

1 **Toward an accurate *ab initio* estimation of compressibility and thermal expansion of diamond in**
2 **the [0, 3000K] temperature, and [0, 30GPa] pressures ranges, at the hybrid HF/DFT theoretical level**

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ABSTRACT

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The volume bulk modulus, together with its temperature dependence, and the thermal expansion of diamond at various pressures, were calculated from first principles in the [0, 30GPa] and [0, 3000K] pressure and temperature ranges. The hybrid HF/DFT functional employed (WC1LYP) proved to be particularly effective in providing a very close agreement between the calculated and the available experimental data. In particular, the bulk modulus at 300K was estimated to be 444.6 GPa ($K' = 3.60$); at the same temperature, the (volume) thermal expansion coefficient was $3.19 \cdot 10^{-6} \text{ K}^{-1}$. To the authors' knowledge, among the theoretical papers devoted to the subject, the present one provides the most accurate thermo-elastic data in high pressure and temperature ranges. Such data can confidently be used in the determination of the pressure of formation using the "elastic method" for minerals found as inclusions in diamonds, thus shading light upon the genesis of diamonds in the Earth's upper mantle.

keywords: diamond, thermo-elastic properties, thermal expansion, ab initio calculations.

27 This work is part of a wider project devoted to the study of diamonds formation in the upper mantle
28 and its growth relationships with those minerals that are commonly found as inclusions in diamonds.
29 In particular, subcratonic diamonds can contain inclusions of other minerals like olivine, garnet,
30 spinel, pyroxenes, sulfides (Nestola et al. 2011; Shirey et al. 2013). Diamonds and their inclusions are
31 among the deepest materials originating from the Earth's interior and reaching the planet surface.
32 Their study plays a key role in understanding and interpreting the geodynamics, geophysics,
33 petrology, geochemistry and mineralogy of the Earth's mantle (Stachel and Harris 2008, and
34 references therein). By the study of such inclusions, *in situ*, by means of diffractometric or
35 spectroscopic techniques, it is possible to determine the pressure (and the corresponding depth in the
36 Earth's mantle) at which the inclusions were formed (Nestola et al. 2011; Izraeli et al. 1999) using the
37 so called "elastic method" (see Shirey et al. 2013 for a review). However, to this end, very accurate
38 data concerning the pressure-volume equation of state, the thermal expansion and the bulk modulus
39 temperature dependence of both diamond and its inclusions are absolutely crucial in order to obtain
40 low error in the pressure of formation.

41 As concerns diamond, previous experimental and theoretical determinations of the elastic parameters
42 and thermal expansion existed. In particular, from the experimental side, the elastic constants
43 measurements from Brillouin scattering, at room or higher temperatures, allowed the estimation of
44 the bulk modulus and its temperature dependence (Grimsditch and Ramdas 1975; McSkimin and
45 Andreatch 1972; Vogelgesang et al. 1996; Zouboulis et al. 1998). Experimental thermal expansion
46 data (from low to high temperature up to 3000K) at room pressure, are available from Stoupin and
47 Shvyd'ko (2011), and from Reeber and Wang (1996). Due to technical difficulties in the experimental

