#### **REVIEWS OF TOPICAL PROBLEMS**

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## Ultrahard nanomaterials: myths and reality

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Abstract. The last 25 years has witnessed a wealth of publications on the creation of carbon materials whose compression bulk modulus and hardness are much higher than those of diamond. This review presents a critical analysis of these studies. Three groups of myths that have emerged lately are discussed. The first is related to the possibility of creating materials whose bulk moduli are significantly higher than those of diamond. The second group is devoted to 'experimentally measured' values of hardness, much higher than that of diamond. The third includes alleged 'theoretical' grounds for a several-fold (!) increase in the hardness of covalent substances due to the effects of quantum confinement. It is shown that materials whose elastic moduli significantly exceed those of diamond cannot in principle be produced under normal conditions. Issues surrounding the quantitative measurement of hardness are discussed; it is noted that the creation of obstacles to the movement of dislocations in nanomaterials may allow a 20-40% increase in the effective measured hardness of ultrahard materials. It is emphasized that alternative hypothetical approaches to increase hardness, for example, due to quantum confinement, actually have no physical grounds whatsoever. The highest mechanical characteristics of diamond are associated with reliably established physical laws, and any assertions regarding possible obtainment of materials whose elastic characteristics or hardness are several times greater than those of diamond may not be regarded as reliable to any extent or even science-based.

Keywords: elastic moduli, hardness, carbon materials, nanostructures, quantum confinement

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## 1. Introduction

Until the early 1990s, the synthesis of and research on new ultrahard materials were quite respectable areas of material science. By that time, the relationship between the elastic characteristics of substances and their atomic and electron density, the degree of electron density anisotropy, and structure, in particular the coordination number, had already been established and explained [1]. It was also realized that operational mechanical characteristics, such as hardness, fracture toughness, and abrasion resistance, can only be considered qualitative comparative characteristics that depend on the method and conditions of measurement or testing. In particular, if hardness is measured using an indenter, the results depend on the load on the indenter, the loading time, the indenter shape, the quality and method of surface finish of the material under testing, the degree of elastic restoration of the indentation, etc. (see [1, 2] and references therein).

There were no doubts 30 years ago that diamond and its isoelectronic analog, cubic boron nitride, have under normal conditions elastic moduli that are the highest among all substances. It should be recalled that the bulk modulus of diamond is 445 GPa, the shear modulus is 530 GPa, and the hardness is 80–120 GPa [1, 3]. New ultrahard materials, i.e., materials whose elastic moduli and hardness exceed the corresponding values for sapphire Al<sub>2</sub>O<sub>3</sub> or hard alloy (sintered tungsten carbide with a binder), starting from the mid-20th century traditionally (and reasonably) were searched for among compounds of light elements (Be, B, C, N, O) and among carbides, borides, oxides, and nitrides of heavy metals (Ta, Mo, Nb, W, Re, Os, Cr, etc.) [1]. It was also well known that the operational mechanical properties of the same material can substantially depend on its structure and state of defects at the micro- and especially at the nanoscale level [1, 2]. However, in contrast to ductile metals, in which the nanocrystalline state can be achieved quite easily (by means of intense plastic deformation, rapid quenching from the melt, etc.), ultrahard materials in the nanocrystalline state

by the beginning of the 1990s had not really been produced and, consequently, not investigated. An exception was TiN-NbN and TiN-VN multilayer nanostructures [2, 4], for which a significant excess of hardness (by a factor of 1.5– 2) compared to that of single crystals of individual compounds was observed.

A series of publications appeared about 25 years ago that announced the production of new ultrahard materials (mainly carbon-based) whose hardness and bulk modulus were 2-4 times higher than the corresponding values for diamond [5-7]. In particular, according to [5], the bulk moduli of the new materials were as high as 1700 GPa (!) and the hardness as high as 300 GPa [7-9]. These were usually highly disordered carbon materials obtained by the thermobaric processing of C<sub>60</sub> fullerenes under pressures of 13-14 GPa. These results, which were subject to criticism [2, 3, 10-13], and, on the whole, were not confirmed by other groups. It was announced recently (in 2014) that such fullerite-based ultrahard materials were obtained at room temperature at relatively low pressures (6.5 GPa) under strong shear deformations using carbon sulfide (CS<sub>2</sub>) as a catalyst for the 3D polymerization of fullerite [14].

The author of this review participated in 2004 in the publication of an open letter to colleagues—physicists, chemists, and material scientists [15]—wherein it was pointed out once again that under normal conditions diamond is and will be the undisputed leader in the shear modulus value among all substances. The letter also called all researchers to be careful and prudent when reporting about 'hardness higher than that of diamond'. The appeal was followed by a short pause of 5–7 years, during which there were virtually no new publications about materials whose elastic moduli and hardness significantly exceed those of diamond.

Significant progress has concurrently been witnessed in the synthesis and exploration of new ultrahard materials with a nanostructure. A number of teams [16-23] produced samples of nano-polycrystalline diamond and, somewhat later, cubic boron nitride. The nanocrystalline diamond state was obtained in this case using various initial substances (graphite, fullerites, nanotubes, soot) (see, for example, [18, 20]). The crystalline grain size in the newly obtained ultrahard polycrystals also varied over a wide range — from 5 to 100 nm [16-23]. The grain morphology (spheres, flakes, needles) also varied widely. The nano-polycrystalline state of diamond and boron nitride turned out to feature hardness, wear resistance, fracture toughness, and heat resistance that are much higher than those of corresponding single crystals [16–23]. It was found that the mechanical characteristics of nano-polycrystalline diamond are the highest if the grain size is 10-20 nm [17-19]. The hardness of such polycrystals measured according to Knoop (various methods for determining and measuring hardness are presented in Section 3) is then as high as 120-140 GPa, i.e., 20-40% higher than the generally accepted hardness of single-crystal diamonds.

Progress was also observed at the same time in theoretical calculations of the mechanical properties of ultrahard materials. Calculations based on first principles, which were made using state-of-the-art computers, allow determining with high accuracy (1–2%) the elastic characteristics of ultrahard materials in the linear region of deformations and their ideal strength under various deformations, including those beyond the linear elastic region (albeit with much less accuracy — with an error of several tens of percent) [24–28].

Since the hardness of materials is a poorly defined parameter, the 'ideal' hardness is usually analyzed in calculations, and is defined as the theoretical shear strength corresponding to certain loads on the indenter [29]. If the load increases further, even in the ideal case of a defect-free single crystal, a local loss of lattice stability and the emergence of dislocation loops or twin boundaries are observed [29]. A number of new empirical formulas have been proposed recently to calculate hardness on the basis of correlations between mechanical properties and elastic moduli, covalence bond character, optical gap width, etc. [30–33]. Although such formulas for calculating hardness are not strict, they are convenient for rapid evaluations of the mechanical properties of hypothetical substances and have been very actively used recently (albeit often uncritically).

A new wave of publications has appeared in the last 5– 10 years, devoted to the synthesis of materials whose elastic moduli and hardness are several times higher than those of diamond. These studies have been carried out primarily by Chinese research teams. Moreover, a number of researchers attempt to substantiate the sensational 'experimental' results by introducing a certain new 'theoretical' base associated with the ideas of quantum confinement. The goal of this review is to analyze the scientific consistency of these reports.

# 2. Myth I: materials with giant elastic moduli significantly exceeding those of diamond

The myth of materials with elastic moduli significantly exceeding those of diamond is the easiest to analyze. Elastic moduli are uniquely determined by interaction between particles and can be calculated from first principles with high accuracy. The effect of the microstructure and defects in the substance on the elastic moduli is small (at the level of several percent). The elastic moduli are apparently greater the greater the binding energy in the material, the greater the atomic and electronic densities, and, consequently, the smaller the interatomic distances.

#### 2.1 Bulk modulus

The physical meaning of the bulk modulus is actually the density of the binding energy in the material. For a degenerate electron gas, the compression modulus B, as well as the electron gas pressure, is uniquely related to the electron density:

$$B \sim \rho^{5/3}$$
,

where *B* is the bulk modulus and  $\rho$  is the electron density.

In the case of real substances, the total energy *E* is some function of the volume *V*:  $E = E_0 f(V/V_0)$ , where  $E_0$  and  $V_0$  are the energy and volume at zero pressure. The bulk modulus at normal pressure is apparently expressed then as [34]

$$B_0 = \frac{E_0}{V_0} f'' \left(\frac{V}{V_0}\right)_{V=V_0} = C \frac{E_0}{V_0}, \qquad (1)$$

where  $C = f''(V/V_0)_{V=V_0}$ .

The cohesion energy may be expressed in some model cases as  $E = A/V^n - B/V^m$ . In this case,  $f''(V/V_0)_{V=V_0} = mn$ , i.e., for the Lennard-Jones potential, for which 3n = 12 and 3m = 6, we have f'' = 8. This value is in good agreement with experimental data for condensed inert gases and a number of molecular substances, for which, indeed,  $B_0 \approx 8E_0/V_0$  [1].



**Figure 1.** (a) Bulk module as a function of the bulk density of binding energy for elemental substances and compounds of group IV of the periodic table. (b) The ratio of the compression modulus to energy density for the same substances. (Data taken from [37] with permission of the author.)

The bulk modulus in the case of metals, covalent substances, and partly ionic compounds is apparently determined primarily by the density of valence electrons. It should be noted that it was established long ago [35] that for many ionic compounds  $B \sim 1/V \sim \rho$ , where V is the specific volume. The relation  $B \sim 1/d^{3.5} \sim \rho^{1.17}$  (d is the interatomic distance) was also established long ago for covalent substances with a diamond-like structure [36]. It should be noted that the value of C in Eqn (1) varies slightly for all substances with a 'strong' type of interaction between particles (covalent substances, most metals, ionic compounds) [1]. For example, the value of C changes in the carbon subgroup by only 10%from ultrahard covalent diamond to soft metallic lead [37] (Fig. 1). Moreover, the values of C in the covalent and metallic modifications of tin ('gray' and 'white' tin) are the same [37]. Thus, the so-called degree of 'covalence' (or nonuniformity of the electron density distribution) makes virtually no contribution to the bulk modulus. The compressibility of a material is primarily determined by the averaged electron density of valence electrons [1-3]. It may be concluded that the record-high value of the bulk modulus of diamond is associated with its electron (and atomic) density, which is record high among all substances. The record-high density of diamond is, in turn, directly related to the position of the carbon atom in the middle of the first filled row in the periodic table. The carbon atom has in compounds a very small ionic radius (effective radius of the orbitals of the inner 'core' electrons) and the largest number of valence electrons—4 [38]. The density of valence electrons indirectly affects the total energy, as a result of which the correlation  $B_0 \sim \rho^{\alpha}$ , where  $\alpha \approx 1.25$ , is observed on average [2] (Fig. 2) for all substances with a 'strong' type of interaction between particles. This correlation is rather close to the relation  $B \sim \rho^{1.17}$  established earlier for covalent substances with a diamond-like structure [36]. Figure 2 is plotted using experimental reference data (see the details given in reviews [1-3]). The 'drop down' of a number of p-element substances from the overall dependence is associated with their quasione-dimensional or quasi-two-dimensional structure (see below). The downward trend from the general dependence for substances on the basis of f-elements is due to strong localization of f-electrons and the calculated number of valence electrons not being unique.

The above arguments refer to weak-anisotropy materials. Quasi-one- or quasi-two-dimensional substances will exhibit strong anisotropy of compressibility along different directions. The bulk modulus will then be naturally smaller than that of an isotropic solid body with the same electron density. For example, the bulk modulus of 3D-bound sp<sup>2</sup> carbon phases  $B \approx 200-300$  GPa, while the bulk modulus for anisotropic graphite is almost ten times smaller ( $B \approx$ 20-30 GPa), although the linear compressibility of graphite in a plane is less than that of diamond [1–3].

The issue of anisotropy is closely related to the issue of topological stiffness [39, 40], i.e., the effect of the extent of connectivity and the number of nearest neighbors on the effective stiffness of the system. If the average coordination number Z diminishes in covalent structures to Z = 2.4-2.7 (depending on the type of topological of bonds), system stiffness is lost, and elastic moduli, including the bulk modulus, steeply decrease (the structure de facto disintegrates into quasi-one- and quasi-two-dimensional regions) [3].

