon structure, first identified from high-pressure high-temperature (HPHT) laboratory syntheses and also found within natural impact-formed diamonds, displays hexagonal (*h*) features in its XRD pattern [19,20]. These diffraction features were associated with an ordered polytype structure in which the stacking pattern includes an orientation reversal between successive sp^3-bonded "diaphane" layers resulting in a 50:50 mix of "chair" and "boat" configurations of the cyclohexane rings. Both this structure type and the new mineral were named "lonsdaleite" to honour the crystallographic contributions of Dame Kathleen Lonsdale [21]. Identification of such hexagonal features in the XRD patterns and corresponding Raman spectra of diamonds recovered from meteorites and bolide impact sites has become established as an important mineralogical marker for the shock conditions experienced during impact events.

Both natural and laboratory-shocked samples are typically described in terms of "pure" cubic diamond and lonsdaleite polytype structures, sometimes accompanied by graphite, that are interpreted as nanoscale mixtures of the proposed end-members. Laboratory experiments carried out to reproduce and extend the P-T conditions of natural shock events have adopted a similar level of interpretation [22,23]. However, this view of describing the complex nanostructures present within natural impact and laboratory-produced diamonds as mixtures of these two polytype structures is now shown to be incorrect.

Cubic-hexagonal stacking disorder and nanotwinned structures within diamond

It was first noted that the hexagonal diffraction features assigned to "lonsdaleite" arise from non-repetitive structures and should instead be interpreted with normal cubic diamond containing a high density of stacking faults and nanoscale twins (Fig. 1) [12]. This interpretation was based on detailed HRTEM studies of samples from the Canyon Diablo meteorite, the type material from which the mineral lonsdaleite was first described [19,20]. A range of *h*-*c* stacked sequences is well known to occur among SiC, BN and other sp^3-bonded materials that exhibit a wide range of ordered (repetitive) polytypes and disordered structures. It is proposed that *h*-*c* sp^3-bonded layered structures are also present in natural and laboratory-shocked diamonds, and these could account for the appearance of hexagonal features in the diffraction patterns [10,11]. The method of DIFFaX analysis, which had been used to interpret the diffraction patterns of layered stacking motifs in H_2O ice, was applied to a range of impact diamonds and laboratory shocked samples to measure their degrees of 'hexagonality'- the percentage of hexagonal stacking units present in the structure [10]. This analysis approach supplemented by Monte Carlo techniques (MCDIFFaX) leads to the practical "stackogram" tool that was developed to identify and describe degrees of *h*-*c* ordered *versus* disordered layering patterns within the sp^3-bonded structures, and also to differentiate among samples that had experienced different shock regimes [11]. The possibility to engineer nanoscale

twinning among cubic and *h-c* diamond polytype structures adds additional capability to improving mechanical performance and thermal resistance [17].

sp^2-bonded domains included within cubic-hexagonal sp^3-bonded diamond structures

Further to layered stacking disorder in diamond, additional structural complexity emerges when sp^2-bonded carbon is brought into play. HRTEM studies of natural impact diamonds and laboratory-shocked materials have led to the recognition of sp^2-bonded graphitic/graphene layered sequences occurring within the cubic/hexagonal diamond structures. These layered sequences are intimately associated with and coherently connected to the sp^3-bonded domains, and the insertions of sp^2-bonded regions are not repetitive [13,14]. A family of these nanostructural motifs could be related to the "diaphite" structures originally described to form at graphene surfaces following laser irradiation [24]. A series of density functional theory (DFT) calculations were undertaken to study the incorporation of graphitic/graphene-like sp^2 layers within the sp^3-bonded domains [14]. The calculations revealed the possibility of entire families of mixed sp^3-sp^2 bonded "diaphite" nanostructures existing within the energy-volume (E-V) phase space between graphitic and diamond-like polymorphs (Fig. 2). By comparison with the E(V) slopes corresponding to different compression regimes, the calculations gave insights into how these sp^3-sp^2 bonded nanostructures might form within diamond-related materials as a result of static or shock-recovery HPHT treatment of diamond or graphitic precursors [14]. It is predicted that these diaphite structures can be produced either during the initial compression or within the rarefaction wave immediately following the initial shock impulse, followed by recovery to ambient conditions. These structures might also be formed metastably during ambient pressure synthesis using suitably designed precursors that can direct the layer-by-layer growth of nanostructured elements containing sp^3- and sp^2-bonded carbon centres, such as those implicated in the formation of functionally-active covalent organic frameworks (COFs) [25]. Tuning the sp^3-sp^2 bonded nanomaterials towards nano- to macroscale composite structures might provide new families of next-generation diamond-related materials [14,26] (Fig. 3).

