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This is a pre print version of the following article:

Original Citation:
High-pressure thermo-elastic properties of beryl (Al₄Be₆Si₁₂O₃₆) from ab initio calculations, and observations about the source of thermal expansion / Mauro Prencipe; Isacco Scanavino; Fabrizio Nestola; Marco Merlini; Bartolomeo Civalleri; Marco Bruno; Roberto Dovesi. - In: PHYSICS AND CHEMISTRY OF MINERALS. - ISSN 0342-1791. - 38(2011), pp. 223-239.

Availability:
This version is available http://hdl.handle.net/2318/74262 since 2016-06-22T14:57:58Z

Published version:
DOI:10.1007/s00269-010-0398-8

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(Article begins on next page)
This is the author's final version of the contribution published as:

Mauro Prencipe; Isacco Scanavino; Fabrizio Nestola; Marco Merlini; Bartolomeo Civalleri; Marco Bruno; Roberto Dovesi. High-pressure thermo-elastic properties of beryl (Al4Be6Si12O36) from ab initio calculations, and observations about the source of thermal expansion. PHYSICS AND CHEMISTRY OF MINERALS. 38 pp: 223-239.
DOI: 10.1007/s00269-010-0398-8

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

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Abstract

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

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

1. Introduction

In the last few years, the increased availability of fast computational resources, at a relatively low cost, allowed the calculation of thermo-elastic and thermodynamics properties of minerals, by following a fully ab initio approach within a statistical-thermodynamics framework (see e.g.
Oganov et al., 2002 for an overview). The method can be applied to the determination of properties of minerals even at conditions of simultaneous very high pressure/high temperature, which are not easily attainable experimentally. In general, however, the reliability of the calculated results and, hence, their usefulness for geophysical modelling of the Earth's crust and mantle, depends upon details concerning (i) the specific type of quantum-mechanical calculation chosen (e.g., pure DFT or hybrid HF/DFT Hamiltonian; exchange and correlation DFT functionals; basis sets; pseudo-potentials employed in connection with plane-waves basis sets, etc...); (ii) the range of validity of various approximations employed, like the quasi-harmonic one (Anderson, 1995), to get phonons frequencies together with their volume and temperature dependence [see also Oganov and Dorogokupets (2004) for an account of intrinsic anharmonic effects evaluated at the quantum-mechanical level, by a perturbative approach], and (iii) the consideration of phonon dispersion.

The present work discusses an application of the whole algorithm, within the limit of the quasi-harmonic approximation (Anderson, 1995), to the determination of the (volume) thermal expansion and compressibility, and their temperature/pressure dependence, of beryl (Al$_4$Be$_6$Si$_{12}$O$_{36}$, space group P6/mcc, Z=1; Deer et al., 1992): a framework silicate according to the Zoltai's classification (Zoltai, 1960), having a moderate structural complexity. Two different hybrid HF/DFT Hamiltonians (that is, containing both an exact non-local Hartree-Fock correction to the DFT exchange functionals) were used to get structures, static energies and frequencies at different cell volumes, namely (i) the well known B3LYP Hamiltonian (Becke, 1993; Koch and Holthausen, 2000), and (ii) a relatively recent hybrid formulation (WC1LYP), due to Wu and Cohen (2006) for the exchange part, and Lee et al. (1988) for the correlation part. See Prencipe and Nestola (2005) for a discussion about the role of the exact non-local Hartree-Fock exchange correction, in calculations of structure and compressibility in silicates (beryl, in particular). The WC1LYP
Hamiltonian seems to perform slightly better than B3LYP, but it is not yet tested on a sufficiently large class of minerals; see Demichelis et al. (2009) for applications to pyrope, forsterite, α-quartz and corundum. B3LYP calculations proved to be highly successful in a number of other cases, either concerning the derivation of thermodynamics properties of minerals within a quantum-statistic framework (α, β and γ polymorphs of Mg2SiO4, Ottonello et al., 2008; stishovite, Ottonello et al., 2009; Anhydrous B phase, MgSi5O24, Ottonello et al., 2010), or the interpretation and assignment of infrared and Raman experimental spectra (see, for instance: calcite, Prencipe et al., 2004; beryl, Prencipe et al., 2006; lizardite, Prencipe et al., 2009, and references therein).

As beryl is concerned, at the B3LYP level the very satisfactory agreement between calculated and experimental vibrational frequencies, at room pressure, has already been demonstrated (Prencipe et al., 2006), and its high pressure properties at the static limit were also investigated in a number of works (Prencipe, 2002; Prencipe and Nestola, 2005, 2007) within the framework of the Quantum Theory of Atoms in Molecules and Crystals (QTAIMC; Bader, 1994).

The mineral consists of sixfold rings of Si-centred tetrahedra stacked along the [001] sixfold symmetry axis, which are interconnected by Be-centred tetrahedra and Al-centred octahedra. Beryl is quoted among those minerals having a low or negative thermal expansion coefficient (Morosin, 1972; Schlenker et al., 1977; Hochella and Brown, 1986; Fey, 1995), together with cordierite and indialite (Mg4Al6Si10O36) which have similar structures. Such peculiar thermal expansion of beryl has been the subject of investigations focussing on (i) thermodynamic properties and their relations with thermal expansion (Schlenker et al., 1977; Pilati et al., 1997); (ii) thermal behaviour of bonds (Hochella and Brown, 1986), and (iii) geometric effects related to tilting of rigid polyhedra leading to negative contributions to the thermal expansion; the latter is the Rigid Unit Model (RUM), concerning the thermal behaviour of framework silicates (Dove et al., 1995; Welche et al., 1998; Heine et al., 1999). Experimental values of thermal expansion,
Compressibility and heat capacity were successfully reproduced by the present calculations. Also, a $P6/mcc \rightarrow P\bar{1}$ soft mode phase transition was predicted to occur at a pressure of about 14GPa, at room temperature. At least in part, the behaviour of thermal expansion and compressibility of beryl was found to be related to the existence of such a soft mode, being it associated to a negative Grüneisen’s parameter; however, as already observed by Welche et al. (1998) in the case of β-quartz, the majority of low frequency modes provides a negative contribution to thermal expansion, which is balanced by positive contributions from the high frequency modes. Consistently with the RUM model of Dove et al. (1995), the low frequency modes, having negative Grüneisen’s parameters, resulted to be describable as rigid tilting of polyhedra, so that a geometric effect determining the low value of thermal expansion could be invoked, according to Heine et al. (1999).

