

Instabilities in Diamond under High Shear Stress

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We investigate, through first-principles calculations, lattice instabilities induced in diamond by the application of high shear stresses. For shear stresses as low as 95 GPa a lattice instability will occur, leading to graphitelike layered structures. This effect is highly anisotropic. The reversal of the direction of the applied shear forces may cause a change of 80 GPa in the shear stress value at which the instability develops. The same reversal also causes different bonds to be broken, resulting in a drastic change in the orientation of the resulting graphitelike structures. We also find that an additional compressive stress of 50 GPa along the (111) direction does not eliminate the shear-induced instability.

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Elemental carbon is known to occur in graphite, diamond, and fullerene-nanotube structures [1]. Among those, graphite is the most stable structure at low pressures, but diamond becomes the most stable one [2,3] at high pressures. This allows the synthesis of diamond from bulk graphite at high pressures [4]. For hypothetical pressures in the thousand-GPa range, transitions to other carbon structures may also be possible [5,6]. The effect of high compressive [7,8] and extensive [9] stresses on diamond have also been investigated theoretically, as well as the role of stress in the formation energy of dislocations in diamond [10].

Recently, the observation of graphitelike vibration properties in a region of a diamond sample subjected to indentation by a diamond tip has been reported [11]. A possible reason [11] for this surprising diamond-graphite transformation is the existence of high shear stresses in the indentation region or in the diamond tip. In this Letter we investigate theoretically, from first-principles calculations, the stability of the diamond structure under a high shear stress. According to our results, shear stresses as low as 95 GPa will cause a lattice instability in the diamond structure leading to graphitelike layered structures. This effect is highly anisotropic: For shear perpendicular to the (111) direction, the reversal of the direction of the applied shear forces may cause a change of 80 GPa in the shear stress value at which the instability develops. The same reversal also causes different bonds to be broken, resulting in a drastic change in the orientation of the resulting graphitelike structures. We also find that an additional compressive stress of 50 GPa along the (111) direction does not eliminate the above-mentioned instabilities. Instead, the compressive stress just increases the minimum critical shear stress, at which the instability develops, by 14%.

Our total-energy calculations are based on the density-functional theory (DFT) [12] and first-principles pseudopotential approach. For the exchange-correlation potential we use the generalized-gradient approximation (GGA) [13]. We make use of norm-conserving Troullier-Martins [14] pseudopotentials in the Kleinman-Bylander

factorized form [15]. The calculations have been performed with a method [16–18] shown to be appropriate for the study of carbon structures [19–21]. Finite-range numerical pseudoatomic wave functions, of the type introduced by Sankey and Niklewski [22], are used to build the atomic-orbital basis sets [23]. A split-valence double- ζ basis set [24] is employed. Test calculations were performed for stress-free diamond and graphite. We obtain bond lengths of 1.554 Å and 1.436 Å for diamond and graphite, and a graphite c/a ratio of 2.730. These compare well with the corresponding experimental results [25] of 1.545, 1.421, and 2.726 Å. We also obtain that the graphite structure is more stable than diamond by 0.022 eV/atom. By adding a zero-point vibrational energy correction [26], the resulting energy difference of 0.036 eV/atom compares well with the experimental estimate [27] of 0.002 Ry/atom.

In our calculations, we consider the diamond lattice subjected to a stress that induces a combination of shear strain perpendicular to the (1, 1, 1) direction and a compressive strain along the (1, 1, 1) direction. This is partly motivated by the experimental situation in Ref. [11], where the indentation is performed on the (111) surface of a diamond crystal. First, let us consider only the effect of a pure shear stress. We will consider two possible directions of the stress, σ and $-\sigma$, defined below. In Fig. 1(a) we show a projection of the diamond lattice in which the y axis is the (1, 1, 1) direction and the x axis is the (2, -1, -1) direction. The (1, 1, 1) and (1, -1, -1) bonds lie in the plane of the paper. In that coordinate system, our choice for positive σ is given by $\sigma_{12} = \sigma_{21} > 0$, the other components of the stress tensor being null. This choice corresponds to the directions of the shear force vectors indicated schematically in Fig. 1(a). The main effect of a small, positive σ is to induce a shear to the left in the horizontal {111} planes in Fig. 1(a), relative to the planes below. For larger values of σ , other effects appear, as we shall see below.