sp^3-bonded domains contained within mainly sp^2-bonded graphitic materials

The diaphite nanostructures extend across the E-V metastable phase diagram reaching towards fully sp^2-bonded graphite (Fig. 2). It is interesting to examine the possibility that diaphane units might be included within predominantly graphitic structures. Cliftonite was described as a form of crystalline graphitic carbon exhibiting unusual cuboidal morphology within the Canyon Diablo iron meteorite [27]. It is thought to form at low pressure by decomposition of iron carbide. Although the structure of cliftonite is currently presumed to be based solely on sp^2-bonded graphitic layers it might also contain some sp^3-bonded elements related to the increased mechanical resistance shown by some samples that have been studied. These sp^3-bonded elements would be produced as a result of the shock wave generated during the impact of the Canyon Diablo asteroid with the Earth. A range of amorphous "hard carbon" materials produced by pyrolysis of carbonaceous precursors including sugar and cellulose are being developed for use as Na-ion battery anodes [28]. The molecular to nanoscale structure of these hard carbons is still under investigation but they are thought to consist of graphitic domains connected by fullerene-like structural units linked by some proportion of sp^3-bonded carbon atoms [28]. Amorphous "diamond-like carbon" (DLC) materials prepared by vapour deposition methods contain a large proportion of sp^3-bonded atoms within their structure and can achieve hardness values that rival those of crystalline diamond [29]. Other high-hardness carbons with mixed sp^2-sp^3 bonding are derived from C_{60} or C_{70} fullerenes treated under HPHT conditions [3].

Towards further complexity among diamond nanostructures

Rounded nanostructures exhibiting concentrically layered geometry have been observed within partly graphitized diamonds and nanodiamonds and have been identified as "onion-like" or "bucky-diamond" structures [16]. Nanoparticles with these structures are thought to evolve by growth from central diamond cores as they transform into surrounding graphitic layers [30]. It is interesting to note

that the cubic diamond structure can achieve five and twelve-fold rotational symmetry through multiple twinning and could also engage in radially symmetric Mackay packing, especially among nanodiamonds such as those produced by detonation shock synthesis [31,32]. DFT studies of diaphite nanocomposite structures subjected to tensile stress conditions show a progressive transformation towards the graphitic phase, growing outwards from the sp^2-sp^3 boundary [26]. This phenomenon that could be described as the "Mozzarella" solution resembles the surface graphitisation predicted for diamond under thermal stress [33]. This transformation mechanism certainly operates within natural and laboratory-shocked samples as they experience the rarefaction regime immediately following initial shock compression, and it could be generated within materials designed for applications that require linear or curved diamond-graphite interface structures.

Prospects of engineering complex nanostructures within diamond-related materials

To date, most of these fascinating and complex nanostructures have been identified among meteorite samples or impacted rocks, or in laboratory-shocked materials. The stacking-disordered and nanotwinned sp^3-bonded materials can be described as diamond-related structures to be considered alongside the ordered cubic and hexagonal diamond polytypes. Stacking-disordered diamond structures are found to be prevalent among millimetre-sized samples obtained using large volume hydraulic press apparatus [10]. The sp^2-bonded layers observed by HRTEM within shocked diamond presumably constitute a small fraction of the overall volume and can be considered as non-periodically inserted graphene regions within the sp^3-bonded matrix. In this case, they do not yet constitute new diamond-related phases. However, DFT calculations demonstrate the stability of periodically extended and structurally coherent diaphite nanostructures with different relative thicknesses of the sp^2- and sp^3-bonded units [14], indicating that such nanostructured assemblies might be engineered in bulk or thin film form by chemical or physical vapour (CVD, PLD) or atomic layer (ALD) deposition from atomic or molecular reactive gases. Diaphite nanostructures have already been produced in the laboratory by laser irradiation of graphene or graphite surfaces [25,34] and similar features are suggested to appear at the diamond surface during thermal degradation [33]. Other sp^2-sp^3 bonded nanostructures could be achieved within diamond-related materials by designed shock-recovery conditions, while unusual carbon morphologies and nanostructured domains with unexpected symmetry properties are known to result from rapid diffusion and exsolution of C from metal carbide phases during the processing of steels [34]. It is certain that the formation and production of complex nanostructures within diamond-related nanomaterials is just entering its infancy. Advances in understanding these complex nanoscale architectures and developing targeted engineering approaches for technological applications will require comprehensive knowledge of the structural relationships and formation conditions of the sp^2-sp^3 bonded nanostructures as well as transformation mechanisms between the two [13,25,35,36] (Fig. 3).