Figure 3 shows the bulk modulus (both experimental and calculated data) as a function of the density for various carbon modifications with various topological connectivities (the sources of data displayed in Fig. 3 are quoted in review [3]). Calculations show that the carbon modification with the BC-8 structure, which is shown in the figure, is a stable high-pressure carbon phase under a pressure higher than 6–8 Mbar.



Figure 2. Bulk modulus as a function of the density of valence electrons for elemental substances.



**Figure 3.** (Color online.) Bulk modulus as a function of density for a number of existing and hypothetical carbon modifications.

Similar to diamond, this modification has a tetrahedral coordination of the nearest-neighbor environment, which is, however, somewhat distorted compared to that of diamond and has a somewhat denser structure. This phase has not been experimentally obtained and maintained under normal conditions. Calculations of the modification with the BC-8 structure and a number of suchlike hypothetical carbon phases with a distorted diamond-like structure (see below) show that their density at normal pressure may be several percent higher than that of diamond.

So, diamond is the record holder under normal conditions in atomic density and valence electron density among all materials known today, and it is this factor that determines its record-setting value of the bulk modulus. Is it possible to create a material less compressible than diamond? This, of course, is not strictly prohibited. The proportionality coefficient C in Eqn (1) for various substances with a 'strong' type of interaction can differ by several tens of percent. Moreover, the electron density of a number of transition metals, such as W, Re, Os, Ir, and a number of their compounds, is close to that of diamond, and the moduli for these substances lie in the range from 300 to 430 GPa (for diamond, B = 445 GPa). It is plausible that stable or metastable compounds with an even lower compressibility may exist. However, the bulk modulus of such materials at normal pressure in any case cannot exceed that for diamond by more than 10-20% [1-3]. It should be noted that pure carbon crystalline modifications are predicted, apart from modifications with the BC-8 structure, whose density is several percent higher than that of diamond, and some of these phases can apparently be metastable under normal pressure [1, 41]. The modulus of such modifications may also exceed the value for diamond by several percent [41]. However, in any case, it is in principle impossible to obtain on the basis of well-known chemical elements a material whose bulk modulus at normal pressure will significantly (by several times) exceed the values for diamond.

It should be noted that experimental studies of carbon modifications obtained from fullerites at high pressures, as well as assertions regarding ultrahigh values of the elasticity moduli or hardness of such materials, were largely fueled and inspired by a series of curious theoretical publications [42–44]. These papers presented estimations of the bulk modulus of an individual  $C_{60}$  molecule. It was assumed that all 60 carbon

atoms, along with electrons, are located within a sphere 7.1 Å in diameter [42-44]. The bulk modulus of such an individual molecule formally turned out to be almost twice that of diamond. Next, an absolutely erroneous assumption was made that a close-packed crystal may be made from contacting C<sub>60</sub> molecules. Again, the estimated bulk modulus of such a crystal formally should be 620-720 GPa, i.e., exceed that of diamond by a factor of about one and a half. Such estimates are not a surprise, since, from a formal point of view, the density of an individual fullerene molecule,  $6.3 \text{ g cm}^{-3}$ , is also almost twice the density of diamond, and the density of a hypothetical crystal that consists of contacting molecules is 1.5 times higher than that of diamond [12, 13]. However, such a crystal cannot exist in principle, since carbon atoms from neighboring molecules must be localized at an impossibly small distance from each other (less than 0.5 Å), while the molecules are not geometric objects and cannot touch each other (!) [12, 13]. Both density and compression moduli of any polymerized modification based on fullerene molecules, are, of course, significantly inferior to those of diamond. It should be noted that even smaller carbon molecules or clusters will have from a formal point of view even higher (and meaningless) values of density and compression moduli. Thus, the density and bulk modulus of an individual hypothetical cube C8 made of carbon atoms are formally nine times higher than that of diamond, while for a carbon tetrahedron  $C_4$  they are 40 times higher (!) [12, 13]. These numbers have no relation whatsoever to the bulk carbon material; it is as pointless to consider the bulk moduli of small clusters as it is to discuss the moduli of individual atoms or molecules. It is of interest that the same error was repeated 27 years later by the authors of [45], who obtained estimated densities of larger carbon fullerene-like onion-type clusters close to that of diamond. It is incorrect to compare the formal densities of small clusters (that consist of several hundred atoms) and a bulk material (diamond), which resulted in an erroneous analysis of the carbon phase diagram [45].

We now consider the experimental and theoretical 'evidence' of the creation of materials whose bulk moduli substantially exceed those of diamond. It should be kept in mind that the first such reports [5] appeared in 1998. Acoustic microscopy was used to measure the velocities of longitudinal and transverse waves in bulk amorphous-crystalline samples of carbon modifications obtained from fullerite  $C_{60}$  at high pressures and temperatures. The bulk and shear moduli of the studied samples were calculated then based on these data. The calculated values of the bulk modulus for a number of samples turned out to be anomalously high, up to 1700 GPa, a value that is four times (!) higher than that of diamond. The density of these carbon phases is in this case 10-20% lower than the density of diamond. It is immediately evident that these results are doubtful. Moreover, the shear modulus for these samples is 2–3 times lower than that for diamond, which leads to anomalously high Poisson's ratios (v > 0.4). These values are characteristic, for example, of rubber or soft metals such as lead, but not of covalent carbon materials, whose Poisson's ratio is in the range of 0.05-0.20. Moreover, the calculated values of shear moduli automatically imply that the hardness of these carbon materials must be much inferior to that of diamond. This is not observed; moreover, the authors themselves argue in [7–9] that these materials are even harder than diamond (see below). As shown in [2, 46], large errors in determining the bulk modulus using data on

sound velocities may be due to anisotropy (nanotexturing) and nonuniformity of sample properties. Such anisotropy emerges in samples very frequently: it is associated with temperature and pressure gradients in the process of synthesis. Nevertheless, some authors keep quoting the unrealistic value of the compression modulus, 1700 GPa, in subsequent studies, both experimental [7, 47] and theoretical [48, 49].

Several reports of abnormally large compression moduli were based on data of X-ray diffraction under pressure. The error, by a factor of 1.5–2.5, was apparently associated with strongly nonhydrostatic experimental conditions [2]. For example, the bulk modulus B = 600 GPa was obtained in [6] using diffraction data for the three-dimensional (3D) polymerized fullerite phase, while subsequent studies of samples obtained with similar parameters of synthesis but under more hydrostatic conditions yielded B = 280 GPa [10] and B = 220 GPa [11].

In addition, bulk samples obtained from fullerite under approximately the same conditions (13–14 GPa, 1200 K) were studied in detail by means of Brillouin spectroscopy [50]. 'Reasonable' values of the bulk and shear moduli were obtained: B = 368 GPa and G = 375 GPa, and 'normal' Poisson's ratio v = 0.12 [50], which is characteristic of carbon covalent modifications.

The bulk moduli of amorphous or strongly disordered phases were often indirectly estimated (and similar estimates are still made [14]) based on measuring Raman frequencies as a function of pressure. An apparently overestimated compression modulus B = 585 GPa is often obtained in this case [14]. If the Grüneisen constant for a given mode is known, compressibility may in principle be estimated in the case of a crystal using the baric dependence of the corresponding vibration frequency. For example, the Grüneisen constant for crystalline diamond is close to one, and the shift of the Raman frequency under pressure may be used to estimate the bulk modulus. However, this is impossible in principle in the case of a highly disordered state, since the very shape of a very wide Raman peak changes significantly in the process of compression, and no fixed Grüneisen constant can be considered. Moreover, an amorphous state may very often exhibit a lower compressibility of individual interatomic bonds than that in the corresponding crystal, and at the same time, a higher compressibility of the entire amorphous sample [51]. This is due to the continuous distortion and transformation of the structure of the amorphous lattice under compression [51]. Finally, the aforementioned Raman studies were primarily carried out also under highly nonhydrostatic conditions, which can lead to a significant error in determining the pressure derivatives of the Raman frequencies.

It was asserted in [20] that carbon material samples were obtained that feature a bulk modulus higher (by 10%) than that of diamond, but also a higher (by 0.2-0.4%) density. The samples, which were also obtained from fullerite C<sub>60</sub> at high pressures and temperatures, were structured as clustered needle-like diamond nanocrystals with an amorphous interlayer between granules. In determining the X-ray density and compression modulus (also using the technique of X-ray diffraction under pressure), only the positions of the maxima of very wide lines were taken into account. The X-ray amorphous regions that constitute about half the sample volume were actually not explored. This is apparently the reason for the erroneous statement about 'the densest and least compressible form of carbon' [20]. It is also possible that

high shear stresses persist in the clustered diamond nanorods, and X-ray data can also yield in this case an overestimated bulk modulus, even though the measurements were carried out under sufficiently hydrostatic conditions. The same authors have recently presented similar data for nanocrystalline diamond microspheres, reporting very high values of the bulk modulus: B = 489 GPa [52] and B = 482 GPa [53]. The density estimated using X-ray diffraction data was 3.54 g cm<sup>-3</sup> (approximately 0.5% higher than that of diamond). In our opinion, these data are also erroneous for the reasons specified above.

A study [54] of similar diamond nanopolycrystals obtained from graphite showed an increase in the longitudinal speed of sound by 3% compared with the averaged value for a diamond single crystal. The measurements were carried out using picosecond ultrasonic spectroscopy. Diamond has a cubic lattice with weak anisotropy (11%), and clusters of twin nanocrystals may be anisotropic (a preferred direction for crystal growth and the emergence of twins related to temperature and pressure gradients in the process of synthesis). Ultrasound data do not correspond then to the standard averaged values for a polycrystal. This is indirectly confirmed by the observation that there was no increase in the longitudinal speed of sound for a number of samples in [54], while the speeds of sound in some samples were lower than in single crystals.

Thus, all the 'experimental' evidence of the creation of carbon materials with a bulk modulus substantially exceeding that of diamond are based either on incorrect experimental data or on their erroneous interpretation.

Curious reports on the synthesis of carbon materials with a bulk module of 600, 800, and 1700 GPa [5, 6, 14] might not have been mentioned in the context of this review but for a series of reports on computer simulation that appeared in recent years [48, 49, 55] that allegedly 'explain' the plausibility of obtaining such materials. The bulk modulus of any carbon modification whose density is lower than that of diamond is in theoretical calculations evidently also lower than the value for diamond (this refers to all authors without exception). This once again confirms the validity of the thesis that the bulk modulus is actually nothing but the bulk density of the binding energy. Thus, the modulus of a uniform carbon phase may not be higher than that of diamond.

To explain the unusual results obtained in [5, 6, 14], it was suggested that a composite material may be created based on two (or more) carbon phases, each of which individually has under normal pressure elastic moduli and a density lower than those of diamond, while in the composite material (also under normal pressure!) they are higher than in diamond [48, 49]. A specific implementation of such composites consisted of nanometer-scale grains of 3D polymers of the C<sub>60</sub> fullerite strongly compressed inside a diamond matrix (Fig. 4). The density of the initial polymerized fullerite phase at normal pressure is  $3.1 \text{ g cm}^{-3}$  and its calculated bulk modulus B = 340 GPa. The authors of [48, 49] suggested that the grains of this fullerite phase may be located inside the diamond matrix in a compressed state with a polymerized phase density of up to 5 g cm<sup>-3</sup> and its bulk modulus over 2000 GPa.