48 determinations of accurate bulk moduli and thermal expansion at simultaneous high pressure and
49 temperature, a number of theoretical works were devoted to the subject, both at the ab initio level
50 (Hebbache 1999; Kunc et al. 2003; Ivanova and Mavrin 2013; Maezono et al. 2007; Mounet and
51 Marzari 2005; Valdez et al. 2012; Xie et al. 1999; Zhi-Jian et al. 2009) or the empirical one (force fields
52 and other techniques based on some specific models; Aguado and Baonza 2006; Gao et al. 2006).
53 Strongly depending upon the specific method employed, the calculated bulk moduli could be
54 overestimated or underestimated by more than 10 GPa with respect to the experimental datum at
55 300K, so that a more reliable ab initio methodology is required to get values which could parallel the
56 experimental techniques in accuracy and under very extreme conditions of P and T. To this end, the
57 equation of state and the thermal expansion of diamond in the [0, 3000K] and [0, 30GPa]
58 temperature and pressure ranges, respectively, have been determined by using the most recent ab
59 initio techniques so far developed. In particular, an hybrid Hartree-Fock/Density Functional Theory
60 (HF/DFT) functional has been employed. Hybrid functionals assure a very high accuracy in reproducing
61 thermo-elastic parameters and vibrational properties of crystals, as it has already been proven in
62 several papers (see for instance: De La Pierre et al. 2011a, Prencipe et al. 2011; Ungureanu et al.
63 2012; Zucchini et al. 2012; Scanavino et al. 2012; Prencipe et al. 2012a; Prencipe et al. 2012b,
64 Scanavino and Prencipe 2013, and references therein).

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COMPUTATIONAL DETAILS

67 Geometry optimization (cell parameter at the equilibrium), energy calculations at the static limit (no
68 zero point and thermal energies) and vibrational frequencies calculations, for a set of different unit

69 cell volumes, were performed by means of the CRYSTAL09 program (Dovesi et al. 2005; Dovesi et al.
70 2009). The chosen functional (WC1LYP) is a hybrid HF/DFT one, based on the WC (GGA) exchange
71 functional proposed by Wu and Cohen (Wu and Cohen 2006), mixed with 16% of the exact non-local
72 Hartree-Fock exchange, and employing the LYP correlation functional (Lee et al. 1988). Such
73 percentage of exact Hartree-Fock exchange is essential for the correct reproduction of the elastic and
74 vibrational properties of crystals, as demonstrated in previous works that had employed this
75 functional (De La Pierre et al. 2011a; Demichelis et al. 2010; Prencipe et al. 2011; Prencipe 2012a;
76 Prencipe et al. 2012b; Scanavino et al. 2012; Scanavino and Prencipe 2013; Ungureanu et al. 2010;
77 Ungureanu et al. 2012; Zicovich-Wilson et al. 2004). With the purpose of testing and comparing our
78 results with those reported from other Authors, static calculations were repeated by employing the
79 B3PW (Becke 1993) and PBE functionals (Perdew et al. 1996). As the localized basis sets are
80 concerned, a 6-111G* basis (B1 in the following), derived from the 6-21G* one by Dovesi et al. (1990)
81 was mainly employed for the calculation of the zero point and thermal pressure contributions (see
82 below), where the computational cost of the proper evaluation of dispersion effects in the phonon
83 spectrum prevented us from the use of a very rich basis set. A very high quality basis set (B2 in the
84 following), precisely a triple-zeta (TPZ) basis by Peintinger et al. (2013) having the (6211/411/1)
85 structure, specifically designed for solid state calculations, was employed for the static equation of
86 state (see below). Such basis is the one indicated as pob-TZVP basis in Table 2 of Peintinger et al.
87 (2013); the notation to specify the basis indicates the number of contracted functions (s/p/d). To get
88 more variational freedom and a better description of directional bonding situations like those in
89 diamond, a B1' basis (6111/111/1) was also employed where, as in the case of the B2 basis and at
90 variance with the B1 one, the ns and np electrons ($n>2$) were associated with different Gaussian

91 functions describing the radial part of the localized orbitals. More details about the procedure which
92 has been followed to calculate energies and vibrational frequencies, and the computational
93 parameters employed are provided in the Appendix. Static energies and vibrational frequencies at the
94 different cell volumes are provided as supplementary material.

95 At each cell volume, the static, zero point and thermal pressure were computed following the
96 algorithms fully described in Prencipe et al. (2011). The procedures to estimate the bulk modulus
97 together with its pressure and temperature dependence, and the thermal expansion are also
98 reported in Prencipe et al. (2011).