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Competing interests

The authors declare no competing interests.

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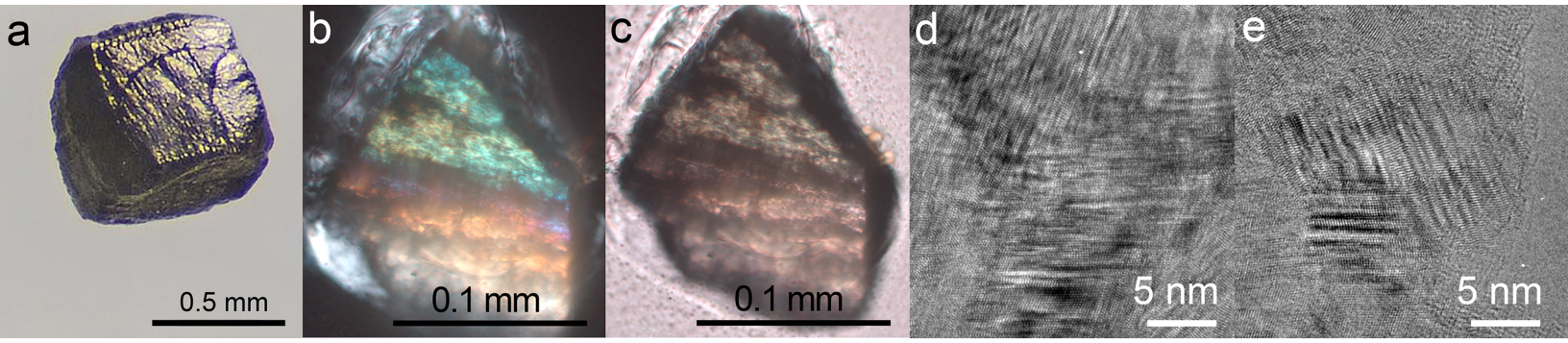
Figure 1. Structural complexity in diamond. a, A cubic diamond grain from Canyon Diablo meteorite [12]. **b**,**c**, optical micrographs from a fragment of a Popigai impact sample taken in normal (b) and polarized (c) light showing the presence of striations associated with regions of different birefringence at the micrometre-scale. **d**,**e**, Low magnification TEM images from fragments of the Canyon Diablo sample that reveal a range of complex structures at the nanoscale. **f-i** different nanostructural elements imaged at high (atomic)-resolution (left column) that are observed in different naturally impacted and laboratory-shocked samples, with corresponding schematics of atomic structures (right column). Cubic-hexagonal sp^3-bonded stacking faults (f) and complex patterns of new types of nanotwins (green dotted line) [12] (g) are demonstrated to occur within diamond-related materials and are proposed to lead to improved mechanical properties. Type 1 (h) and Type 2 (i) diaphite nanostructures [13,14] are identified using a combination of HRTEM and DFT techniques in natural and laboratory-shocked diamond specimens. These unique nanostructures could be engineered to improve fracture toughness among diamond materials. **j,** HRTEM evidence in the left panel for core-shell sp^2-sp^3 bonded nanostructures observed in shock-formed meteorite and naturally- or laboratory-shocked samples, with its schematic in the right panel. **k,** HRTEM images of nanostructures revealing five- and twelve-fold rotational symmetries formed by multiple twinning and radially symmetric Mackay packing [15,16,32] in the left column, with schematics in the right column. Panels adapted with permission from: a,f,g, ref. [12], Springer Nature Ltd; h, ref.[13], Mineralogical Society of America; i, ref.[14], American Chemical Society; j, ref.[16], Mineralogical Society of America; k, ref.[15], Springer Nature Ltd.

