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1 **High pressure thermo-elastic properties of beryl ($\text{Al}_4\text{Be}_6\text{Si}_{12}\text{O}_{36}$) from *ab initio***
2 **calculations, and observations about the source of thermal expansion**
3

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24 **Abstract**

25
26 *Ab initio* calculations of thermo-elastic properties of beryl ($\text{Al}_4\text{Be}_6\text{Si}_{12}\text{O}_{36}$) have been carried out at
27 the hybrid HF/DFT level, by using the B3LYP and WC1LYP Hamiltonians. Static geometries and
28 vibrational frequencies were calculated at different values of the unit cell volume, to get static
29 pressure and mode- γ Grüneisen's parameters. Zero point and thermal pressures were calculated
30 by following a standard statistical-thermodynamic approach, within the limit of the quasi-
31 harmonic approximation, and added to the static pressure at each volume, to get the total
32 pressure (P) as a function of both temperature (T) and cell volume (V). The resulting $P(V,T)$ curves
33 were fitted by appropriate EoS', to get bulk modulus (K_0) and its derivative (K'), at different
34 temperatures. The calculation successfully reproduced the available experimental data concerning
35 compressibility at room temperature (the WC1LYP Hamiltonian provided K_0 and K' values of
36 180.2Gpa and 4.0, respectively), and the low values observed for the thermal expansion
37 coefficient. A zone-centre soft mode $P6/mcc \rightarrow P\bar{1}$ phase transition was predicted to occur at a
38 pressure of about 14 GPa; the reduction of the frequency of the soft vibrational mode, as the
39 pressure is increased, and the similar behaviour of the majority of the low frequency modes,
40 provided an explanation of the thermal behaviour of the crystal, which is consistent with the RUM
41 model (Rigid Unit Model; Dove et al., 1995), where the negative contribution to thermal expansion
42 is ascribed to a *geometric* effect connected to the tilting of rigid polyhedra in framework silicates.

43 **Keywords:** thermal expansion, compressibility, bulk modulus, thermo-elastic properties, ab
44 initio calculations, beryl.

45
46 **1. Introduction**

47
48 In the last few years, the increased availability of fast computational resources, at a relatively low
49 cost, allowed the calculation of thermo-elastic and thermodynamics properties of minerals, by
50 following a fully *ab initio* approach within a statistical-thermodynamics framework (see *e.g.*

51 Oganov et al., 2002 for an overview). The method can be applied to the determination of
52 properties of minerals even at conditions of simultaneous very high pressure/high temperature,
53 which are not easily attainable experimentally. In general, however, the reliability of the
54 calculated results and, hence, their usefulness for geophysical modelling of the Earth's crust and
55 mantle, depends upon details concerning (i) the specific type of quantum-mechanical calculation
56 chosen (e.g., *pure* DFT or *hybrid* HF/DFT Hamiltonian; exchange and correlation DFT functionals;
57 basis sets; pseudo-potentials employed in connection with plane-waves basis sets, etc...); (ii) the
58 range of validity of various approximations employed, like the quasi-harmonic one (Anderson,
59 1995), to get phonons frequencies together with their volume and temperature dependence [see
60 also Oganov and Dorogokupets (2004) for an account of *intrinsic* anharmonic effects evaluated at
61 the quantum-mechanical level, by a perturbative approach], and (iii) the consideration of phonon
62 *dispersion*.

63 The present work discusses an application of the whole algorithm, within the limit of the
64 quasi-harmonic approximation (Anderson, 1995), to the determination of the (volume) thermal
65 expansion and compressibility, and their temperature/pressure dependence, of beryl
66 ($\text{Al}_4\text{Be}_6\text{Si}_{12}\text{O}_{36}$, space group *P6/mcc*, $Z=1$; Deer et al., 1992): a framework silicate according to the
67 Zoltai's classification (Zoltai, 1960), having a *moderate* structural complexity. Two different hybrid
68 HF/DFT Hamiltonians (that is, containing both an *exact non-local* Hartree-Fock correction to the
69 DFT exchange functionals) were used to get structures, static energies and frequencies at different
70 cell volumes, namely (i) the well known B3LYP Hamiltonian (Becke, 1993; Koch and Holthausen,
71 2000), and (ii) a relatively recent hybrid formulation (WC1LYP), due to Wu and Cohen (2006) for
72 the exchange part, and Lee et al. (1988) for the correlation part. See Prencipe and Nestola (2005)
73 for a discussion about the role of the *exact non-local* Hartree-Fock exchange correction, in
74 calculations of structure and compressibility in silicates (beryl, in particular). The WC1LYP

75 Hamiltonian seems to perform slightly better than B3LYP, but it is not yet tested on a sufficiently
76 large class of minerals; see Demichelis et al. (2009) for applications to pyrope, forsterite, α -quartz
77 and corundum. B3LYP calculations proved to be highly successful in a number of other cases,
78 either concerning the derivation of thermodynamics properties of minerals within a quantum-
79 statistic framework (α , β and γ polymorphs of Mg_2SiO_4 , Ottonello et al., 2008; stishovite, Ottonello
80 et al., 2009; *Anhydrous B* phase, $\text{Mg}_{14}\text{Si}_5\text{O}_{24}$, Ottonello et al., 2010), or the interpretation and
81 assignment of infrared and Raman experimental spectra (see, for instance: calcite, Prencipe et al.,
82 2004; beryl, Prencipe et al., 2006; lizardite, Prencipe et al., 2009, and references therein).

83 As beryl is concerned, at the B3LYP level the very satisfactory agreement between
84 calculated and experimental vibrational frequencies, at room pressure, has already been
85 demonstrated (Prencipe et al., 2006), and its high pressure properties at the *static limit* were also
86 investigated in a number of works (Prencipe, 2002; Prencipe and Nestola, 2005, 2007) within the
87 framework of the Quantum Theory of Atoms in Molecules and Crystals (QTAIMC; Bader, 1994).
88 The mineral consists of sixfold rings of Si-centred tetrahedra stacked along the [001] sixfold
89 symmetry axis, which are interconnected by Be-centred tetrahedra and Al-centred octahedra.
90 Beryl is quoted among those minerals having a low or negative thermal expansion coefficient
91 (Morosin, 1972; Schlenker et al., 1977; Hochella and Brown, 1986; Fey, 1995), together with
92 cordierite and indialite ($\text{Mg}_4\text{Al}_8\text{Si}_{10}\text{O}_{36}$) which have similar structures. Such peculiar thermal
93 expansion of beryl has been the subject of investigations focussing on (i) thermodynamic
94 properties and their relations with thermal expansion (Schlenker et al., 1977; Pilati et al., 1997); (ii)
95 thermal behaviour of bonds (Hochella and Brown, 1986), and (iii) geometric effects related to
96 tilting of rigid polyhedra leading to negative contributions to the thermal expansion; the latter is
97 the Rigid Unit Model (RUM), concerning the thermal behaviour of framework silicates (Dove et al.,
98 1995; Welche et al., 1998; Heine et al., 1999). Experimental values of thermal expansion,

99 compressibility and heat capacity were successfully reproduced by the present calculations. Also, a
100 $P6/mcc \rightarrow P\bar{1}$ soft mode phase transition was predicted to occur at a pressure of about 14GPa,
101 at room temperature. At least in part, the behaviour of thermal expansion and compressibility of
102 beryl was found to be related to the existence of such a soft mode, being it associated to a
103 negative Grüneisen's parameter; however, as already observed by Welche et al. (1998) in the case
104 of β -quartz, the majority of low frequency modes provides a negative contribution to thermal
105 expansion, which is balanced by positive contributions from the high frequency modes.
106 Consistently with the RUM model of Dove et al. (1995), the low frequency modes, having negative
107 Grüneisen's parameters, resulted to be describable as rigid tilting of polyhedra, so that a
108 *geometric effect* determining the low value of thermal expansion could be invoked, according to
109 Heine et al. (1999).

110 The very successful reproduction of thermo-elastic properties by the method here
111 discussed, coupled with the use of the WC1LYP Hamiltonian (Wu and Cohen, 2006), makes the
112 latter suitable for analogous calculations concerning minerals existing in the Earth's mantle, at
113 simultaneous high pressure/high temperature conditions.

114 115 **2. Computational details**

116
117 Geometry optimizations, energy calculations at the static limit (no zero point and thermal
118 energies), and vibrational frequencies at the Γ point, for a set of different unit cell volumes, were
119 calculated by means of the CRYSTAL06 program (Dovesi et al. 2006), by using two different hybrid
120 HF/DFT Hamiltonians: B3LYP (Becke, 1993) and WC1LYP (Wu and Cohen, 2006). Details about the
121 procedure which has been followed, and the computational parameters employed are provided in
122 Appendix.

