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Carbon

Diamond: Electronic Ground State of Carbon at Temperatures Approaching 0 K**

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Dedicated to Professor Robert G. Parr

Abstract: *The relative stability of graphite and diamond is revisited with hybrid density functional theory calculations. The electronic energy of diamond is computed to be more negative by 1.1 kJ mol^{-1} than that of graphite at $T = 0$ K and in the absence of external pressure. Graphite gains thermodynamic stability over diamond at 298 K only because of the differences in the zero-point energy, specific heat, and entropy terms for both polymorphs.*

Carbon, the element crucial to the development of organic life, exhibits a particularly large flexibility of its electronic structure, with facile s-p mixing and sp, sp^2, and sp^3 hybridizations all available for chemical bond formation. These correspond to linear, trigonal planar, and tetrahedral coordinations, respectively, and even for the element alone lead to a large number of carbon forms, with graphite (G) and diamond (D) (and now C_{60}) being the prototypical exemplifications of allotropy, as taught to every elementary school pupil worldwide (Figure 1).[1,2] Indeed, it was in 1772 that Lavoisier showed in an elegant (but quite expensive!) experiment that the only product of the combustion of a diamond was carbon dioxide, thus proving that D is simply another form of carbon. A quarter century later, Tennant expanded that experiment; by demonstrating that burning D and G releases the same amount of gas he unequivocally established the chemical equivalence of these substances.

The received textbook dictum is that graphite (itself a variety of polytypes) is the thermodynamically favored form of elemental carbon in the solid state, while diamond is metastable at ambient (p,T) conditions and may be formed only at elevated pressures exceeding 4.5 GPa.[3] A vast literature exists on this topic, which is both of fundamental and technological importance (cf. the Supporting Information).[4] The phase diagram of carbon continues to fascinate chemists and physicists alike;[5] aside from the late 20-century discoveries of fullerenes,[6] nanotubes,[7] and a recent graphene rush,[8] many more fascinating forms of carbon are proposed each year by theoretical research.[9] It is probably fair to say that graphitic materials, ultra-hard forms of carbon, fullerenes, nanotubes, and graphene—each constitute well-researched self-standing fields of contemporary materials science.[10]

But is G a true “ground state” of carbon not at “standard conditions” ($p = 1$ atm, $T = 298$ K) but—less arbitrarily—at p approaching 0 atm, and T approaching 0 K? And how do the thermodynamic contributions to the stability of both allotropes evolve? Here we attempt to get insight into the relative stability of G and D with the use of state-of-the-art hybrid density functional theory (DFT) methods,[11,12] compare the results obtained with the comprehensive set of experimental data available, and discuss the discrepancies.

The HSE06[11,12] hybrid functional is capable of much more accurate predictions of lattice constants (even for highly anisotropic systems with weak van der Waals (vdW) interactions,[13] or with systems exhibiting a shallow potential energy surface, such as those containing the Jahn–Teller-active species),[14] equation of state, bulk modulus, electronic band gap at the Fermi level, energetics and thermodynamics, than the classical local density approximation (LDA) or generalized gradient approximation (GGA) functionals. But, of course, at the cost of elongated CPU time.[15] Use of HSE06 is particularly advised for G, which is a computationally demanding system[16,17] because of both large structural anisotropy, as well as its semimetallic nature.[18] Reproduction of weak interlayer interactions of G is important for accurate

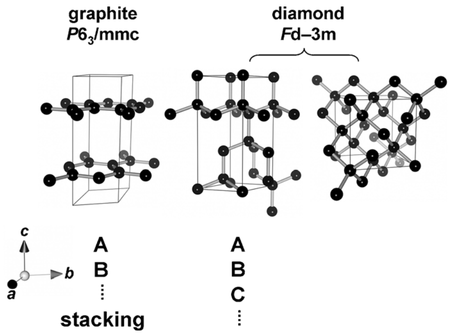

Figure 1. Crystal structures of Bernal graphite and diamond emphasising the relationships between them. The crystallographic unit cells are marked with solid lines. Both the hexagonal (middle) and classical cubic (right) representation of diamond are shown. Note, the hexagonal representation of cubic diamond is not equivalent to lonsdaleite (i.e. true hexagonal diamond).