Figure 2. An energy-volume (E-V) map of crystalline carbon structures. The relative E(V) relations for stable and metastable structures are established using density functional theory (DFT) calculations [14]. Known and predicted carbon allotropes from the SACADA database [9] are plotted as dark grey dots. The inset (rectangle) shows the range of energies for stacking disordered sp^3-bonded polytypes (turquoise) between cubic (3C) (orange dot) and the hexagonal (2H) diamond structure (blue) [11]. Points for Type 1 and Type 2 diaphite structures described in [14] are shown as yellow and red dots, respectively. The two graphite points (green dots) correspond to the 2H and 3R polymorphs. Data for fullerene and single walled carbon nanotube crystalline structures are shown for comparison. The dashed line passing through the E(V) point for stable 2H graphite constitutes a baseline for the datasets at T=0 K. Adapted with permission from ref.[14], American Chemical Society.

Figure 3. Projected properties of diamond-related materials containing complex nanostructures. **a,** Inclusion of cubic-hexagonal layer stacking polytype structures and nanotwinned domains within fully sp^3-bonded diamond structures leads to increased bulk and shear moduli. Adding sp^2 content in diaphite nanostructures maintains high elastic modulus values while contributing new features to the mechanical and other properties. Values for graphite, amorphous hard carbon and diamond-like carbon materials are indicated for comparison. **b,** Stress-strain relations under tension. Ideal diamond is predicted to achieve >40% longitudinal strain under application of tensile stresses up to ~220 GPa but real materials fracture at significantly