Comment on "Pentadiamond: A Hard Carbon Allotrope of a Pentagonal Network of sp² and sp³ C Atoms"

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In a recent Letter, Fujii et. al. [1] predicted a new carbon allotrope, pentadiamond (PD), with remarkable mechanical properties: elastic moduli comparable or larger than diamond, and negative Poisson’s ratio $\mu = -0.241$. The estimated Vicker’s hardness ($V_H$) is 422 GPa, $\sim 4.6$ times higher than in diamond ($\sim 92$ GPa [2]), the hardest material known to date. PD, however was not investigated.

In the study of Avery et al. [2] on hardness of different carbon allotropes (i) $V_H$ is lower than in diamond in all cases, (ii) the hardest allotropes are dominated by diamond and/or lonsdaleite motifs. PD, with its record hardness and only $\sim 45.5\%$ sp³ bonds, would be an exceptional outlier in this picture. What, as claimed in Ref. [1], causes its extreme hardness?

Motivated by this question, we tried to reproduce the results of Ref. [1], recomputing the elastic properties of PD with different approximations based on Density Functional Theory (DFT). Surprisingly, although we correctly reproduced the structural data, electronic band structure and phonon dispersion of Ref. [1], we consistently obtained very different results for the elastic properties [3].

A summary of our results is reported in Table I.

Table I. Calculated independent elastic constants $C_{11}$, $C_{12}$ and $C_{44}$, Bulk modulus $B_0$, Young’s modulus $E$, Shear modulus $G_0$, Vicker’s hardness $V_H$ in GPa and dimensionless Poisson’s ratio $\mu$.

| Method       | $C_{11}$ | $C_{12}$ | $C_{44}$ | $B_0$ | $E$  | $G_0$ | $V_H$ | $\mu$ |
|--------------|----------|----------|----------|-------|------|-------|-------|-------|
| Pentadiamond | S-S      | 509      | 94       | 142   | 23   | 404   | 166   | 23    | 0.21  |
|              | E-S      | 541      | 109      | 142   | 253  | 412   | 168   | 22    | 0.23  |
|              | Dir-PBE  | 538      | 108      | 142   | 252  | 411   | 167   | 22    | 0.23  |
|              | Dir-LDA  | 568      | 121      | 143   | 270  | 424   | 171   | 21    | 0.24  |
|              | E-S (QE) | 541      | 107      | 142   | 252  | 414   | 169   | 22    | 0.21  |
|              | Ref. [1] | 1715 -283 | 1187 | 381 | 1691 | 1113 | 422 | -0.24 |
| Diamond      | S-S      | 1026     | 107      | 563   | 416  | 1098  | 518   | 97   | 0.06  |
|              | E-S      | 1052     | 133      | 565   | 439  | 1118  | 520   | 91   | 0.08  |
|              | Dir-PBE  | 1049     | 121      | 567   | 430  | 1117  | 523   | 95   | 0.07  |
|              | Dir-LDA  | 1113     | 154      | 601   | 474  | 1188  | 549   | 92   | 0.08  |
|              | Ref. [4] | 1051     | 128      | 561   | 435  | 1114  | 519   | 92   | 0.07  |
|              | Ref. [1] | 468      | 1273     | 608   | 112  | 112   | 0.05  |

Unless otherwise specified, we employed the Vienna Ab-initio Simulation Package (VASP) [3, 8], with Projected Augmented Wave(PAW) pseudopotentials [7] for the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [8].

The three independent cubic elastic constants $C_{11}$, $C_{12}$ and $C_{44}$ were estimated both from the linear stress-strain (S-S) and quadratic energy-strain relations (E-S). We created strains in the unit cell along appropriate directions and calculated the total energy and the stress tensor after relaxation of the internal atomic coordinates.

From the elastic constants, we obtained the bulk modulus $B_0$, Young’s modulus $E$, shear modulus $G_0$, $V_H$, and $\mu$ based on the Voigt-Reuss-Hill approximation [10]. The same quantities were also evaluated using the built-in implementation of VASP for the calculation of elastic constants from stress-strain relations, based on Ref. [11] (Dir). As an independent check of our setup, the same calculations were repeated for diamond.

The elastic constants computed in the three approaches are consistent with each other to within 5% and, for diamond, with literature results. On the other hand, a strong discrepancy exists between our results for PD and Ref. [1]: our elastic constants are 3-10 times smaller, and $C_{12}$ even exhibits another sign. As a result, our estimated $V_H$ (22 GPa) is twenty times smaller than in Ref. [1], and a factor four smaller than in diamond, while the Poisson’s ratio ($\mu$) is positive. We also did test runs for other hard carbon allotropes (positive Poisson’s ratio) and they match with the literature results.

Ref [1] did not provide sufficient computational details to reproduce the results. In order to rule out other possible sources of discrepancy, we repeated our calculations for PD using VASP-PAW pseudopotentials in the Local Density Approximation [12] (LDA) (Dir-LDA), and PBE norm-conserving pseudopotentials [13, 14] in Quantum Espresso, version 6.4.1 [15] (E-S (QE)). Again, the same strong discrepancy is found.

The most plausible conclusion of our tests is that the elastic constants and elastic moduli of PD reported in Ref [1] are incorrect, and pentadiamond should be considered a non-auxetic soft carbon allotrope.

Computational Details: For VASP calculations, we employed a kinetic energy cutoff of 800 eV, and a Γ-centered mesh of resolution of $2\pi \times 0.15$ Å⁻¹ for reciprocal space integration, with a Gaussian smearing of width 0.10 eV. For QE-6.4.1, an energy cut-off of 80 Ry with Gaussian smearing of 0.02 Ry and $8 \times 8 \times 8$ mesh on the reciprocal (k) space was used. This ensured a convergence of 0.4 GPa on the components of the stress.
tensor. The primitive cell of both the PD and diamond was used for all the calculations.

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