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description of phonon modes connected with soft inter-layer motions, which in turn influence zero-point vibrational energy, heat capacity, and absolute entropy. Moreover, very large supercells are needed to eliminate imaginary phonon modes appearing in the computed phonon dispersion of G even at standard DFT level (LDA or GGA).[17] All this, taken together, renders rigorous calculations for graphite very CPU-demanding.

We have found in the literature only one preceding computational study for G using hybrid functionals, focused on prediction of lattice constants.[19] For D two reports were located, one on accurate lattice constant and band-gap prediction[20] and another on optical spectra of defects.[21] Consistent comparative study of G and D has not yet been made at the same level of hybrid DFT. However, the recent HSE06 results obtained for related silicon point out to excellent performance of this functional for prediction of the insulator–metal phase transition of this element and thus to successful estimation of relative energies of semiconducting and metallic forms of the same element.[22]

Results of our own HSE06/PBEsol[23] total energy calculations for D and G are shown in Table 1. For important comparison with LDA and GGA results as well as for geometrical parameters and phonon dispersion see the Supporting Information. Before we analyze the results of diverse contributions to the Gibbs free energy it is advisable to focus on the lowest-frequency Raman-active E_{2u} mode of graphite, which governs such properties as energy of dissociation of graphite to free graphene sheets,[24,25] and directly influences the zero-point energy, vibrational entropy, and heat capacity of G, and in consequence the predicted free Gibbs energy difference between D and G. This normal mode, which is notoriously difficult to predict from theory,[17] and it is underestimated by as much as 50 % in the LDA and GGA calculations (see Table S9 in the Supporting Information), has been calculated here with HSE06/PBEsol to fall at 41.6–42.1 cm^{-1}, that is, in excellent agreement with experimental values of 42–45 cm^{-1} (cf. Table S7). Simultaneously, the sum of all observable normal mode frequencies at the center of the Brillouin zone is overestimated by about 4 % for G and by about 2 % for D. We take this fact into account in the quantitative considerations below by introducing the corrected zero-point energy term (ZPE_corr in Table 1).

Table 1: The HSE06/PBEsol-calculated electronic energy, E(el), zero-point energy, ZPE term (cf. the Supporting Information for further correction of this term leading to $\mathrm{ZPE_{corr}}$), total energy, $E(t)$ (all formally at 0 K), as well as absolute vibrational entropy, $S_\mathrm{vib}{}^0$(298 K), heat capacity at constant volume, $C_\mathrm{v}{}^0$ (298 K), standard Gibbs free energy, G^0(298 K), atomic volume, V, and residual pV term, p(res)V, for G and D. Selected experimental values are given in the Table footnotes. The corrected $E(t)_\mathrm{corr}$ and $G^0(298\ \mathrm{K})_\mathrm{corr}$ terms are based on the $\mathrm{ZPE_{corr}}$ value.