For each value of the stress tensor, corresponding to a given value of σ , we fully optimize the atomic coordinates and the lattice translation vectors. The geometry

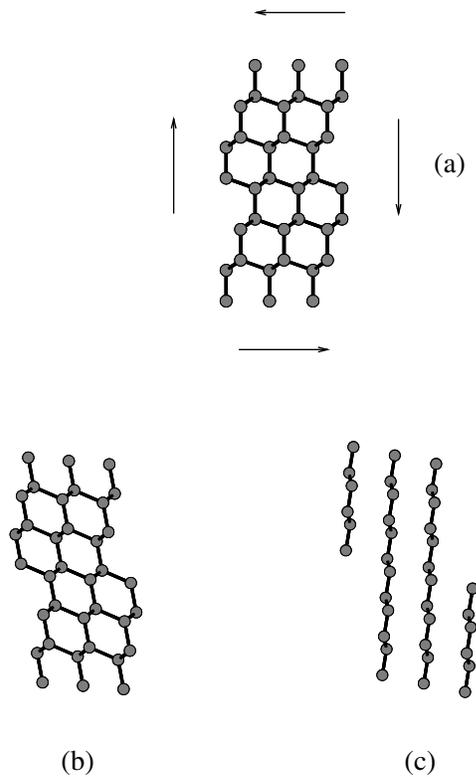


FIG. 1. Deformation of the diamond lattice under shear stresses corresponding to positive σ , as defined in the text. The vertical direction in the figure corresponds to the $(1, 1, 1)$ crystalline direction and the horizontal direction in the figure to the $(2, -1, -1)$ crystalline direction. (a) Lattice for zero stress. The arrows indicate the directions of the shear forces corresponding to our choice of positive σ . (b) Lattice geometry corresponding to the critical stress of 95 GPa. (c) "Snapshot" of the graphitelike instability driven by small perturbations at the critical stress.

optimization is performed with the conjugate-gradient method, considering the atomic coordinates and the components of the lattice translation vectors as a set of generalized coordinates [24]. The components of the gradient of the total energy with respect to the atomic coordinates are given by the negative of the forces on the atoms. The components of the (constrained) gradient with respect to the lattice vectors are obtained from the calculated stress minus the target stress (which is the only constraint in the calculation). The geometry optimization is performed by searching for the zeros of the projection of the gradient along the successive directions of the conjugate-gradient procedure [28].

Figure 1 shows the deformation of the diamond lattice under positive σ . In Fig. 1(a) we show the lattice for zero stress. As the stress increases, the lattice deforms to a stable geometry until a critical stress is achieved, beyond which the lattice is unstable. The lattice geometry corresponding to the critical stress of 95 GPa is shown in Fig. 1(b). For this critical stress value, the lattice is unstable with respect to small perturbations. The corresponding lattice instability leads, in the dynamics of

the conjugate-gradient procedure, to graphitelike layered structures which continuously increase in volume as the instability develops. In Fig. 1(c) we show a "snapshot" of this instability corresponding to an increase of 9.5% in the cell volume, with the atomic positions optimized to the energy minimum. It is clearly a layered structure, with small intralayer bond lengths (1.46, 1.46, and 1.48 Å) and a large interlayer bond length (2.16 Å). This interlayer bond length is, in fact, already larger than the breaking-bond length at the saddle point in a diamond-graphite transformation [3]. That is, this structure can be considered as graphitelike rather than diamondlike. In Fig. 1(c), we emphasize the layered nature of the graphitelike structure by depicting only the intralayer bonds. One can see that the graphitelike planes are almost vertical in the figure. This results from the stress-induced breaking of the $(1, -1, -1)$ bonds of the diamond structure.