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

2. Computational details

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

Total pressures, bulk moduli, thermal expansion and specific heat were obtained in the limit of the quasi-harmonic approximation (Anderson, 1995), through the evaluation of the unit
cell volume dependence of the frequencies of the vibrational normal modes (mode-γ Grüneisen’s parameters) at the Γ point. Dispersion effects in the phonon spectra at various pressures were not taken into account as the large volume of the unit cell makes it impossible the required calculation of the vibrational frequencies in the case of super-cells, due to limitation of the available computational resources. On the other hand, the Grüneisen’s parameters corresponding to the zone-centre vibrational modes, can reasonably be considered representative of the whole set of parameters, due to their large number which depends upon the number of atoms in the unit cell. Indeed, as demonstrated by other Authors (Ottonello et al., 2008, 2009, 2010), highly reliable estimations of thermo-elastic and thermodynamics quantities can be obtained by neglecting dispersion effects, even in case of systems having relatively small unit cells. This is consistent with the general observation that thermodynamic properties, which are obtained as averages over the relevant quantities at the atomic level, can reliably be derived even without a detailed knowledge of the phonon density of state (Kieffer, 1979a). For the same reasons, LO/TO splitting of the IR active modes was not taken into account (see discussion in Ottonello et al., 2008).

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

A correction to the specific heat at zero pressure was done in order to take into account the contributions from the three acoustic branches of the phonon spectrum. In this case, a Kieffer’s model was employed (limited to the acoustic branches only), where a sinusoidal
dispersion relation is assumed to exist between the wavelengths and the frequencies of the acoustic modes (Kieffer, 1979a; Kieffer, 1979b, Ottonello et al., 2010). The maximum frequencies of the transversal and longitudinal acoustic waves (that is, the frequencies at the borders of the Brillouin zone) were estimated from the calculated values of the elastic and compliances constants, following a method described in Ottonello et al. (2010). The elastic constants were obtained by using a development version of the CRystal code. Details on the latter procedure, together with those concerning the formalism employed to derive thermo-elastic properties from vibrational frequencies (following Anderson, 1995) are given below.

2.1 Pressures

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

\[
P(V,T) = - \left( \frac{\partial E_{st}}{\partial V} \right) + \frac{h}{2V} \sum_j \gamma_j \nu_j + \frac{h}{V} \sum_j n_j(\nu_j, T) \nu_j \nu_j
\]

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

\[
\gamma_j = - \frac{\partial \ln \nu_j}{\partial \ln V} = - \frac{\nu_j}{\nu_j} \frac{\partial v_j}{\partial v}
\]
Actually, the $\gamma$ here defined is the mode-$\gamma$ Grüneisen’s parameter, whereas, more properly $\gamma$ (thermal Grüneisen’s parameter) is defined as: $\gamma = (\partial P/\partial U)_V$ (Grüneisen, 1912); for short, in the following the mode-$\gamma$ parameter will simply be indicated with $\gamma$.

Such parameters were estimated by the analytical derivatives with respect to $V$, at the static equilibrium cell volume ($V_{st}^0$), of quadratic polynomials fitting the numerically determined $\gamma_j(V)$ curves. The sums in equation (1) run on all the vibrational modes at the $\Gamma$ point ($k=0$) of the reciprocal space. The first term on the right hand of equation (1) is the static pressure $P_{st}(V)$; the second term is the zero point pressure $P_{zp}(V)$ and the third one is the thermal pressure $P_{th}(V,T)$.

The sum $P_{ath}(V)=P_{st}(V)+P_{zp}(V)$ is here named athermal pressure, whereas the sum $P_{vib}(V,T)=P_{zp}(V)+P_{th}(V,T)$ is named vibrational pressure.

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

$$F_{zp}(V) = U_{zp}(V) = \frac{1}{2} N_0 \sum_j h \nu_j$$

$$F_{th}(V,T) = U_{th} - TS = N_0 \sum_j n_j(\nu_j, T) h \nu_j - TS$$

$$S(V,T) = N_0 k \sum_j \left[ n_j(\nu_j, T) \frac{h \nu_j}{kT} - \ln(1 - e^{-h \nu_j/kT}) \right]$$

and $N_0$ is the Avogadro’s number. Though the methods (i) and (ii) of getting zero point and thermal pressures are formally identical, in general the resulting values might depend upon the detailed implementations of both, by making use of fittings and/or numerical derivatives which
could differ in accuracy. Moreover, method \((i)\) implicitly assumes the constancy of the Grüneisen’s parameters as the cell volume is reduced in a finite interval; in the present case, such assumption is not strictly valid for all the normal modes, and a check of the possible differences in the results obtained by applying the two different methods was required.

2.2 Equation of State

The equation of state (EoS) has been determined by several methods differing in the way static, zero point and thermal pressures were obtained. As already explained in the section above, the static contribution to the pressure (which does not depend on \(T\)) must be derived from the \(E_{st}(V)\) static energy curve calculated by CRYSTAL. Static pressures were then added to zero point and thermal pressures, to get total \(P(V,T)\) curves which were subsequently fitted by appropriate EoS’s.