It should be noted that such a change in density corresponds to an external pressure on grains of  $\approx 500$  GPa (the authors themselves give an incorrect estimate of 60 GPa); consequently, the same negative pressure (tensile stresses) must act on the diamond matrix. The maximum tensile

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Figure 4. (Color online.) Simulation of a compressed grain of polymerized  $C_{60}$  fullerite in an also compressed diamond matrix. Figure from [48], reproduced with permission of the American Chemical Society (ACS) C 2015.

strength of diamond is  $\approx 100$  GPa; at higher tensile stresses, a plastic flow of diamond occurs [24-26, 56]; therefore, this degree of compression of fullerite polymers in the composite is, of course, unrealizable. However, this is not the most important flaw. As follows from the theory of elasticity [57], in the simplest case, when the matrix and the inclusions are made of the same material, if a finite inclusion volume is created in a compressed state inside the matrix, the total change in volume is strictly equal to zero. Shear stresses emerge in the system, which lead to bulk changes whose values for the compressed inclusion and for the matrix are the same but have opposite signs. As a result, the density of a hypothetical composite based on the same substance should be equal to that of the initial unstressed mixture of phases with the same phase ratio. This, of course, is not true if materials are not the same. If a strained composite material is created, the more compressible substance undergoes a greater change in density and bulk modulus than the denser and incompressible one. However, it is fundamentally impossible to create, based on materials with different bulk moduli, a composite material whose specific volume and bulk modulus are higher than those of each of the components. Roughly speaking, it is not possible to create on the basis of rubber and steel a composite material whose moduli and specific volume are higher than those of steel. Or, if completely reducing the issue to absurdity, it is not possible to create a porous material whose modulus and density are higher than those of the continuous counterpart. The maximum pressures at which grains of polymerized fullerite may persist in the diamond matrix in the elastic mode are actually less than 100 GPa; this fullerite will be compressed then by about 15%, while the diamond matrix (with the same volume as the fullerite grains) is stretched by 10%. This implies that the composite density in any case does not exceed  $3.4 \text{ g cm}^{-3}$ , and the bulk modulus does not exceed 400 GPa.

The authors of [48, 49] do not report the average density of the entire simulated system. The value of this density (like that of the bulk modulus of the entire system) should actually be intermediate between the densities of diamond ( $3.5 \text{ g cm}^{-3}$ ) and polymerized fullerite ( $3.1 \text{ g cm}^{-3}$ ). If this is not so (judging by the data in [48, 49]), then the simulated system was effectively subjected to high pressure (200–300 GPa) at a very high density (about 4.5 g cm<sup>-3</sup>), and the authors

considered incorrectly the boundary conditions. The authors of the calculations acknowledged in a recent private conversation that they really had considered a composite material with periodic conditions, in which both polymerized fullerite nanograins and diamond nanosized layers (see Fig. 4) were in a highly compressed state, and the outer boundary of the sample was not considered. Both phases compress each other (while external pressure is zero), similarly to Baron Munchausen pulling himself out of a swamp by his own hair. Such a situation, of course, contradicts Newton's third law. It apparently corresponded to a large external pressure (200– 300 GPa) applied to the entire sample, which was not taken into account by the authors of [48, 49] (external boundaries at infinity were not considered).

It should be noted that, to analyze possible errors, it is useful to consider a composite material under stress in which the matrix and the grains consist of the same substance, for example, diamond. The diamond grains inside the diamond matrix will be compressed; the diamond layers between them will be stretched; the total change in volume will be zero; and the compression modulus of such a diamond will decrease slightly (the negative contribution from the stretched regions will prevail over the positive contribution from the compressed regions).

A conceptually similar approach was used in Ref. [54] to explain the increase in the moduli of nano-polycrystalline diamond in comparison with those of a single crystal. The contribution from twin boundaries under stress was considered in this case. It is shown that a large concentration of twin boundaries can lead to an increase in the elastic moduli by, however, only a few tenths of a percent, while the variation of the results depending on the interatomic potential used in the calculations is several percent. Such a small increase is actually possible for shear or Young moduli for certain directions in the anisotropic system, but it is forbidden for the bulk modulus under the laws of thermodynamics (and ultimately, simply under Newton's third law). If the external pressure is zero (atmospheric), the total compression modulus in the state under any complex stress can only decrease. A possible increase in the compression modulus of nanopolycrystalline diamond was also explained in [52] by a complex anisotropic shear stress in some grains. However, as was said above, shear stresses cannot lead to an increase in

the density and bulk modulus (but can only cause the opposite effect). It is worth noting that recent precision measurements of elastic moduli of nanocrystalline diamond using two methods—gigahertz ultrasonic interferometry and the 'resonance sphere' method [58]—failed to reveal with an accuracy of 0.05% (!) any differences among the moduli from the average values for diamond single crystals.

Thus, there is no theoretical basis whatsoever for the existence of lower-density carbon materials whose bulk moduli would be substantially higher than those of diamond.

# 2.2 Shear modulus and Young's modulus, anisotropic systems

Shear and Young's moduli are more important for the operational characteristics of a material, such as strength, hardness, fracture toughness, and wear resistance than the compression bulk module, since shear stresses emerge in all mechanical tests. Depending on the symmetry of single crystals, there are several (up to 21) elastic constants. We primarily discuss the shear module G and Young's module E of polycrystalline or amorphous materials. It should be recalled that Young's modulus characterizes the ability of a material to resist one-sided compression or tension in an elastic region. In the case of one-sided tension (compression), components of both shear and hydrostatic compression are present. There are only two moduli that are independent in the linear region of small strains for an isotropic body, while a third modulus, like Poisson's ratio, is expressed in terms of these two moduli. In particular, for Young's modulus, E = 9BG/(3B+G). The shear modulus and Young's modulus (as well as the compression modulus) are also associated with the density of the energy of bonds and, consequently, with the atomic and electron density in the material [1, 2].

However, of importance for shear moduli is not only the average density of valence electrons, but also the degree of its spatial localization, which, as noted above, is not really essential for determining the bulk modulus. The importance of the spatial distribution of electron density is apparent, since any shear deformation leads to a change in this distribution (so-called angular stiffness emerges). The dependences of the shear modulus on the average electron density for various groups of substances range from  $G \sim \rho$  to  $G \sim \rho^{5/3}$  (Fig. 5).

The plot in Fig. 5 is based on experimental reference data; details are given in review [2]. A high degree of covalency and, consequently, a high degree of angular stiffness can increase the shear modulus by a factor of 1.5-3 compared with that for a more uniform distribution of electron density, as in metals [1, 2]. For example, the shear moduli of covalent compounds such as SiC and B<sub>4</sub>C are higher than those of metals such as W and Re, although their bulk modulus is significantly lower [1, 2]. Both the density and bulk modulus of metallic white tin exceed those of semiconductor gray tin by 20%, while the polycrystalline shear modulus is almost 1.5 times smaller [1, 2]. Covalent modifications with a nonuniform distribution of electron density, as a rule, are realized in structures with a small coordination number. However, similar to the case of the bulk modulus, the topological stiffness of the system is a critical factor [39, 40]. As a result, the coordination number of covalent structures with a high shear modulus ranges from 3 to 6, and the coordination number 4 (as in a diamond lattice) is close to optimal (see the discussion in [1-3]).

The degree of covalence can be characterized from a formal point of view by Pugh's ratio k = G/B or Poisson's



**Figure 5.** (a) Polycrystalline shear modulus of elemental substances as a function of the corresponding density of valence electrons. (b) The same with a division of substances into groups.

ratio v = (3 - 2G/B)/(6 + 2G/B). Among metals with a high coordination number, only beryllium has a high Pugh ratio and, consequently, a small Poisson's ratio because of the very small size of the Be ion and the strongly nonuniform distribution of electron density (actually, a significant angular stiffness of bonds emerges in this metal).

Thus, the shear modulus (like Young's modulus) is also primarily determined by the atomic density of the material and the density of valence electrons. However, unlike the bulk modulus, the shear modulus may vary by a factor of 1.5–3, depending on the degree of spatial nonuniformity of electron density (the degree of bond 'covalence').

It should be noted that diamond is the record holder in terms of shear modulus (and hardness) even among all hypothetical carbon materials, including predicted materials with a higher density and bulk modulus [41]. In contrast to the 'sensational' assertions about the bulk modulus, there are virtually no similar assertions in both experimental and theoretical publications about shear moduli or Young's modulus that exceed those of diamond. It is only for nanopolycrystalline diamond with a large number of twin boundaries that theoretical calculations predict a possible increase in the shear modulus by several tenths of a percent [54], although the data obtained are very sensitive to the empirical effective interatomic potentials used in calculations. Moreover, as mentioned above, precision studies of the elastic characteristics of polycrystalline diamonds using gigahertz ultrasonic interferometry [58] confirmed that both the shear modulus and the bulk modulus for such materials coincide with very high accuracy with the corresponding averaged values for diamond single crystals. We also note that, according to nanoindentation data, Young's modulus of the abovementioned clusters of needle-shaped diamond nanocrystals [20] is  $1070 \pm 54$  GPa, a value that is even slightly lower than that of diamond (1140 GPa) [21].

Although diamond is (and will be) the undisputed recordholder among all substances (including hypothetical ones) in terms of the averaged polycrystalline shear modulus and Young's modulus, the situation for highly anisotropic materials is much more interesting and promising. It is known that, for example, a graphite single crystal in a layer features shorter and stronger interatomic bonds and, consequently, lower compressibility and a higher Young's modulus along the planes of atomic layers than diamond. Chains of carbine (linearly coupled quasi-one-dimensional carbon material) should have also a record high modulus for uniaxial compression-tension. Filaments based on nanotubes or carbinoid structures can feature not only record-high moduli in a single direction, but, consequently, also recordhigh mechanical properties (tensile strength). Observed in many anisotropic multilayer nanostructures is not only a several-fold increase in hardness, but also an increase in Young's modulus along certain directions by several tens of percent [2, 4].

It should be noted that all elastic moduli are determined for small deformations (linear approximation of the theory of elasticity). Large deformations (changes in volume) simply make it necessary in the case of hydrostatic compression to take into account the dependence of the bulk modulus on pressure. The pressure may be, in this case, arbitrarily large if the possibility of phase transitions and the effects of quantum 'cold melting' at ultrahigh pressures are ignored. However, the situation regarding shear deformations is more complicated. The crystal lattice loses stability at a critical deformation [24–29] (Fig. 6a). The theoretical shear strength  $\sigma$  was previously considered in simplified models (see, e.g., the famous Frenkel formula, which is almost one hundred years old:  $\sigma \approx G/(2\pi)$  [29]). We have as a result a theoretical estimate of the shear strength for diamond:  $\sigma \approx 85$  GPa. Similar estimates are still widely used to this day.

At the same time, state-of-the-art computers made it possible to calculate the ideal shear, tensile, or uniaxial compression strengths of a crystal starting from the first principles. Such calculations have been actively carried out in the last 20 years. Despite the high accuracy of firstprinciple-based calculations that predict the binding energy and the electron density distribution, the dispersion of the calculated shear strength is quite large. The main reason for this dispersion is that changes in the spatial distribution of electron density should be very meticulously taken into account for large deformations (this change can be ignored in calculating elastic moduli in a linear elastic region) (Fig. 6b). For example, for a defect-free single-crystal diamond, the ideal shear strength in various directions varies, depending on the specific study, from 60 GPa to 200 GPa [24-26]. The most accurate calculations yield values that range from 95 GPa to 115 GPa [27]. Semi-quantitative experimental measurements yield critical shear stresses of  $\approx 130$  GPa [56].

It should be noted that the ideal strength (which corresponds to the loss of stability of the crystal lattice



**Figure 6.** Calculated stress in diamond as a function of (a) shear deformation  $\varepsilon$  and (b) tensile deformation [26]. (Reproduced from [26] with permission of the American Physical Society © 2001.) (c) Electron density distribution in diamond under normal conditions and at a critical degree of tension, when covalent bonds are 'broken' [24]. (Reproduced from [24] with permission of the American Physical Society © 2000.)

under a load containing shear components) for deformations of various types, like elastic moduli, is determined only by the structure and interaction between particles, i.e., is a uniquely defined microscopic parameter. In other words, these are actually the same elastic moduli or their combinations, but manifested in a strongly nonlinear region of large deformations. It is worth pointing out that shear deformations inevitably lead in the nonlinear region of large deformations to a minor change (decrease) in volume, whereas, according to the linear theory of elasticity, shear deformations do not cause any change in volume [26]. Summarizing, we can conclude that there are neither reliable experimental data nor theoretical grounds for creating materials whose elastic moduli at normal pressure significantly exceed the corresponding values for diamond. The experimental problems of measuring the moduli are associated with the small size of the samples, often their disordered and nonuniform structure, their anisotropy and texturing at the nano- and micro-levels, nonhydrostatic conditions in the experiment, etc. The record-high moduli of diamond are ensured from a theoretical point of view by diamond's record-high density of valence electrons (in fact, energy density) and a high degree of electron density localization. The creation of any composite materials cannot provide any significant changes in this area.

