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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11

12 **ABSTRACT**

13 The volume bulk modulus, together with its temperature dependence, and the thermal expansion of

14 diamond at various pressures, were calculated from first principles in the [0, 30GPa] and [0, 3000K]

15 pressure and temperature ranges. The hybrid HF/DFT functional employed (WC1LYP) proved to be

16 particularly effective in providing a very close agreement between the calculated and the available

17 experimental data. In particular, the bulk modulus at 300K was estimated to be 444.6 GPa (K' = 3.60);

18 at the same temperature, the (volume) thermal expansion coefficient was $3.19 \cdot 10^{-6}$ K^{-1}. To the

19 authors' knowledge, among the theoretical papers devoted to the subject, the present one provides

20 the most accurate thermo-elastic data in high pressure and temperature ranges. Such data can

21 confidently be used in the determination of the pressure of formation using the "elastic method" for

22 minerals found as inclusions in diamonds, thus shading light upon the genesis of diamonds in the

23 Earth's upper mantle.

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

25

INTRODUCTION

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 diffrattometric 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).

65

66   **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).

99

100   **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.

110

111

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 an 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 (442-445GPa; 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

Thermal Equation of State

By adding the static pressures (from the higher quality B2 basis set calculation) to the zero point and thermal pressures estimated from the vibrational frequencies and their volume derivative (B1 and B2 calculations) of a 2x2x2 supercell of the conventional FCC diamond cell (32 $\underline{k}$ points of the reciprocal lattice, 189 normal modes of vibration), the total pressure at a given temperature could be estimated, for a set of values of the unit cell volume. For any given fixed temperature value, the P(V) data were fitted by a BM3-EoS, so that the bulk modulus K_{0T}, its pressure derivative K'_T and the equilibrium volume V_{0T} could be estimated. Results are summarized in Table 2 for the two different basis sets, at the reference temperature of 300K. The significant difference between the bulk moduli estimated by using the B1 and B2 basis sets (more than 10 GPa, as in the static calculation reported in Table 1) is due to the differences of the static contributions to the total pressure. Indeed, using the EoS parameters estimated with the B2 basis set for the static part, together with the frequencies and their volume derivatives for the vibrational part [in the latter cases, having rescaled by a factor $V_{0,st}(B2)/V_{0,st}(B1)$ the unit cell volumes at which the vibrational frequencies were calculated, being $V_{0,st}(Bx)$ the equilibrium static volume optimized by using the Bx basis set; in this way, the frequencies at any given value of the static pressure for the B1 base were assigned to cell volumes corresponding to the same static pressure for the B2 base] and fitting the resulting P(V) data, yielded a K_{0T} of 439.0GPa (V_{0T}=45.694 Å^3, K'=3.65; B1* data in Table 2), which is only about 0.7GPa higher than the bulk modulus estimated by using the frequencies calculated with the B2 basis set. This means that, even if the quality of the basis set had a significant impact on the estimated static elastic parameters, frequencies calculated with a poorer basis set could confidently be used for the evaluation of the 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 $0.77|a*|$

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 Å^3 (a_0=3.575 Å).

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

218   with $K_0(300K)$ = 444.8 GPa and B_T = -1.2·10^{-5}GPa/K^2. By performing the same fit on our $K_0(T)$ B1**

219   data, we got $K_0(300K)$ = 443.9(4) GPa, and B_T = -0.96(3)·10^{-5}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 been 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 = 0GPa [-0.96(3)·10^{-5}

227   GPa/K^2].

228

229   *Thermal expansion*

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

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

232   has been plotted in Figure 5 in the [1, 300K] temperature range. The most recent and highly accurate

233   experimental α_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 α_V =3α_L]. The two curves nearly

236   overlap; in particular the difference between the calculated and experimental coefficients, at 300K

237   (3.19·10^{-6} and 3.22·$10^{-6}$$K^{-1}$, respectively), is 2.7·$10^{-8}$$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 $3.05 \cdot 10^{-6} K^{-1}$ (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 $1.71 \cdot 10^{-5} K^{-1}$ respectively, to be compared with the calculated data of

243   respectively $1.25 \cdot 10^{-5}$, $1.50 \cdot 10^{-5}$ and $1.60 \cdot 10^{-5} K^{-1}$.

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, 2000K] 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    $$\frac{V_P(T)}{V_P(300K)} = 1 + C_1 T + C_2 T^2 + C_3 T^3 + \frac{C_4}{T} + \frac{C_5}{T^2}$$ (3)

251   where $V_P(300K)$ is the cell volume at pressure P and T=300K. This relation can confidently be used in

252   the [300, 2500K] temperature range; the five C_i coefficients are reported in Table 3 for seven different

253   values of the pressure in the [0, 30GPa] 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, 1500K] 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 $\alpha_V = 3 \cdot \alpha_L = 3.6 \cdot 10^{-6} K^{-1}$ 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 $3.05 \cdot 10^{-6} K^{-1}$, respectively), but in

262 substantial agreement with older experimental data from Slack and Bartram (1975), which they use as

263 reference.

264

265 **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; Monkhrost 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).

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Captions to the Tables:

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

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

Table 3: Coefficients of the equation (3) for the interpolation of the ratio $V_P(T)/V_P(300K)$ at several 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 K^{-3}, C_4 in K and C_5 in K^2.

Captions to the Figures:

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

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

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

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

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

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

1   **Tables**

2

3   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	-

[a]Zhi-Jian*et al.* (2009)
[b]Mounet and Marzari (2005)

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6   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	$c_1 (\times 10^6)$	$c_2 (\times 10^9)$	$c_3 (\times 10^{13})$	c_4	c_5
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