123 Total pressures, bulk moduli, thermal expansion and specific heat were obtained in the
124 limit of the quasi-harmonic approximation (Anderson, 1995), through the evaluation of the unit

125 cell volume dependence of the frequencies of the vibrational normal modes (mode- γ Grüneisen's
126 parameters) at the Γ point. Dispersion effects in the phonon spectra at various pressures were not
127 taken into account as the large volume of the unit cell makes it impossible the required calculation
128 of the vibrational frequencies in the case of super-cells, due to limitation of the available
129 computational resources. On the other hand, the Grüneisen's parameters corresponding to the
130 zone-centre vibrational modes, can reasonably be considered representative of the whole set of
131 parameters, due to their large number which depends upon the number of atoms in the unit cell.
132 Indeed, as demonstrated by other Authors (Ottonello et al., 2008, 2009, 2010), highly reliable
133 estimations of thermo-elastic and thermodynamics quantities can be obtained by neglecting
134 dispersion effects, even in case of systems having relatively small unit cells. This is consistent with
135 the general observation that thermodynamic properties, which are obtained as averages over the
136 relevant quantities at the atomic level, can reliably be derived even without a detailed knowledge
137 of the phonon density of state (Kieffer, 1979a). For the same reasons, LO/TO splitting of the IR
138 active modes was not taken into account (see discussion in Ottonello et al., 2008).

139 Intrinsic anharmonic effects (Oganov and Dorogokupets, 2004) were not taken into
140 account, thought they could play a role in determining frequencies and Grüneisen's parameters
141 of the lower frequency modes, especially at very high temperature. At the not exceedingly high
142 temperatures of our calculation (1000K), and at high pressures, they are however expected to be
143 small (Oganov and Dorogokupets, 2004). See the last section of the present paper for an
144 evaluation of the relative importance of anharmonic terms of the potential, with reference to a
145 few *key* modes of the beryl structure.

146 A correction to the specific heat at zero pressure was done in order to take into account
147 the contributions from the three acoustic branches of the phonon spectrum. In this case, a
148 Kieffer's model was employed (limited to the acoustic branches only), where a sinusoidal

149 dispersion relation is assumed to exist between the wavelengths and the frequencies of the
 150 acoustic modes (Kieffer, 1979a; Kieffer, 1979b, Ottonello et al., 2010). The maximum frequencies
 151 of the transversal and longitudinal acoustic waves (that is, the frequencies at the borders of the
 152 Brillouin zone) were estimated from the calculated values of the elastic and compliances
 153 constants, following a method described in Ottonello et al. (2010). The elastic constants were
 154 obtained by using a development version of the CRYSTAL code. Details on the latter procedure,
 155 together with those concerning the formalism employed to derive thermo-elastic properties from
 156 vibrational frequencies (following Anderson, 1995) are given below.

157
 158 *2.1 Pressures*

159
 160 The total pressure (P) at each cell volume (V) and temperature (T) is given by the expression:

161
 162
$$P(V, T) = -\left(\frac{\partial E_{st}}{\partial V}\right) + \frac{h}{2V} \sum_j \gamma_j \nu_j + \frac{h}{V} \sum_j n_j(\nu_j, T) \gamma_j \nu_j \quad (1)$$

163
 164
$$n_j(\nu_j, T) = \frac{1}{e^{h\nu_j/kT} - 1} \quad (2)$$

165
 166 where h and k are respectively the Planck's and Boltzmann's constants; E_{st} is the static energy
 167 calculated by CRYSTAL at a given cell volume; ν_j is the frequency of the j^{th} vibrational normal
 168 mode; $n_j(\nu_j, T)$ is the number of phonons of frequency ν_j , at the temperature T (or, from a different
 169 point of view, the excitation level of the corresponding normal mode). Equation (2) follows directly
 170 from the Bose-Einstein statistics applied to the phonon gas; γ_j is the Grüneisen's parameter,
 171 defined by the expression:

172
 173
$$\gamma_j = -\frac{\partial \ln \nu_j}{\partial \ln V} = -\frac{V}{\nu_j} \frac{\partial \nu_j}{\partial V} \quad (3)$$

174
 175

176 Actually, the γ here defined is the mode- γ Grüneisen's parameter, whereas, more properly γ
 177 (thermal Grüneisen's parameter) is defined as: $\gamma = (\partial P/\partial U)_V$ (Grüneisen, 1912); for short, in the
 178 following the mode- γ parameter will simply be indicated with γ .

179 Such parameters were estimated by the analytical derivatives with respect to V , at the *static*
 180 *equilibrium* cell volume (V_{st}^0), of quadratic polynomials fitting the *numerically* determined $\gamma_j(V)$
 181 curves. The sums in equation (1) run on all the vibrational modes at the Γ point ($\mathbf{k}=\mathbf{0}$) of the
 182 reciprocal space. The first term on the right hand of equation (1) is the *static* pressure $P_{st}(V)$; the
 183 second term is the *zero point* pressure $P_{zp}(V)$ and the third one is the *thermal* pressure $P_{th}(V,T)$.
 184 The sum $P_{ath}(V)=P_{st}(V)+P_{zp}(V)$ is here named *athermal* pressure, whereas the sum
 185 $P_{vib}(V,T)=P_{zp}(V)+P_{th}(V,T)$ is named *vibrational* pressure.

186 Static pressures were determined by interpolating the $E_{st}(V)$ curve by either (i) a volume
 187 integrated 3rd order Birch-Murnaghan equation of state (V_{int} -BM3), or (ii) Legendre's polynomials
 188 up the 3rd or 4th-order (L3 and L4, respectively), to get static pressures as derivatives of the
 189 resulting analytical curves. Zero points and thermal pressures were obtained either by (i) direct
 190 application of equations (1) and (2), or (ii) numerical derivative, with respect to V , of the (molar)
 191 Helmholtz $F_{zp}(V)$ and $F_{th}(V,T)$ functions, where:

$$192 \quad F_{zp}(V) = U_{zp}(V) = \frac{1}{2} \mathcal{N}_0 \sum_j h\nu_j \quad (4.1)$$

$$193 \quad F_{th}(V, T) = U_{th} - TS = \mathcal{N}_0 \sum_j n_j(\nu_j, T) h\nu_j - TS \quad (4.2)$$

$$194 \quad S(V, T) = \mathcal{N}_0 k \sum_j \left[n_j(\nu_j, T) \frac{h\nu_j}{kT} - \ln(1 - e^{-h\nu_j/kT}) \right] \quad (4.3)$$

195

196 and \mathcal{N}_0 is the Avogadro's number. Thought the methods (i) and (ii) of getting zero point and
 197 thermal pressures are *formally* identical, in general the resulting values might depend upon the
 198 detailed implementations of both, by making use of fittings and/or numerical derivatives which

199 could differ in accuracy. Moreover, method (i) implicitly assumes the constancy of the Grüneisen's
200 parameters as the cell volume is reduced in a finite interval; in the present case, such assumption
201 is not strictly valid for all the normal modes, and a check of the possible differences in the results
202 obtained by applying the two different methods was required.

203
204

205 *2.2 Equation of State*

206
207 The equation of state (EoS) has been determined by several methods differing in the way static,
208 zero point and thermal pressures were obtained. As already explained in the section above, the
209 static contribution to the pressure (which does not depend on T) must be derived from the $E_{st}(V)$
210 static energy curve calculated by CRYSTAL. Static pressures were then added to zero point and
211 thermal pressures, to get total $P(V,T)$ curves which were subsequently fitted by appropriate EoS's.
212 In this respect, the notation employed below is composed by two symbols, the first one referring
213 to the way static pressure contributions have been calculated, and the second one indicating the
214 type of EoS used to fit the total $P(V,T)$ curve. Precisely: (i) BM3-BM3 and BM3-BM4 notations
215 respectively indicate (second symbol) that 3rd or 4th-order Birch-Murnaghan EoS' have been used
216 to fit the total $P(V,T)$ pressure as a function of V , at a fixed T , whereas a V_{int} -BM3 (referring to the
217 first symbol in the notation) has been used to get static pressures only; (ii) L3-BM3, L3-BM4, L4-
218 BM3 and L4-BM4 notations indicate that static pressures were evaluated through L3 or L4
219 Legendre polynomial fittings; (iii) BM3-BD, L3-BD and L4-BD notations indicate that the bulk
220 modulus at a given cell volume (pressure) and temperature has been calculated by a numerical
221 derivative, with respect to V , of the $P(V,T)$ curve at the corresponding volume, and that static
222 pressures were obtained by the V_{int} -BM3, L3 or L4 fittings, respectively. Finally (iv) a V_{int} -BM3_t
223 notation indicates that a volume integrated BM3 EoS has been used to fit the total (static + zero
224 point + thermal) Helmholtz free energy as a function of V (*one* fit only, at each temperature).