# 3. Myth II: materials whose hardness far exceeds that of diamond

The myth of the hardness of 'ultrahard' materials is the issue that is most complex and convoluted for a coherent analysis. The main reason for this difficulty is the extreme vagueness of the very concept of 'hardness'. Hardness is a qualitative rather than a quantitative characteristic, which depends not only on the properties of the material, but also on the measurement method, as well as on the interpretation of measurement results.

# 3.1 Concept of hardness, definitions, and measurement methods

One of the most common definitions is formulated as follows: hardness is the degree of resistance of a material when a harder body (indenter) is introduced into it or when the material is scratched with an indenter. The definition is extended in most cases by adding words 'in the process of plastic deformation'. Sometimes, the term 'hardness in the elastic mode' is used, but if so, this value is uniquely determined by the elastic moduli of the material, the indenter shape, and the magnitude of the load.

Historically, the first technique employed to measure (estimate) hardness was the 'comparative scratching' method referred to as sclerometry. Depending on the ability of one mineral to scratch another, conventional hardness is assigned to minerals in Mohs mineralogical scale units, which range from 1 (talc) to 10 (diamond). This technique became obsolete by the mid-20th century due to the advent of quantitative methods for measuring hardness based on indentation. Recently, however, in obtaining micrometer-sized samples at ultrahigh pressures, a conclusion about their hardness is also often made on whether they can scratch a flat diamond anvil [8, 59, 60]. It should be noted that microindentation actually occurs in the process of scratching, and a particle of the sample is able to plastically deform the flat surface of the anvil even if the sample hardness is 3-4 times lower (see the discussion in Section 3.3).

Dynamic techniques for measuring hardness include the 'rebound hardness' method. This technique consists of measuring the height of the 'bounce' of a diamond-tipped hammer dropped from a fixed height onto the surface of the material under testing. This method is not used to study small samples.

The most common methods to measure hardness involve using various indenters made of ultrahard materials (diamond, hard alloy, hard steel, etc.). The techniques used to measure hardness include the Brinell test (spherical indenter),

Rockwell test (conical indenter), and the Vickers, Berkovich, or Knoop test (pyramidal indenters of various profiles and vertex angles). Indentation hardness is defined as the ratio of the load to the imprint surface area (sometimes to the imprint projection area, to the imprint depth, or to its volume). The hardness corresponds in the standard definition to the average pressure in the plastic deformation region. Also distinguished are 'restored hardness' if the imprint is examined after the load is removed, and 'unrestored hardness' if the imprint area or more often the indenter penetration depth is investigated directly under load. 'Unrestored hardness' is measured, in particular, using the nanoindentation technique. It is clear that if 'restored hardness' is measured, for the measurements to be correct, a significant plastic deformation of the sample is required. Otherwise, if indenting is carried out in the elastic mode, no imprint will persist after the load is removed, which formally means infinitely high hardness. Moreover, these absurd results may be obtained not only for hard materials, but also, for example, for soft but elastic rubber.

It is clear in connection with the foregoing that the most correct data in measuring hardness can be obtained by recording the *in situ* movement of the indenter in the process of nanoindentation. The initial stage of nanoindentation always corresponds to the elastic mode, and the data obtained may be used to measure Young's modulus of the material with good accuracy [29]. As the indenter is introduced further and stresses grow, a sharp elastic-plastic transition (pop-in) may occur at a certain depth in the nanocontact as a result of the rapid spontaneous emergence of dislocations or twin boundaries in the region beneath the imprint [29]. If the nano-region beneath the imprint does not contain any movable defects (primarily in the case of single crystals), the pressure at the beginning of this transition corresponds to the 'ideal' hardness of the material. This value is uniquely determined by the material moduli in a strongly nonlinear region of large deformations, the 'theoretical strength' (see above). During the elastoplastic transition in the process of nanoindentation, a homogeneous avalanchelike nucleation of dislocations and their movement occurs, which, as a rule, leads to a sharp decrease in the measured hardness. Several hundred or thousand dislocations are formed simultaneously in single crystals of metals when pop-in occurs, while in brittle solids, for example in sapphire, they only number a few dozen [29].

A sharp elastic-plastic transition during nanoindentation is not observed, as a rule, in nanomaterials or amorphous substances. On the one hand, such materials always contain in the region underneath the imprint potentially movable defects, and the stresses that correspond to the lattice instability are not attained. As a result, the transition to the plastic regime is smooth. On the other hand, the dislocation mobility in these materials is very low, and the onset of plastic deformation does not lead to a noticeable decrease in contact pressure or sinking of the indenter (pop-in). Figure 7 displays the nanoindentation curve of the 3D polymerized fullerite  $C_{60}$ [3] showing that the elastic-plastic transition has just begun (elastic restoration is 93%). The curve does not contain popin anomalies. The load that corresponds to the onset of plastic deformation can be estimated in the case of smooth nanoindentation curves using various methods [61–63]. The most correct but labor-consuming method is the technique in which the maximum loads are consequently increased in a large number of experiments. The load is fixed, after the



**Figure 7.** Nanoindentation curve for a sample of 3D polymerized fullerite [3].

application of which the indentation curve ceases to be completely reversible (reversibility corresponds to the elastic regime). A simpler method is to approximate the initial segment of the indentation curve by a simple function (usually a power function). For the quasispherical part of the indenter in the Hertz contact problem,  $F \sim h^{1.5}$ , where F is the load and h is the indenter penetration depth. By fitting this or a similar approximation to the entire loading curve, it is possible to find where the increase in mean pressure begins slowing down and, consequently, the plastic flow commences.

Although in situ studies of nanoindentation provide the most reliable information, the use of nanoindenters to study ultrahard materials is limited. This is due to several reasons. First, because of the high price and complexity of operation, nanoindentation devices may not be used as desktop testers for measuring hardness by all research groups. Second, strict requirements are set for nanoindentation regarding the quality of the sample surface and the indenter tip. And finally, the main point: in studying materials whose hardness is comparable to that of diamond, as a rule, only elastic sections of the loading curves can be captured, since the indenter often collapses before the onset of the elastic-plastic transition (pop-in) in the sample [29]. No sharp pop-in transition in single crystal diamond has ever been observed by anyone. It was only recently that the pop-in transition in single-crystal cubic boron nitride c-BN with a low dislocation density was observed for the first time at a load of 7 mN [61] (Fig. 8a). The average pressure of the onset of plastic deformation before the pop-in for the (111) face of c-BN was 84 GPa, and the nanohardness in the plastic regime was 62 GPa. Figure 8b shows for comparison the nanoindentation curve of polycrystalline boron nitride with fine grains (size from 100 to 400 nm) [61]. The pressure that corresponds to the onset of plastic deformation is in this case even slightly lower than that for a single crystal, but the hardness in the plastic regime is higher (approximately 72 GPa) [61].

All methods to measure hardness using indenters were initially developed for only those cases when the indenter hardness and elastic moduli are at least several times higher than the corresponding values of the material under study. It is assumed that a change in the indenter size and shape in the process of its elastic deformation under loading may be



**Figure 8.** Nanoindentation curves and calculated contact pressure for (a) a single crystal and (b) a polycrystal of cubic boron nitride. (Data taken from [61] with permission of the author.)

disregarded. Plastic deformation of the indenter is, moreover, not allowed, implying that an 'ideal' indenter must be incompressible and nondeforming. If a diamond indenter is used, this requirement is almost always satisfied for most of the materials studied, i.e., a diamond indenter can be considered 'ideal' for most materials. However, if the elastic and mechanical properties of the indenter and the test sample are comparable, indentation is only a comparative and qualitative rather than an accurate quantitative measurement method. If the hardness of a material whose characteristics are close to those of diamond is measured using a diamond indenter, values of hardness may be obtained that are several times higher than those obtained when a hypothetical absolutely hard and incompressible indenter is used.

Hardness is measured in three load ranges: macro-, micro-, and nano-scale. The nanoscale only sets the indenter penetration depth, which should be less than 0.2  $\mu$ m. It should be noted that a value of 0.1–0.2  $\mu$ m exactly corresponds to the standard curvature radius of the vertex of the sharpest trihedral Berkovich pyramid used in nanoscale hardness testers [29]. As a result, the pyramid vertex in nanoindentation is actually a spherical indenter. The micro-range (micro-hardness) sets the magnitude of the load up to 2 N and the indenter penetration depth significantly greater than 0.2  $\mu$ m, so that the pyramidal or conical part of the indenter starts 'working'. The characteristic curvature radius of the Vickers and Knoop pyramid vertex is 0.2–0.4  $\mu$ m. The macro-range sets the load from 2 N to 30 kN.

The measured hardness depends on many factors, primarily on the load on the indenter. The average pressure below the imprint increases for a spherical indenter with a load (the Hertz problem known in the theory of elasticity), and, consequently, the measured hardness also increases. For a conical and pyramidal indenter, the pressure below the imprint does not depend on the load [64, 65]; the measured restored hardness decreases as load increases and almost plateaus at high loads. Due to the almost spherical rounding near the vertex of the pyramid or cone, the measured hardness can start growing as load increases and afterwards starts decreasing (in the case of a conical or pyramidal part of the indenter). The reason for the decrease in measured hardness with an increase in load is a reduction in the relative fraction of the elastic deformation energy of the material compared to the energy spent on creating a new surface in the process of plastic deformation [1, 2]. The measured hardness for ultrahard materials is saturated at high loads, starting from 10-100 N [1], i.e., standard devices that measure microhardness are not applicable to explore such materials. It should be noted that the proportionality between the load and the imprint area is not strict even in the plastic regime [2]. Mayer's empirical law  $F \sim d^n$  is usually applicable in this case, where F is the load, d is the linear size of the imprint, and *n* is the exponent, usually n = 1.5 - 2 [66]. The exponent *n* for ultrahard materials significantly differs from two: for diamond,  $n \approx 1.5$ , while for nano-polycrystalline diamond,  $n \approx 1.4$  (!) [17]. Thus, a slight decrease in the measured hardness with an increase in load is observed even in the plastic region. For example, a slow decrease in the measured hardness is observed for ultrahard silicon carbide SiC at loads up to 200 N [15].

Apart from the load, the hardness measured using even the same method is affected by many factors, in particular, the surface quality of the sample under study and the method of preparing a smooth flat surface (polishing, etching, processing with an ion beam, etc.), since the type and amount of structural defects depend on this, and the quality of the indenter (type of diamond, sharpness of edges and vertex, etc.). Of importance in many cases are the indenter loading and unloading rates, as well as the time of exposure under load and the time between unloading and the start of measurement. The process of plastic deformation involves certain kinetics; if exposure to the load is long, new dislocation loops, twin boundaries, and other defects may emerge. Many materials exhibit viscoelastic properties, and the imprint obtained after unloading 'heals' (partially or completely disappears) over time. A number of complicating circumstances arise in studying materials whose moduli and hardness are comparable to those of diamond; the factors are considered below. Finally, it should be noted that hardness is primarily measured under normal conditions. Plasticity (i.e., ease of formation and mobility of dislocations and twin boundaries) of brittle solid materials rapidly increases at high temperatures, which can lead to a significant decrease in the measured hardness. For example, the measured Vickers hardness of a diamond single crystal decreases at a temperature of 1400 K almost five-fold, to about 20 GPa, i.e., diamond becomes less hard than silicon carbide SiC at the same temperature ( $\approx 25$  GPa) [2].

All of the above refers to measuring the hardness of a particular material sample. If various samples of the same material are studied, the measured hardness, of course, depends on the grain size, defects, and stresses in each specific sample. This issue is considered in Sections 3.2 and 3.3.

