Theoretical Strength and Cleavage of Diamond

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The theoretical strength of diamond has been calculated for the ⟨100⟩, ⟨110⟩, and ⟨111⟩ directions using a first principles approach and is found to be strongly dependent on crystallographic direction. This elastic anisotropy, found at large strains, and particularly the pronounced minimum in cohesion in the ⟨111⟩ direction, is believed to be the reason for the remarkable dominance of the {111} cleavage plane when diamond is fractured. The extra energy required to cleave a crystal on planes other than {111} is discussed with reference to simple surface energy calculations and also the introduction of bond-bending terms.

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For centuries, people involved in the handling and shaping of diamond have been aware of the tendency for diamond crystals to cleave quite easily when they are struck by a well-oriented blow parallel to certain planes. There is no shortage of experimental evidence demonstrating that the fracture of diamond occurs predominantly along a preferred set of planes [1–7], and many mineralogical texts describe its cleavage as perfect, yet a definitive explanation has not emerged. The scale of observations ranges from the remarkably flat (or stepped) surfaces often produced by whole-crystal cleavage, to the microscopic, distorted "ring" cracks that appear upon Hertzian loading of diamond surfaces.

In an attempt to explain the "easy" or {111} cleavage of diamond, Ramaseshan [1], and more recently Field [8,9], employed the method used by Harkins [10] to calculate the energies required to cleave a crystal parallel to a particular plane. The cleavage energy was assumed equal to twice the surface energy of that plane. In this approximate method, the energy is calculated as the number of bonds cut per unit area multiplied by the thermodynamic energy of the carbon-carbon bond, irrespective of whether the "cut" is at an angle to the bonding direction. As the bond density on {111} planes is the lowest, the cleavage energy of these planes is the lowest. However, as Ramaseshan has pointed out, the cleavage energy calculated in this way is not greatly different from that for other nearby planes, e.g., (332), which is only about 10% higher. Bearing in mind the fact that in the crude method used for cleaving diamonds the energies employed may be much in excess of what is required to effect cleavage in any direction, one would expect to have a fracture rather than a perfect cleavage. Ramaseshan then revised this simple model, based on the fact that there are two distinct atomic planes parallel to {111} with spacings in the ratio 1:3. The number of bonds cut per unit area is 3 times smaller on the widely spaced planes than for the narrowly spaced planes. He then suggested that cleavage on the former type of plane is bound by the heavily bonded planes above and below, imposing upon any planar deviation, "a threefold increase in energy." However, if the simple bond-cutting ideas were the whole story, a crack could, in principle, easily avoid this energy barrier by following atomic-sized steps in the desired crystallographic direction, especially if favored by the applied stress field.

Ansell [11] proposed an explanation for {111} cleavage based on the idea that maximum relief of nonbonded, repulsive interactions accompanies the separation of such planes. Indeed, nonbonding interactions can be responsible for the rotation of free molecular structures in adopting low-energy/low-strain configurations. For example, the hydrogens in ethane on opposing carbons avoid eclipsing each other as viewed along the C-C axis. As a result of this type of interaction, O'Keefe and Hyde [12] argue that there is an effective compression normal to the {111} planes in diamond. Ansell then describes the process of fracture as proceeding by a chain reaction whereby the C-C bonds adjacent to a ruptured bond "keel over" as a result of the repulsion from their immediate nonbonded neighbors.

The process of cleavage can be influenced by nonbonded interactions for the case of heteroatom, and therefore partially ionic, isostructural compounds, e.g., ZnS [13,14]. Here, because of electrostatic dipolar interactions, cleavage is found predominantly on {110} planes such that the separated plane is electrically neutral. In such cases the eclipsed bond repulsions are easily overcome. Nonbonded interactions are smaller in magnitude and range when compared with the superior bonding interactions, and in a strong homopolar solid like diamond their contribution will be very small. Their influence may aid the confinement of fracture to {111} during dynamic growth, but this is almost certainly a secondary effect and does not adequately explain the cleavage phenomenon.

A further explanation for the dominant cleavage plane of diamond is that fracture follows planar weaknesses caused by faulted growth and/or impurity incorporation along {111} since these are the primary growth planes of natural diamond. Cleavage surfaces on diamonds with few impurities but a large number of dislocations are found to be more orderly and perfect than on diamonds with these characteristics reversed [3]. However, there is no clear picture yet as to the role of impurities and defects on the room-temperature fracture behavior of diamond. In this work we show that the cleavage behavior can be satisfactorily

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explained without resorting to the influence of defects and thus the phenomenon is intrinsic to the diamond lattice. Of course, this is not to say that defects will have no effect.

Abraham and Gao [15] have explored the fracture behavior of fcc crystals using powerful molecular dynamics simulations. In particular, they examined the competition between ductile and brittle failure in metals and rare-gas solids with interatomic interactions described by empirical potentials. They too note the failure of simple surface energy arguments to explain cleavage behavior and turn instead to the strong anisotropy in elasticity near the cohesive limit as their explanation. The essence of their approach is adopted here; however, their results are not directly applicable to covalent solids. Note that the interatomic potentials for diamond are not spherically symmetric as they are for metals and rare-gas solids, so that our analysis necessarily differs from theirs in this regard.