Parameter	D (theor.)	G (theor.)	Δ(D vs. G)
E(el) [kJ mol^{-1}]	−1087.47	−1086.39	−1.08
ZPE [kJ mol^{-1}]	+18.26	+17.49	+0.77
$\mathrm{ZPE_{corr}}$ [kJ mol^{-1}]	+17.93	+16.78	+1.15
$E(t)$ [kJ mol^{-1}]	−1069.21	−1068.90	−0.31
$E(t)_\mathrm{corr}$ [kJ mol^{-1}]	−1069.54	−1069.61	+0.07
$S_\mathrm{vib}{}^0$(298 K) [J mol^{-1} K^{-1}]	2.205	4.575	−2.370
$S_\mathrm{vib}{}^0(298\ \mathrm{K})_\mathrm{exp}$ [J mol^{-1} K^{-1}]	2.377[a]	5.740[b]	−3.363
$C_\mathrm{v}{}^0$(298 K) [J mol^{-1} K^{-1}]	5.723	7.926	−2.203
$C_\mathrm{v}{}^0$ $(298\ \mathrm{K})_\mathrm{exp}$ [J mol^{-1} K^{-1}]	6.116–6.117[c]	8.517[d]	−2.401
G^0(298 K) [kJ mol^{-1}]	−1069.04	-1069.37	+0.33
$G^0(298\ \mathrm{K})_\mathrm{corr}$ [kJ mol^{-1}]	−1069.37	-1070.08	+0.71[e]
V [Å^{-3}]	5.535[f]	9.364[g]	−3.829
p(res)V [kJ mol^{-1}]	−0.04	−0.06	+0.02

The recommended experimental values: [a,b,d] Ref. [26]. [c] Ref. [26,27]. [e] 2.87–2.90.[4b,26] [f] 5.671 (10 K).[28] [g] 8.730 (4.2 K).[29]

The outcome of the HSE06/PBEsol calculations is quite surprising: D turns out to be the electronic ground state of carbon at $T \rightarrow 0$ K, stabilized with respect to G by about 1.1 kJ mol^{-1}. The change of the percent of the exact exchange within reasonable limits (25–35 %) and of the screening parameter (within recommended limits 0.2–0.3 Å^{-1}) does not influence qualitatively this result (Table S12). The decrease of the percent of exact exchange diminishes the relative electronic energy of D versus G; the increase of the screening parameter leads to the same result. Only in one case when both parameters simultaneously depart from their default values for the HSE06 functional (i.e. the ones which were found previously to lead to correct results for a number of systems including Si), the relative E(el) becomes marginally positive (by +0.15 kJ mol^{-1}). This result is not unexpected since reduction of the Hartree–Fock exchange to null must result in convergence towards the incorrect GGA result.

Importantly, the difference of vibrational ZPE between the two polymorphs is reversed with respect to the electronic term—and of the comparable size. This has been observed previously based on LDA calculations.[30] In consequence, the two terms largely cancel out and the difference of total energies of D and G is (accidentally) close to null[31] (compare also the values of $E(t)$ and $E(t)_\mathrm{corr}$ in Table S1). Thus, according to HSE06/PBEsol D and G are quasi-degenerate at $T \rightarrow 0$ K/$p \rightarrow 0$ GPa. The ΔE(el) and ΔZPE_corr values for carbon are both close to ±1.1 kJ mol^{-1} and at first sight they may seem too small to reliably judge the relative stability of G and D. Note, however, that the difference of the Gibbs free energy for two polymorphic forms of another important mineral, SiO_2, (quartz vs. cristobalite) reportedly reaches a comparable value of 1.4 kJ mol^{-1}.[24]

The phonon calculations permitted us to derive the values of the heat capacity at constant volume, $C_\mathrm{v}{}^0$, and of the absolute vibrational entropy, $S_\mathrm{vib}{}^0$, of both carbon allotropes. The obtained values show discrepancies with experimental values,[32] and they are usually underestimated. The largest discrepancy is that for $S_\mathrm{vib}{}^0(298\ \mathrm{K})$ of G which should certainly be improved in the future calculations. However, the experimental $S_\mathrm{vib}{}^0$ of G has a large uncertainty of 0.21 J mol^{-1} K^{-1}[33] (3.7 %). Values of the heat capacity of G also show substantial differences up to 0.86 J mol^{-1} K^{-1}[34] (10.1 %) depending on what specimen of graphite has been used for the study. Moreover, what matters for relative stability of both polymorphs at a given finite T value are the differences between the respective $C_\mathrm{v}{}^0$ and $S_\mathrm{vib}{}^0$ values for both polymorphs, $\Delta C_\mathrm{v}{}^0$ and $\Delta S_\mathrm{vib}{}^0$. These have smaller discrepancies to experiment because of error cancelling. What is most important for our considerations is that these differential terms again favor G over D, just like the ZPE term.