In this respect, the notation employed below is composed by two symbols, the first one referring to the way static pressure contributions have been calculated, and the second one indicating the type of EoS used to fit the total \(P(V,T)\) curve. Precisely: \((i)\) BM3-BM3 and BM3-BM4 notations respectively indicate (second symbol) that 3rd or 4th-order Birch-Murnaghan EoS’ have been used 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 first symbol in the notation) has been used to get static pressures only; \((ii)\) L3-BM3, L3-BM4, L4-BM3 and L4-BM4 notations indicate that static pressures were evaluated through L3 or L4 Legendre polynomial fittings; \((iii)\) BM3-BD, L3-BD and L4-BD notations indicate that the bulk modulus at a given cell volume (pressure) and temperature has been calculated by a numerical derivative, with respect to \(V\), of the \(P(V,T)\) curve at the corresponding volume, and that static pressures were obtained by the \(V_{int}\)-BM3, L3 or L4 fittings, respectively. Finally \((iv)\) a \(V_{int}\)-BM3 notation indicates that a volume integrated BM3 EoS has been used to fit the total (static + zero point + thermal) Helmholtz free energy as a function of \(V\) \((one\ fit\ only,\ at\ each\ temperature)\).
2.3 Thermal expansion

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

\[
\alpha_T = \frac{1}{K_T} \left( \frac{\partial P}{\partial T} \right)_T
\]

(5)

where $K_T$ is the bulk modulus estimated at the given pressure (cell volume) and temperature, or (ii) direct evaluation of the $\alpha_T K_T$ product (Anderson, 1995):

\[
\alpha_T K_T = \frac{N_0 k}{V} \sum_j v_j e^{h v_j / k T} \left( e^{h v_j / k T} - 1 \right)^2
\]

(6)

2.4 Acoustic phonon frequencies at the Brillouin zone border, and Kieffer’s model

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

\[
\bar{v}_j = \bar{v}_j \frac{1}{2\pi} \left( \frac{6\pi^2 N_0}{V} \right)^{1/3}
\]

(7)

where $\bar{v}_j$ is the corresponding average wave velocity. In turn, velocities were obtained through the well known relations $\bar{v}_s = (\bar{\mu}_{VRH} / \rho)^{1/2}$ and $\bar{v}_p = \left[ (\bar{K}_{VRH} + 4\bar{\mu}_{VRH} / 3) / \rho \right]^{1/2}$, where $\rho$ is the density, $\bar{K}_{VRH}$ and $\bar{\mu}_{VRH}$ are the Voigt and Reuss’ average of the bulk and shear moduli, respectively:

\[
\bar{\mu}_{VRH} = \frac{1}{2} (\mu_{\rho} + \mu_{s}); \quad \bar{K}_{VRH} = \frac{1}{2} (K_{\rho} + K_{s})
\]

(8.1)

\[
\mu_{\rho} = \frac{1}{15} (c' - c'' + 3c'''); \quad \mu_{s} = 15 (4s' - 4s'' + 3s''')
\]

(8.2)

\[
K_{\rho} = \frac{1}{9} (c' + 2c''); \quad K_{s} = (s' + 2s'')^{-1}
\]

(8.3)
and \( c', c'', c''', s', s'', s''' \) are respectively the sums over the elastic constants and compliances 

\[(c_{11}+c_{22}+c_{33}), (c_{12}+c_{13}+c_{23}), (c_{44}+c_{55}+c_{66}), (s_{11}+s_{22}+s_{33}), (s_{12}+s_{13}+s_{23}) \text{ and } (s_{44}+s_{55}+s_{66}) \]. The elastic and compliances tensors were calculated by using CRYS.

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

\[
C_V = 3kN_0 \left(\frac{2}{\pi}\right)^3 \sum_{i=1}^{3} \int_0^{X_i} \frac{[\arcsin(X/X_i)]^2 X^2 e^X}{(X_i^2-X^2)^{3/2} e^{X_i^2-X^2}} dX + kN_0 \sum_{i=4}^{3n} e^{e(1-e^{-X_i+1})/2} \] (9)

where \(X_i = \hbar \nu_i / KT\). In equation (9), the first sum runs over the three acoustic branches and, in 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 \(\Gamma\) point.

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

\[
C_P = C_V + T\alpha^2 \kappa T V_T \] (10)

where \(V_T\) is the cell volume at the temperature \(T\).

3. Results and discussion

3.1 Grüneisen’s parameters, zero point, thermal pressures and thermal expansion

Equilibrium geometries, static energies and zone-centre vibrational frequencies \((\nu_j, j=1,3n-3; n=58\) is the number of atoms in the unit cell) were determined for sets of \((i)\) 11 different cell volumes \(V\) ranging from 697 to 650Å\(^3\) (B3LYP Hamiltonian), and \((ii)\) 9 different \(V\)'s in the [691, 650 Å\(^3\)] range (WC1LYP Hamiltonian); details are provided in Appendix. For each normal mode, the Grüneisen’s parameter \(\gamma_j\) was determined. In the low frequency region of the vibrational spectrum (ranging from 100 to about 400 cm\(^{-1}\)) the majority of the vibrational modes are associated to a negative
Grüneisen’s parameter, whereas for frequencies above 600 cm\(^{-1}\), all of such parameters are positive [see Figure (1)]. The average Grüneisen’s parameter \(\bar{\gamma}\) is positive, and equal to 0.41 for both the B3LYP and WC1LYP Hamiltonians.

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

At higher temperatures, a phonon gas is produced inside the crystal which contributes a thermal pressure whose value depends by \((i)\) the average number of phonons associated to each normal mode, \((ii)\) the corresponding frequencies and \((iii)\) the Grüneisen’s parameters [see equation (1)]. The Bose-Einstein distribution of phonons at three different temperatures (300, 600 and 900K), and at zero total pressure, is shown in Figure (2):
at room temperature (300K) no phonons exist corresponding to modes having frequencies higher
than about 900 cm$^{-1}$, so that the thermal pressure is mainly determined by the low frequencies
phonons having negative $\gamma$'s [see Figure (3)].