225

226 *2.3 Thermal expansion*

227

228 The thermal expansion coefficient at any given cell volume (pressure), as a function of T , has been
 229 obtained either by (i) numerical derivative of the total pressure with respect to the temperature,
 230 according to the expression:

231

$$232 \alpha_T = \frac{1}{K_T} \left(\frac{\partial P}{\partial T} \right)_T \quad (5)$$

233

234 where K_T is the bulk modulus estimated at the given pressure (cell volume) and temperature, or

235 (ii) direct evaluation of the $\alpha_T K_T$ product (Anderson, 1995):

236

$$237 \alpha_T K_T = \frac{N_0 k}{V} \sum_j \gamma_j e^{h\nu_j/kT} \left(\frac{h\nu_j/kT}{e^{h\nu_j/kT} - 1} \right)^2 \quad (6)$$

238

239

240

241 *2.4 Acoustic phonon frequencies at the Brillouin zone border, and Kieffer's model*

242

243 Average longitudinal (ρ) and transversal (s) acoustic phonon frequencies ($\bar{\nu}_j$, $j=p,s$) at the Brillouin
 244 zone boundary were estimated through the relation (Kieffer, 1979b)

245

$$246 \bar{\nu}_j = \bar{\nu}_j \frac{1}{2\pi} \left(\frac{6\pi^2 N_0}{V} \right)^{1/3} \quad (7)$$

247

248 where $\bar{\nu}_j$ is the corresponding average wave velocity. In turn, velocities were obtained through

249 the well known relations $\bar{\nu}_s = (\bar{\mu}_{VRH}/\rho)^{1/2}$ and $\bar{\nu}_p = \left[\left(\bar{K}_{VRH} + \frac{4\bar{\mu}_{VRH}}{3} \right) / \rho \right]^{1/2}$, where ρ is the

250 density, \bar{K}_{VRH} and $\bar{\mu}_{VRH}$ are the Voigt and Reuss' average of the bulk and shear moduli,

251 respectively:

252

$$253 \bar{\mu}_{VRH} = \frac{1}{2}(\mu_V + \mu_R); \quad \bar{K}_{VRH} = \frac{1}{2}(K_V + K_R) \quad (8.1)$$

254

$$255 \mu_V = \frac{1}{15}(c' - c'' + 3c'''); \quad \mu_R = 15(4s' - 4s'' + 3s''') \quad (8.2)$$

256

$$257 K_V = \frac{1}{9}(c' + 2c''); \quad K_R = (s' + 2s'')^{-1} \quad (8.3)$$

258
 259 and c' , c'' , c''' , s' , s'' , s''' are respectively the sums over the elastic constants and compliances
 260 $(c_{11}+c_{22}+c_{33})$, $(c_{12}+c_{13}+c_{23})$, $(c_{44}+c_{55}+c_{66})$, $(s_{11}+s_{22}+s_{33})$, $(s_{12}+s_{13}+s_{23})$ and $(s_{44}+s_{55}+s_{66})$. The elastic and
 261 compliances tensors were calculated by using CRYSTAL as detailed in Appendix.

262
 263 The heat capacity at constant volume (C_V), as a function of T , has been calculated at zero pressure
 264 through the formula (Ottonello et al., 2010)

265
 266
$$C_V = 3k\mathcal{N}_0 \left(\frac{2}{\pi}\right)^3 \sum_{i=1}^3 \int_0^{X_i} \frac{[\arcsin(X/X_i)]^2 X^2 e^X}{(X_i^2 - X^2)^{1/2} (e^X - 1)^2} dX + k\mathcal{N}_0 \sum_{i=4}^{3n} e^{X_i} \left(\frac{X_i}{e^{X_i} - 1}\right)^2 \quad (9)$$

267
 268 where $X_i = \hbar\nu_i/KT$. In equation (9), the first sum runs over the three acoustic branches and, in
 269 our model, $\nu_1 = \nu_2 = \bar{\nu}_s$; $\nu_3 = \bar{\nu}_p$; the second sum runs over all the optic modes at the Γ point.

270
 271 The specific heat at constant pressure (C_P) were calculated at zero pressure through the usual
 272 formula

273
 274
$$C_P = C_V + T\alpha_T^2 K_T V_T \quad (10)$$

275
 276 where V_T is the cell volume at the temperature T .

279 3. Results and discussion

281 3.1 Grüneisen's parameters, zero point, thermal pressures and thermal expansion

282
 283 Equilibrium geometries, static energies and zone-centre vibrational frequencies (ν_j , $j=1,3n-3$; $n=58$
 284 is the number of atoms in the unit cell) were determined for sets of (i) 11 different cell volumes (V)
 285 ranging from 697 to 650 Å³ (B3LYP Hamiltonian), and (ii) 9 different V 's in the [691, 650 Å³] range
 286 (WC1LYP Hamiltonian); details are provided in Appendix. For each normal mode, the Grüneisen's
 287 parameter γ_j was determined. In the low frequency region of the vibrational spectrum (ranging
 288 from 100 to about 400 cm⁻¹) the majority of the vibrational modes are associated to a negative

289 Grüneisen's parameter, whereas for frequencies above 600 cm^{-1} , all of such parameters are
290 positive [see Figure (1)]. The average Grüneisen's parameter ($\bar{\gamma}$) is positive, and equal to 0.41 for
291 both the B3LYP and WC1LYP Hamiltonians.

292

293 Figure 1

294

295 According to equation (1), modes having a negative γ_j produce a negative contribution to the
296 vibrational pressure, however since $\bar{\gamma}$ is positive and the high frequencies modes have positive γ_j 's,
297 the zero point pressure is positive and amount to 1.27 GPa at the static equilibrium cell volume
298 (V_{st}^0), where $P_{st} = (\partial E_{st} / \partial V)_{V_{st}^0} = 0$. At zero total pressure and at the athermal limit ($T=0\text{K}$, where
299 the thermal pressure is zero) the static pressure must exactly counterbalance the zero point
300 pressure ($P_{st} + P_{zp} = 0$), so that $P_{st} = -1.27 \text{ GPa}$; this corresponds to an athermal equilibrium volume
301 (V_{ath}^0) larger than the static one: V_{ath}^0 is equal to 697.46 \AA^3 ($V_{st}^0 = 692.22$) at the B3LYP level, and
302 692.10 \AA^3 ($V_{st}^0 = 687.05$) at the WC1LYP one.

303 At higher temperatures, a phonon gas is produced inside the crystal which contributes a
304 thermal pressure whose value depends by (i) the average number of phonons associated to each
305 normal mode, (ii) the corresponding frequencies and (iii) the Grüneisen's parameters [see
306 equation (1)]. The Bose-Einstein distribution of phonons at three different temperatures (300, 600
307 and 900K), and at zero total pressure, is shown in Figure (2):

308

309 Figure 2

310

311 at room temperature (300K) no phonons exist corresponding to modes having frequencies higher
312 than about 900 cm^{-1} , so that the thermal pressure is mainly determined by the low frequencies
313 phonons having negative γ_j 's [see Figure (3)].

314

315 Figure 3

316

317 At higher temperatures, the number of high frequency phonons increases and, since such phonons
318 are associated to positive γ_j 's, an overall positive thermal pressure is produced. The static, zero
319 point and thermal pressure contributions to the (zero) total pressure, as functions of temperature,
320 are plotted in Figure (4): zero point pressure is almost constant along the [0, 1000K] interval (its
321 little variation is due to the small thermal expansion of the cell volume, see below); thermal
322 pressure decreases from 0 to about -0.1 GPa at 290K, and then starts to increase, reaching positive
323 values at temperatures higher than 500K. To maintain the equilibrium with the (imposed) external
324 pressure of 0GPa, the static pressure must mirror the behaviour of the thermal pressure (in fact,
325 by neglecting the slight variation of P_{zp} with temperature, $\Delta P_{st} = -\Delta P_{th}$), that is: P_{st} increases by
326 about 0.1 Gpa from 0 up to 290K, and decreases at higher temperatures.

327

328 Figure 4

329

330 The relative increase of the (negative) static pressure in the [0, 290K] interval is realized through a
331 slight reduction of the cell volume, so that the estimated thermal expansion coefficient is negative
332 at low temperatures. At higher temperatures, thermal expansion is positive but its magnitude
333 remains however small, due to the negative contribution of the low frequency phonons to the
334 thermal pressure.

335 At higher total pressures, the low frequency modes having negative Grüneisen's
336 parameters decrease significantly their frequencies and, consequently, their negative
337 contributions to the thermal pressure is enhanced due the large increment of the associated
338 number of phonons. This results in thermal pressures that are negative even at relatively high
339 temperatures, and negative thermal expansions are thus estimated up to temperatures well above
340 the room one [about 500K at $P=6$ GPa]. Such behaviour is illustrated in Figures (5) and (6),
341 reporting the isobaric curves (0, 3 and 6 GPa) of the $\alpha_T K_T$ product and of the thermal expansion
342 coefficient α_T in the [0, 1200K] temperature interval, as determined from equations (6) and (5),
343 respectively.