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The $\Delta G^0(298\ \mathrm{K})_{\mathrm{corr}}$ which governs the relative stability of G versus D is computed to be $+0.71\ \mathrm{kJ\,mol^{-1}}$; this value accounts only for one quarter of the recommended experimental value of 2.87–$2.90\ \mathrm{kJ\,mol^{-1}}$ but the emerging picture is qualitatively correct. In other words, there is no fundamental disagreement between the supposition that D is the electronic ground state of carbon at $T \rightarrow 0$ K and the experimentally observed thermodynamic preference for G at $T = 298$ K.[35] Certainly, the quantitative discrepancies between theory and experiment beg to be discussed.

Undoubtedly, the CPU-demanding HSE06/PBEsol method, although constituting the current state-of-the-art for solid-state calculations, has its drawbacks, and is still a compromise. The theoretical results presented here may certainly be improved in the future, once more accurate methods become available and larger supercomputer resources are harnessed. But there are a few obvious limitations on the side of experiment as well. Most importantly, the G to D pressure-induced transformation has a very large energy barrier, which results in immeasurably sluggish transformation at $T < 1000$ K, even if the pressures involved are larger than necessary for transformation. Hence, the position of the diamond/graphite equilibrium line[36] (Figure 2) has been established by thermodynamic calculations based upon 1) experiments on growth or graphitization of diamond in the temperature range from 1100 to about 2200 K[29,37] and 2) the measured physical properties of graphite and diamond in the temperature range from 300 to about 1200 K.[38–40] By necessity, many properties at 0 K are obtained by extrapolations from these data sets.

Substantial discrepancies exist between various experimental data sets even without including error bars. The deviations between the most separated experimental equilibrium lines reach 0.38 GPa at 298 K and as much as 1.08 GPa at 3000 K. One may also draw lines connecting point (0 K, 0 GPa) and the point (1950 K, 6.1 GPa) where most experimental curves intersect (note, the kinetics of the $G \rightleftarrows D$ transformation are fast at high temperatures and pressures, so the equilibrium line at this (p,T) point is likely to be precise). This new limiting equilibrium line falls departs from the "best calorimetric" line in the low T region (the deviation at 0 K is about 0.8 GPa) but it is close to the "Jacob Minimum Deviation" in the high T region 1950–3000 K (the deviation at 3000 K is ca. 0.1 GPa). It is probably fair to say that—given a very small computed difference of free energies of G and D at 0 K and the limited accuracy of the experimental measurements—one cannot determine the position of the equilibrium line at this time with satisfactory precision. One must be also cautious when assessing very small energy differences with DFT.[41] But without doubt a better agreement of experimental and theoretical $\Delta G^0(298\ \mathrm{K})$ is now needed; it is possible that the preference of D versus G because of the electronic energy term at $T \rightarrow 0$ K will prove in the future to be less pronounced than the current best value of $-1.1\ \mathrm{kJ\,mol^{-1}}$, but still slightly negative. Having all what was said in mind, the purpose of this theoretical work is in fact to call for rigorous revisiting various properties of D and G in experiment and theory, in particular in the low-T regime (0–300 K).