#### 3.2 'Theoretical' models of hardness

The data quoted in Section 3.1 seem to be an unambiguous indication that hardness is not a clearly defined quantitative characteristic. The measured hardness of a material can vary by several tens of percent and sometimes several times, even within the same method. Therefore, by definition, there can be neither a strict theory of hardness nor unambiguous quantitative theoretical models of hardness. Moreover, hardness as a technological characteristic is an almost useless concept. In machining materials (cutting, lathe turning, grinding, drilling, etc.) it is naturally highly desirable that the hardness of tool elements be superior to that of the processed material, or at least not much inferior to it. No other requirement is set. Moreover, machining can be carried out by means of abrasive processing and grinding using a powder whose hardness is lower by a factor of 1.5-2 (see Section 3.3). Much more important in industrial machining of materials are other technological properties of solid materials, such as fracture toughness, wear resistance, heat resistance, and chemical inertness to the processed material. However, these more important technological characteristics have always been and still are 'eclipsed' by hardness in both research and pop-science articles. Moreover, interest in new ultrahard materials is only growing, and new empirical formulas for determining hardness are continuously being proposed. The main reason for this phenomenon is that the concept of 'hardness' (the ability to scratch or indent) seems to be clearly evident, and the words 'hard' and 'soft' are widely used in everyday language (in contrast, e.g., to the use of the terms 'wear resistance' or 'fracture toughness'). In addition, the development of the industry of synthetic ultrahard materials (diamond and cubic boron nitride) is one of the most prominent milestones of the technological revolution of the 20th century. The global production of synthetic diamonds and cubic boron nitride is currently several thousand tons per year (several hundred times greater than mining of natural diamonds). Several hundred billion dollars circulate annually in the global industry of ultrahard materials. It is therefore understandable why the terms 'new ultrahard material' or 'material harder than diamond' are so popular in publications and grant applications. Material scientists, physicists, and chemists are naturally tempted to develop a more solid theoretical foundation for the fuzzy concept of hardness.

The most straightforward idea is to find a correlation between measurable (by some method) hardness and the uniquely defined characteristics of the material-elastic moduli. Such correlations have been studied for almost 100 years (see [1-3, 67] and the references therein). A correlation between hardness and bulk modulus does exist, but it is very weak and flawed by many exceptions [1, 3]. Many metals exhibit a very high bulk modulus and relatively low hardness. Stricter correlations are observed between hardness and the shear modulus, as well as between hardness and Young's modulus [2, 3, 68] (Fig. 9). This, of course, is not accidental, since all methods to measure hardness involve shear deformation of the material [1]. Moreover, as mentioned above, in loading with an ideally sharp nondeforming conic or pyramidal indenter (with angle  $2\varphi$  at the tip), the pressure in the elastic region ('ideal' 'elastic' hardness) is uniquely determined by only Young's modulus of the



**Figure 9.** Correlation between hardness and the elastic polycrystalline shear modulus (a) and Young's modulus (b) [2] and more complete data for the correlation between hardness and the shear modulus (c) [31]. (Reproduced from [31] with permission of Elsevier © 2011.)

material and does not depend on the load [1]:

$$\mathbf{P} = \frac{E\cot\varphi}{2-2v^2} \,,$$

Ì

where E is Young's modulus and v is Poisson's ratio. Such an 'ideal' hardness in the elastic region lies for diamond in a range from 200 GPa to 300 GPa, depending on the vertex angle of the indenter used. It should be noted that if the vertex angle is sufficiently small, this value always exceeds the plastic flow stress, i.e., if indentation is performed using a pyramid or cone with an ideally sharp angle, the plastic flow should immediately begin, and the elastic region will be absent.

Actually, by the end of the 20th century, all the 'theories' of hardness only consisted of these correlations between the measured hardness and the elastic moduli. However, as noted above, there was a temptation to make calculations of the hardness of hypothetical predicted materials more rigorous. For example, a semi-quantitative approach to indentation applied in [31] yielded estimated hardness  $H \approx 0.151G$ . Such a proportionality coefficient, indeed, describes rather well the correlation between the measured hardness and the shear modulus [2, 3, 31]. This 'new' formula is not far ahead of the century-old Frenkel estimate of theoretical shear strength:  $H \approx G/(2\pi)$ . The hardness obtained for diamond, 81 GPa, is slightly lower than the generally accepted values. However, it is known that if the shear moduli of various substances have close values, the measured hardness is higher for the material with a higher Pugh coefficient, k = G/B. An approximate relation for hardness has been derived recently:  $H \sim k^2 G$  [31]. However, this correlation is not directly used in this specific form. A large array of experimental data was used in its stead to obtain the relation  $H = 2(k^2G)^{0.585} - 3$  [31], which, of course, can in no way be considered 'theory-based'. This is a purely empirical formula, whose dimensionality is, moreover, incorrect: all numerical coefficients depend on the units in which the values of the moduli and hardness are measured (the empirical formula is obtained for the case when B, G, and H are all measured in GPa). It should be stressed that such 'accurate' formulas for hardness give rise to a paradoxical situation: the hardness values predicted in most calculation articles are accurate to a few tenths of a percent, while the experimental hardness of a material cannot be determined, even within the same measurement method, with an error of less than  $\pm 10\%$ , and for very hard materials the measurement error is much higher.

A large and actively developing area of the 'theory' of hardness for covalent substances is related to the correlation between the maximum shear strength of an ideal crystal and the semiconductor gap width. This empirical correlation was found by J J Gilman more than 50 years ago [69, 70], and the shortcomings of this approach have also been well known for a long time [71, 72]. However, these empirical estimates have 'magically' transformed in the last decade into a 'theory of hardness' [30, 32, 33, 73]. The shortcomings of these approaches are discussed in detail in Section 4, devoted to quantum confinement.

It is well known experimentally that the measured hardness may depend on the size of crystalline grains in a polycrystal and on the concentration of various defects (dislocations, point defects, chemical impurities) [1-3, 74]. Real crystals almost always contain a noticeable concentration of dislocations or twin boundaries that maintain plastic deformation even at moderate shear stresses. At the same time, if the concentration of grain boundaries and other defects and impurities is very high, they hinder the movement of dislocations. Most materials exhibit, as a result, an enhancement of mechanical characteristics (hardness, strength) with a decrease in grain size, the Hall-Petch effect (see [1] and the references therein). An increase in hardness with a decrease in grain size is well described in a certain range of grain sizes by the empirical relation  $H = H_0 + Ad^{-1/2}$ , where d is the grain size (Hall–Petch law). Starting from a certain grain size (usually 5-10 nm), a further decrease leads to a deterioration of mechanical characteristics (inverse Hall-Petch effect). This phenomenon is due to the active slip and rotation of very small grains relative to each other and to the emergence of coherent twin boundaries [75]. The contribution due to the Hall-Petch effect is taken into account in a number of recent 'theoretical' expressions for hardness [33]. It is assumed that the total hardness is just a sum of the 'theoretical' hardness for a single crystal and various contributions from grain boundaries (Hall-Petch effect) and other defects. Such an approach is partially justified only if empirical expressions fitted to experimental data are used for the hardness of a single crystal (as in [31]). However, the hardness of an ideal defect-free single crystal should be considered as the theoretical shear strength at which the crystal lattice loses stability (this actually corresponds to the emergence of the first dislocation loop(s) and the onset of plastic deformation). Of course, no contributions from grain boundaries and other defects to the value for hardness need be added in this case: the Hall-Petch effect only allows the hardness of a real sample to get close to the 'ideal' value for a defect-free single crystal.

#### 3.3 Experimental studies

#### of materials 'harder' than diamond

We analyze in this section major reports on experimental studies of materials, which, allegedly, are substantially harder than regular single-crystal diamonds.

As mentioned earlier, the first wave of such reports dates back to the 1990s [7-9]. A Russian team synthesized ultrahard carbon phases from fullerite C<sub>60</sub> during polymerization and partial destruction of molecules at high pressures and temperatures. The first experiments showed that the phases obtained from fullerite under ultrahigh pressures make scratches on diamond anvils of a high-pressure chamber (Fig. 10). The ability to scratch diamond anvils to this day is often considered 'evidence' of the unusually high hardness of newly synthesized materials [59, 60]. These conclusions are, of course, incorrect: the sharp edge of a material can scratch under a heavy load the flat surface of another material, even if the hardness of the first material is 3-4 times lower than that of the second substance (see the discussion below). Ultrahard fullerite-based materials were obtained later in the form of bulk samples several millimeters in size, which made it possible to perform quantitative studies. The obtained carbon modifications featured a strongly disordered (nanocrystalline or quasi-amorphous) structure and a density of  $3.10-3.35 \text{ g cm}^{-3}$ .

It should be stressed that the authors of [7–9] correctly noted that the hardness measured by the indentation method in the case of comparable mechanical characteristics of the sample and the indenter are not fully reliable, and proposed a method of semi-quantitative sclerometry of their own [8, 9]. Scratches on various materials are studied in this method in a comparative way using an atomic force microscope. The key measured parameter is the scratch width at a fixed load. It was found that the scratches on the surface of the diamond single crystal under the same experimental conditions are deeper and have a greater number of micro-cracks than those on the 'ultrahard fullerite' surface [8], which indicates a higher hardness and fracture toughness of new materials. Moreover, the 'ultrahard fullerite' tip makes scratches on the surface of diamond that are smoother and have fewer cracks than the diamond tip. Semi-quantitative sclerometry measurements of new samples yielded a hardness from 170 to 300 GPa [7–9]. However, it should be noted that the hardness of various diamond faces measured using the same technique ranged from 140 to 170 GPa, which is almost twice as high as



**Figure 10.** Scratches on the surface of a diamond anvil produced as a result of shear deformation under the pressure of ultrahard fullerite particles [14]. (The photo, from [14], is reproduced with permission of Elsevier © 2014.)

generally accepted values. The authors of [7-9] recognized that the absolute values of the estimated hardness should be treated with caution. It can only be argued that the hardness of the new material, 'ultrahard fullerite', is apparently no lower than that of diamond, and the anvils made of the new material make imprints on the faces of the hardest singlecrystal diamonds (nitrogen-free diamonds, type IIa) during indentation. It should be noted that bulk samples obtained from fullerite by another group under approximately the same conditions (13-14 GPa, 1200 K) [50] had a Vickers hardness of 80-90 GPa at a 10 N load, i.e., their hardness was no greater than that of diamond. It should be noted that the authors of [8, 9], acknowledging that their measurements of hardness (and the concept itself) are not unambiguous, paid some attention to studying other, more important, technological characteristics, such as wear resistance. They found that samples of new carbon materials are significantly superior to commercial diamond polycrystals in terms of wear and fracture toughness [9]. It should be noted that it is just the higher fracture toughness rather than hardness of 'ultrahard fullerites' compared to that of ordinary diamond that can explain the comparative sclerometry data.

A team of researchers from Japan (Irifune group) was the next to report the synthesis of ultrahard nano-polycrystalline diamonds [16–19]. The first bulk (several cubic millimeters) samples of nano-polycrystalline diamond were obtained and investigated by this group at the beginning of the 21st century [16]. The samples were produced by direct noncatalytic conversion of graphite into diamond with ultrafine grains at high pressures (> 15 GPa) and temperatures (> 2300 K). This team systematically studied over the next 15 years the structure and properties of the obtained nanopolycrystals using various carbon sources (graphite, soot, fullerite, nanotubes, etc.) in a wide range of the P, T parameters of synthesis; the eventual sample size was of the order of centimeters [18, 19]. The results of a detailed study of various nano-polycrystalline diamonds and the prospects for their use in tools and as elements of high-pressure chambers were also presented in later publications by this group [76–80].

Depending on the initial carbon material and the synthesis parameters, diamond polycrystals with a crystal grain size of 3 to 100 nm have been synthesized [17–19, 76–80]. Many of

the nanopolycrystals had a lamellar (laminar or needleshaped) grain morphology. The hardness of the materials obtained was investigated using 'classical' indentation methods. It was found that the Vickers and Berkovich indenters collapse in testing the hardest of the nanopolycrystal samples under even moderate loads at the first loading, which indicates a very high hardness of the new materials [17]. Reliable reproducible prints could only be obtained using a Knoop indenter, and only at loads less than 7 N. These imprints have been studied in detail using atomic force and electron scanning microscopes [17-19, 76-78]. Most of the measurements of the new materials were carried out as a result at only one load of 4.9 N. The dependence of hardness on load is not yet saturated at this load value; therefore, the measured value of hardness is to a great extent conventional. This technique allows at the same time a quantitative comparison of the corresponding indicators for various ultrahard materials. It was found that the maximum hardness is attained for nanopolycrystals obtained from graphite with a lamellar structure and a grain size of 10–20 nm [17–19]. The Knoop hardness of such materials (at a load of 4.9 N) lies in the range of 120-145 GPa [17-19, 76-80]. At the same time, the hardness of the hardest single crystal diamond (group IIa) measured in the same way did not exceed 130 GPa, and the hardness of ordinary single crystal diamond (group lb) did not exceed 105 GPa [17]. The hardness of nanopolycrystals obtained from other carbon materials (including fullerite  $C_{60}$ ) measured using the same Knoop-indenter technique ranged from 80 to 120 GPa, depending on the size of the grains and their morphology [17, 18, 76].