lower stress-strain values due to defects within the sp^3-bonded structure. Graphene can be extended by over 25% before breaking. It is predicted that the presence of graphene-like domains within the diaphite structures should permit much greater lateral strain when subjected to lower tensile stresses depending on the width of the graphitic regions. **c,** The inclusion of diaphite nanostructures is expected to improve the fracture toughness of diamond materials as the energy of a propagating crack causes the sp^3 atoms at the graphene-diamond interface to transform into a graphitic state. **d,** Electronic properties. Inclusion of graphitic/graphene domains into diaphite nanostructures should result in the appearance of nanoconducting channels inside the insulating diamond matrix. **e,** Optical properties. The incorporation of graphitic regions into the diamond structure as well as internal scattering due to nanoscale domains and interface boundaries causes impact diamonds to appear black[12]. **f,** Thermal properties. The presence of layered polytype structures and nanoscale graphitic domains will hinder phonon propagation and cause the thermal conductivity to be significantly lowered compared with diamond or graphite (in plane). This can result in development of thermoelectric properties in diaphites containing nanoscale conducting channels. Panel e adapted with permission from ref.[12], Springer Nature Ltd.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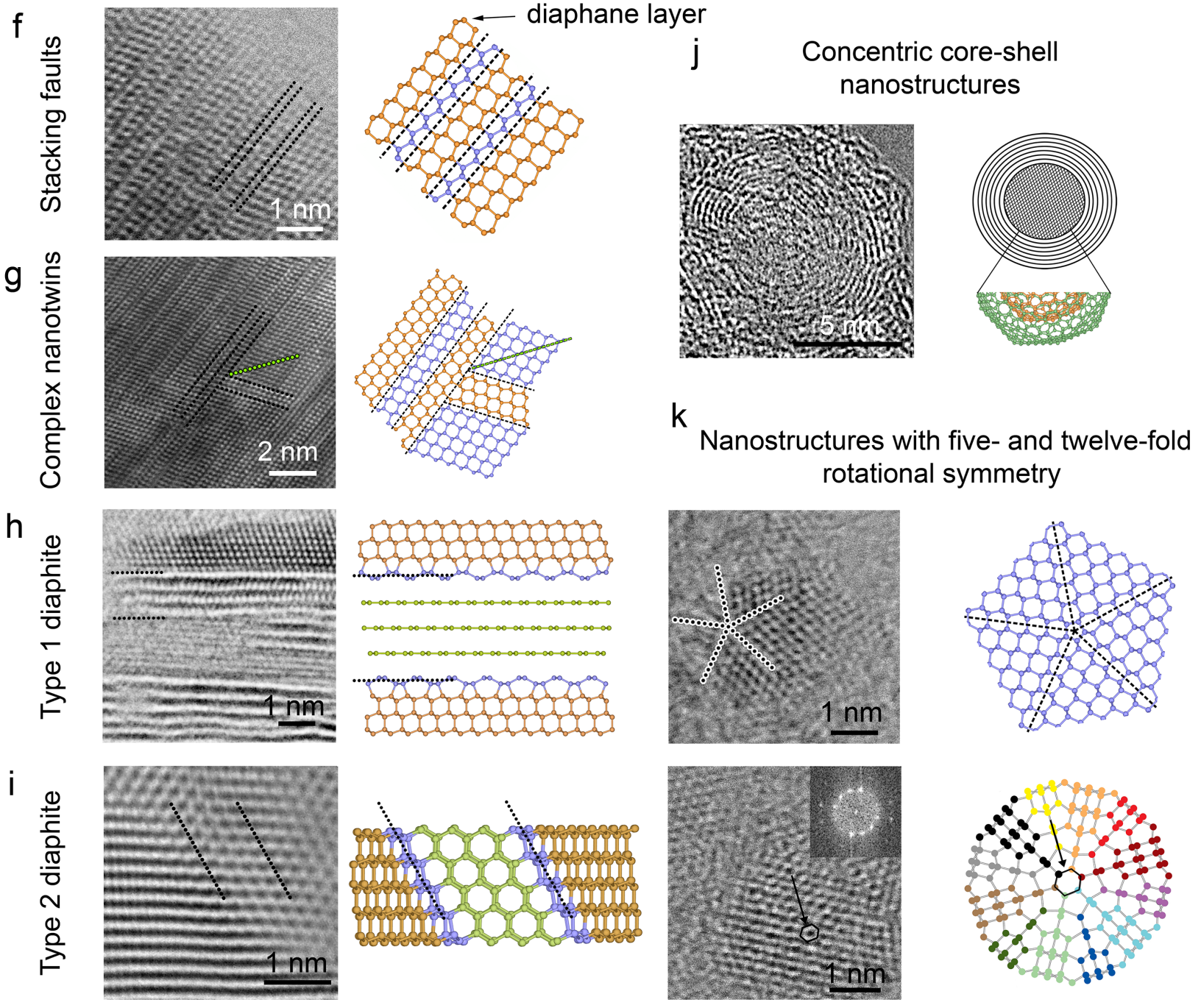
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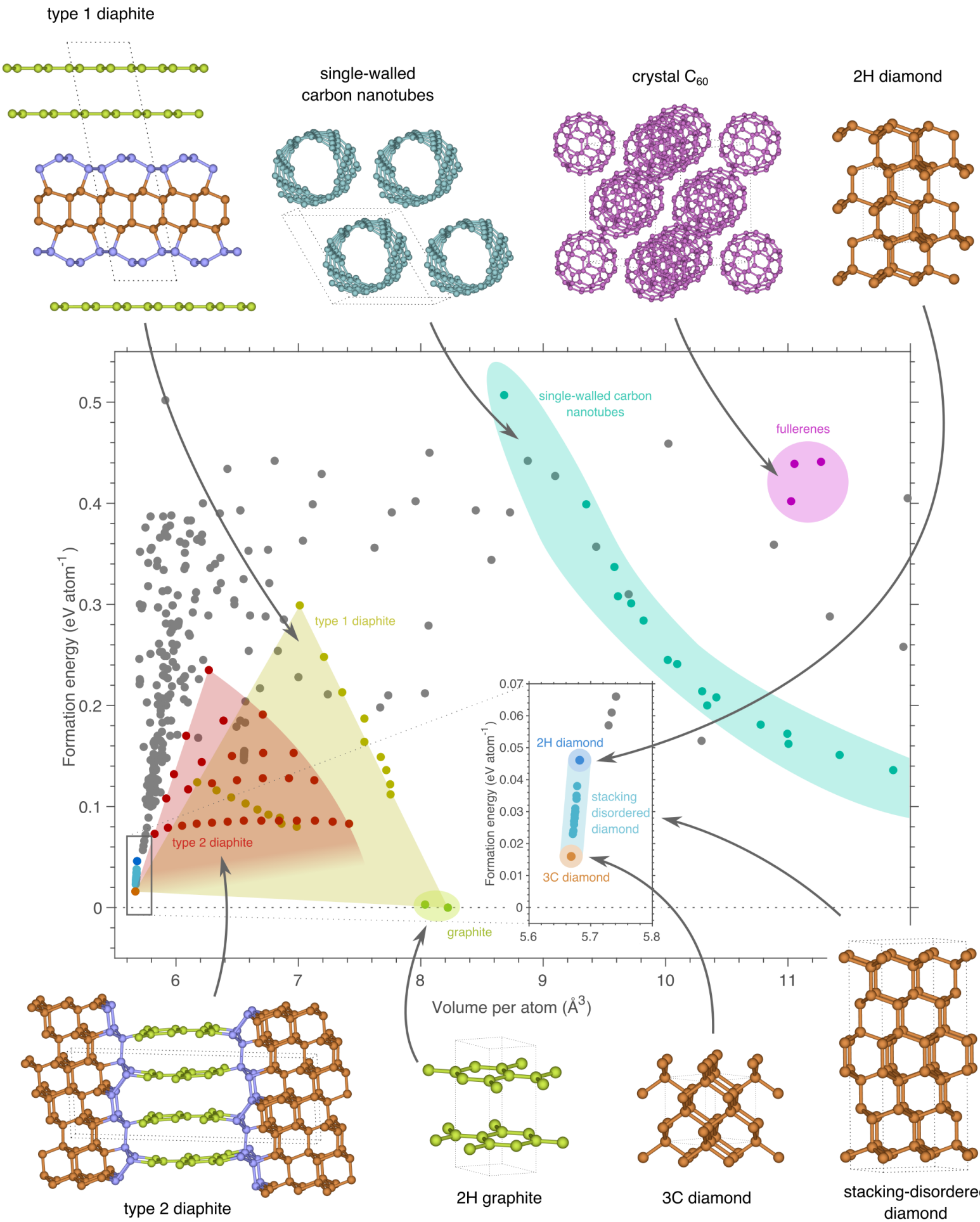
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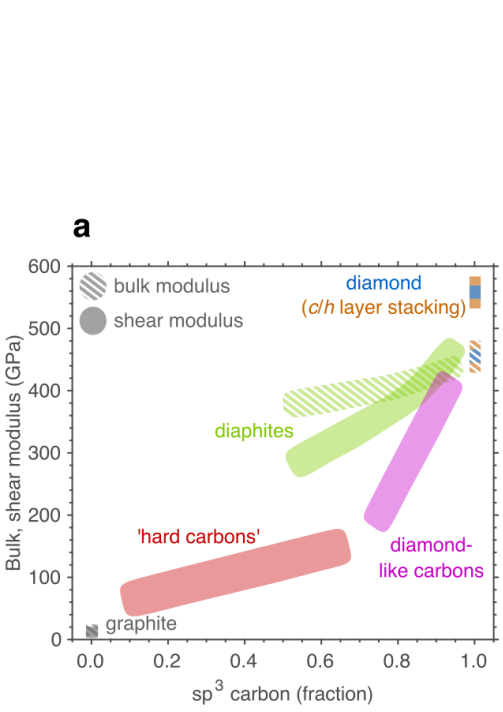