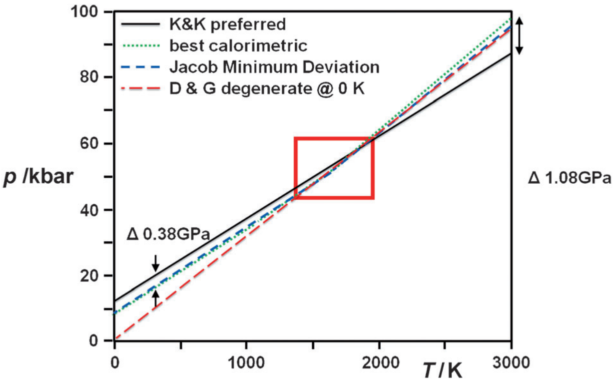

Figure 2. The diamond/graphite equilibrium line according to various researchers (black, green, and blue lines) as collected and corrected in 2012 by Day.[28] The red box (according to Day) stands for the (p,T) range where most experiments were performed on direct $G \rightleftarrows D$ transformations. Our redrawing of Day's Figure 7 includes dotted red line which passes through the (1950 K, 6.1 GPa) point where most curves intersect and represents a limiting case when D and G are truly degenerate at 0 K.

Summarizing, the most important finding of this work is certainly that D is the electronic ground state of carbon at 0 K, and that thermodynamic stability of graphite at 298 K is only due to the combined effect of the ZPE term as well as due to entropy and specific heat terms at finite temperature.[42] The difference of total energies of G and D seems to be large enough ($1.1\ \mathrm{kJ\,mol^{-1}}$) to lay ground for such a statement.[35] Importantly, this is similar to what has recently been found with DFT in the relative stability of various polymorphs of elemental boron (stability reversal because of the ZPE term).[43–45] In this way the carbon allotrope which has the larger band gap at the Fermi level (D) and thus it is "electronically harder"—is also electronically more stable than the softer allotrope with negligible band gap (G). This could be viewed as a spectacular manifestation of the maximum hardness principle[46,47] applied to extended solids. The properties of carbon calculated here confirm the non-metallic nature of this element which is placed in between semiconducting boron and insulating nitrogen in the periodic table.

In a following study we will compare at the HSE06/PBEsol as well as B3LYP level a broader set of carbon polymorphs including hexagonal diamond (lonsdaleite), rhombohedral, and simple hexagonal graphite as well as the as-yet unknown NiAs-type structure, and we will show that hybrid DFT is capable of excellent reproduction of a broader set of physical properties of carbon allotropes.

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[1] http://www.sciencekids.co.nz/sciencefacts/chemistry/diamond.html.
[2] http://encyclopedia.kids.net.au/page/gr/Graphite.

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[3] As popularized via WWW, see for example: "The reaction D→G has a negative change in the Gibbs free energy and is therefore thermodynamically favorable at 25 °C and 1 atm. However, even though favorable, it is so slow that it is not observed." http://en.wikipedia.org/wiki/Gibbs_free_energy.

[4] The most recent comprehensive review on the phase diagram of carbon relies on experimental data up to 20 years old: a) F. P. Bundy, A. A. Bassett, M. S. Weathers, R. J. Hemley, H. K. Mao, A. F. Goncharov, *Carbon* **1996**, *34*, 141–153. Importantly, the **G/D** transition curve has been revised in 2012: b) H. W. Day, *Am. Mineral.* **2012**, *97*, 52–62.

[5] J. M. Zazula, LHC Project Note 78/97, 18 Jan **1997**, available at www.

[6] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature* **1985**, *318*, 162–163.

[7] S. Iijima, *Nature* **1991**, *354*, 56–58.

[8] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* **2004**, *306*, 666–669.

[9] For M-, bct-, W- and Z-carbon, n-diamond and hypothetical superhard forms of carbon see for example: a) Z. Li, F. Gao, Z. Xu, *Phys. Rev. B* **2012**, *85*, 144115; b) B. Wen, J. Zhao, T. Li, C. Dong, *New J. Phys.* **2006**, *8*, 62; c) C. He, L. Sun, C. Zhang, X. Peng, K. Zhang, J. Zhong, *Phys. Chem. Chem. Phys.* **2012**, *14*, 8410–8414; d) Q. Zhu, A. R. Oganov, M. A. Salvadó, P. Pertierra, A. O. Lyakhov, *Phys. Rev. B* **2011**, *83*, 193410, and references therein. For schwarzite see for example: e) S. Gaito, L. Colombo, G. Benedek, *Europhys. Lett.* **1998**, *44*, 525–530; f) V. Rosato, M. Celino, G. Benedek, S. Gaito, *Phys. Rev. B* **1999**, *60*, 16928–16933.