The study of ultrahard nano-polycrystalline diamond by the nanoindentation method at loads up to a record-high 250 mN (penetration depth of 450 nm) shows that the character of loading is close to elastic [17]. The elastic restoration coefficient exceeded in this case 90%, but no attempts were made to estimate hardness using the obtained nanoindentation curve. My own estimates based on fitting the nanoindentation curve of nano-polycrystalline diamond reported in [17] yield a hardness of 130 GPa. It should be kept in mind that no elastic-plastic transition (pop-in) has been previously observed in studies of regular diamond crystals using nanoindentation (penetration depth of less than 100-200 nm [29]. Although the hardness of diamond nanopolycrystals at room temperature is only slightly superior to that of single crystal group-IIa diamond, this difference becomes dramatic at high temperatures. For example, the hardness of diamond nanopolycrystals at a temperature of 1000 K becomes almost twice as high as that of single crystals (!) [19]. This is apparently due to easier plastic deformation and greater mobility of dislocations in single crystals at high temperatures. Diamond nanopolycrystals also feature significantly higher fracture toughness and wear resistance than those of single crystals and commercial polycrystals [17-19, 76-80]. Synthesis of centimeter-sized nano-polycrystalline diamond samples has been deployed recently; these products may be used after processing as elements of megabar-range high-pressure chambers (Fig. 11).

The next team to announce the obtainment of materials whose hardness is significantly higher than that of diamond was a US Geophysical Laboratory group [81]. This group grew large diamond single crystals using chemical vapor deposition (CVD). The single crystals were then subjected to thermal annealing at high pressures (2200 K, 7 GPa). The



Figure 11. Large samples of nanopolycrystalline diamond used as elements of high pressure chambers [80]. (The photo, from [80], is reproduced with permission of Elsevier © 2014.)



**Figure 12.** Photo of the imprint after indentation with a Vickers pyramid on an 'ultrahard' CVD diamond [81]:  $d_1$ ,  $d_2$  are the imprint diagonals for calculating hardness;  $c_1$  and  $c_2$  are the imprint diagonals with cracks for calculating fracture toughness. (The photo is reproduced from [81] with permission of John Wiley and Sons © 2004.)

Vickers hardness of the single crystals obtained as a result of such annealing, according to the data of [81], is higher than 160 GPa, although rather large loads (10–30 N) were used.

Indenter imprints were examined using an optical microscope, while the quality of the imprints left much to be desired (Fig. 12). The authors indicate that the Vickers indenter did not collapse and produced imprints even under heavy loads, although it could only be used once or twice. The Knoop hardness of these single crystals has not been measured. The actual hardness of these single crystals is apparently much inferior to that of the Irifune group's nanopolycrystals, since the Vickers indenters always disintegrated during their indentation at loads above 5 N [17]. It may be assumed that the actual hardness of the annealed CVD diamonds did not exceed 120–130 GPa.

The mechanical characteristics of the abovementioned polycrystals consisting of diamond nano-needle clusters, which were obtained by the Dubrovinskii group by a direct transition at ultrahigh pressures from  $C_{60}$  fullerite [20], have also been investigated in detail [21]. It turns out that the Vickers hardness of these samples cannot be reliably measured, while the Knoop hardness at a load of 5 N varied from 90 to 115 GPa, a value that is consistent with the results for the Irifune group's samples, whose microstructure is similar [17-19]. The only difference is the morphology of nanopolycrystal grains. The polycrystals obtained from graphite in [17-19, 76-80] had a laminar or needle-shaped grain morphology, while fullerite-based polycrystals mainly featured a rounded morphology that differs from that of the samples studied in [20, 21]. The difference in the microstructure of the samples may be related to the synthesis conditions (various temperature and pressure gradients). Similar to the nanopolycrystals obtained by the Irifune group, diamond nano-needle clusters had very high wear and fracture toughness [21]. Nanoindentation of these samples was only studied in a purely elastic regime at low loads [21].

Finally, many reports of Chinese groups have appeared in the last five years, in which the synthesis of ultrahard materials based on diamond and boron nitride has been reported [82–88]. Diamond polycrystals with nanotwinned diamond were obtained at high pressures and temperatures (20 GPa, 2200 K) from a compact set of onion carbon nanoparticles [83]. Several Chinese teams subsequently produced nanotwinned diamonds using other initial materials (nanotubes, fullerites, etc.).

These activities were kindled by the synthesis of cubic boron nitride also with a nanotwinned structure and outstanding mechanical characteristics [82]. It should be kept in mind that the shear modulus of cubic boron nitride is the second largest among all materials and only inferior to that of diamond by 30% [1]. At the same time, the measured hardness of boron nitride single crystals is 2–2.5 times worse than that of diamond, which is apparently due to the easier formation and propagation of dislocations. Creating a nanostructure in boron nitride enabled an increase in its hardness to 80–85 GPa [22, 23]. These values agree well with the results of *in situ* measurements by nanoindentation [61].

According to the authors of [82], nanotwinned boron nitride has an even higher hardness: up to 108 GPa according to Vickers and 78 GPa according to Knoop. These results were subjected to intense criticism [89], to which the authors of [82] attempted to respond [90], albeit, in our opinion, not too convincingly. Moreover, the reported values significantly exceed those obtained in recent *in situ* studies of single crystals [61], according to which the ideal hardness of c-BN before pop-in is 80–85 GPa. The Vickers hardness by definition should be less than the nanohardness (due to different vertex angles of the Vickers and Berkovich pyramids) [29]; therefore, the results of [82] cannot be considered reliable.

The hardness of nanotwinned diamond samples (average thickness of twins is 5 nm), according to the authors of [83],

was (under a load of 5 N) 175-203 GPa according to Vickers and 168-196 GPa according to Knoop. The hardness was measured at loads up to 8 N, and in measuring fracture toughness, loads of 9.8 and 19.6 N were used. Neither fracture nor deformation of the Vickers indenter was observed even at such high loads [83] (which, on the contrary, were observed by the Irifune group in testing nanopolycrystals). The recordhigh hardness of nanotwinned diamonds was explained in [83] by quantum confinement effects (similar to earlier explanations of the anomalous hardness of twinned boron nitride crystals [82]). The discussion of the possible relationship between hardness and quantum confinement effects is continued in Section 4. It was predicted in the same study [83] that a further decrease in the size of twins may lead to an increase in hardness to 400 GPa (!). It should be noted that neither information on the surface roughness of the samples under study, nor the curvature radius of the indenter tip, nor photographs of the imprints were presented in [83]. It should be noted that at a load of 5 N the depth of Vickers pyramid penetration for the declared hardness should be 0.8-1.0 µm, a value that is comparable to both the roughness of the polished surface  $(0.3-1.0 \,\mu\text{m})$  and the indenter tip-blunting radius  $(0.2-0.4 \ \mu m)$ . A review by the same authors [84] announced once again that a Vickers hardness significantly exceeding 200 GPa was attained, but the obtained imprints have been neither displayed nor discussed. Imprints on the surface of ultrahard samples explored using optical and atomic force microscopes were presented in a later publication [82] (Vickers pyramid, load 9.8 N) (Fig. 13). The Vickers hardness reported for a number of samples is as high as 200-250 GPa. The imprint depth after indentation under a load of 9.8 N is as small as 0.2  $\mu$ m [85], which evidences an immense degree of elastic restoration after indentation. It should be noted that the Berkovich indenter penetration depth in the case of *in situ* nanoindentation of diamond nanopolycrystals is 0.45  $\mu$ m (twice as much) at a low load of 0.25 N (40 times smaller!) [17]. Because of the quality and profile of the imprints displayed in Ref. [82], it is not possible to draw any conclusions about the hardness with an accuracy better than 40-70%. A significant plastic deformation in the imprint is actually only observed near the Vickers pyramid vertex and edges. Given the quoted loads, indentation apparently has not yet reached the saturation regime (significant plastic deformation).

It was reported in subsequent studies [86, 87] of nanotwinned diamonds that a hardness of 300–400 GPa (!) was attained according to both Vickers and Knoop, and it was predicted that a hardness of 600 GPa (!) is attainable for twins of minimum size. Recent paper [88] also predicts unique mechanical properties of hypothetical structures based on nanotwinned diamond multilayers and cubic boron nitride.

A large number of publications by Chinese groups regarding the production of diamonds from nanotwins with a hardness of up to 400 GPa (to be increased in the future up to 600 GPa) caused well-founded criticism and many questions. First of all, the question arises as to whether materials this hard can be indented using a standard diamond indenter. To explain their results, the authors of [82–85] note that the sample undergoes tensile shear stresses during indentation, while the indenter pyramid is subject to compressive stresses. Therefore, in the opinion of the authors, the indenter can produce an imprint on a material which is five times harder than the indenter itself, since the tensile and compression strength of diamond differ by approximately the



**Figure 13.** (a) Image of the imprint on the surface of nanotwinned diamond after indentation with a Vickers pyramid (load 9.8 N) obtained using an atomic force microscope; the inset shows the optical image of the imprint. (b) Imprint depth profiles along two diagonals obtained using an atomic force microscope [85]. (The figure, from [85], is reproduced with permission of the Chinese Physical Society © 2018.)

same factor. This assertion is not quite true—the profiles of both shear and compressive stresses in the indenter and the sample are very complex and change in the process of indentation. The spherical part of the indenter operates at the initial stage of indentation, and the contact is flattened, after which the pyramidal part starts penetrating into the sample. In addition, it is necessary to take into account the friction force between the indenter and the sample, which is also different for different sections of the indenter. The indenter generates the greatest stress at a small depth beneath the contact spot and near the sharp edges of the pyramid. It is experimentally known that the plastic flow of a diamond indenter (like diamond anvils with a similar vertex angle) commences at pressures of 180-190 GPa [56], values that are almost twice the pressure at the onset of plastic deformation of a flat diamond surface beneath the indenter. This implies that the indenter in the elastic mode can indeed make a plastic imprint on a sample whose hardness is approximately twice that of the indenter. If plastic deformation and disintegration of the indenters have not been observed, this implies that the contact pressures (and hardness of the sample) were significantly less than 180 GPa. Interestingly, an insignificant plastic flow of the anvil ( $\approx 3 \,\mu$ m) is almost completely 'healed' in several years (dislocations 'emerge' on the surface) [91].

The pressure beneath the indenter, of course, can continue to increase with an increase in load also after the onset of plastic deformation of the indenter, and the maximum pressure can additionally increase by a factor of 2–2.5 [56], but the irreversible deformation of the indenter will be in this case very significant. Thus, a flat surface may be scratched by a micro-sample with sharp edges whose hardness is 3–4 times worse (the scratching particles themselves naturally also experiences severe strains and disintegrate). It is for this reason that the presence of scratches on the diamond anvil sites may not be used as evidence of the anomalously high hardness of the micro-samples that make traces (see above).

The quality of the imprints presented in [85] is, of course, not quite satisfactory; nevertheless, the authors appeal to the standard definition of hardness based on the size of the 'restored' imprint (after unloading). The fraction of elastic restoration is anomalously large, and the sizes of the restored and unrestored imprints apparently significantly differ in all studies of these diamond materials. Moreover, an elastoplastic 'healing' of the imprint may occur for a number of materials after unloading. Therefore, the quantitative results obtained using this measurement method are largely meaningless: no imprint is left on a rubber sample after indentation, but this does not imply that its hardness is infinitely high.