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RESULTS AND DISCUSSION

101 **Equation of State**

102 The discussion concerning the estimation of the equation of state (EoS) is here divided in two parts.
103 The first one is devoted to the *static* EoS where the only contribution to the pressure at any given cell
104 volume is from the electrostatic interactions among nuclei and electrons (no zero point and kinetic
105 contributions from the vibrational motion of the atomic nuclei); the second part is devoted to the
106 thermal equation of state where all of the contributions to the pressure are taken into account. As
107 results for the static part are significantly dependent upon the quality of the basis set (see above the
108 *computational details* section), at variance with those concerning the zero point and thermal pressure
109 contributions, as it will be shown below, such separated discussion makes the issues clearer.

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112 *Static Equation of State*

113 The parameters obtained from a volume-integrated third-order Birch-Murnaghan (BM3) fitting of the
114 static energies, calculated with the two different B1 and B2 basis sets, are reported in Table 1. With
115 respect to the B2 basis, the B1 basis set significantly overestimates the static equilibrium cell volume
116 and underestimates the static bulk modulus. The particularly high sensitivity of the static bulk
117 modulus of diamond to the basis set quality was also noted by De La Pierre (2011): indeed, low quality
118 basis sets gave lower values of the static bulk modulus than those obtained with higher quality bases
119 (De La Pierre 2011b). The B1' basis set differs from the B1 one by having a different description of the
120 *s* and *p* orbitals (by contrast, in B1, *s* and *p* electrons are described by *sp* shells; see above the
121 Computational details section); this should allow a better description of the electronic distribution in
122 the case of systems involving directional bonds, as in diamond. Such split of the *s* and *p* electrons has
123 a small effect on the geometry, but increases the static bulk modulus by about 5 GPa (B1'/WC1LYP
124 data in Table 1), approaching the value obtained by the B2 basis which also has splitted *s* and *p* orbital
125 descriptions.

126 Static results from Zhi-Jian *et al.* (2009) are also reported in Table 1: the localized basis set they
127 employed (B3) was a 6-21G* and the chosen functionals/Hamiltonians were the B3PW (Becke 1993;
128 this is a hybrid Hamiltonian containing 20% of the *exact, non local* HF exchange), and the Hartree-
129 Fock (RHF) one. As $K_{0,st}$ is concerned, B3PW gave results comparable to those from WC1LYP, whereas
130 the RHF datum is largely overestimated, as it could be expected on the basis of the widely known
131 behavior of the Hartree-Fock Hamiltonian (see for instance Prencipe and Nestola 2005). Calculations
132 of the static bulk moduli with our B1 and B2 basis sets, and the B3PW functional (as in the work by
133 Zhi-Jian *et al.* 2009), gave values of 460.3 GPa (B1/B3PW) and 476.3 GPa (B2/B3PW data in Table 1),

134 which are to be compared with the B1/WC1LYP and B2/WC1LYP calculations (same bases, different
135 functionals) respectively giving $K_{0,st}=445.0$ and 456.4 GPa, thus showing the significant effect of the
136 DFT functional on such calculated elastic parameter. The increase in $K_{0,st}$, and the reduction of $V_{0,st}$ in
137 passing from the WC1LYP to the B3PW functional is likely due to the corresponding increase of the
138 Hartree-Fock weight in the exchange functional (16% in WC1LYP, 20% in B3PW), as it was already
139 observed in Prencipe and Nestola (2005) in a study of the compressibility of a silicate (beryl) by means
140 of functionals based on a B3LYP scheme, having increasingly higher HF exchange contributions.