To separate a diamond crystal along $\{111\}$, we can more or less justify the approach of Harkins. Here, the direction of the tension is parallel to a bonding direction $\langle 111 \rangle$, and thus the energy to separate each pair of atoms to infinity is essentially the radially directed work done (strain is accommodated predominantly by the parallel bonds). However, to separate the crystal on a $\{100\}$ plane, for example, the forces are resolved through an angle of 54.74° onto the C–C bonds. In the case of $\{110\}$ the angle is 35.26°. Thus we can see qualitatively that more energy must be supplied to break the crystal. This arises from the work done in bringing the nonbonded atoms closer together and in rotating the bonds, schematically illustrated in Fig. 1.

To determine the magnitude of this effect we have used a parameter-free, first principles, quantum mechanical technique to describe the intrinsic strength of diamond. The calculations were performed using density functional theory [16,17] within the plane-wave pseudopotential approach [18]. In particular, the so-called ultrasoft pseudopotentials of Vanderbilt [19] were used to efficiently describe the electron-ion interaction. The exchange and correlation energy was evaluated using the local density approximation with Perdew-Zunger parametrization [20]. The total energy was converged to 0.1 eV per atom, and the stress [21] to about 5 GPa with respect to changes in the size of the basis set and quality of Brillouin zone integration. Appropriate cuboid unit cells were used for each set of calculations, and the internal coordinates were fully relaxed for each applied strain (strictly necessary for the $[111]$ stretch). Poisson contractions were made until the total energy and the orthogonal components in the output stress tensor were minimized for a given strain.

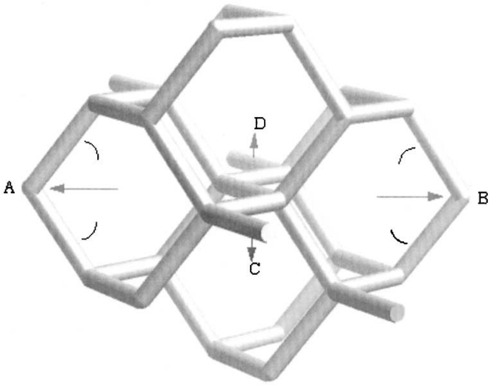

FIG. 1. Perspective section of diamond crystal schematically illustrating uniaxial tensions parallel to $\langle 100 \rangle$ (in the direction of a line through points A and B) and $\langle 110 \rangle$ (along the zigzag in the direction CD) clearly showing the tendency for strain accommodation as the crystal is stretched. The curved lines indicate the bond-bending tendency for $\langle 100 \rangle$ tension.

The total energies and the uniaxial stresses are plotted as a function of the applied strain (Fig. 2). The points of inflection in the total energy plots correspond to the maxima in the stress. These maxima are then taken as the limits of crystal cohesion, i.e., the maximum strengths. Figure 3 illustrates the change in electron distribution caused by a large uniaxial strain in the $[111]$ direction. It is clear from Fig. 2 that a strong anisotropy exists in the intrinsic strength of a diamond crystal. For tension parallel to $[100]$ the strength and strain to failure are highest, followed by $[110]$ then $[111]$. The maximum strengths are 225, 130, and 90 GPa, respectively.

Using a semiempirical method whereby the stress-strain relations were found using experimentally determined elastic constants up to third order in strain, Whitlock and Ruoff [22] calculated strength values of 98.4, 53.6, and 52.6 GPa for the $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ directions, respectively. These values appear to be low given that experimentally a tensile strength for fracture of 60 GPa has been recorded at the edge of contact of a 2.5 μm

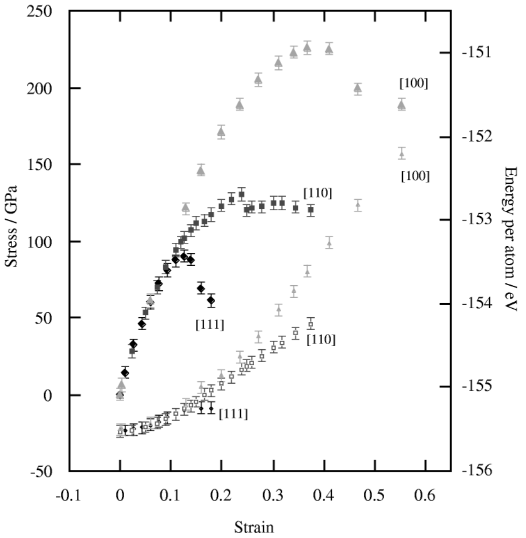

FIG. 2. Theoretical data for the uniaxial stress (upper curves) and the total energy per atom (lower curves) plotted as a function of the uniaxial tensile strain for the [100], [110], and [111] directions.