Thus, almost all recent reports about materials whose hardness is significantly higher than that diamond refer to carbon materials with a nanocrystalline (sometimes partially amorphous) structure. The nanostructure actually enables increasing the hardness to the 'ideal' value for elastic loading. The creation of a nanostructure in the case of cubic boron nitride makes it possible to increase the hardness almost twofold. Accurate estimates in the case of diamond are a very difficult task. The creation of a nanostructure apparently makes it possible to increase the measured hardness by no less than 20-40% (from 90-100 GPa to 120-140 GPa). At the same time, the absolute values of hardness of diamond and other carbon materials above 120-130 GPa should be treated with caution. Even the most reliable results for a Knoop hardness of 140 GPa, which were obtained by the Irifune group, relate to fairly small loads (4.9 N), when the percentage of elastic restoration is a priori high. Such values for the same loading parameters can only be considered as comparative in studying various materials.

The structure of samples obtained by Blank's, Dubrovinskii's, and Tian's groups is in many respects similar to that of the Irifune group's samples. Samples of a diamond nanopolycrystal with lamellar grains 10 nm in size are probably the hardest, since the Vickers diamond indenter disintegrates if samples are indented, even at light loads [17]. The hardness of the ultrahard carbon samples obtained by other groups are apparently slightly inferior to the hardness of these materials, since they can be indented under significant loads by a Vickers diamond pyramid without collapse of the latter. The nanotwinned structure of diamonds obtained by groups of Chinese researchers possibly facilitates very high degrees of elastic restoration of the imprint after unloading. Finally, we note that the formal 'ideal' hardness of diamond in the elastic linear mode (prior to the onset of plastic deformation) is 200–250 GPa [29]; therefore, any values of the 'restored' hardness (after removing the load) higher than 200 GPa are apparently meaningless. The absence of significant plastic deformation of the diamond indenter tip or its disintegration after indentation also implies that the hardness of the material under study could not exceed 180 GPa.

Thus, all assertions regarding the hardness of carbon materials in excess of 150 GPa should be regarded as unreliable, and the results of measuring the hardness in the range of 120–150 GPa should be treated with great caution and only used as qualitative comparative data.

#### 3.4 Are quantitative *in situ* studies

#### of the hardness of ultrahard materials possible?

So, accurate quantitative methods for measuring hardness above 100 GPa (actually, 100 GPa is the hardness of the diamond indenter itself) do not exist. At the same time, there is an accurate value of the critical shear stresses for various types of loading, at which the crystal lattice becomes unstable. Such an 'ideal' hardness in the regime of strongly nonlinear deformations can be calculated from first principles, but so far, unfortunately, with low accuracy. A cascade of dislocations or coherent twin boundaries concurrently occurs in the lattice after loss of stability, while the contact pressure and, consequently, the measured hardness sharply decrease [29]. If multiple barriers to the movement and multiplication of dislocations are created, the hardness of the sample will come close to the ideal shear strength for a given type of loading.

For example, the 'elastic' ideal hardness (determined by elastic moduli in the linear region of the theory of elasticity) for a sapphire single crystal is for the Berkovich pyramid 57 GPa; the ideal hardness in the nonlinear deformation region before the avalanche-like nucleation of dislocation loops (pop-in) is 47 GPa, and after the transition, the hardness in the plastic deformation mode is 28 GPa [29]. Even simple grinding of the sapphire surface leads to an increase in the concentration of near-surface dislocations and an increase in the measured hardness to 32 GPa, i.e., the creation of the sapphire nanocrystalline structure can apparently bring the measured hardness in the plastic deformation regime closer to the 'ideal' values before the elastic-plastic pop-in transition-up to 47 GPa [29]. The in situ nanoindentation method enables correct and unambiguous determination for most single-crystal materials of both the 'ideal' hardness (before pop-in) and the actual hardness of the sample after the pop-in transition, which is controlled by grain size, concentration of dislocations, and other defects. Materials whose hardness is close to that of diamond are an exception, since it is not possible to observe the beginning of an elastic-plastic transition in such materials, and, consequently, to determine the ideal shear strength of the material under a load of this type.

Thus, the situation with the quantitative *in situ* study of materials whose hardness is higher than 80–100 GPa is unsatisfactory. Imprints can only be analyzed after loading. If the indenter has neither experienced plastic deformation nor collapsed, imprints of normal quality can only be obtained at moderate loads, when the fraction of elastic restoration of the imprint is still very large, and the measured hardness 'has not plateaued'. The hardness values obtained in

this case could be used in comparing materials, but this is not always correct either. A material with smaller elastic moduli and lower ideal shear strength can at the same time feature a higher fraction of elastic restoration (like rubber), and the imprints obtained after indentation will formally correspond to higher hardness, although in reality the mechanical properties of the material are much worse. To compare the ideal shear strength in the indentation of various ultrahard materials, it is apparently necessary to conduct *in situ* measurements.

It should be recalled that, during indentation using a spherical indenter, the contact pressure increases as load and penetration depth increase, while in loading with a conical or pyramidal ideally hard and ideally sharp indenter, the pressure is only determined by Young's modulus of the material and the indenter vertex angle. If actual Vickers or Knoop indenters are used at the initial indentation stage, the almost spherical part (rounded at the vertex) penetrates the material. Starting with an indentation depth of 0.2–0.4 µm, the pyramidal part of the indenter is involved in the 'operation'. Plastic deformation of materials whose hardness is close to that of diamond begins at a penetration depth of 0.2–0.5 µm (see the nanoindentation curves for diamond and cubic boron nitride in [17, 61]). The regions of plastic deformation in the sample are localized in this case beneath the imprint center (at a depth of 100 nm beneath the contact) and near the pyramid edges (at a distance of about 20-50 nm from the contact point). The stresses corresponding to plastic flow in a diamond-like material will apparently emerge only at sufficiently high loads ( $\approx 0.2 - 1.0$  N), at which the indenter also begins to deform and disintegrate.

To solve the problem of the *in situ* hardness testing of ultrahard materials, in my opinion, the nanoindentation method should be revived, albeit at a new technological level. First, the maximum possible quality polishing (or etching) of the test material is required, with possibly fine finishing using an ion beam to a roughness of no more than 10-20 nm. Second, indenters should be manufactured from defect-free diamonds (type IIa). The indenter top and edges should also be 'finished' after grinding to the maximum sharpness using an ion beam. It should be noted that diamond nano-needles under loading exhibit record-high (up to 9%!) elastic deformation without fracture [92]. The curvature radius at the indenter vertex and near its edges should not exceed 20-50 nm. The pyramid type and angle optimal for indentation should be selected in the process of testing. Indentation should be carried out in the slowest loading mode. The elastic-plastic transition in an ultrahard material should occur in this case at a penetration depth of  $\approx 100$  nm at loads of less than 100 mN. Such homemade indenters will possibly enable in-depth in situ studies of the elastic-plastic transition and determining experimentally the 'ideal' shear strength of ultrahard diamond-based and other carbon nanomaterials. As mentioned above, a sharp pop-in transition is usually not observed in nanostructured materials. Nevertheless, there are methods to estimate loads that correspond to the onset of plastic deformation and measure hardness by nanoindentation using loading curves [61] (see above). Let us recall that there are successful examples of nanoindentation of ultrahard nano-polycrystalline diamonds at very high loads, up to 250 mN (penetration depth 450 nm), which already show that loading is not completely elastic [17]. Unfortunately, no quantitative processing of nanoindentation curves has been done in [17].

## 4. Myth III: quantum nanoconfinement as a 'theoretical' mechanism for creating ultrahard materials

The myth of the quantum confinement contribution to the record-high hardness of nanomaterials is arguably the most ridiculous one. It has taken shape due to the piling up of errors, incorrect interpretations, and unjustified extrapolations of various theoretical and experimental results. It should be kept in mind that empirical formulas are widely used for the 'theoretical' prediction of the hardness of a new material (see, e.g., [31]). A high concentration of defects and nanostructuring are known to impede plastic deformation and improve mechanical production characteristics: hardness, fracture toughness, wear resistance, etc. [1, 2]. These effects are usually taken into account using empirical formulas (Hall-Petch law, etc.). However, intense efforts have been made lately to develop a quantitative 'theoretical' basis for predicting an improvement in the mechanical characteristics of nanomaterials [33, 73]. For example, an additional mechanism was proposed to increase the hardness of nanostructured materials due to the effects of so-called quantum confinement [73]. 'Quantum confinement' means in this case a change in the electronic wave functions and a corresponding change in the semiconductor band gap and other physical properties of materials upon transition to nanoscale.

Briefly, the evolution of the 'theory' of an increase in hardness due to quantum confinement effects may be summarized in a positive way as follows:

(1) the activation energy of plastic deformation in semiconductors, including diamond-like ones, is associated with the semiconductor band gap width [69, 70];

(2) the same energy is proportionally related to the hardness of the material (resistance force at bond breaking), which implies that hardness is associated with the band gap width [30];

(3) an increase in the semiconductor band gap or exciton energy is observed for many semiconductor nanoparticles with a decrease in the particle size [93–99] due to quantum confinement effects (restriction of the scale of the wave function of the electron and the hole);

(4) a comparison of the results of the Kubo–Halperin theory [100] for nanoparticles with experimental data for a number of semiconductors made it possible to establish a certain universal relationship between the increase in the semiconductor band gap and the nanocrystal size [73];

(5) this ratio, along with the contribution from the Hall– Petch effect, was used later to construct the 'microscopic theory of hardness' of nanomaterials [33];

(6) the same ratio was used to explain the anomalously high hardness of nanotwinned cubic boron nitride and nanotwinned diamond [82, 83];

(7) it was predicted that for minimum-size twins in diamond the contribution to hardness due to confinement effects is over 300 GPa, which, along with the possible contribution from the Hall–Petch effect (about 200 GPa), should result in a possible hardness of nanotwinned diamonds of up to 600 GPa [82–87].

This series of arguments at first glance looks nice and to some extent convincing, but in reality each of the above points contains errors and falsifications, in several points blatant.

First, the absurdity of the numbers in item 7 is immediately evident. The fourfold increase in hardness, and hence

**Figure 14.** Activation energy of the plastic flow of covalent diamond-like semiconductors as a function of the semiconductor band gap width [69]. (The figure is reproduced from [69] with permission of AIP Publishing © 1975.)

the shear modulus, due to the effects of quantum confinement is predicted. This implies that actually the local density of valence electrons should increase by a factor of four. At the same time, the confinement effects are a change in the envelope of the wave function of electrons on a cluster-size scale. This change slightly modifies the electron spectrum, but can only change the local electron density on covalent bonds by a few percent. We now analyze all the items in more detail.

Researchers noticed in the early 1970s that the activation energy for plastic deformation of covalent crystals with a diamond-like lattice is close to double the semiconductor band gap width [69] (Fig. 14). This observation actually implies that for a dislocation loop to emerge a covalent bond should be broken, which in turn leads to the excitation of two valence electrons and their transition to the conduction band. This simplified picture was later subjected to constructive criticism [71, 72]. It turned out that the simple relation between the plastic flow activation energy and the band gap width fails for narrow-band-gap semiconductors: the activation energy remains finite when the band gap width tends to zero [71]. It was found next that a correct description of plasticity activation parameters requires taking into account not only the band gap size but also the value of the Pugh coefficient G/B [72]. In most studies on this subject, researchers were primarily interested not in the absolute magnitude of hardness but in its temperature dependence at high temperatures, although a correlation between hardness at moderate temperatures and the semiconductor band gap width was also noted [69].

F Gao et al. [30] revived 30 years later the idea of a correlation between hardness and the semiconductor band





Figure 15. (Color online). (a) Illustration of the response of bonds between atoms in indenting. (b) Excitation of two electrons in the valence band accompanied by the breakdown of a covalent bond and subsequent transition to the conduction band. (c) Spatial distribution of valence electrons for purely covalent and polar coupling. (The figure, from [33, 84], is reproduced with permission of Elsevier © 2012.)

gap width for semiconductor crystals. The role of high temperature is played in this approach by the indentation process itself: bonds break in the plastic deformation mode, and hardness is approximately proportional to the covalent bond energy (Fig. 15). Such a model is, of course, applicable to a very narrow class of substances and fails to describe the high hardness of metal borides and carbides. This correlation (for a narrow class of substances) is in principle quite justified and is no worse than other models. Indeed, a high degree of covalence and a large band gap imply a high electron density (and, hence, high values of elastic moduli) and a high degree of electron density localization (and, therefore, a large value of the G/B ratio) [2]. F Gao group's ideas regarding the relation between hardness and the magnitude of the semiconductor band gap and the ideas of X Chen et al. on the importance of the Pugh coefficient G/B [31] have been combined and further developed in a number of studies (see, e.g., [32]). The only problem is that none of these correlations is rigorous, and that the formulas based on them should only be regarded as empirical.