141 Another paper is that from Hebbache (1999), reporting a value of 463.1 GPa for the static bulk
142 modulus, calculated at the DFT-LDA level. A static calculation of K_0 by means of a purely DFT-GGA
143 functional (PBE; Perdew et al. 1996), together with a plane-wave basis set and pseudopotentials, was
144 reported by Mounet and Marzari (2005): they found a value of 432 GPa (PW/PBE data in Table 1). For
145 comparison, in this work a calculation with the B2 basis set and the PBE Hamiltonian gave 444.02 GPa
146 (B2/PBE data in Table 1); such difference of more than 10 GPa is very likely be attributed to
147 differences in the basis set structure (plane-waves vs localized basis sets). Although, the quality of the
148 different basis sets cannot here be judged on the basis of the agreement with the experimental data
149 as, by definition, no zero point and thermal effects are taken into account at the static level, it is
150 known (see next section) that such effects do decrease the bulk modulus by up to 10 GPa; in this
151 view, *static* bulk moduli which are equal or even smaller than the experimental room temperature
152 value ($442-445$ GPa; Grimsditch and Ramdas 1975; Zouboulis et al. 1998) will likely be off the
153 experimental datum by at least 10 GPa.

154 Smaller effects of both basis sets and Hamiltonians are observed for K'_{st} which is about 3.6 .

155

156 *Thermal Equation of State*

157 By adding the static pressures (from the higher quality B2 basis set calculation) to the zero point and
158 thermal pressures estimated from the vibrational frequencies and their volume derivative (B1 and B2
159 calculations) of a 2x2x2 supercell of the conventional FCC diamond cell (32 k points of the reciprocal
160 lattice, 189 normal modes of vibration), the total pressure at a given temperature could be estimated,
161 for a set of values of the unit cell volume. For any given fixed temperature value, the $P(V)$ data were
162 fitted by a BM3-EoS, so that the bulk modulus K_{0T} , its pressure derivative K'_T and the equilibrium
163 volume V_{0T} could be estimated. Results are summarized in Table 2 for the two different basis sets, at
164 the reference temperature of 300K. The significant difference between the bulk moduli estimated by
165 using the B1 and B2 basis sets (more than 10 GPa, as in the static calculation reported in Table 1) is
166 due to the differences of the static contributions to the total pressure. Indeed, using the EoS
167 parameters estimated with the B2 basis set for the static part, together with the frequencies and their
168 volume derivatives for the vibrational part [in the latter cases, having rescaled by a factor
169 $V_{0,st}(B2)/V_{0,st}(B1)$ the unit cell volumes at which the vibrational frequencies were calculated, being
170 $V_{0,st}(Bx)$ the equilibrium static volume optimized by using the Bx basis set; in this way, the frequencies
171 at any given value of the static pressure for the B1 base were assigned to cell volumes corresponding
172 to the same static pressure for the B2 base] and fitting the resulting $P(V)$ data, yielded a K_{0T} of
173 439.0GPa ($V_{0T}=45.694 \text{ \AA}^3$, $K'=3.65$; B1* data in Table 2), which is only about 0.7GPa higher than the
174 bulk modulus estimated by using the frequencies calculated with the B2 basis set. This means that,
175 even if the quality of the basis set had a significant impact on the estimated static elastic parameters,
176 frequencies calculated with a poorer basis set could confidently be used for the evaluation of the
177 thermal and zero point contributions to the total pressure.

178 The reduced computational cost of the B1 basis set allowed for the calculation of vibrational
179 frequencies also in the case of larger supercells, thus allowing a more accurate estimation of the
180 influence of dispersion effects upon the elastic parameters. By employing the B1 basis set, the
181 calculations of the frequencies were repeated for the 3x3x3 and 1x1x4 supercells, thus reaching a
182 total of 148 \underline{k} points having $|\underline{k}|$'s in the range $[2^{1/2}/8 |\underline{a}^*|, |\underline{a}^*|]$, where $|\underline{a}^*|$ is the module of the
183 reciprocal lattice parameter, and 885 normal modes. The distribution of the number of modes versus
184 their frequencies (VDOS: vibrational density of states) is reported in Figure 1, whereas a drawing of
185 the dispersion curves along the $[001]^*$ direction in the reciprocal lattice (Δ path, from the Γ toward
186 the X point) is shown in Figure 2; the agreement with the experimental data from inelastic neutron
187 scattering (Warren et al. 1967), which are reported in the inset of Figure 2, is quite satisfactory.