[10] Search of the Web of Knowledge database conducted on Aug 3, 2013, reveals +28 000 hits for keyword "fullerene" and close to 140 000 hits for a more general term "nanotube", as well as +101 000 for graphite, +84 000 for diamond, and nearly 38 000 for graphene.

[11] J. Heyd, G. E. Scuseria, M. Ernzerhof, *J. Chem. Phys.* **2003**, *118*, 8207–8215; V. Barone, O. Hod, J. E. Peralta, G. E. Scuseria, *Acc. Chem. Res.* **2011**, *44*, 269–279; T. M. Henderson, J. Paier, G. E. Scuseria, *Phys. Status Solidi B* **2011**, *248*, 767–774.

[12] A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, G. E. Scuseria, *J. Chem. Phys.* **2006**, *125*, 224106.

[13] W. Grochala, M. K. Cyrański, M. Derzsi, T. Michałowski, P. J. Malinowski, Z. Mazej, D. Kurzydłowski, W. Koźminski, A. Budzianowski, P. J. Leszczyński, *Dalton Trans.* **2012**, *41*, 2034–2047.

[14] P. J. Malinowski, Z. Mazej, M. Derzsi, Z. Jagličić, J. Szydłowska, T. Gilewski, W. Grochala, *CrystEngComm* **2011**, *13*, 6871–6879; *cf.* ESI.

[15] L. Schimka, J. Harl, G. Kresse, *J. Chem. Phys.* **2011**, *134*, 024116.

[16] M. Lazzeri, C. Attaccalite, L. Wirtz, F. Mauri, *Phys. Rev. B* **2008**, *78*, 081406.

[17] G. Kresse, J. Furthmüller, J. Hafner, *Europhys. Lett.* **1995**, *32*, 729–734; *cf.* also O. Dubay, G. Kresse, *Phys. Rev. B* **2003**, *67*, 035401.

[18] N. García, P. Esquinazi, J. Barzola-Quiquia, S. Dusari, *New J. Phys.* **2012**, *14*, 053015. The direct band gap is measured to be 40 meV, the indirect band gap is closed, as typical of semimetals.

[19] P. V. Avramov, S. Sakai, S. Entani, Y. Matsumoto, H. Naramoto, *Chem. Phys. Lett.* **2011**, *508*, 86–89.

[20] X. Liu, L. Li, Q. Li, Y. Li, F. Lu, *Mater. Sci. Semicond. Process.* **2013**, *16*, 1369–1376.

[21] A. Gali, E. Janzén, P. Deák, G. Kresse, E. Kaxiras, *Phys. Rev. Lett.* **2009**, *103*, 186404.

[22] B. Xiao, J. Sun, A. Ruzsinszky, J. Feng, R. Haunschild, G. E. Scuseria, J. P. Perdew, *Phys. Rev. B* **2013**, *88*, 184103.

[23] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, K. Burke, *Phys. Rev. Lett.* **2008**, *100*, 136406.

[24] M. O'Keeffe, *Phys. Chem. Chem. Phys.* **2010**, *12*, 8580.

[25] M. Hasegawa, K. Nishidate, H. Iyetomi, *Phys. Rev. B* **2007**, *76*, 115424; H. Rydberg, M. Dion, N. Jacobsen, E. Schröder, P. Hyldgard, S. I. Simak, D. C. Langreth, B. L. Lundqvist, *Phys. Rev. Lett.* **2003**, *91*, 126402.

[26] Knovel database, http://why.knovel.com/accessed Oct **2013**.

[27] A. C. Victor, *J. Chem. Phys.* **1962**, *36*, 1903.