The awareness of the relationship between the mechanical characteristics of covalent crystals and the semiconductor band gap width stimulated at the same time the emergence of new ideas regarding the mechanism of the effect of nanostructure on the hardness of substances. Reference [73] was pioneering in this regard. To explain the increase in hardness of nanocrystalline diamonds compared to that of ordinary single crystals, the authors of [73] considered instead of the well-known Hall–Petch effect the option that hardness grows due to an increase in the semiconductor band gap, which in turn is driven by quantum confinement effects. However, a number of unfounded assumptions were made in this approach.

The Kubo theory [100] is used to calculate the increase in the band gap in an individual nanocrystal. This step is, at the very least, strange. First, electronic levels of *metal* nanoparticles are considered in the cited review by V Halperin [100], and the formula taken from this review and used in Ref. [73] is nothing but a trivial energy difference between levels that is equal to the Fermi energy divided by the number of electrons. This value is extremely small ( $\sim 1 \text{ meV}$ ) even for particles with a size of  $\sim 1 \text{ nm}$ , and the effects considered in review [100] have nothing to do with quantum confinement in semiconductors—they can only manifest themselves in metal nanoparticles at very low temperatures. Second, this energy 'gap' is, of course, inversely proportional to the



**Figure 16.** Coefficient that determines the increase in the semiconductor band gap width due to quantum confinement effects as a function of the cluster size [73]. (The figure, from [73], is reproduced with permission of the American Physical Society © 2006.)

number of atoms and simply the nanoparticle volume  $(\delta \sim 1/V)$  [73, 100]. Third, the additional energy  $\delta$  is replaced in [73], without any explanation, with a quantity  $\delta_P$  that only differs in the ad hoc dimensionless parameter K, which, moreover, may depend in an unknown way on the nanoparticle size (!). The authors of [73] then approximate a set of heterogeneous data [96-98] on the increase in the exciton energy and the band gap for nanocrystals of several semiconductors as a function of their size (Fig. 16). A conclusion is made as a result in [73] that the increase in the semiconductor band gap energy for nanocrystals of semiconductors can be described by a certain universal dependence, and this increase is inversely proportional to the nanocluster size rather than volume, as is the case in the original study [100]. This implies that the increase in hardness due to nanoconfinement effects is also inversely proportional to the nanocrystal size  $D: \Delta H \sim 1/D$ . The major part of the data shown in Fig. 16 was taken from [97], where an increase in the exciton energy with a decrease in the cluster size of the CdS semiconductor was observed, which is only indirectly related to an increase in the semiconductor band gap. However, the theoretical consideration suggested in Ref. [73]

has in reality no relation whatsoever to the theory of quantum confinement in semiconductor materials.

The concept of quantum confinement has been known since the mid-20th century. The general idea of confinement is that, if the spatial scale of the electron wave function (or de Broglie wavelength of the carrier) becomes comparable in some dimension to the size of the particle (cluster), the energy spectrum of carriers may change due to a change in the boundary conditions for the wave function. The quantum confinement effects for semiconductors often imply as well a change in the exciton spectrum for small clusters, since the luminescence spectra (de-excitation of the exciton) provide basic experimental information. These effects become significant when the Bohr radius of the exciton (the bound state of an electron and a hole) is comparable to the nanoparticle size. It should be noted that there is no direct relation between the exciton energy and the semiconductor band gap width, although in most cases they are correlated. The quantum confinement effects are, to some extent, threshold, albeit smooth, phenomena. An accurate theoretical description of the energy shift of bands and changes in the carrier spectrum due to quantum confinement effects is a rather challenging problem [101-104]. The increase in the effective semiconductor band gap in the nanocluster has, in any case, no relation whatsoever to the Kubo theory or the Halperin review [100] and is in no way described by the equations from [73]. The main contribution to the energy shift, naturally, is made by the term that corresponds to the kinetic energy, which is inversely proportional to the cluster size squared rather than cubed (as in [100]) or simply to cluster size (as in [73]). The correct kinetic quantum contribution differs from the formula in [73] by the factor D/a, where D is the nanoparticle size and *a* is the interatomic distance.

Rapid development of the concept of quantum confinement occurred in the early 1990s in connection with the production and study of porous silicon [93–95]. Strong luminescence was observed in porous silicon samples, which are an aggregate of weakly coupled filament-like nanoclusters, both the valence and conduction bands being significantly shifted with respect to those for bulk silicon samples. An explanation for the observed effects involved quantum confinement of electrons (and holes) in porous silicon [93–95]. Further studies showed that silicon nanoclusters obtained by other methods also exhibit an increase in the exciton energy and an increase in the effective semiconductor band gap as the cluster size decreases [96].The increase in the band gap for ultra-small clusters ( $\sim 1$  nm) is approximately 1 eV.

It should be noted that the data from various studies disagree with each other due to the complexity of the characterization and exploration of nanoparticles and the effect of chemical impurities that are inevitably present on the cluster surface.

The influence of dimensional quantum effects on the exciton energy was studied in detail for CdS semiconductor clusters varying in size from 1 to 6 nm [97]. An increase in the exciton excitation energy of about 1 eV was detected for the smallest clusters, i.e., approximately 30% compared with a bulk semiconductor (Fig. 17). Attempts were made to theoretically describe the results obtained for CdS both in the original paper [97] and in subsequent studies, e.g., in [104]. Possible effects of nanoconfinement for diamonds were explored in only a few studies both for individual clusters [98] and for island nanofilms [99]. A significant increase in the band gap (of about 10–20%) was only observed for ultra-



**Figure 17.** Exciton energy for CdS nanoclusters as a function of cluster size according to [97]. (The figure is reproduced from [97] with permission of the American Physical Society © 1990.)



**Figure 18.** Energy of the conduction band edge  $E_{CB}$  and the exciton state energy  $E_{ex}$  as a function of the nanodiamond crystal size (in the inset, the exciton energy shift as a function of the cluster size) [99]. (The figure, from [99], is reproduced with permission of the American Physical Society  $\bigcirc$  1999.)

small diamond clusters (1–2 nm) [98, 99] (Fig. 18). An important role is played in this case by surface atoms, the number of which is comparable to the number of atoms inside the nanoparticle. The cluster surface structure is also rearranged in the case of diamond nanoparticles into a fullerene-like structure, a phenomenon that also affects the observed effects [98] (Fig. 19).

A significant increase in the band gap is observed for all the studied semiconductor nanocrystals with cluster sizes of less than 1-3 nm, and the maximum increase in the



**Figure 19.** (Color online.) Illustration of the restructuring of the nanodiamond surface into a fullerene-like structure according to calculations based on the first-principles [98]. (The figure is reproduced from [98] with permission of the American Physical Society © 2003.)

semiconductor band gap is approximately 20–40%. It should be noted that the increase in the band gap is not directly related in this case to hardness or impeded plastic deformation. First, the correlation between the band gap size and the energy of bond 'breaking' is largely empirical. The entire picture of electron density should actually be considered. As the particle size decreases to the nanoscale, an increase in the lattice parameter is usually observed, and the bonds become kind of effectively stretched, a phenomenon that may result in an increase in the semiconductor band gap, but the bond energy does not increase and, moreover, in many cases it decreases. Second, dislocations in nanocrystal can hardly emerge at all with such a nanocrystal size [105], and a conglomerate of nanoparticles can exhibit super-elastic behavior even at ultra-high pressures [106].

Moreover, quantum confinement effects are only observed for individual nanoparticles or loosely coupled cluster aggregates. The boundary conditions for the electron wave function at the grain boundary radically differ in the case of a nanopolycrystal from those for a free surface, and no reliable data on the increase in the semiconductor band gap in any bulk nanopolycrystal are available. The coherent twin boundaries considered in [82–87] stand apart in this regard, since the structural-disorder effects at the boundaries of such twins are minimal, and any dimensional effects of quantum confinement are completely irrelevant. Moreover, twin boundaries, on the contrary, may perform themselves as agents of plastic deformation under load.

As noted above, empirical formulas for quantum confinement effects were added in further studies to the 'new' 'microscopic theory' of hardness [33], which allegedly made it possible to explain the 'observed' hardness of 200–300 GPa and 'predict' possible further increase in hardness in nanomaterials up to 600 GPa [82–87].

The absence of any significant quantum confinement effects for bulk nanopolycrystals, especially those with coherent boundaries between grains, is, of course, a strong argument against the 'new' theories of hardness. However, this argument is actually not required in this case. The situation is even more ludicrous. The 'fundamental' empirical equations (6) and (7) in [73] for the increase in the band gap and hardness due to the growth of the band gap contain the cluster size D measured in angstroms. The same formulas with the same coefficients were reproduced one-for-one in the main 'theoretical' work of the Chinese group [33] (see Eqns (18) and (19) there) and were used in all subsequent articles on ultrahard materials. However, the nanocrystallite

size *D* in all these studies is measured in *nanometers* rather than *angstroms*! This implies that the hypothetical contribution due to nanoconfinment apparently was inadvertently enhanced by a factor of 10. It follows from the formulas derived in [73] that the maximum hypothetical increase in the gap and hardness in the obtained nanotwinned diamond at a twin thickness of 5 nm = 50 Å (as in Ref. [83]) may not exceed 5%. As mentioned earlier, the increase in the band gap does not exceed 20% even for ultra-small diamond clusters ~ 1 nm in size [98, 99]. Let us recall that the estimated contribution of the size effect to hardness found in original study [73], where a mechanism for increasing hardness due to quantum confinement was proposed, was precisely 10–20% for minimum crystal sizes of 1–1.5 nm.

Thus, the 'nice' model of the effect of 'quantum confinement' on the hardness of semiconductor materials described at the beginning of this section should be corrected as follows.

(1) The activation energy of plastic deformation for a number of covalent crystals correlates with the semiconductor band gap width, although this correlation is not strict.

(2) The measured hardness and the semiconductor gap width are correlated for certain classes of semiconductor materials, but this correlation is even less precise than that of item 1.

(3) An increase in the exciton energy and band gap size is observed in many semiconductor nanoparticles (clusters) as the cluster size diminishes to the nanometer range. This increase is only observed for individual or weakly bound clusters and has never been observed for bulk nano-polycrystalline material.

(4) The behavior of the band gap depends in a complex way on the cluster size and the structure of its surface and is in no way connected with the Kubo–Halperin theory [100].

(5) There are no grounds to use data on quantum nanoconfinement in small clusters to explain a possible increase in hardness in nanopolycrystals.

(6) The hypothetical effect of quantum confinement on the hardness of nanotwinned diamond and cubic boron nitride is overestimated by a factor of 10 due to the incidental (or intentional) replacement of units used for measuring the cluster size.

(7) Nanostructuring actually provides an increase in hardness by a factor of 1.5-2 for most materials and by 20-40% for diamond, but only due to the well-known Hall–Patch effect, known for a long time (inhibition of dislocations).

Consequently, there are no actual scientific grounds for an additional increase in hardness in nanopolycrystals due to quantum confinement effects.

## 5. Conclusion

Summarizing the content of this review, it may be concluded that diamond still remains the hardest material under normal conditions and the record holder as regards elastic moduli. Moreover, shown here was the fundamental impossibility of creating in the future any materials whose elastic moduli and hardness would be significantly (severalfold) larger than those of diamond. Consequently, any assertions regarding obtainment of new ultrahard substances with giant elastic moduli cannot be considered scientifically reliable. At the same time, a number of production characteristics associated with the structure of materials at the nano- and mesoscale levels, such as wear resistance, fracture toughness, and heat resistance, can actually be several times larger due to the formation of a special morphology of grains, defects, etc.

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