344

345 Figures 5 and 6

346

347 Thermal expansion coefficients evaluated through equations (5) or (6) are nearly identical;
348 the B3LYP values (at zero total pressure) at 300, 600 and 900K are $1.0 \cdot 10^{-6}$, $6.5 \cdot 10^{-6}$ and
349 $9.0 \cdot 10^{-6} \text{ K}^{-1}$, respectively (the required K_T values are from a BM3-BD fitting of data up to a P_{max} of
350 6GPa; see next section). WC1LYP values at the same temperatures are lower and, respectively,
351 $-0.7 \cdot 10^{-6}$, $4.2 \cdot 10^{-6}$ and $6.1 \cdot 10^{-6} \text{ K}^{-1}$. Experimental data were derived from the work of Morosin et al.
352 (1972), by calculating cell volumes at different temperatures from the a and c lattice constants
353 plotted in their graph (14 points in the [298, 873K] temperature range), and fitting the resulting
354 $V(T)$ set by using Legendre's polynomials up to the 2nd order (higher order polynomials produced
355 unphysical *waving* of the fitted $V(T)$ curve, due to considerable *noise* in the experimental values);
356 the subsequent derivation, with respect to T , of the $V(T)$ curve, yielded α_T values of $3.2 \cdot 10^{-6}$,
357 $6.0 \cdot 10^{-6}$ and $8.7 \cdot 10^{-6} \text{ K}^{-1}$ at 300, 600 and 900K respectively, in reasonable agreement with the
358 calculated results. By limiting the fit of the experimental $V(T)$ curve to a maximum temperature of

359 720K (11 points), yielded α_T values of $2.4 \cdot 10^{-6}$ and $7.4 \cdot 10^{-6} \text{ K}^{-1}$ at 300 and 600K, respectively. The
360 analysis of the Morosin's data made by Schlenker et al. (1977) resulted in α_T values of $2.1(0.4) \cdot 10^{-6}$,
361 $4.7(0.2) \cdot 10^{-6}$ and $7.3(0.4) \cdot 10^{-6} \text{ K}^{-1}$, at 300, 600 and 900K, respectively (standard uncertainties in
362 parentheses). The B3LYP calculated thermal expansion appears to be in closer agreement with the
363 experimental data, than the WC1LYP one. However, the possible errors affecting the experiment
364 must be stressed, especially in such a case of very low thermal expansion, whose estimation would
365 require highly accurate and precise cell volume data, at each temperature, in order to reach a
366 relatively low uncertainty.

367 368 3.2 Bulk Modulus

369
370 The values of the bulk modulus at zero pressure (K_0) determined at the B3LYP level by using the
371 various methods described in the *computational details* section, are reported in Table (1).

372
373 Table 1

374
375 The four columns under the $P_{max}=6\text{GPa}$ heading refer to the EoS' determined by fitting the $P(V,T)$
376 curves up to 6GPa (*low pressure* case, in what follow); the last four columns refer to fittings
377 extended to the [0, 12GPa] pressure range (*high pressure* case). Static values are also reported [2nd
378 and 6th columns in Table (1)] as determined (i) by fitting the V_{int} -BM3 EoS' (BM3) to the $E_{st}(V)$ curve
379 (these are identical with a V_{int} -BM3_t calculation when the only contribution to the energy
380 considered is the static one), or (ii) through the analytic second derivative, with respect to V and at
381 the static equilibrium volume, of n^{th} -order Legendre polynomials (L3 or L4) fitting the same curve.
382 In the high pressure case, the L3, L5 and L6 fittings of the static energy curve have also been tried,
383 in addition to the L4 one reported in Table (1): the values of the bulk moduli, at the static limit and
384 at the various temperatures, were not significantly different from those obtained by the L4 fitting.

385 Static bulk modulus has also been obtained as a *by-product* of the calculation of the elastic
386 constants C_{ij} (see the Appendix): its value of 179.4 GPa is in close agreement with the
387 corresponding values of Table (1).

388 As it clearly appears in Table (1), in the low pressure case no significant differences in the
389 values of the bulk modulus emerge as a function of the algorithm employed to calculate it. In
390 particular, the static bulk modulus has a value of about 178 GPa, and it decreases to about 172
391 GPa at the athermal limit (due to the presence of zero point effects), and to 168 and 162 GPa, at
392 300 and 600K, respectively (due to thermal effects). In the high pressure case, however, significant
393 differences are observed among the BM3, BM4 and BD values at 300 and 600K (whereas static and
394 athermal values are nearly identical). In particular, due to the effect of the behaviour of the
395 thermal pressure with the temperature (see the previous section), at temperatures greater than
396 zero the inadequacy of the BM3 EoS is evident: indeed the value of K_0 , when the $P_{\text{tot}}(V, T)$ curve is
397 fitted by a BM3 EoS, does not decrease with T , at variance with what could be expected [see BM3-
398 BM3, L4-BM3 and $V_{\text{int-BM3}_t}$ values, for the high pressure case, in Table (1)]. A F_E - f_E plot (Angel,
399 2000), where $f_E = [(V_0/V)^{2/3} - 1]/2$ is the Eulerian strain and $F_E = P/[3f_E(1 + 2f_E)^{5/2}]$ is the
400 *normalized* pressure, is shown in Figure (7): apart the static and athermal cases where the linear
401 and almost flat plots indicates the adequacy of a BM3 curve to fit the $P(V)$ data (indeed, even a 2nd
402 order EoS could describe the data), at higher temperatures the non linearity of the curves is
403 evident, so that $P(V, T)$ data cannot be fitted by a BM3 EoS.

404

405 Figure 7

406

407 A *normal* behaviour with temperature is observed when K_0 is calculated either by (i) using a
408 4th-order Birch-Murnaghan EoS to fit the $P_{\text{tot}}(V, T)$ curve [BM3-BM4 or L4-BM4 cases in Table (1)],

409 or (ii) numerical derivation [BM3-BD and L4-BD cases in Table (1)]. Significant differences of the
410 BM4 and BD bulk moduli at high temperatures, for the high pressure case, are also observed [see
411 BM3-BM4 and BM3-BD, or L4-BM4 and L4-BD in Table (1)], which may reflect the inadequacy of
412 the BM4 EoS to describe high P/T conditions. This is clearly seen in Figure (8), where $K_T(P)$ curves,
413 directly calculated by numerical derivation of the $P(V,T)$ curves, at fixed T (L4-BD or BM3-BD
414 algorithms; we recall here that, in the L4-BD algorithm, the L4 fitting is *limited* to the $E_{st}(V)$ curve,
415 to get the *static* pressure at each V), are plotted together with $K_T(P)$ *point* values determined by
416 using the $K_T(0)$ (*i.e.* K_0), K'_0 and K''_0 parameters from L4-BM4 fittings, at the three different
417 temperatures.

418

419 Figure 8

420

421 Indeed, even if at the athermal limit the bulk moduli obtained through the L4-BD and L4-BM4
422 algorithms are identical all along the [0, 12GPa] pressure range [this fact can also be seen in Table
423 (1)], at higher temperatures the shapes of the L4-BD curves (almost linear for $P < 5$ Gpa, and *bent*
424 toward low values, at higher P , at least for the T=600K case) are definitely not well reproduced by
425 the BM4- $K_T(P)$ based functions. Concerning the low pressure linear region, the slopes for $P \rightarrow 0$
426 (K'_0) of the three L4-BD functions reported in Figure (8) slightly decrease from 3.9, at the athermal
427 limit, to 3.0 at 600K. Instead, the K'_0 values obtained by the L4-BM4 fittings increase strongly from
428 4.0 at the athermal limit, to 6.8 at 300K, and 10.4 at 600K. Meanwhile, the K''_0 values decrease
429 from -0.05 GPa^{-1} , at the athermal limit, to -0.93 and -2.2 GPa^{-1} , at 300 and 600K respectively. The
430 correlation among the K_0 , K'_0 and K''_0 values of the BM4 fittings produces lower values of K_0 than
431 those from the BD calculations [Table (1)]. In the present case, therefore, the most reliable values

432 of the bulk moduli, at each temperature and pressure, are those obtained through the application
433 of a Ln-BD (or a BM3-BD) algorithm.

434 The last row of Table (1) reports the $V_{\text{int-BM3}_t}$ bulk moduli obtained by the $V_{\text{int-BM3}}$ fit of
435 the *total* $F(V,T)$ Helmholtz function. Such values are very close to the BM3-BM3 ones, at each
436 temperature, and for the low and high pressure cases. Other EoS's we tried to fit our $P(V)$ data
437 (e.g. Vinet's EoS) gave results nearly identical to the BM3 ones.

438 Similar trends of the bulk modulus behaviour as a function of temperature, pressure and
439 maximum pressure of fitting were observed in the case of the WC1LYP Hamiltonian, as it can be
440 seen from the results reported in Table (2).

441

442 Table 2

443

444 The WC1LYP K_0 values are generally higher than the corresponding B3LYP ones by more than 10
445 GPa. The experimental value of the bulk modulus measured by Prencipe and Nestola (2005) on
446 $P(V)$ data collected up to a pressure of 6 GPa, and fitted by a BM3 EoS, is also reported in Table (2):
447 the agreement with the calculated datum is excellent, suggesting at least for this case, a very good
448 performance of the WC1LYP Hamiltonian.