188 The impact on the bulk modulus of the increasingly larger number of sampled \underline{k} points, as the
189 minimum value of $|\underline{k}|$ is reduced (by enlarging the size of the supercell) moving \underline{k} toward the Γ point
190 (B1** data in Table 2; static parameters were from the B2 basis calculations), can be clearly seen in
191 Figure 3, where K_0 is plotted against the minimum value of $|\underline{k}|$ characterizing each studied supercell
192 (B1** data in Table 2; static parameters were from the B2 basis calculations): K_0 reaches the
193 convergence with respect to the number of \underline{k} points when $|\underline{k}|$ is smaller than about $0.77|\underline{a}^*|$
194 (corresponding to 59 \underline{k} points sampled). The small variations of K_0 with $|\underline{k}|$, for $|\underline{k}| < 0.77|\underline{a}^*|$, allowed
195 us to derive an uncertainty (*precision*) of the estimated K_0 of about 0.1GPa over an average value
196 445.4 GPa. However, as discussed above, this datum is likely to be overestimated of almost 1 GPa
197 with respect to the one that could be derived by using the higher quality B2 basis set for the
198 calculation of the frequencies. In conclusion, our best estimate of K_0 for diamond at 300K was 444.6

199 GPa, with an uncertainty (*accuracy*: mainly due to the basis set bias) of 0.8 GPa. K' and V_0 were
200 respectively 3.60 and 45.689 \AA^3 ($a_0=3.575 \text{ \AA}$).

201 Other *ab initio* estimations of the bulk modulus were available for diamond. From temperature
202 dependent elastic constant calculations, Valdez et al. (2012) found a value of 453.54 GPa by using the
203 purely DFT-LDA functional. Another paper by Xie et al. (1999) was devoted to the *ab initio* equation of
204 state of diamond; however they did not report a numerical value of the bulk modulus at 300K, which
205 had to be inferred from the figure they published (Figure 6 in Xie et al. 1999), where it appeared to be
206 slightly overestimated with respect to the experimental datum. Nor it was clear the functional they
207 employed (LDA perhaps); in this case, their results were consistent with those from Valdez et al.
208 (2012). By employing a GGA-PBE functional (Perdew *et al.* 1996), Mounet and Marzari (2005) gave a
209 value of 422 GPa at 300K from a volume-integrated BM4-EoS fit of their $E(V)$ data. It should be
210 stressed that differences in the evaluated bulk moduli from different authors were due to either the
211 different DFT functionals employed in each case, or the basis sets, as already discussed above in the
212 section concerning the static EoS.

213 Experimental data from measurements of the elastic constants of diamond, at variable temperature,
214 gave value of 442.3 GPa (Grimsditch and Ramdas 1975) and 444.8 GPa (Zouboulis et al. 1998); in the
215 latter case, the value of the bulk modulus at 300K was obtained from a fit of $K_0(T)$ values measured in
216 the [300, 1600K] temperature range, according to the function

$$217 \quad K_0(T) = K_0(300K) + B_T(T^2 - 300^2) \quad (1)$$

218 with $K_0(300K) = 444.8 \text{ GPa}$ and $B_T = -1.2 \cdot 10^{-5} \text{ GPa/K}^2$. By performing the same fit on our $K_0(T)$ B1**
219 data, we got $K_0(300K) = 443.9(4) \text{ GPa}$, and $B_T = -0.96(3) \cdot 10^{-5} \text{ GPa/K}^2$ (in parentheses are the errors from

220 the fit). Even by considering the bias due to the basis set quality (see above), our datum fell very close
221 and between the two experimental data available.