Figure 3

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

Figure 4

The relative increase of the (negative) static pressure in the [0, 290K] interval is realized through a
slight reduction of the cell volume, so that the estimated thermal expansion coefficient is negative
at low temperatures. At higher temperatures, thermal expansion is positive but its magnitude
remains however small, due to the negative contribution of the low frequency phonons to the
thermal pressure.
At higher total pressures, the low frequency modes having negative Grüneisen’s parameters decrease significantly their frequencies and, consequently, their negative contributions to the thermal pressure is enhanced due the large increment of the associated number of phonons. This results in thermal pressures that are negative even at relatively high temperatures, and negative thermal expansions are thus estimated up to temperatures well above the room one [about 500K at $P=6$ GPa]. Such behaviour is illustrated in Figures (5) and (6), reporting the isobaric curves (0, 3 and 6 GPa) of the $\alpha_T K_T$ product and of the thermal expansion coefficient $\alpha_T$ in the [0, 1200K] temperature interval, as determined from equations (6) and (5), respectively.

Figures 5 and 6

Thermal expansion coefficients evaluated through equations (5) or (6) are nearly identical; the B3LYP values (at zero total pressure) at 300, 600 and 900K are $1.0 \cdot 10^{-6}$, $6.5 \cdot 10^{-6}$ and $9.0 \cdot 10^{-6} \text{K}^{-1}$, respectively (the required $K_T$ values are from a BM3-BD fitting of data up to a $P_{\text{max}}$ of 6GPa; see next section). WC1LYP values at the same temperatures are lower and, respectively, $-0.7 \cdot 10^{-6}$, $4.2 \cdot 10^{-6}$ and $6.1 \cdot 10^{-6} \text{K}^{-1}$. Experimental data were derived from the work of Morosin et al. (1972), by calculating cell volumes at different temperatures from the $a$ and $c$ lattice constants plotted in their graph (14 points in the [298, 873K] temperature range), and fitting the resulting $V(T)$ set by using Legendre’s polynomials up to the 2$\text{nd}$ order (higher order polynomials produced unphysical waving of the fitted $V(T)$ curve, due to considerable noise in the experimental values); the subsequent derivation, with respect to $T$, of the $V(T)$ curve, yielded $\alpha_T$ values of $3.2 \cdot 10^{-6}$, $6.0 \cdot 10^{-6}$ and $8.7 \cdot 10^{-6} \text{K}^{-1}$ at 300, 600 and 900K respectively, in reasonable agreement with the calculated results. By limiting the fit of the experimental $V(T)$ curve to a maximum temperature of
720K (11 points), yielded $\alpha_T$ values of $2.4 \cdot 10^{-6}$ and $7.4 \cdot 10^{-6}$ K$^{-1}$ at 300 and 600K, respectively. The analysis of the Morosin's data made by Schlenker et al. (1977) resulted in $\alpha_T$ values of $2.1(0.4) \cdot 10^{-6}$, $4.7(0.2) \cdot 10^{-6}$ and $7.3(0.4) \cdot 10^{-6}$ K$^{-1}$, at 300, 600 and 900K, respectively (standard uncertainties in parentheses). The B3LYP calculated thermal expansion appears to be in closer agreement with the experimental data, than the WC1LYP one. However, the possible errors affecting the experiment must be stressed, especially in such a case of very low thermal expansion, whose estimation would require highly accurate and precise cell volume data, at each temperature, in order to reach a relatively low uncertainty.

3.2 Bulk Modulus

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

The four columns under the $P_{\text{max}}$=6GPa heading refer to the EoS' determined by fitting the $P(V,T)$ curves up to 6GPa (low pressure case, in what follow); the last four columns refer to fittings extended to the [0, 12GPa] pressure range (high pressure case). Static values are also reported [2nd and 6th columns in Table (1)] as determined (i) by fitting the $V_{\text{int}}$-BM3 EoS' (BM3) to the $E_{\text{st}}(V)$ curve (these are identical with a $V_{\text{int}}$-BM3$_t$ calculation when the only contribution to the energy considered is the static one), or (ii) through the analytic second derivative, with respect to $V$ and at the static equilibrium volume, of $n^{\text{th}}$-order Legendre polynomials (L3 or L4) fitting the same curve.

In the high pressure case, the L3, L5 and L6 fittings of the static energy curve have also been tried, in addition to the L4 one reported in Table (1): the values of the bulk moduli, at the static limit and at the various temperatures, were not significantly different from those obtained by the L4 fitting.
Static bulk modulus has also been obtained as a by-product of the calculation of the elastic
costants $C_{ij}$ (see the Appendix): its value of 179.4 GPa is in close agreement with the
corresponding values of Table (1).

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

Figure 7

A normal behaviour with temperature is observed when $K_0$ is calculated either by (i) using a
$4^{th}$-order Birch-Murnaghan EoS to fit the $P_{tot}(V,T)$ curve [BM3-BM4 or L4-BM4 cases in Table (1)],
or (ii) numerical derivation [BM3-BD and L4-BD cases in Table (1)]. Significant differences of the
BM4 and BD bulk moduli at high temperatures, for the high pressure case, are also observed [see
BM3-BM4 and BM3-BD, or L4-BM4 and L4-BD in Table (1)], which may reflect the inadequacy of
the BM4 EoS to describe high P/T conditions. This is clearly seen in Figure (8), where \( K_\tau(P) \) curves,
directly calculated by numerical derivation of the \( P(V,T) \) curves, at fixed \( T \) (L4-BD or BM3-BD
algorithms; we recall here that, in the L4-BD algorithm, the L4 fitting is limited to the \( E_{st}(V) \) curve,
to get the static pressure at each \( V \) ), are plotted together with \( K_\tau(P) \) point values determined by
using the \( K_\tau(0) \) (i.e. \( K_0 \)), \( K_0' \) and \( K_0'' \) parameters from L4-BM4 fittings, at the three different
temperatures.