449 Isobaric curves of the bulk modulus variation with temperature, at 0, 3, 6 and 9 GPa (L4-BD
450 algorithm) are reported in Figure (9). Apart from the very low temperature region, such curves
451 show negative and nearly constant slopes which increase in magnitude with the pressure;
452 precisely, $(\partial K_T/\partial T)_P = -0.020, -0.022, -0.028$ and -0.048 GPa/K at 0, 3, 6 and 9 GPa, respectively.

453

454 Figure 9

455

456 Such increase of the magnitude of the slope, at high pressure, is due to the enhanced negative
457 contribution to the thermal pressure of the low frequency phonons; indeed this fact parallels what
458 has been discussed above, concerning thermal expansion: as the low frequency modes are
459 associated to negative Grüneisen's parameters, their frequencies are reduced at high pressure, so
460 that an increasingly large number of phonons is created, and a consequent increased negative
461 contribution to the thermal pressure is produced.

462 463 3.3 Heat capacity

464
465 Constant volume and constant pressure (C_p , at zero total pressure) specific heats were
466 calculated by means of equations (9) and (10). The calculated (B3LYP Hamiltonian) $C_p(T)$ curve, in
467 the [0, 1000K] temperature range and referring to the $\text{Al}_2\text{Be}_3\text{Si}_6\text{O}_{18}$ formula unit, is plotted in
468 Figure (10) and reported in Table (3), together with the experimental values by Hemingway et al.
469 (1986).

470
471 Table 3 and Figure 10

472
473 As it appears from the data shown in Table (3), no significant differences have been observed in
474 the C_p calculated at the B3LYP and WC1LYP levels. In Figure (10) circles refer to experimental data
475 measured at temperature higher than the room one, whereas triangles refer to low temperature
476 measurements on a sample that contains 0.72 H_2O molecules pfu (on 36 oxygen atoms). Such
477 water is presumably lost at high temperature and, in fact, Hemingway et al. (1986) provided two
478 different tables of values of C_p : one for the low temperature region, and another one for high
479 temperatures. The calculated curve in the high temperature region compares quite well with the
480 experimental data, even if some discrepancy is observed for temperatures higher than 900K; such
481 discrepancy could possibly be due to the failure, at high T , of the quasi-harmonic approximation

482 used in our calculation, as well as to some problem in the experimental measurements as reported
483 by Hemingway et al. (1986). At low temperature, it is likely that the experimental C_p contains a
484 significant contribution from the vibrations of the water molecules inside the channels of the
485 structure, which lead to higher C_p values than those referring to the pure beryl. However,
486 Hemingway et al. (1986) tried to correct for such an effect (and even for the presence of Cr^{3+}
487 impurities in the sample) but, in spite of the correction, the value of C_p remained relatively much
488 higher than that expected at low temperature. The reason of such *anomaly* in the experimental
489 low temperature C_p was not identified (Hemingway et al., 1986), nor it is by looking at our
490 calculated data [Table (3)] which confirms the somewhat low values that could be expected from
491 Debye's temperature based considerations, as discussed by Hemingway et al. (1986).

492 With the purpose of a comparison with the experimental data of Hemingway et al. (1986),
493 a fit of the C_p versus T has been done, in the [200-1000K] temperature range, according to the
494 expression:

495

$$C_p = c_1 + c_2T + c_3T^2 + c_4T^{-0.5} + c_5T^{-2}$$

496
497

498 The refined values of the c_1 , c_2 , c_3 , c_4 and c_5 coefficients were respectively 1594.12, -0.4186,
499 $1.0819 \cdot 10^{-4}$, -19331.40, $6.1187 \cdot 10^6$, in appropriate units (C_p is in J/mol·K and T is in K). The
500 correspondent values of the same coefficients refined by Hemingway et al. (1986) were 1625.84,
501 -0.4252, $1.2038 \cdot 10^{-4}$, -20180.94, $6.8254 \cdot 10^6$. The range of T over which the experimental C_p 's were
502 interpolated was [200, 1800K] (Hemingway et al., 1986); we have chosen a lower maximum
503 temperature (1000K) due to the possible failure, at very high temperatures, of the quasi-harmonic
504 approximation employed in our calculations.

505
506
507

508 3.4 Soft mode and the $P6/mcc \rightarrow P\bar{1}$ phase transition

509

510 A zone-centre E_g soft mode was identified (at both the B3LYP and WC1LYP levels), whose
511 frequency went to zero at a cell volume lower than 650\AA^3 , corresponding to a static pressure
512 higher than 14 GPa, starting from a value of 136 cm^{-1} at the static equilibrium cell volume [see
513 Figure (11)].

514

515 Figure 11

516

517 This was the sign of a possible soft mode transition to a lower symmetry phase. By initially shifting
518 the atoms of the unit cell along the two eigenvectors associated to this 2-dimensional E_g normal
519 mode, a $P\bar{1}$ space group symmetry resulted. By optimizing the geometry in such a space group, by
520 keeping the cell volume fixed at values lower than 650\AA^3 , triclinic structures were obtained, having
521 static energies systematically lower than those resulting from the optimization, at the same cell
522 volumes, in the $P6/mcc$ space group [Table (4)].

523

524 Table 4

525

526 The stability field of the $P\bar{1}$ phase, at temperatures higher than 0K, was not determined since it
527 would require the calculation of the vibrational frequencies in $P\bar{1}$: a too demanding task by
528 considering the available computational resources.

529 Geometry (cell parameters and fractional coordinates) resulting from the optimization at
530 cell volumes of 630\AA^3 , in the $P\bar{1}$ symmetry, is provided as supplementary material. A full
531 discussion concerning the geometry of such a phase will be presented in a subsequent paper
532 together with results from experimental findings: preliminary single-crystal and powder diffraction

533 data collected at the ESR synchrotron facility, in Grenoble, showed that a symmetry reduction
534 does indeed occur at pressures close to 14 GPa (Merlini; private communication). The
535 interpretation of the experimental data is however difficult due to the possible presence of
536 twinning. On the theoretical side, as geometry is concerned, it is here anticipated that the
537 deviation from the hexagonal symmetry increases with the reduction of the unit cell volume. At a
538 cell volume of 630\AA^3 , the six independent lattice constants a , b , c , α , β and γ were respectively
539 optimized to 9.061, 9.045, 8.881 \AA , 90.2°, 89.7° and 120.1°; at the same cell volume, a and c lattice
540 constants of the hexagonal phase were 9.028 and 8.924 \AA , respectively. Thus, apart from the
541 changes in the unit cell angles, the transition to the triclinic system produces a contraction of the c
542 axis length, whereas the a and b parameters are increased. Some details of the $P\bar{1}$ structure, in
543 particular concerning the ring of Si-centred tetrahedra, are represented in Figure (12): the unique
544 Si site in $P6/mcc$ splits in three sites Si1, Si2, Si3; likewise, the unique O1 atom in the hexagonal
545 phase splits in the O1a, O1b and O1c inequivalent atoms. Polyhedra are tilted either around axes
546 parallel to [001] [Figure (12a)] or around directions normal to it [Figure (12b)].

547

548 Figure 12

549

550 The Si-O1-Si angles are reduced from the value of 164.3° in $P6/mcc$, to 154.8° (Si1-O1a-Si3), 159.6°
551 (Si2-O1b-Si1) and 160.4° (Si2-O1c-Si3) in $P\bar{1}$; such reduction of the angle is accompanied by a
552 parallel increase of the Si-O1 distances of about 0.01 \AA on average, in going from the hexagonal
553 phase to the triclinic one; this is consistent with the increase of the a and b lattice constants, and
554 the decrease of the c parameter (indeed, even in the hexagonal phase, the c axis appears to be
555 more compressible than the other two axes). These modifications of the structure of beryl as it
556 transforms to the triclinic phase are anticipated in the vibrational properties of the high symmetry

557 polymorph: by looking at the low frequencies normal modes which mainly involve the tilting of
558 Si-centred tetrahedra (see animations at the web page
559 <http://www.personalweb.unito.it/mauro.prencipe/vibs/beryl/index.html>,
560 calculated for the hexagonal beryl at a cell volume of 650\AA^3 , close to the phase transition) and
561 examining the Si-O1 distances during the excursion of such low frequencies vibrations, it is seen
562 that a significant lengthening of the average Si-O1 distance accompanies the tilting [Figure (13)].