[28] K. Haruna, H. Maeta, K. Ohashi, T. Koike, *Jpn. J. Appl. Phys.* **1992**, *31*, 2527–2529.

[29] Y. Baskin, L. Meyer, *Phys. Rev.* **1955**, *100*, 544.

[30] M. T. Yin, M. L. Cohen, *Phys. Rev. B* **1984**, *29*, 6996.

[31] This corresponds to a D→G transition pressure of +0.03 GPa in the phase diagram at $T\rightarrow 0$ K, not far from the Jacob Min. Dev. line in the phase diagram (Figure 2).

[32] Note, we compute the values of C_v^0 while the tabulated experimental values are those of C_p^0. However, the difference between C_v^0 and C_p^0 is usually small for extended solids.

[33] M. W. Chase, Jr., (**1998**) NIST-JANAF Thermochemical Tables, Fourth Edition Part 1, AI-Co. Journal of Physical and Chemical Reference Data, Monograph, 9.

[34] S. Picard, D. T. Burns, P. Roger (**2006**) Measurement of the Specific Heat Capacity of Graphite, International Bureau of Weights and Measures, Sèvres France (report available at www).

[35] We notice that similar value of ΔE(el)has been previously calculated using LDA, likely due to error cancelling (Ref. [29] and F. J. Ribeiro, P. Tangney, S. G. Louie, M. L. Cohen, *Phys. Rev. B* **2006**, *74*, 172101). These authors, however, followed an incorrect assumption that the preference for D over G in electronic energy at 0 K cannot be true "since G is thermodynamically favored over D at 298 K".

[36] F. P. Bundy, H. P. Bovenkerk, H. M. Strong, R. H. Wentorf, Jr, *J. Chem. Phys.* **1961**, *35*, 383–391.

[37] C. S. Kennedy, G. C. Kennedy, *J. Geophys. Res.* **1976**, *81*, 2467–2470.

[38] F. D. Rossini, R. S. Jessup, *J. Res. Natl. Bur. Stand.* **1938**, *21*, 491–497.

[39] O. I. Leipunskii, *Usp. Khim.* **1939**, *8*, 1519–1534.

[40] R. Berman, F. Simon, *Z. Elektrochem.* **1955**, *59*, 333–338.

[41] See for example: a) X. Liu, P. Müller, P. Kroll, R. Dronskowski, *Inorg. Chem.* **2002**, *41*, 4259–4265; b) X. Liu, P. Müller, P. Kroll, R. Dronskowski, W. Wilsmann, R. Conradt, *ChemPhysChem* **2003**, *4*, 725–731. This is of particular importance for systems where weak van der Waals interactions have substantial contribution to overall stability, for example: c) K. Rościszewski, B. Paulus, P. Fulde, H. Stoll, *Phys. Rev. B* **2000**, *62*, 5482–5488. One possible but still incomplete solution is offered by incremental approach, see e.g.: d) H. Stoll, *J. Chem. Phys.* **1992**, *97*, 8449.

[42] Interestingly, the nature of the ground state of the C_2 molecule was also subject to discussions until it was unequivocally established that the ground-state singlet ($^1\Sigma_g^+$) is lower in energy by ca. 8.6 kJ mol^{-1} than the first excited triplet state ($^3\Pi_u$).

[43] M. J. van Setten, M. A. Uijttewaal, G. A. de Wijs, R. A. de Groot, *J. Am. Chem. Soc.* **2007**, *129*, 2458–2465.

[44] M. Widom, M. Mihalkovič, *Phys. Rev. B* **2008**, *77*, 064113.

[45] T. Ogitsu, F. Gygi, J. Reed, Y. Motome, E. Schwegler, G. Galli, *J. Am. Chem. Soc.* **2009**, *131*, 1903–1909.

[46] R. G. Pearson, *J. Chem. Educ.* **1987**, *64*, 561–567.

[47] R. G. Parr, P. K. Chattaraj, *J. Am. Chem. Soc.* **1991**, *113*, 1854–1855.

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