Indeed, even if at the athermal limit the bulk moduli obtained through the L4-BD and L4-BM4
algorithms are identical all along the [0, 12GPa] pressure range [this fact can also be seen in Table
(1)], at higher temperatures the shapes of the L4-BD curves (almost linear for \( P < 5 \) Gpa, and bent
toward low values, at higher \( P \), at least for the T=600K case) are definitely not well reproduced by
the BM4-\( K_\tau(P) \) based functions. Concerning the low pressure linear region, the slopes for \( P \rightarrow 0 \n(\bar{K}_0') \) of the three L4-BD functions reported in Figure (8) slightly decrease from 3.9, at the athermal
limit, to 3.0 at 600K. Instead, the \( K_0' \) values obtained by the L4-BM4 fittings increase strongly from
4.0 at the athermal limit, to 6.8 at 300K, and 10.4 at 600K. Meanwhile, the \( K_0'' \) values decrease
from -0.05 GPa\(^{-1}\), at the athermal limit, to -0.93 and -2.2 GPa\(^{-1}\), at 300 and 600K respectively. The
correlation among the \( K_0, K_0' \) and \( K_0'' \) values of the BM4 fittings produces lower values of \( K_0 \) than
those from the BD calculations [Table (1)]. In the present case, therefore, the most reliable values
of the bulk moduli, at each temperature and pressure, are those obtained through the application
of a Ln-BD (or a BM3-BD) algorithm.

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

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

Table 2

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

Isobaric curves of the bulk modulus variation with temperature, at 0, 3, 6 and 9 GPa (L4-BD
algorithm) are reported in Figure (9). Apart from the very low temperature region, such curves
show negative and nearly constant slopes which increase in magnitude with the pressure;
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.
Such increase of the magnitude of the slope, at high pressure, is due to the enhanced negative contribution to the thermal pressure of the low frequency phonons; indeed this fact parallels what has been discussed above, concerning thermal expansion: as the low frequency modes are associated to negative Grüneisen’s parameters, their frequencies are reduced at high pressure, so that an increasingly large number on phonons is created, and a consequent increased negative contribution to the thermal pressure is produced.

3.3 Heat capacity

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

Table 3 and Figure 10

As it appears from the data shown in Table (3), no significant differences have been observed in the $C_p$ calculated at the B3LYP and WC1LYP levels. In Figure (10) circles refer to experimental data measured at temperature higher then the room one, whereas triangles refer to low temperature measurements on a sample that contains 0.72 H$_2$O molecules pfu (on 36 oxygen atoms). Such water is presumably lost at high temperature and, in fact, Hemingway et al. (1986) provided two different tables of values of $C_p$: one for the low temperature region, and another one for high temperatures. The calculated curve in the high temperature region compares quite well with the experimental data, even if some discrepancy is observed for temperatures higher than 900K; such discrepancy could possibly be due to the failure, at high $T$, of the quasi-harmonic approximation.
used in our calculation, as well as to some problem in the experimental measurements as reported
by Hemingway et al. (1986). At low temperature, it is likely that the experimental $C_p$ contains a
significant contribution from the vibrations of the water molecules inside the channels of the
structure, which lead to higher $C_p$ values than those referring to the pure beryl. However,
Hemingway et al. (1986) tried to correct for such an effect (and even for the presence of $Cr^{3+}$
impurities in the sample) but, in spite of the correction, the value of $C_p$ remained relatively much
higher than that expected at low temperature. The reason of such anomaly in the experimental
low temperature $C_p$ was not identified (Hemingway et al., 1986), nor it is by looking at our
calculated data [Table (3)] which confirms the somewhat low values that could be expected from
Debye’s temperature based considerations, as discussed by Hemingway et al. (1986).

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

$$C_p = c_1 + c_2 T + c_3 T^2 + c_4 T^{-0.5} + c_5 T^{-2}$$

The refined valued of the $c_1$, $c_2$, $c_3$, $c_4$ and $c_5$ coefficients were respectively 1594.12, -0.4186,
1.0819·10$^{-4}$, -19331.40, 6.1187·10$^6$, in appropriate units ($C_p$ is in J/mol·K and $T$ is in K). The
correspondent values of the same coefficients refined by Hemingway et al. (1986) were 1625.84,
-0.4252, 1.2038·10$^{-4}$, -20180.94, 6.8254·10$^6$. The range of $T$ over which the experimental $C_p$’s were
interpolated was [200, 1800K] (Hemingway et al., 1986); we have chosen a lower maximum
temperature (1000K) due to the possible failure, at very high temperatures, of the quasi-harmonic
approximation employed in our calculations.
3.4 Soft mode and the $P\overline{6}/mcc \rightarrow P\overline{1}$ phase transition

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

This was the sign of a possible soft mode transition to a lower symmetry phase. By initially shifting the atoms of the unit cell along the two eigenvectors associated to this 2-dimensional $E_g$ normal mode, a $P\overline{1}$ space group symmetry resulted. By optimizing the geometry in such a space group, by keeping the cell volume fixed at values lower than 650Å$^3$, triclinic structures were obtained, having static energies systematically lower than those resulting from the optimization, at the same cell volumes, in the $P\overline{6}/mcc$ space group [Table (4)].