222 Isobar curves of the estimated bulk moduli as functions of temperature, in the [0, 2000K] range, are
223 reported in Figure 4, for pressures of 0, 10, 20 and 30 GPa; as it can be seen from the Figure, all of
224 the curves exhibited the same behavior with respect to the temperature; indeed, fitting the $K_p(T)$ data
225 with the same quadratic function as above, gave $K_p(300K) = 479.5(4)$, $514.4(3)$ and $548.8(3)$ GPa for P
226 = 10, 20, and 30 GPa respectively, and the same B_T values as the case of $P = 0$ GPa [$-0.96(3) \cdot 10^{-5}$
227 GPa/K²].

228

229 *Thermal expansion*

230 The quasi-harmonic estimation of the thermal expansion coefficient as a function of temperature

$$231 \alpha_V(T) = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (2)$$

232 has been plotted in Figure 5 in the [1, 300K] temperature range. The most recent and highly accurate
233 experimental $\alpha_V(T)$ curve from Stoupin and Shvyd'ko (2011) is also reported in the same figure [taking
234 into account that, in the latter work, the thermal expansion coefficient of the lattice parameter (α_L)
235 has been measured, and the relation between the two coefficients is $\alpha_V = 3\alpha_L$]. The two curves nearly
236 overlap; in particular the difference between the calculated and experimental coefficients, at 300K
237 ($3.19 \cdot 10^{-6}$ and $3.22 \cdot 10^{-6} \text{K}^{-1}$, respectively), is $2.7 \cdot 10^{-8} \text{K}^{-1}$, which is consistent with the accuracy of 10^{-8}K^{-1} ,
238 estimated for the experimental measurements by Stoupin and Shvyd'ko (2011). Very good agreement
239 exists with other literature data like those from Reeber and Wang (1996): at 300K the experimental

240 datum for α_V is $3.05 \cdot 10^{-6} \text{K}^{-1}$ (slightly underestimated with respect to the experimental data of Stoupin
 241 and Shvyd'ko 2011); at 1000, 2000 and 3000K the experimental thermal expansion coefficients are
 242 $1.34 \cdot 10^{-5}$, $1.64 \cdot 10^{-5}$ and $1.71 \cdot 10^{-5} \text{K}^{-1}$ respectively, to be compared with the calculated data of
 243 respectively $1.25 \cdot 10^{-5}$, $1.50 \cdot 10^{-5}$ and $1.60 \cdot 10^{-5} \text{K}^{-1}$.

244 The very high reliability of the thermal expansion behavior, as demonstrated by the comparison of the
 245 calculated data with the experimental ones at room pressure, makes us confident about thermal
 246 expansion data at higher pressures. Figure 6 reports the calculated $\alpha_V(T)$ curves for the pressures of
 247 $P=0, 10, 20$ and 30 GPa , in the $[0, 2000\text{K}]$ temperature range. As what it is frequently required is the
 248 cell volume at a given pressure and temperature $[V_P(T)]$, an empirical relation has been derived of the
 249 form:

$$250 \quad \frac{V_P(T)}{V_P(300\text{K})} = 1 + C_1 T + C_2 T^2 + C_3 T^3 + \frac{C_4}{T} + \frac{C_5}{T^2} \quad (3)$$

251 where $V_P(300\text{K})$ is the cell volume at pressure P and $T=300\text{K}$. This relation can confidently be used in
 252 the $[300, 2500\text{K}]$ temperature range; the five C_i coefficients are reported in Table 3 for seven different
 253 values of the pressure in the $[0, 30\text{GPa}]$ range. Coefficients for other values of pressure in the range
 254 can easily be derived by interpolation. As concerns other ab initio determinations of thermal
 255 expansion at high pressure and temperature, substantial agreement exists between our data and
 256 those from Xie et al. (1999), who employed an unspecified *standard* purely DFT functional, and a
 257 plane wave basis set. Ivanova and Mavrin (2013) also reported the calculation of thermal expansion of
 258 diamond in the $[0, 1500\text{K}]$ temperature range (at the LDA-DFT level of the theory); from the plot they
 259 reported (Figure 4 in Ivanova and Mavrin 2013) it appears that $\alpha_V = 3 \cdot \alpha_L = 3.6 \cdot 10^{-6} \text{K}^{-1}$ at 300K , which is
 260 somewhat overestimated with respect to the experimental data from Reeber and Wang (1996) and

261 Stoupin and Shvyd'ko (2011) at the same temperature ($3.22 \cdot 10^{-6}$ and $3.05 \cdot 10^{-6} \text{K}^{-1}$, respectively), but in
262 substantial agreement with older experimental data from Slack and Bartram (1975), which they use as
263 reference.