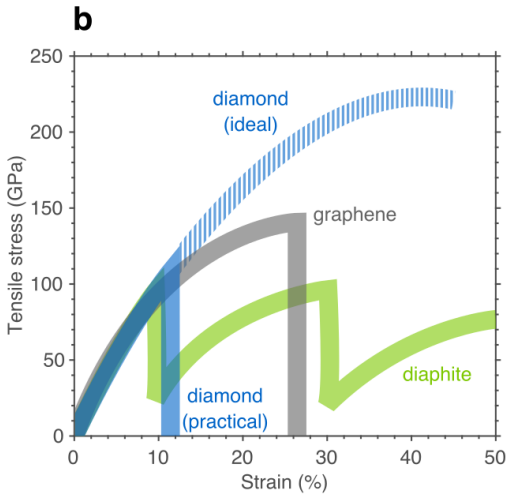

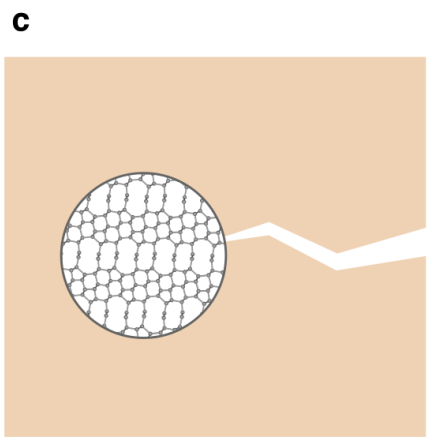

Complex diamond and diaphite nanostructures. Influence on materials properties