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

Geometry (cell parameters and fractional coordinates) resulting from the optimization at cell volumes of 630Å$^3$, in the $P\overline{1}$ symmetry, is provided as supplementary material. A full discussion concerning the geometry of such a phase will be presented in a subsequent paper together with results from experimental findings: preliminary single-crystal and powder diffraction
data collected at the ESR synchrotron facility, in Grenoble, showed that a symmetry reduction does indeed occur at pressures close to 14 GPa (Merlini; private communication). The interpretation of the experimental data is however difficult due to the possible presence of twinning. On the theoretical side, as geometry is concerned, it is here anticipated that the deviation from the hexagonal symmetry increases with the reduction of the unit cell volume. At a cell volume of 630Å³, the six independent lattice constants \(a, b, c, \alpha, \beta\) and \(\gamma\) were respectively optimized to 9.061, 9.045, 8.881Å, 90.2°, 89.7° and 120.1°; at the same cell volume, \(a\) and \(c\) lattice constants of the hexagonal phase were 9.028 and 8.924 Å, respectively. Thus, apart from the changes in the unit cell angles, the transition to the triclinic system produces a contraction of the \(c\) axis length, whereas the \(a\) and \(b\) parameters are increased. Some details of the \(\mathcal{P}\overline{1}\) structure, in particular concerning the ring of Si-centred tetrahedra, are represented in Figure (12): the unique Si site in \(\text{P6/mcc}\) splits in three sites \(\text{Si1, Si2, Si3}\); likewise, the unique O1 atom in the hexagonal phase splits in the O1a, O1b and O1c inequivalent atoms. Polyhedra are tilted either around axes parallel to [001] [Figure (12a)] or around directions normal to it [Figure (12b)].

The Si-O1-Si angles are reduced from the value of 164.3° in \(\text{P6/mcc}\), to 154.8° (Si1-O1a-Si3), 159.6° (Si2-O1b-Si1) and 160.4° (Si2-O1c-Si3) in \(\mathcal{P}\overline{1}\); such reduction of the angle is accompanied by a parallel increase of the Si-O1 distances of about 0.01Å on average, in going from the hexagonal phase to the triclinic one; this is consistent with the increase of the \(a\) and \(b\) lattice constants, and the decrease of the \(c\) parameter (indeed, even in the hexagonal phase, the \(c\) axis appears to be more compressible than the other two axes). These modifications of the structure of beryl as it transforms to the triclinic phase are anticipated in the vibrational properties of the high symmetry
polymorph: by looking at the low frequencies normal modes which mainly involve the tilting of Si-centred tetrahedra (see animations at the web page http://www.personalweb.unito.it/mauro.prencipe/vibs/beryl/index.html, calculated for the hexagonal beryl at a cell volume of 650Å³, close to the phase transition) and examining the Si-O1 distances during the excursion of such low frequencies vibrations, it is seen that a significant lengthening of the average Si-O1 distance accompanies the tilting [Figure (13)].

Figure 13

It could be said that, for pressures lower than 14GPa (hexagonal phase), the increase of the repulsion among the nuclei due to the volume contraction (see the relevant discussion in Prencipe and Nestola, 2007) is dynamically partially compensated by vibrations along the low frequencies modes (the $E_g$ soft mode in particular) which reduce the Si-O1-Si angles and increase the internuclear distances. Such reverse correlation between the Si-O-Si angle and Si-O bond length has also been observed in silicates, both in static calculations and experimental measurements, and interpreted within the framework of the QTAIMC theory (Bader, 1994; Prencipe, 2002; Prencipe and Nestola, 2007; Gibbs et al., 2009). As the cell volume decreases, the shortening of the interatomic distances (Si-O1 ones in particular: the shortest in the structure) increases the energy of the minima of the Born-Oppenheimer surface which correspond to the positions of the nuclei at the static equilibrium. Moreover, the lengthening of the average Si-O1 distance, as the Si-O1-Si angle decreases, is more pronounced at high pressures than at low ones: in fact, the nearly linear curves $d_{(Si-01)}((Si-O1-Si))$ had slopes of $-2.20\cdot10^{-3}$ and $-1.92\cdot10^{-3}$ Å/degree at cell volumes of 650Å³ (high pressure) and 692Å³ (zero static pressure) respectively. In other words, the tilting of the Si-centred tetrahedra becomes less rigid as the pressure increases. Consequently,
potential wells become shallower and vibrational frequencies are reduced (negative Grüneisen’s parameters). This fact can also be analyzed by considering the total pressure and its contributions: the energy required to statically compress the structure, and which is measured by the static pressure, is lowered by the dynamic distortion of the structure that moves along its low frequency normal modes; such lowering is measured by the zero point and thermal pressures, to which the latter modes contribute negatively. The (total) pressure required to compress the (hexagonal) beryl at a given volume is therefore lower than the (static) pressure that would be required to compress it \textit{statically}. At pressures higher than 14GPa the dynamic distortion is \textit{frozen} and the symmetry of beryl is reduced to the $P\overline{1}$ space group.