563

564 Figure 13

565

566 It could be said that, for pressures lower than 14GPa (hexagonal phase), the increase of the
567 repulsion among the nuclei due to the volume contraction (see the relevant discussion in Prencipe
568 and Nestola, 2007) is *dynamically* partially compensated by vibrations along the low frequencies
569 modes (the E_g soft mode in particular) which reduce the Si-O1-Si angles and increase the
570 internuclear distances. Such *reverse* correlation between the Si-O-Si angle and Si-O bond length
571 has also been observed in silicates, both in *static* calculations and experimental measurements,
572 and interpreted within the framework of the QTAIMC theory (Bader, 1994; Prencipe, 2002;
573 Prencipe and Nestola, 2007; Gibbs et al., 2009). As the cell volume decreases, the shortening of
574 the interatomic distances (Si-O1 ones in particular: the shortest in the structure) increases the
575 energy of the minima of the Born-Oppenheimer surface which correspond to the positions of the
576 nuclei at the static equilibrium. Moreover, the lengthening of the average Si-O1 distance, as the
577 Si-O1-Si angle decreases, is more pronounced at high pressures than at low ones: in fact, the
578 nearly linear curves $d_{\langle\text{Si-O1}\rangle}(\langle\text{Si-O1-Si}\rangle)$ had slopes of $-2.20\cdot 10^{-3}$ and $-1.92\cdot 10^{-3}$ Å/degree at cell
579 volumes of 650\AA^3 (high pressure) and 692\AA^3 (zero static pressure) respectively. In other words, the
580 tilting of the Si-centred tetrahedra becomes less *rigid* as the pressure increases. Consequently,

581 potential wells become shallower and vibrational frequencies are reduced (negative Grüneisen's
582 parameters). This fact can also be analyzed by considering the total pressure and its contributions:
583 the energy required to statically compress the structure, and which is measured by the static
584 pressure, is lowered by the dynamic distortion of the structure that *moves* along its low frequency
585 normal modes; such lowering is measured by the zero point and thermal pressures, to which the
586 latter modes contribute negatively. The (total) pressure required to compress the (hexagonal)
587 beryl at a given volume is therefore lower than the (static) pressure that would be required to
588 compress it *statically*. At pressures higher than 14GPa the dynamic distortion is *frozen* and the
589 symmetry of beryl is reduced to the $P\bar{1}$ space group.

590

591 **4. Conclusive (general) remarks on thermal expansion**

592

593 As reported in the previous section, low frequency modes consist essentially of tilting of M-centre
594 polyhedra (M=Si, Al, Be) associated to only minor variations of the M-O distances (as discussed
595 above the latter ones are nevertheless determinant for the decrease of the vibrational frequencies
596 as the pressure increases); in other words, such vibrations can be regarded as *rigid unit modes*
597 (RUM) according to the definition given in Dove et al. (1995). Indeed the origin of negative or very
598 low thermal expansion coefficients in some framework silicates has been interpreted within the
599 RUM model, by invoking a *geometrical* effect of the tilting of rigid polyhedra, which acts in the
600 direction of decreasing the cell volume as the temperature (amplitude of the vibrational motion) is
601 increased. Such effect is generally compensated by *normal anharmonic* effects which, instead,
602 produce a cell volume expansion as the temperature is increased (Welche et al., 1998; Heine et al.,
603 1999). The interpretation of the thermal expansion data proposed in the current work is not in
604 contradiction with the *geometrical* RUM model: in fact, RUM's are observed and they are
605 associated to negative Grüneisen's parameters (that is, they contribute negatively to the thermal
606 expansion). Indeed, it is explicitly stated in Heine et al. (1999) that "the Grüneisen theory as a

607 general formulation must be able to encompass the geometrical effect”, and a relation is
608 proposed between γ^{red} [equal to $(2\pi\nu)^2\gamma$] and η , the latter being a geometrical constant specific
609 to the RUM mode, which determines the magnitude of the volume contraction as the temperature
610 increases (Welche et al., 1998). However, whilst by following the approach of Welche et al. (1998),
611 one could *explain* the sign of γ^{red} on the basis of the sign of η (the variation of the frequency with
612 the volume would be a *consequence* of the geometry of vibration), in our approach it is the sign of
613 γ^{red} , ultimately due to the shape of the Born-Oppenheimer surface, that determines the sign of η
614 and hence the geometry of vibration. It is also emphasised here that, in our opinion, such
615 geometrical effect is just one type of *anharmonicity*. The distinction between *geometrical* and
616 *anharmonic* effects in the terms discussed by Welche et al. (1998) and Heine et al. (1999) could be
617 misleading in that it seems to attribute a component of thermal expansion (or *contraction*) to
618 effects not related to the anharmonicity of the atomic interactions, whilst it is clear that thermal
619 expansion (or contraction) is possible if and only if the Born-Oppenheimer’s surface deviates from
620 the harmonic shape: if the surface were perfectly harmonic, the Grüneisen’s parameters would be
621 zero, as well as the zero point and thermal pressures, and no thermal expansion would be
622 observed (Ashcroft and Mermin, 1976; Born and Huang, 1954).

623 Another issue concerning thermal expansion is related to the asymmetry of the interatomic
624 potential. It is often said that *normal* thermal expansion in solids is ultimately due to the
625 *asymmetry* of potential wells on the Born-Oppenheimer surface, whose minima are occupied by
626 atoms (see for instance Miller et al., 2009). This view stems from considerations based on the
627 simple quantum oscillator usually invoked to explain the behaviour of biatomic molecules. Indeed,
628 in a biatomic molecule, the increase of bond length with temperature can be ascribed to the
629 asymmetric shape of the interatomic potential leading to the well known asymmetric vibrational
630 eigenfunctions of the anharmonic oscillator, whose average positions are progressively shifted to

631 values corresponding to higher interatomic distances, as the vibrational quantum number is
632 increased; in this case, as excited vibrational energy levels are being populated by heating the
633 molecular gas, the thermally averaged equilibrium distance of the nuclei is larger than the distance
634 at $T=0\text{K}$, where the oscillator is at the fundamental level. Thus, bond lengthening can be directly
635 view as an effect of the asymmetry of the potential which, in general, is just *one* type of
636 anharmonicity (it is however here stressed that the thermal expansion of the gas, at constant
637 pressure, is of course *never* interpreted as an effect of bond lengthening). By following this line of
638 reasoning, an anharmonic but symmetric potential should not lead to any thermal expansion,
639 since the eigenfunctions of such *peculiar* symmetric oscillator are symmetric with respect to the
640 static equilibrium position. In a solid, if the shape of the Born-Oppenheimer surface around a
641 minimum associated to the equilibrium position of the nuclei (q_0), were hypothetically described
642 by a potential of the form $V(q) = V(q_0) + 1/2 k_2 (q-q_0)^2 + k_4(q-q_0)^4$ (where q is some normal
643 coordinate, and $q_0=0$ corresponds to the equilibrium position) *symmetric* eigenfunctions would
644 result, that is: *no* thermal expansion, according to the model translated from the molecular
645 experience. Even in this case, however, the corresponding frequencies would depend upon the
646 volume, since the above potential is anharmonic by the presence of the quartic term; in turn, this
647 would lead to Grüneisen's parameters different from zero, and a *non* zero thermal expansion
648 would result. It should be noted that, at variance with the zone-centre vibrational modes that
649 could be asymmetric with respect to the q_0 position, a symmetric $V(q)$ potential should be
650 characteristic of all the off-centre modes: this is obvious, for instance, in the zone-border case
651 where, for any motion in the reference zero cell (*e.g.* a M-X bond lengthening) there is a motion,
652 in an adjacent cell, which is exactly in anti-phase with the first one (a M-X bond shortening); when
653 the sign of q is reversed, the M-X bond in the zero cell shortens, whereas the corresponding bond,
654 in the adjacent cell, lengthens; this means that V does not depend upon the sign of q and,

655 therefore, it is symmetric. Thus, the argument concerning the role played by the asymmetry of the
656 potential energy surface, in connection with the asymmetry of the resulting eigenfunctions, in
657 determining the thermal expansion (negative or positive, as it may be) is, in general, not fully
658 appropriate.

659 Another objection that could be raised against such *asymmetric-potential* model of thermal
660 expansion concerns the principle of conservation of energy: imagine a crystal at $T=0\text{K}$ subjected to
661 an external zero pressure; by heating such a crystal to a temperature T , it will generally expand. If
662 such an expansion were exclusively due to the asymmetry of the vibrational eigenfunctions, after
663 heating the (static) equilibrium positions of the nuclei would be unchanged with respect to those
664 at $T=0\text{K}$: indeed, it is often said that the temperature affects the population of vibrational levels,
665 but not the structure of the vibrational spectrum (position of the energy levels); in turns, this
666 means that either static and zero point energies would be exactly the same as they were at 0K , as
667 well as the corresponding pressures. Now, it can be said that (i) as a reaction to the temperature
668 increase, the crystal expands in order to equilibrate its internal pressure with the external zero
669 one, and (ii) by heating it at constant volume, phonons are created which contribute a thermal
670 pressure according to what has been discussed in the sections above; therefore, if the nuclei did
671 not change their equilibrium position at high T , the only way to equilibrate the external and
672 internal pressures would be that of reducing the thermal pressure to zero. This is clearly a paradox
673 since, if the Grüneisen's parameters are different from zero, a zero thermal pressure would be
674 possible only if *no* phonons existed in the crystal, even at a *non* zero temperature, in open
675 contradiction with the Bose-Einstein statistics. Moreover, since no work is done in the expansion
676 process (against the zero external pressure), all of the energy carried by phonons at a certain T
677 (which would be equal to the energy provided during heating) would be lost and the energy-
678 conservation principle would be violated.