264

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APPENDIX

266 Static energies and vibrational frequencies at the (static) equilibrium, and at fixed cell volumes, were
267 performed by means of the ab initio CRYSTAL09 code (Dovesi et al. 2009), which implements the
268 Hartree–Fock and Kohn–Sham, Self Consistent Field (SCF) method for the study of periodic systems
269 (Pisani et al. 1988), by using a Gaussian type basis set. The present choice of the Hamiltonian and the
270 basis set employed were discussed above in the Computational Details section. The DFT exchange and
271 correlation contributions to the total energy were evaluated by numerical integration, over the cell
272 volume, of the appropriate functionals; a (99, 1454) p grid was used, where the notation (nr, nx) p
273 indicates a pruned grid with nr radial points and nx angular points on the Lebedev surface in the most
274 accurate integration region (see the ANGULAR keyword in the CRYSTAL09 user's manual, Dovesi et al.
275 2009). Such a grid corresponds to 2920 integration points in the unit cell at the equilibrium volume.
276 The accuracy of the integration can be measured from the error in the integrated total electron
277 density, which amounts to $5 \cdot 10^{-5} |e|$ for a total of 12 electrons in the cell. The thresholds controlling
278 the accuracy of the calculation of Coulomb and exchange integrals were set to 10 (ITOL1 to ITOL4)
279 and 22 (ITOL5; Dovesi et al. 2009). The diagonalization of the Hamiltonian matrix was performed at 16
280 independent \underline{k} vectors in the reciprocal space (with reference to the primitive unit cell. Monkhorst
281 net; Monkhorst and Pack 1976) by setting to 6 the shrinking factor IS (Dovesi et al. 2009).

282 The cell parameter at the static conditions was optimized by analytical gradient methods, as
283 implemented in CRYSTAL09 (Civalleri et al. 2001; Dovesi et al. 2009). Geometry optimization was
284 considered converged when each component of the gradient (TOLDEG parameter in CRYSTAL09) was
285 smaller than 0.00001 hartree/bohr and displacements (TOLDEX) with respect to the previous step
286 were smaller than 0.00004 bohr. Static energies at each cell volume are provided as supplementary
287 material (Table S1a and S1b, for the B1 and B2 basis sets, respectively). Vibrational frequencies and
288 normal modes were calculated at different cell volumes, within the limit of the harmonic
289 approximation, by diagonalizing a mass-weighted Hessian matrix, whose elements are the second
290 derivatives of the full potential of the crystal with respect to mass-weighted atomic displacements
291 (see Pascale et al., 2004 for details). The threshold for the convergence of the total energy, in the SCF
292 cycles, was set to 10^{-10} hartree (TOLDEE parameter in CRYSTAL09). Results are provided as
293 supplementary material (Tables S2a and S2b for the B1 and the B2 basis sets, respectively).
294 Total pressures (sum of static, zero point and thermal pressures) at different unit cell volumes and
295 temperatures are reported as supplementary materials (Table S3).

296

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432 **Captions to the Tables:**

433

434 **Table 1:** Static cell volume ($V_{0,st}$; in \AA^3) and cell parameter ($a_{0,st}$; in \AA) at the static equilibrium ($P_{st}=0$);
435 static bulk moduls ($K_{0,st}$; in GPa) and its pressure derivative (K'_{st}), obtained with different basis
436 sets/Hamiltonians (see text for explanations concerning both the basis sets and the Hamiltonians).