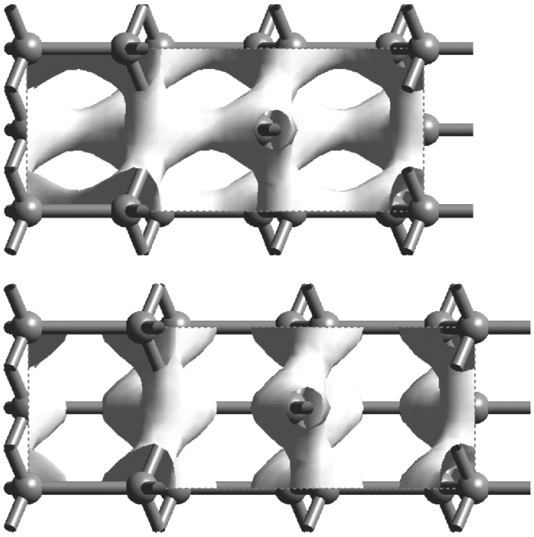

FIG. 3. Surface plots of the valence charge density at 1.2 electrons per angstrom^3 superimposed onto the diamond cell stretched in the [111] direction and viewed from the [112] direction. The strains from equilibrium are 0 in the top picture and 0.125 in the bottom picture. The charge density between the atoms is clearly depleted at the larger strain (corresponding to a point just past the maximum stress) which is consistent with the covalent bonds having been broken.

radius Hertzian indenter and a diamond flat [23]. Their predictions may be low as a result of uncertainties in the values for the elastic constants or due to the absence of higher-order terms in their calculation (especially given the magnitudes of the strain). More significantly, they did not predict a large strength anisotropy in diamond, particularly, little difference between the $\langle 110\rangle$ and $\langle 111\rangle$ directions.

It should be pointed out that although {111} cleavage is by far the most commonly observed fracture plane, {110} fractures can be observed in diamond. For example, these have been observed in compressive loading of diamond grits [24] and also under sharp indentations [25] or blunt indentations at elevated temperature [26], where shear stresses and plastic flow are thought to dictate the failure and the stress fields are inhomogeneous.

For the equilibrium growth of a crack we may, to a first approximation, equate the stored elastic strain energy up to the point of fracture with the potential energy of the two fracture surfaces produced. This energy, proportional to the area under each of the curves in Fig. 2 and bound by a vertical line drawn at the appropriate breaking strain, will more or less determine the propensity for fracture normal to that direction (strictly, it will be determined by the given resolved stress and the surface energy related fracture toughness of given planes ahead of the crack tip). We find the ratio of these energies as approximately 7:2.8:1 for the planes {100}:{110}:{111}, respectively. This compares with the modest ratio 1.73:1.22:1 found using the method of Harkins. Thus, even when a stress is applied uniaxially at a large angle to the {111} we would, on the basis of our calculations, still expect fracture to proceed along these “easy cleavage” planes. For example, the farthest angle away from {111} to resolve an applied stress is 54.74°, corresponding to tension applied normally to a {100} plane. The resolved stress on {111} is then about 0.6 of the stress on {100} and 0.8 of the stress on {110}. These reductions in stress, however, are insufficient to favor fracture on these other planes given their significantly larger stresses and energies to fracture. We might expect the ensuing fracture to be macroscopically parallel to {100} but composed of stepped {111} surfaces. Experimental studies [7,27] on apparently noncrystallographic fracture surfaces in diamond-structure crystals have found that, on a microscopic level, such surfaces are indeed stepped.

We have shown that in diamond the intrinsic strength varies significantly with the direction of tensile stress applied to the crystal, despite only a modest variation in Young’s modulus (using averaged experimental constants [28,29] we get values of 1050, 1165, and 1207 GPa in the {100}, {110}, and {111} directions, respectively). The high resistance of the bonds in diamond to angular distortion certainly contributes to the macroscopic strength anisotropy (diamond generally has a very low Poisson ratio: minimum value $= 0.007\,86$ for in-plane $\langle 110\rangle$ strains arising from a stress applied in a {100} plane, maximum value $= 0.115$ for out-of-plane strains in the $\langle 110\rangle$ direction for stress applied in a {100} plane; the averaged value over all directions is 0.0691 [30]). This resistance to distortion can be attributed to the absence of nearby, unfilled electronic states, thus making distortion of the sp^3 hybrid costly in terms of energy [31].

In conclusion, the dominance of {111} cleavage in the fracture of diamond is explained by the markedly lower strength and energy for fracture on these planes. This is inferred from first principles calculations and also qualitatively explained by strain accommodation and the introduction of powerful “bond-bending” energy terms upon stretching the crystal away from the $\langle 111\rangle$ direction.

This work could be extended to examine the strength anisotropy of other highly brittle, elastic solids. Of particular interest would be the case of partially ionic crystals with the sphaelerite (ZnS) structure, e.g., cubic boron nitride, and whether the shift to {110} cleavage is observed. Examining the role of common impurities such as hydrogen and nitrogen on the mechanical properties of diamond would also be very informative.

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