679 Therefore, even if the asymmetry of the interatomic potential, and the consequent
680 asymmetry of the vibrational eigenfunctions, cannot in general be ruled out [the asymmetry of the
681 resulting vibrational eigenfunctions could be related to a component of what is generally termed
682 *intrinsic* anharmonicity (Oganov and Dorogokupets, 2004) which could also contribute a fraction to
683 the total thermal expansion], the reason of the thermal expansion must be searched in the
684 anharmonicity of the potential, independently by its symmetry, through the effects it has on the
685 thermal pressure *via* the Grüneisen's parameters. Such effects are exactly those which are
686 properly taken into account at the quasi-harmonic level.

687 In the present case of beryl, the calculation of the static energies as the structure is
688 deformed along the normal coordinates corresponding to low frequency modes, gave perfectly
689 symmetric curves about the respective equilibrium points even if, as discussed above, such modes
690 are associated to large (and negative) Grüneisen's parameters, and thus do contribute
691 substantially to the thermal pressure and to the thermal expansion. For instance, a fit up to the 4th
692 power of the (static) energy *v.s.* the normal coordinate q associated to the B_{1g} mode at 72 cm⁻¹,
693 (cell volume equal to 650 Å³) gave k_2 , k_3 and k_4 values of $1.08 \cdot 10^{-2}$ hartree/Å², $3.39 \cdot 10^{-5}$ hartree/Å³
694 and $3.23 \cdot 10^{-3}$ hartree/Å⁴ respectively; in particular, the k_3 value associated to the cubic term is
695 much smaller than the values of both the quadratic (k_2) and quartic (k_4) coefficients. Indeed, the
696 $E(q)$ curve appears to be perfectly symmetric with respect to the origin ($q=0$). Similar calculations
697 carried out for the normal modes corresponding to the A_{2g} symmetric and A_{1u} antisymmetric Si-O2
698 stretching modes, at 1101 and 1217 cm⁻¹ respectively, gave symmetric $E(q)$ curves: k_2 , k_3 and k_4
699 equal respectively to 2.56 hartree/Å², $4.79 \cdot 10^{-3}$ hartree/Å³ and $4.73 \cdot 10^{-3}$ hartree/Å⁴, for the A_{2g}
700 mode, and 3.70 hartree/Å², $4.68 \cdot 10^{-6}$ hartree/Å³ and 0.249 hartree/Å⁴, for the A_{1u} mode; it should
701 be noted the much lower value of k_3 for the A_{1u} mode (anti-phase stretching of the two Si-O2
702 bonds: for each SiO₄ tetrahedron, one bond shortens and the other one lengthens), than the

703 corresponding value obtained for the A_{2g} one (in-phase stretching of the two Si-O2 bonds). The A_{1g}
704 symmetric Al-O2, Be-O2 stretching mode at 667 cm^{-1} [Figure (14)] has a k_3 value comparable in
705 magnitude to the quartic coefficient ($k_2=0.998\text{ hartree/\AA}^2$, $k_3=-9.14\cdot 10^{-3}\text{ hartree/\AA}^3$, $k_4=1.16\cdot 10^{-2}$
706 hartree/\AA^4).

707

708 Figure 14

709

710 The curve appears to be reasonably well described by an harmonic fit [dotted line in Figure (14)]
711 and the asymmetry is not evident, even if in this case the k_3 value is higher than the values
712 obtained for the other modes. The shift of the average q position from the equilibrium one ($q=0$)
713 at the 6th excited vibrational level (which corresponds to the average number of phonons of that
714 mode at $T=900\text{K}$), calculated by following the method of Viswanathan (1957), amount to 0.0005\AA
715 only. Therefore, on the whole it could be said that, at least in the case of beryl, the asymmetry of
716 the $E(q)$ plays very little or no role at all in determining the thermal expansion of the crystal. The
717 observed structural changes with temperature should be an effect of the *real* shift of the
718 equilibrium static positions of the nuclei, which determines variations of the total energy (both
719 static and vibrational contributions) and entropy, driving the crystal toward the minimum free
720 energy at given pressure and temperature. On the other hand, the condition

721

$$P = - \left(\frac{\partial F}{\partial V} \right)_T = 0$$

722

723 expressing the total pressure of the crystal in equilibrium with a zero external pressure, can
724 obviously be read as the condition of minimum free energy at a given temperature.

725 The analysis of the effects of thermal expansion on the crystal energy can also be
 726 considered under a different point of view. Let $E_{th}(\nu, T)$ be the contribution to the thermal
 727 energy, at the temperature T , due to the vibrational mode at frequency ν , that is:

728

$$E_{th}(\nu, T) = n(\nu, T) \cdot h\nu$$

729

730 where $n(\nu, T)$ is the number of phonons having frequency ν at the temperature T [equation (2)].

731

The variation of $E_{th}(\nu, T)$ with the volume is given by the expression

732

$$\frac{dE_{th}(\nu)}{dV} = \gamma \frac{KT}{V} F(y)$$

733

734 where y is the ratio $h\nu/kT$, γ is the Grüneisen's parameter and the F function [plotted in figure
 735 (15)] is defined as

736

$$F(y) = y \frac{e^y(y-1) + 1}{(e^y - 1)^2}$$

737

738

739 Figure 15

740

741 The $F(y)$ function is always positive and, if γ is positive too, the thermal energy increases as the
 742 volume increases (at constant T). This is due to the fact that, even if the energy *per* phonon
 743 decreases as the volume increases (because of the reduction of the frequency), the number of
 744 phonons increases. By taking into account the zero point energy contribution [$E_{zp}(\nu)$], the volume
 745 derivative of the total vibrational energy of the single mode considered [$E_{vib}(\nu, T) = E_{zp}(\nu) +$
 746 $E_{th}(\nu, T)$] is:

747

$$\frac{dE_{vib}}{dV} = \gamma \frac{KT}{V} G(y)$$

748

749 where the G function is defined as:

750

$$G(y) = -\frac{y(\sinh y - 1)}{2(\cosh y - 1)}$$

751

752 Such G function is always negative and, consequently, as the cell volume increases (isothermically)
753 the vibrational energy decreases due to a decrease of the zero point contribution which outweighs
754 the thermal one. The vibrational energy *lost* during expansion, plus the energy provided by the
755 environment to keep the temperature constant (if the expansion was adiabatic, the crystal would
756 generally decrease its temperature with a reduction of the number of phonons), is transferred to
757 the *static lattice*, to shift the nuclear positions against the static potential whose relative value
758 increases as the crystal expands.

759

760 **Appendix**

761

762 Geometry optimizations, static energies and vibrational frequencies at the (static) equilibrium, and
763 at fixed cell volumes, were performed by means of the *ab initio* CRYSTAL06 code (Dovesi et al.,
764 2006), which implements the Hartree-Fock and Kohn-Sham, Self Consistent Field (SCF) method for
765 the study of periodic systems (Pisani et al., 1988), by using a Gaussian type basis set.

766

767 *Basis set, Hamiltonian and computational parameters*

768

769 The basis set employed was already used for the calculation of the vibrational spectrum of beryl at
770 zero pressure (basis set D2 in Prencipe et al., 2006); it consisted of a 6-31G* contraction for Be, a
771 88-31G* contraction for both Al and Si, and a 8-411G* contraction for O.

772

773

774

775

776

The B3LYP (Becke, 1993) and the WC1LYP (Wu and Cohen, 2006) Hamiltonians have been
chosen which contain hybrid Hartree-Fock/Density-Functional exchange terms. B3LYP is one of the
most suitable Hamiltonian for *the ab initio* calculation of the vibrational properties of molecules,
as documented by Koch and Holthausen (2000), as well as for solid state calculations, where it has
been shown to provide excellent results for geometries and vibrational frequencies, superior to

777 the one obtained by LDA- or GGA- type functionals (Pascale et al., 2004a; Prencipe et al., 2004;
778 Pascale et al., 2005a; Pascale et al., 2005b; Prencipe et al., 2009). WC1LYP (Wu and Cohen, 2006) is
779 a relatively new Hamiltonian not yet sufficiently tested on solids; in the present case, it appears to
780 perform slightly better than B3LYP as geometry is concerned, and to provide vibrational
781 frequencies nearly identical to those from the B3LYP calculations, consistently with the findings of
782 Demichelis et al. (2009) on pyrope ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$), forsterite ($\alpha\text{-Mg}_2\text{SiO}_4$), α -quartz ($\alpha\text{-SiO}_2$) and
783 corundum ($\alpha\text{-Al}_2\text{O}_3$).