4. Conclusive (general) remarks on thermal expansion

As reported in the previous section, low frequency modes consist essentially of tilting of M-centre polyhedra (M=Si, Al, Be) associated to only minor variations of the M-O distances (as discussed above the latter ones are nevertheless determinant for the decrease of the vibrational frequencies as the pressure increases); in other words, such vibrations can be regarded as \textit{rigid unit modes} (RUM) according to the definition given in Dove et al. (1995). Indeed the origin of negative or very low thermal expansion coefficients in some framework silicates has been interpreted within the RUM model, by invoking a \textit{geometrical} effect of the tilting of rigid polyhedra, which acts in the direction of decreasing the cell volume as the temperature (amplitude of the vibrational motion) is increased. Such effect is generally compensated by \textit{normal anharmonic} effects which, instead, produce a cell volume expansion as the temperature is increased (Welche et al., 1998; Heine et al., 1999). The interpretation of the thermal expansion data proposed in the current work is not in contradiction with the \textit{geometrical} RUM model: in fact, RUM’s are observed and they are associated to negative Grüneisen’s parameters (that is, they contribute negatively to the thermal expansion). Indeed, it is explicitly stated in Heine et al. (1999) that “the Grüneisen theory as a
general formulation must be able to encompass the geometrical effect”, and a relation is
proposed between $\gamma^{red}$ [equal to $(2\pi\nu)^2 \gamma$] and $\eta$, the latter being a geometrical constant specific
to the RUM mode, which determines the magnitude of the volume contraction as the temperature
increases (Welche et al., 1998). However, whilst by following the approach of Welche et al. (1998),
one could explain the sign of $\gamma^{red}$ on the basis of the sign of $\eta$ (the variation of the frequency with
the volume would be a consequence of the geometry of vibration), in our approach it is the sign of
$\gamma^{red}$, ultimately due to the shape of the Born-Oppenheimer surface, that determines the sign of $\eta$
and hence the geometry of vibration. It is also emphasised here that, in our opinion, such
geometrical effect is just one type of anharmonicity. The distinction between geometrical and
anharmonic effects in the terms discussed by Welche et al. (1998) and Heine et al. (1999) could be
misleading in that it seems to attribute a component of thermal expansion (or contraction) to
effects not related to the anharmonicity of the atomic interactions, whilst it is clear that thermal
expansion (or contraction) is possible if and only if the Born-Oppenheimer’s surface deviates from
the harmonic shape: if the surface were perfectly harmonic, the Grüneisen’s parameters would be
zero, as well as the zero point and thermal pressures, and no thermal expansion would be
observed (Ashcroft and Mermin, 1976; Born and Huang, 1954).

Another issue concerning thermal expansion is related to the asymmetry of the interatomic
potential. It is often said that normal thermal expansion in solids is ultimately due to the
asymmetry of potential wells on the Born-Oppenheimer surface, whose minima are occupied by
atoms (see for instance Miller et al., 2009). This view stems from considerations based on the
simple quantum oscillator usually invoked to explain the behaviour of biatomic molecules. Indeed,
in a biatomic molecule, the increase of bond length with temperature can be ascribed to the
asymmetric shape of the interatomic potential leading to the well known asymmetric vibrational
eigenfunctions of the anharmonic oscillator, whose average positions are progressively shifted to
values corresponding to higher interatomic distances, as the vibrational quantum number is increased; in this case, as excited vibrational energy levels are being populated by heating the molecular gas, the thermally averaged equilibrium distance of the nuclei is larger than the distance at \( T=0 \text{K} \), where the oscillator is at the fundamental level. Thus, bond lengthening can be directly view as an effect of the asymmetry of the potential which, in general, is just one type of anharmonicity (it is however here stressed that the thermal expansion of the gas, at constant pressure, is of course never interpreted as an effect of bond lengthening). By following this line of reasoning, an anharmonic but symmetric potential should not lead to any thermal expansion, since the eigenfunctions of such peculiar symmetric oscillator are symmetric with respect to the static equilibrium position. In a solid, if the shape of the Born-Oppenheimer surface around a minimum associated to the equilibrium position of the nuclei \((q_0)\), were hypothetically described 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 coordinate, and \( q_0=0 \) corresponds to the equilibrium position) symmetric eigenfunctions would result, that is: no thermal expansion, according to the model translated from the molecular experience. Even in this case, however, the corresponding frequencies would depend upon the volume, since the above potential is anharmonic by the presence of the quartic term; in turn, this would lead to Grüneisen’s parameters different from zero, and a non zero thermal expansion would result. It should be noted that, at variance with the zone-centre vibrational modes that could be asymmetric with respect to the \( q_0 \) position, a symmetric \( V(q) \) potential should be characteristic of all the off-centre modes: this is obvious, for instance, in the zone-border case where, for any motion in the reference zero cell (e.g. a M-X bond lengthening) there is a motion, in an adjacent cell, which is exactly in anti-phase with the first one (a M-X bond shortening); when the sign of \( q \) is reversed, the M-X bond in the zero cell shortens, whereas the corresponding bond, in the adjacent cell, lengthens; this means that \( V \) does not depend upon the sign of \( q \) and,
therefore, it is symmetric. Thus, the argument concerning the role played by the asymmetry of the potential energy surface, in connection with the asymmetry of the resulting eigenfunctions, in determining the thermal expansion (negative or positive, as it may be) is, in general, not fully appropriate.

Another objection that could be raised against such asymmetric-potential model of thermal expansion concerns the principle of conservation of energy: imagine a crystal at $T=0K$ subjected to an external zero pressure; by heating such a crystal to a temperature $T$, it will generally expand. If such an expansion were exclusively due to the asymmetry of the vibrational eigenfunctions, after heating the (static) equilibrium positions of the nuclei would be unchanged with respect to those at $T=0K$: indeed, it is often said that the temperature affects the population of vibrational levels, but not the structure of the vibrational spectrum (position of the energy levels); in turns, this means that either static and zero point energies would be exactly the same as they were at 0K, as well as the corresponding pressures. Now, it can be said that (i) as a reaction to the temperature increase, the crystal expands in order to equilibrate its internal pressure with the external zero one, and (ii) by heating it at constant volume, phonons are created which contribute a thermal pressure according to what has been discussed in the sections above; therefore, if the nuclei did not change their equilibrium position at high $T$, the only way to equilibrate the external and internal pressures would be that of reducing the thermal pressure to zero. This is clearly a paradox since, if the Grüneisen’s parameters are different from zero, a zero thermal pressure would be possible only if no phonons existed in the crystal, even at a non zero temperature, in open contradiction with the Bose-Einstein statistics. Moreover, since no work is done in the expansion process (against the zero external pressure), all of the energy carried by phonons at a certain $T$ (which would be equal to the energy provided during heating) would be lost and the energy-conservation principle would be violated.
Therefore, even if the asymmetry of the interatomic potential, and the consequent asymmetry of the vibrational eigenfunctions, cannot in general be ruled out [the asymmetry of the resulting vibrational eigenfunctions could be related to a component of what is generally termed intrinsic anharmonicity (Oganov and Dorogokupets, 2004) which could also contribute a fraction to the total thermal expansion], the reason of the thermal expansion must be searched in the anharmonicity of the potential, independently by its symmetry, through the effects it has on the thermal pressure via the Grüneisen’s parameters. Such effects are exactly those which are properly taken into account at the quasi-harmonic level.