We have also investigated the deformation of the diamond lattice under negative σ . This corresponds to forces opposite to those in Fig. 1(a). We shall mention that there is no reversal symmetry in this specific problem. In fact, the critical stress for negative σ is 175 GPa, which is 84% larger than the one for positive σ . The lattice geometry at the critical stress is shown in Fig. 2(a). At the critical stress, the lattice also becomes unstable upon small perturbations. The instability leads, as in the previous case, to a graphitelike lattice. A snapshot of this instability is shown in Fig. 2(b). One can see that, unlike in the previous case, the graphitelike planes are almost horizontal in the figure. This results from the stress-induced breaking of the $(1, 1, 1)$ bonds of the diamond structure.

We have also considered the deformation of the diamond lattice under a combination of positive σ and a compressive stress along the $(1, 1, 1)$ direction. We fixed the compressive stress to a constant value of 50 GPa and varied the shear stress to verify if the shear-induced instability still exists under compressive stress. We found that the instability still exists and that the critical stress value is

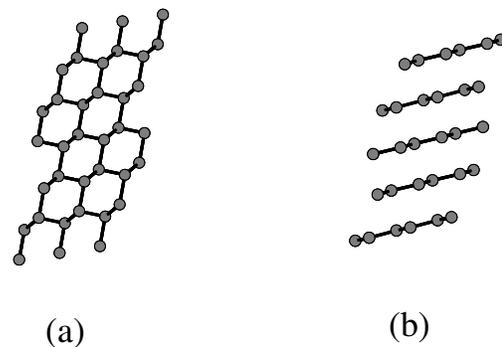


FIG. 2. Deformation of the diamond lattice under shear stresses corresponding to negative σ , as defined in the text. (a) Lattice geometry corresponding to the critical stress of 108 GPa. (b) "Snapshot" of the graphitelike instability driven by small perturbations at the critical stress.

108 GPa, which corresponds to a 14% increase relative to the case without compressive stress. Such a small increase is a surprising result, because pressure strongly favors diamondlike structures over graphitelike structures [3]. We propose that the explanation for the small increase of the critical stress lies in the orientation of the graphitelike layers of the instability-induced structures relative to the applied compressive stress. The orientation of such layers is very similar to that of Fig. 1(c). That is, the compressive stress is almost parallel to the graphitelike layers, and therefore it barely affects the bonds that are being broken. As a result, the effect of the compressive stress is relatively small [29].

In the three cases considered (positive or negative σ , and additional compressive stress), the applied stress causes the increase of one bond length relative to the others. This is shown in Fig. 3, where we plot the long bond length as a function of the applied shear stress. For positive σ , the $(1, -1, -1)$ diamond bond is the one that increases the most under stress. For negative σ , the $(-1, 1, -1)$ and the $(-1, -1, 1)$ bonds are the long ones for stresses up to 171 GPa, and for stresses above that the $(1, 1, 1)$ bond length (which is the one we depict in Fig. 3) becomes the largest. Figure 3 clearly shows that the shear stress due to positive σ is much more effective in causing a bond elongation than that due to negative σ . This partly explains the smaller critical stress in the former case. The figure also shows that the effect of an additional compressive stress of 50 GPa on the long bond lengths is relatively small, which is consistent with its small effect in the critical stress value.