784 The DFT exchange and correlation contributions to the total energy were evaluated by
785 numerical integration, over the cell volume, of the appropriate functionals; a (75, 974) ρ grid has
786 been used, where the notation (n_r, n_ω) ρ indicates a pruned grid with n_r radial points and n_ω
787 angular points on the Lebedev surface in the most accurate integration region (see the ANGULAR
788 keyword in the CRYSTAL06 user's manual, Dovesi et al., 2006). Such a grid corresponds to 77420
789 integration points in the unit cell at the equilibrium volume. The accuracy of the integration can be
790 measured from the error in the integrated total electron density, which amounts to $-3 \cdot 10^{-4} |e|$ for
791 a total of 532 electrons. The thresholds controlling the accuracy of the calculation of Coulomb and
792 exchange integrals have been set to 6 (*ITOL1* to *ITOL4*) and 14 (*ITOL5*; Dovesi et al., 2006). The
793 diagonalization of the Hamiltonian matrix was performed at 6 independent \mathbf{k} vectors in the
794 reciprocal space (Monkhorst net; Monkhorst and Pack, 1976) by setting to 3 the shrinking factor IS
795 (Dovesi et al., 2006).

796
797 *Geometry, Γ point phonon frequencies and elastic constants*

798
799 Cell parameters and fractional coordinates were optimized by analytical gradient methods, as
800 implemented in CRYSTAL06 (Civalleri et al., 2001; Dovesi et al., 2006). Geometry optimization was
801 considered converged when each component of the gradient (TOLDEG parameter in CRYSTAL06)
802 was smaller than 0.00001 hartree/bohr and displacements (TOLDEX) with respect to the previous

803 step were smaller than 0.00004 bohr. The volume ranges over which geometries were refined, and
804 static energies calculated, were [703-650Å³] in the B3LYP case (12 different volume values; static
805 equilibrium found at 692.22Å³), and [691-650Å³] in the WC1LYP one (9 volume values; static
806 equilibrium at 686.74Å³). Results (cell volumes, cell parameters, optimized fractional coordinates
807 and static energies) are provided as supplementary material (Tables S1a and S1b, for the B3LYP
808 and WC1LYP cases, respectively).

809 Vibrational frequencies and normal modes were calculated at different cell volumes, within
810 the limit of the harmonic approximation, by diagonalizing a mass weighted Hessian matrix, whose
811 elements are the second derivatives of the full potential of the crystal with respect to mass
812 weighted atomic displacements (see Pascale et al., 2004b for details). The threshold for the
813 convergence of the total energy, in the SCF cycles, was set to 10⁻¹⁰ hartree (TOLDEE parameter in
814 CRYSTAL06). Results are provided as supplementary material (Tables S2a and S2b for the B3LYP
815 and WC1LYP calculations, respectively).

816 The elastic constants are the 2nd derivative of the energy with respect to the strain
817 components. They were evaluated through a numerical differentiation of the analytical energy
818 gradient with respect to the cell parameters, by imposing a certain amount of strain along the
819 crystallographic direction corresponding to the component of the elastic tensor. Calculations were
820 carried out by using an automatic scheme recently implemented in the CRYSTAL code (Perger et
821 al., 2009). The calculated (B3LYP) values are provided in Table (5), together the experimental data
822 of Yoon and Newnham (1973).

823

824 Table 5

825

826 The K_V , K_R [equation (8.3)] values were 179.9 and 179.4 GPa, respectively; the average value \bar{K}_{VHR}

827 [equation (8.1)] was 179.7 GPa. The shear moduli μ_V , μ_R and $\bar{\mu}_{VHR}$ [equations (8.2) and (8.1)] were
828 79.1, 77.1 and 78.1 GPa, respectively. The calculated average longitudinal and transversal acoustic
829 waves (\bar{v}_p and \bar{v}_s) were 10.50 and 5.51 Km/sec, respectively, which are very close to the
830 experimental data of Yoon and Newnham (1973). Finally, the average longitudinal and transversal
831 frequencies of the acoustic wave at the Brillouin zone boundary [ν_l and ν_s , equation (7)] were
832 245.5 and 128.8 cm^{-1} , respectively.

833
834
835

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Captions to the Tables

952 **Table 1:** Bulk modulus (GPa) at zero pressure calculated with the B3LYP Hamiltonian. The order (n)
953 of the Legendre polynomials (L_n), used to fit the static curve, is 3 for $P_{max}=6\text{GPa}$ and 4 for
954 $P_{max}=12\text{GPa}$. See text for further details.

955
956 **Table 2:** Bulk modulus (GPa) at zero pressure and K'_0 (in parentheses) calculated with WC1LYP
957 Hamiltonian. The experimental data (Exp) are from Prencipe and Nestola (2005); the estimated
958 error on the experimental K_0 is 1 GPa. See text for further details.

959

960 **Table 3:** Heat capacity at constant pressure (C_p , at zero total pressure, J/mol K), at a selected set of
961 temperatures (T , in K). Experimental data (EXP) are from Hemingway et al. (1986). Δ (in J/mol K)
962 and $\Delta\%$ are, respectively, the difference and the percentage difference between the experimental
963 data and the B3LYP calculated ones.

964

965 **Table 4:** Energies (in hartree) of the $P6/mcc$ and $P\bar{1}$ structures of beryl at unit cell volumes (V , in
966 \AA^3) lower than 650\AA^3 . Δ is the $P\bar{1} - P6/mcc$ energy difference (in hartree).

967

968 **Table 5:** Elastic constants (GPa) calculated at the B3LYP level, and experimental data from Yoon
969 and Newnham (1973). The value of the bulk modulus (K_0) derived from the elastic constants is also
970 provided.

971

972 **Captions to the Figures:**

973

974 **Figure 1:** Grüneisen's parameters (γ) at zero pressure as a function of frequency (ν).

975

976 **Figure 2:** Bose-Einstein distributions of phonons at 300, 600 and 900K, as a function of the
977 frequency of the corresponding normal modes.

978

979 **Figure 3:** Thermal pressure contribution of phonons, as a function of the frequency of the
980 associated normal modes, at three different temperatures.

981

982 **Figure 4:** Static, zero point and thermal pressure contributions to the (zero) total pressure, in the
983 [0, 1000K] temperature range. The zero point pressure scale is reported on the right-hand axis; the
984 static and thermal pressures scale is on the left-hand axis.

985

986 **Figure 5:** $\alpha_T K_T$ product [isobaric curves, equation (6)] as a function of temperature, at 0, 3 and
987 6 GPa.

988

989 **Figure 6:** Thermal expansion coefficient α_T as a function of temperature, at 0, 3 and 6 GPa.

990

991 **Figure 7:** $F_E f_E$ plot of the $P(V)$ data (minimum volume: 650\AA^3), at the static and athermal limits,
992 300K and 600K. See text for details.

993

994 **Figure 8:** Bulk modulus as a function of pressure, at different temperatures. See text for
995 explanation.

996

997 **Figure 9:** Bulk modulus as a function of temperature. Isobaric curves at 0, 3, 6 and 9 GPa.

998
999 **Figure 10:** Constant pressure specific heat as a function of temperature.

1000
1001 **Figure 11:** Pressure dependence of the lowest frequency normal modes.

1002
1003 **Figure 12:** View of the $P\bar{1}$ structure of beryl, along the [001] axis of the channel (a), and along a
1004 direction normal to it (b). Light grey: Si-centred tetrahedra; grey: Be-centred tetrahedra; dark grey:
1005 Al-centred octahedra.

1006
1007 **Figure 13:** Average Si-O1 bond length (\AA) versus average Si-O1-Si angle (degree) during the
1008 excursion along one of the two eigenvectors associated to the E_g vibrational mode at 28 cm^{-1} (soft
1009 mode; cell volume 650.00 \AA^3). Full circles are positioned at steps of 1 unit along the path, where
1010 the unit corresponds to the maximum distance from the equilibrium reached when the oscillator is
1011 in the first excited energy level (one phonon). The minimum excursion refers to the equilibrium
1012 position; the maximum excursion corresponds to a path length of 5 units (about 20 phonons).

1013
1014 **Figure 14:** Energy variations (E; hartree) along the normal mode associated to the symmetric Al-O2
1015 stretching mode at 667 cm^{-1} (cell volume 650\AA^3). The q coordinate of the normal mode is
1016 expressed in unit of q_{max} , the maximum classical amplitude of vibration at the fundamental energy
1017 level ($q_{\text{max}}=0.055\text{\AA}$). The positions of the fundamental level and of the first 5 excited ones is
1018 shown. Black circles indicate the calculated actual energy values; dotted line is the harmonic curve
1019 which best fits the data. The values of the M-O bond lengths, at the extremes of the considered
1020 excursion and at the equilibrium, are also shown.

1021
1022 **Figure 15:** Plot of the $F(y)$ universal factor (adimensional) of the volume derivative of the thermal
1023 energy associated to a vibrational mode at frequency ν . The adimensional variable y is the ratio
1024 $h\nu/kT$. (See text for details).