437

438 **Table 2:** Equilibrium cell volume (V_{0T} ; in \AA^3) and cell parameter (a_{0T} ; in \AA); bulk moduls (K_{0T} ; in GPa)
439 and its pressure derivative (K'_T), at the temperature of 300K, calculated with different basis sets
440 (WC1LYP functional).

441

442 **Table 3:** Coefficients of the equation (3) for the interpolation of the ratio $V_p(T)/V_p(300K)$ at several
443 pressures, in the [300, 2500K] temperature range. See text for explanations. C_1 is in K^{-1} , C_2 in K^{-2} , C_3 in
444 K^{-3} , C_4 in K and C_5 in K^2 .

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447 **Captions to the Figures:**

448

449 **Figure 1:** Vibrational density of state of diamond (VDOS). See text for explanation.

450

451 **Figure 2:** Phonon dispersion in diamond along the [001]* path in the reciprocal space (Δ path), from
452 the Γ point (Brillouin zone center) to the X point (zone border). The inset represents the experimental
453 data along the same path, from the work of Warren et al., 1967. Reprinted excerpt with permission
454 from Warren, J.L., Yarnell, J.L., Dolling, G., and Cowley, R.A., Physical Review, 158, 805, 1967.
455 Copyright (1967) by the American Physical Society.

456

457 **Figure 3:** Bulk modulus at 300K (K_0 in GPa) as a function of the size of the supercell employed for the
458 calculation, the latter being measured by the module of the corresponding smallest \underline{k} vector (in unit
459 of $|\underline{a}^*|$). Note that $|\underline{k}|=1 |\underline{a}^*|$ corresponds to a vector of the reciprocal lattice, which is therefore
460 equivalent to the Γ point.

461

462 **Figure 4:** Bulk modulus (K_p) as a function of temperature, at four different pressures (isobar curves).

463

464 **Figure 5:** Thermal expansion coefficient (α_v ; referred to the volume of the unit cell) as a function of
465 temperature (low temperature data). The experimental data (dashed curve) are from the fit as it is
466 reported in Stoupin and Shvyd'ko (2011).

467

468 **Figure 6:** Thermal expansion coefficient (α ; referred to the unit cell volume) as a function of
469 temperature, at four different pressures (isobar curves).

470

1 **Tables**

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Table 1

Basis set/Hamiltonian	$V_{0,st}$	$a_{0,st}$	$K_{0,st}$	K'_{st}
B1/WC1LYP	45.872	3.5797	445.0	3.62
B1'/WC1LYP	45.878	3.5799	450.3	3.58
B2/WC1LYP	45.187	3.5618	456.4	3.62
B1/B3PW	45.478	3.5694	460.3	3.62
B2/B3PW	44.793	3.5514	476.3	3.61
B2/PBE	45.477	3.5694	444.0	3.66
B3/B3PW ^a	45.526	3.5707	442.8	3.43
B3/RHF ^a	45.358	3.5663	508.7	3.58
PW/PBE ^b	45.432	3.5682	432	-

^aZhi-Jianet *al.* (2009)^bMounet and Marzari (2005)

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Table 2

	V_{0T}	a_{0T}	K_{0T}	K'_T
B1	46.399	3.5934	427.7	3.65
B2	45.717	3.5757	438.3	3.66
B1*	45.694	3.5751	439.0	3.65
B1**	45.689	3.5750	445.4	3.60

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Table 3

P	c₁(x10⁶)	c₂(x10⁹)	c₃(x10¹³)	c₄	c₅
0	2.78	5.62	-8.47	-1.48	330.61
5	2.57	5.47	-8.26	-1.41	316.17
10	2.37	5.33	-8.07	-1.34	302.75
15	2.19	5.20	-7.90	-1.28	290.18
20	2.03	5.07	-7.72	-1.22	278.52
25	1.88	4.95	-7.55	-1.17	267.50
30	1.74	4.83	-7.39	-1.12	257.44

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