In the present case of beryl, the calculation of the static energies as the structure is deformed along the normal coordinates corresponding to low frequency modes, gave perfectly symmetric curves about the respective equilibrium points even if, as discussed above, such modes are associated to large (and negative) Grüneisen’s parameters, and thus do contribute substantially to the thermal pressure and to the thermal expansion. For instance, a fit up to the 4th power of the (static) energy v.s. the normal coordinate $q$ associated to the $B_{1g}$ mode at 72 cm$^{-1}$, (cell volume equal to 650 Å$^3$) gave $k_2$, $k_3$ and $k_4$ values of $1.08 \times 10^{-2}$ hartree/Å$^2$, $3.39 \times 10^{-5}$ hartree/Å$^3$ and $3.23 \times 10^{-3}$ hartree/Å$^4$ respectively; in particular, the $k_3$ value associated to the cubic term is much smaller than the values of both the quadratic ($k_2$) and quartic ($k_4$) coefficients. Indeed, the $E(q)$ curve appears to be perfectly symmetric with respect to the origin ($q=0$). Similar calculations carried out for the normal modes corresponding to the $A_{2g}$ symmetric and $A_{1u}$ antisymmetric Si-O2 stretching modes, at 1101 and 1217 cm$^{-1}$ respectively, gave symmetric $E(q)$ curves: $k_2$, $k_3$ and $k_4$ equal respectively to $2.56$ hartree/Å$^2$, $4.79 \times 10^{-3}$ hartree/Å$^3$ and $4.73 \times 10^{-3}$ hartree/Å$^4$, for the $A_{2g}$ mode, and $3.70$ hartree/Å$^2$, $4.68 \times 10^{-6}$ hartree/Å$^3$ and $0.249$ hartree/Å$^4$, for the $A_{1u}$ mode; it should be noted the much lower value of $k_3$ for the $A_{1u}$ mode (anti-phase stretching of the two Si-O2 bonds: for each SiO$_4$ tetrahedron, one bond shortens and the other one lengths), than the
corresponding value obtained for the $A_{2g}$ one (in-phase stretching of the two Si-O bonds). The $A_{1g}$ symmetric Al-O$_2$, Be-O$_2$ stretching mode at 667 cm$^{-1}$ [Figure (14)] has a $k_3$ value comparable in magnitude to the quartic coefficient ($k_2=0.998$ hartree/Å$^2$, $k_3=-9.14\cdot10^{-3}$ hartree/Å$^3$, $k_4=1.16\cdot10^{-2}$ hartree/Å$^4$).

Figure 14

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

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

expressing the total pressure of the crystal in equilibrium with a zero external pressure, can obviously be read as the condition of minimum free energy at a given temperature.
The analysis of the effects of thermal expansion on the crystal energy can also be considered under a different point of view. Let \( E_{th}(\nu, T) \) be the contribution to the thermal energy, at the temperature \( T \), due to the vibrational mode at frequency \( \nu \), that is:

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

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

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

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

where \( y \) is the ratio \( h\nu/kT \), \( \gamma \) is the Grüneisen’s parameter and the \( F \) function [plotted in figure (15)] is defined as

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

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

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

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

Appendix

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

Basis set, Hamiltonian and computational parameters

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

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

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

**Geometry, $\Gamma$ point phonon frequencies and elastic constants**

Cell parameters and fractional coordinates were optimized by analytical gradient methods, as implemented in CRYSTAL06 (Civalleri et al., 2001; Dovesi et al., 2006). Geometry optimization was considered converged when each component of the gradient (TOLDEG parameter in CRYSTAL06) was smaller than 0.00001 hartree/bohr and displacements (TOLDEX) with respect to the previous
The volume ranges over which geometries were refined, and static energies calculated, were [703-650\AA^3] in the B3LYP case (12 different volume values; static equilibrium found at 692.22\AA^3), and [691-650\AA^3] in the WC1LYP one (9 volume values; static equilibrium at 686.74\AA^3). Results (cell volumes, cell parameters, optimized fractional coordinates and static energies) are provided as supplementary material (Tables S1a and S1b, for the B3LYP and WC1LYP cases, respectively).

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

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

Table 5

The $K_V, K_R$ [equation (8.3)] values were 179.9 and 179.4 GPa, respectively; the average value $\overline{K}_{VHR}$
[equation (8.1)] was 179.7 GPa. The shear moduli \( \mu_V, \mu_R \) and \( \mu_{VHR} \) [equations (8.2) and (8.1)] were 79.1, 77.1 and 78.1 GPa, respectively. The calculated average longitudinal and transversal acoustic waves (\( \bar{v}_p \) and \( \bar{v}_s \)) were 10.50 and 5.51 Km/sec, respectively, which are very close to the experimental data of Yoon and Newnham (1973). Finally, the average longitudinal and transversal frequencies of the acoustic wave at the Brillouin zone boundary [\( \nu_l \) and \( \nu_s \), equation (7)] were 245.5 and 128.8 cm\(^{-1} \), respectively.
References


**Captions to the Tables**

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

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

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

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

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

Figure 1: Grüneisen’s parameters ($\gamma$) at zero pressure as a function of frequency ($\nu$).

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

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

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

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

Figure 6: Thermal expansion coefficient $\alpha_T$ as a function of temperature, at 0, 3 and 6 GPa.

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

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

Figure 9: Bulk modulus as a function of temperature. Isobaric curves at 0, 3, 6 and 9 GPa.
**Figure 10**: Constant pressure specific heat as a function of temperature.

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

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

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

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

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