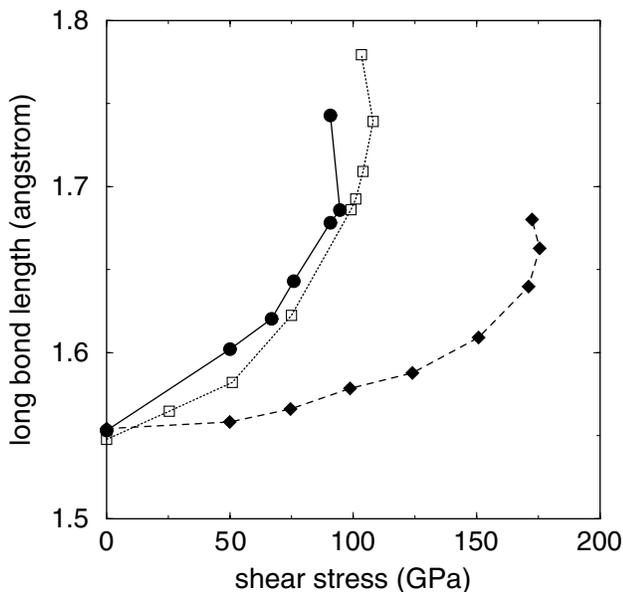


FIG. 3. Long bond length in diamond as a function of the applied shear stress. Solid dots: pure shear stress, positive σ . Solid diamonds: pure shear stress, negative σ . Open squares: combination of shear stress (positive σ) and a compressive stress of 50 GPa along the $(1, 1, 1)$ direction.

The points corresponding to the largest bond length in each curve of Fig. 3 are not local minima in the energy surface. Instead, they are saddle points that arise from the fact that we are not fixing the *strain* in our calculations, but rather the *stress*. These are points on an upper branch of the total energy as a function of stress. This is seen in Fig. 4, where we plot the total energy per atom as a function of the applied stress. In each case considered ($+\sigma$, $-\sigma$, $+\sigma$ with additional compressive stress), the total energy of the stable structures (lower branch) increases continuously as a function of the stress, up to the critical stress. There is also an upper branch in the energy versus stress curve. The upper branch is characterized by a larger energy (see Fig. 4) and a larger bond length (see Fig. 3). At the critical stress, the upper and the lower branches merge to the same point.

One of the results of our calculations is a relatively small critical shear stress of 95 GPa. This quantity, also called ideal shear strength [30], is an upper limit for the mechanical strength of a material [30], in our case diamond. Another measure of the mechanical strength of diamond is its critical value of the tensile stress, recently calculated as 90 GPa [9]. As mentioned before, a large anisotropy was found in our calculated shear response at large stresses. This is possibly the cause of the relatively small minimal value of the critical shear stress: small values of the critical shear stress along some directions are compensated by large values along other directions. That is, the shear strength of diamond is reduced due to the large anisotropy of the covalent bonds. In the indentation experiment of Gogotsi *et al.* [11], the nominal compressive stress at which the formation of the graphitelike

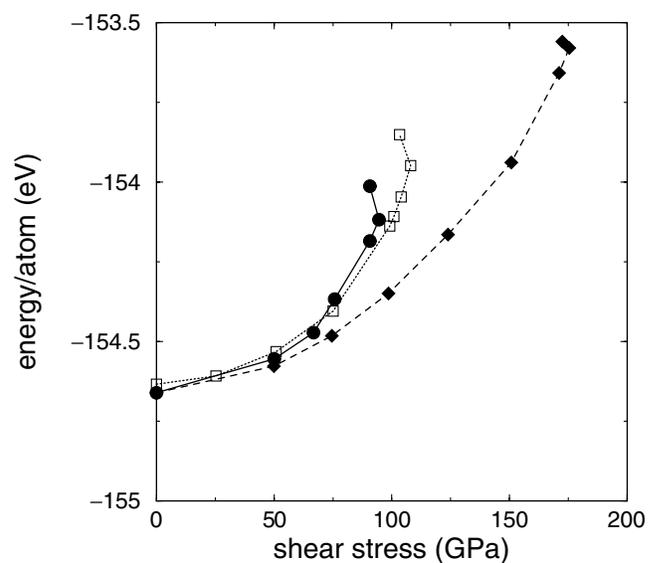


FIG. 4. Total energy per atom in diamond as a function of the applied shear stress. Solid dots: pure shear stress, positive σ . Solid diamonds: pure shear stress, negative σ . Open squares: combination of shear stress (positive σ) and a compressive stress of 50 GPa along the $(1, 1, 1)$ direction.

material (graphitization) was observed was estimated as slightly below 100 GPa, with possibly larger values at regions of the indentation area. Although the amount of shear stress in the experiment was not determined, it is possible that the relatively small value of stress necessary to induce the graphitization originates from the anisotropy-induced reduction of the shear strength.

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Note added.—After the completion of this work, we became aware of a related unpublished work by Roundy and Cohen [31].

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